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SYMPOSIUM FA - Advanced Fossil Fuel Energy Technologies: the Materials Demand

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SYMPOSIUM FB - Materials and Process Innovations in Hydrogen Production and Storage

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SYMPOSIUM FC - Fuel Cells: Materials and Technology Challenges

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SYMPOSIUM FD - Electrochemical Energy Storage Systems: the Next Evolution

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SYMPOSIUM FE - Advances in Materials and Technologies for Efficient Direct Thermal-to-electrical Energy Conversion

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SYMPOSIUM FF - Materials Challenges for Future Nuclear Fission and Fusion Technologies

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SYMPOSIUM FG - Photovoltaic Solar Energy Conversion: Materials and Technology Challenges

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SYMPOSIUM FH - Concentrating Solar Technologies: Materials and Technology Solutions for CPV and CSP Competitiveness

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SYMPOSIUM FI - Recent Developments in the Research and Application of Transparent Conducting and Semiconducting Oxides

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SYMPOSIUM FJ - Materials and Technologies for Solid State Lighting

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SYMPOSIUM FM - Electromagnetic Metamaterials

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FK - *6th International Conference* "Science and Engineering of Novel Superconductors"

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FL - *9th International Conference* "Medical Applications of Novel Biomaterials and Nano-biotechnology"

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ABSTRACTS

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CIMTEC 2010

5th Forum on New Materials

June 13-18, 2010

OPENING SESSION

Plenary Lectures

F:PL1 **Graphene: Magic of Flat Carbon**
André Geim, University of Manchester, UK

Graphene - a free-standing atomic plane of graphite - is a wonder material. It has many superlatives to its name. It is the thinnest material in the universe and the strongest one ever measured. Its charge carriers exhibit the highest intrinsic mobility, have zero effective mass and can travel micron distances without scattering at room temperature. Graphene can sustain current densities million times higher than that of copper, shows record thermal conductivity and stiffness, is impermeable to gases and reconciles such conflicting qualities as brittleness and ductility. Electron transport in graphene is described by a Dirac-like equation (rather than the standard Schrodinger equation), which allows the investigation of relativistic quantum phenomena in a bench-top experiment. I will overview our work on graphene concentrating on its fascinating electronic and optical properties and speculate about future applications.

F:PL2 **Programmed Molecular Assembly for Tailored Functional Materials**
Takuzo Aida, JST ERATO-SORST NANOSPACE PROJECT, Center for Nanobio Integration, and Dept. of Chemistry & Biotechnology, The University of Tokyo, Tokyo, Japan

Utilization of π-electronic conjugation has become of increasing importance in materials sciences, particularly, for molecular electronics, and a variety of molecules and substances, which show interesting optoelectronic properties, have been reported so far. In 2003, we found that bucky gels, prepared by grinding single-walled carbon nanotubes in imidazolium ion-based ionic liquids[1, 2], serve as highly powerful capacitors, and can be applicable to the fabrication of fully plastic actuators by layer-by-layer casting[3] and stretchable electronics[4, 5]. There are many other potential applications, as summarized in our recent review article[6]. In 2004, we have also reported that an amphiphilic hexa-peri-hexabenzocoronene self-assembles into graphite nanotubes[7], which are highly interesting as designer electronic nanomaterials[8]. Later, we succeeded in obtaining a pseudo-crosslinked version of this graphite nanotube by ADMET-triggered self-assembly of an allyl group-appended new amphiphilic hexa-peri-hexabenzocoronene[9]. More recent examples include photo[10], redox[11], and coordination chemistry[12] - mediated stabilization of the graphite nanotubes. These developments will allow for enhancing the practical utilities of these assembly-based nanomaterials. Use of a chiral amphiphilic hexa-*peri*-hexabenzocoronene with stereogenic centers results in the formation of graphite nanotubes with one-handed helical chirality[13, 14]. Water-dispersible graphite nanotubes and surface-polymerized graphite coils have also been fabricated[15-17]. The most recent achievement includes the successful fabrication of a photoconductive graphite nanotube with a coaxial architecture[18, 19]. By using click chemistry, dendrons can be grafted on selectively on the exterior surface of the nanotubes, allowing for the second click reaction selectively in their interior[20]. Very recently, by using a synchrotron facility, we succeeded in complete structural analysis of the graphite nanotubes[21]. We also started a new project for liquid crystalline materials for electronics[22-24]. The most recent example along this line highlights a bawl-shaped corannulene derivative, forming a hexagonal columnar LC mesophase, which perfectly responds to an applied electric field.

*[1]Fukushima et al., Science **2003**, 300, 2072. [2]Fukushima et al., Small **2006**, 2, 554. [3]Fukushima et al. Angew, Chem., Int. Ed. **2005**, 44, 2410. [4]Sekitani et al., Science **2008**, 321, 1468. [5]Sekitani et al., Nature Mat. **2009**, 8, 494. [6]Fukushima et al. Chem. Eur. J. (Concepts) **2007**, 13, 5048. [7]Müllen et al., Chem. Rev. **2007**, 107, 718. [8]Hill et al., Science **2004**, 304, 1481. [9]Jin et al., J. Am. Chem. Soc. **2005**, 127, 10020. [10]Motoyanagi et al., J. Am. Chem. Soc. **2006**, 128, 4220. [11]Motoyanagi et al., JPS., Part A, Polym. Chem. Ed. **2006**, 44, 5120. [12]Wei et al., Angew. Chem., Int. Ed. **2009**, 48, in press. [13]Jin et al., Proc. Natl. Acad. Sci., USA **2005**, 102, 10801. [14]Yamamoto et al., Adv. Mater. **2006**, 18, 1297. [15]Zhang et al., J. Am. Chem. Soc. **2007**, 129, 719. [16]Yamamoto et al. J. Am. Chem. Soc. **2006**, 128, 14337. [17]Yamamoto et al. Angew. Chem. Int. Ed. **2008**, 47, 1672. [18]Yamamoto et al., Science **2006**, 314, 1761. [19]Yamamoto et al., J. Am. Chem. Soc. **2007**, 129, 9276. [20]Mynar et al., J. Am. Chem. Soc. **2008**, 130, 1530. [21]Jin et al., J. Am. Chem. Soc. **2008**, 130, 9434. [22]Li et al., J. Am. Chem. Soc. **2008**, 130, 8886. [23]Sakurai et al., J. Am. Chem. Soc. **2008**, 130, 13812. [24]Miyajima et al. J. Am. Chem. Soc. **2009**, 131, 44.*

F:PL3 First Principles Multiscale Methods Applied to Materials Science

William A. Goddard, III, Materials and Process Simulation Center (MSC), California Institute of Technology, Pasadena, CA, USA

Advances in theoretical and computational chemistry, materials science, and physics are making it practical to consider first principles (de novo) predictions of important systems and processes in the Chemical, Biological, and Materials Sciences. Our approach to applying first principles to such systems is to build a hierarchy of models each based on the results of more fundamental methods but coarsened to make practical the consideration of much larger length and time scales. Connecting this multi-paradigm multi-scale hierarchy back to quantum mechanics enables the application of first principles to the coarse levels essential for practical simulations of complex systems. We will highlight some recent advances in methodology and will illustrate them with recent applications to problems selected from: · Metal-graphene and metal-carbon nanotube interconnects; · Low energy electron enhanced etching in microelectronics processing; · Dynamical processes in highly excited electronic systems; · DNA origami based self-assembly of CNT devices; · Prediction of improved cuprate superconductors; · Simulation of battery, photovoltaic, and fuel cell materials; · MOF, COF, ZIF storage materials for H_2, CH_4, CO_2.

Symposium FA

ADVANCED FOSSIL FUEL ENERGY TECHNOLOGIES: THE MATERIALS DEMAND

Oral Presentations

Session FA-1
Fossil Fuel Combustion

FA-1.1 Improved or New Materials

FA-1.1:IL01 **Materials Issues in Oxy-fuel Technology for Carbon Capture and Storage**
Terry Wall, Chemical Engineering, University of Newcastle, Callaghan, NSW, Australia

Oxy-fuel is one of three carbon capture and storage (CCS) technologies currently being developed through demonstrations, the others being post-combustion capture and IGCC with CCS. (Wall et al, 2009). Amongst the three CCS technologies, CO2 gas quality has the greatest potential variability, uncertainty and impact in oxy-fuel. This is due to the presence of O2, N2, Ar, SOx, NOx, Hg and other trace elements. This quality can be controlled either by gas cleaning in the power plant or the compression operation, or both. The final quality will be influenced by future regulations for CO2 storage and identified impacts in transport and storage. The cost and process energy requirements may potentially be minimised and CO2 recovery optimised, but at present the technical possibilities are still being established. Materials issues detailed include high temperature steels for improved steam temperatures and electricity generation efficiency, sulfur related corrosion due to higher SO3 levels in furnace gases, mercury gas corrosion of aluminium heat exchangers used in CO2 compression and solid oxygen carriers for future oxygen systems of lower energy penalty than current air separation units (ASU).

FA-1.1:IL02 **New Metallic Materials for Advanced Fossil Fuel Power Generation**
W.J. Quadakkers, Forschungszentrum Jülich, IEF2, Jülich, Germany

Today, fossil fuels provide the majority of worldwide energy resources. Even though the use of renewable energy sources is growing rapidly, fossil fuels will remain an indispensable part of the global energy mix for the foreseeable future. However, the global rise in energy consumption will inevitably result in a shortage of fossil fuels in the medium term. Additionally, legislations in respect to emission of greenhouse gases, will require a substantial reduction and eventually even a total prevention of CO2 emissions. For these reasons, a large number of research projects are being carried out worldwide which focus on new strategies to increase conversion efficiency in combination with carbon capture technologies. The new plant designs and changed operating conditions result in more demanding service conditions for the construction materials for heat exchanging components in boilers as well as for the various components in gas and steam turbines. The present presentation will describe the service conditions which will prevail in the various types of high efficiency power plants with or without carbon capture technology. Differences in materials requirements in respect to mechanical properties as well as oxidation and corrosion resistance compared to application in conventional plants will be described. Concepts for realizing the new demanding energy conversion systems using optimized existing construction and coating materials will be discussed.

FA-1.1:IL03 **Materials Design of Ni Base Superalloy for 700 °C-class Steam Turbine**
Shinya Imano*, Jun Sato, Material Research Laboratory, Hitachi, Ltd, Hitachi-shi, Japan

To improve the microstructure stability and avoid the segregation of Nb, we modified the chemical composition of Alloy 706. It is known that Alloy 706 is strengthened by the GAMMA' (Ni3Al) and GAMMA''(Ni3Nb) phases up to about 600 °C. But these phases are unstable after long-term exposure to high temperatures and transform into the Nb rich DELTA or ETA phases. The modified alloy (FENIX-700) contains lower amounts of Nb and higher amounts of Al than Alloy 706. Also, using the CALPHAD method, it is designed as a GAMMA' (Ni3Al) strengthened alloy without GAMMA'' (Ni3Nb), DELTA, and ETA phases. Furthermore, we could not find DELTA or ETA phases in the modified alloy after creep and long-term aging at 700 °C. And it appears that the creep temperature capability has improved from 650 °C to 700 °C or more. In this presentation, the alloy design and experimental results of FENIX-700 will be shown, and the alloy design of Ni-base welding materials for welding type rotors (Ni-base/12Cr Steel) for 700 °C-class steam turbines using the CALPHAD method will also be shown.

FA-1.1:IL04 **Control of Microstructure and Defects in Cast TiAl**
R. Yang*, Y.Y. Cui, Q. Jia, R.H. Liu Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China

Alloys based on the titanium aluminide TiAl, owing to their light weight, good corrosion and oxidation resistance, and temperature capacity up to 850 °C for long time service, have great potential for use in both air and land based turbines. Cost considerations make investment casting the most viable route for manufacturing TiAl blades. This talk will summarize our research on the microstructure and defects (both surface and internal) in cast TiAl and three topics will be discussed: surface microstructure in relation to the shell mould material; precision casting of model industrial gas turbine blades; investigation of directional solidification of TiAl with a long term view to producing blades with more robust performance under service.

FA-1.1:IL05 **Directional Solidification by Liquid Metal Cooling Process**
J. Shen, J. Zhang*, L.H. Hong, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China

Recent progress of high gradient directional solidification assisted by the liquid metal coolant (Sn) was reported. The microstructure, heat treatment response and mechanical properties of large castings which were directionally solidified using high rate solidification (HRS) and liquid metal cooling (LMC) techniques were compared. Effect of withdrawal rates on microstructure and creep strength of a nickel base superalloy which produced by LMC was studied. The thermal field and the grain structure were simulated and compared with the experimental results. The key challenges of LMC process, namely, the contamination of low melting metal coolant, and ceramic core and shell issue were discussed based on the experimental results. For demonstration, large blades with columnar and single crystal structures were cast using the optimized LMC process.

FA-1.1:IL06 **Long-term Stabilization of Creep-resistant Ferritic Steels forHighly Efficient Ultra-supercritical Power Plants**
Fujio Abe, National Institute for Materials Science (NIMS), Tsukuba, Japan

Alloy-designing of ferritic steels, which can be used in highly efficient ultra-supercritical power plant with maximum steam temperature of 700 °C, has been investigated in terms of long-term creep strength and oxidation resistance including welded joints. The target temperature for ferritic steels as a main steam pipe is 650 °C, while the maximum allowable temperature of conventional ferritic steels is 610 °C. The boundary and sub-boundary hardening is shown to be the most important strengthening mechanism in creep of the 9% Cr steel base metal and welded joints. The addition of boron reduces the coarsening rate of M23C6 carbides along boundaries near prior austenite grain boundaries during creep, enhancing the boundary and sub-boundary hardening. This improves long-term creep strength of base metal. The enhancement of boundary and sub-boundary hardening is significantly reduced in fine-grained region of Ac3 HAZ simulated specimens of conventional steel P92. In NIMS 9% Cr boron steel welded joints, the grain size and distribution of carbonitrides are substantially the same between the HAZ and base metal, where fine carbonitrides are distributed along the lath and block boundaries as well as along prior austenite grain boundaries. This is essential for the suppression of Type IV fracture in

NIMS 9% Cr boron steel welded joints. Newly alloy-designed 9Cr steel with 160 ppm boron and 85 ppm nitrogen exhibits much higher creep rupture strength of base metal than P92 and also no Type IV fracture in welded joints at 650 °C.

FA-1.1:IL07 Simplified Processing of Oxide Dispersion Strengthened (ODS) Ferritic Alloys using Gas Atomized Precursor Powders

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Oxide dispersion strengthened ferritic stainless steel microstructures were processed by a simplified powder-based method in this research. Instead of mechanical alloying, precursor ferritic stainless steel powders were oxidized in situ using a gas atomization reaction synthesis technique. As-atomized powders contained an ultra-thin kinetically favored (i.e., Cr-enriched) surface oxide. This surface layer was used as a vehicle to carry oxygen into the as-consolidated alloy microstructure, where heat treatments were designed to drive oxygen exchange between the less stable prior particle boundary oxide and dissolved Y and other additions. Exchange reactions and subsequent thermal-mechanical processing resulted in nano-metric Y-enriched oxide dispersoids and strengthening from dislocation sub-structures. Transmission electron microscopy and synchrotron X-ray diffraction helped evaluate the evolution of the alloy microstructure and elevated temperature tensile testing was used to assess the strength of the alloy.

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FA-1.1:IL09 Alloy Design and Processing Challenges for Advanced Power Systems: an Alloy Producer's Perspective

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The alloys required for advanced fossil fuel power systems such as advanced ultra-super critical steam turbines are transitioning from stainless steels that operate below 600 °C to nickel-based alloys that can operate up to 760 °C for extremely long service lives. This transition brings with it major metallurgical as well as economic challenges related to alloy design, melt processing and fabrication of the large size components never before attempted. The alloys in general will be required to maintain creep resistance over 100,000 hours of service life while at the same time maintaining resistance to severe hot corrosion and oxidation. A need exists for nickel-based alloys that are not only highly alloyed but are also impervious to phase instabilities during initial processing and service. The potential exists for severe segregation when casting large ingots. This possibility must be dealt with during thermo-mechanical processing to obtain the wrought structures that can be inspected to necessary design defect levels. This paper will detail these challenges as they have been addressed in smaller aerospace turbines and discuss strategies to overcoming problems. New computation modeling tools will play a critical role in engineering solutions for alloy design, solidification, forging and heat treatment. Since any solution needs to be economically viable, the paper also discusses processing cost issues in terms of the process yields and operational strategies. The use of powder metallurgy will be reviewed as a cost effective alternative.

FA-1.1:IL10 Computational and Experimental Development of Novel High Temperature Alloys

M.J. Kramer*, M. Akinc, P. Ray, Ames Laboratory and Dept. of Materials Science and Engineering, Iowa State University, Ames, Iowa, USA

Discovery of new alloys is a multidimensional problem which encompasses the intrinsic thermodynamic stability of the alloy and their thermomechanical and thermochemical response to the combustion environment. Even when only considering economically viable refractory base metals in combination with stable oxide formers, the number of ternary combinations > 104. Thus, the traditional Edisonian approaches not an efficient means for developing new alloy systems. We propose a hierarchical scheme for identifying potential alloy systems which involves sifting through large regions of phase space with increasingly more accurate analysis. Our coarsest sieve is an extended Miedema model for initial screening of prospective alloy followed by more detailed thermodynamic assessments. Our ternary Miedema model has been used to evaluate prospective alloy systems having high melting temperatures, with good probability of having a high strength matrix. This winnows the prospective phase space to a handful of potential alloy systems. Candidate alloys are then evaluated with more accurate methods. Compounds having the highest enthalpies of formation are then evaluated. Highest melting compounds then tested for their stability in an oxidizing environment. Specific examples will be presented.

FA-1.1:L12 Reaction Synthesis Mo-Si-B Alloys; Strength, Oxidation, Microstructural Engineering

J.K. Cochran*, M.R. Middlemas, W.L. Daloz, P.E. Marshall, Georgia Tech, Atlanta, GA, USA; K.S. Kumar, P. Jain, Brown University, Providence, RI, USA

Mo-Si-B alloys are promising candidates for next generation turbine engine blades with the potential to increase the service temperature 200-300 °C higher than nickel-based superalloys. RS-Mo-Si-B forms a composite microstructure of molybdenum solid solution (Moss) and two intermetallic phases, Mo3Si and Mo5SiB2, where the Moss phase increases ductility and the intermetallic phases enhance strength and provide oxidation resistance. Using powder processing, the three-phase alloys are produced through the reaction of sub-micron molybdenum, Si3N4 and BN particles. The resulting microstructures are a fine dispersion of the intermetallic phases in a Moss matrix. High temperature tensile strengths of these alloys will be compared to similar compositions from other processes and the oxidization resistance from cyclic oxidation will be presented. The properties of these alloys are dependent on morphology of the microstructure. By manipulating green state elemental arraignment, a variety of microstructural scenarios are being investigated.

FA-1.1:L13 Effect of Alloying Elements on Phase Equilibria in New Co-based Superalloy

T. Omori*, J. Sato, K. Oikawa, I. Ohnuma, R. Kainuma, K. Ishida, Tohoku University, Sendai, Japan

Recently, our research group has found a new ternary compound Co3(Al,W)[1], and it has been reported that the mechanical properties of Co-Al-W alloys having the gamma/gamma' two-phase structure are sufficient for this alloy system to be considered as constituting high-temperature materials[2]. The phase diagram is one of the most important sources of information for development of a new type of precipitation hardened Co-based superalloy, and we have determined the phase equilibria in the Co-Al-W ternary system. In this study, the effect of alloying elements was investigated. Co-Al-W-2at%X alloys were annealed at 1173 K or 1273 K, and their equilibrium compositions were determined by EPMA. DSC measurements were also conducted. The phase equilibria between the gamma, gamma', D019 and B2 phases were determined, and it was found that Ti, V, Nb, Ta and Mo tend to concentrate in the gamma' or D019 phase in the gamma/gamma' or gamma/D019 equilibria, respectively, while Cr, Mn and Fe tend to be distributed in the gamma phase. A correlation between the partition and the gamma' solvus temperature was found. The effect of B on the mechanical properties was also examined.

[1] J. Sato et al., Science 312 (2006) 90; [2] A. Suzuki, T. M. Pollock, Acta Mater. 56 (2008) 12 88.

FA-1.2 Membranes for O_2 Separation and Adsorbents for CO_2 Capture

FA-1.2:IL01 Oxygen Transport Membranes for Oxyfuel Combustion

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Greenhouse gas emissions in power production can be largely reduced byCO2 capture and subsequent subterranean storage. Three major capture options are being researched e.g. post combustion capture of CO2, precombustion capture and oxyfuel combustion i.e. combustion with pure oxygen. The latter option is pursued in three stages of development: conventional high efficiency cryogenic air separation, high temperature oxygen transport (OTM) membranes and finally the integration of (partial) oxidation in an OTM membrane reactor. The majority of materials used for this purpose are mixed oxide and electronic conducting ceramics largely based on the oxygen deficient cubic perovskite structure, ABO3-δ. Crucial to the performance as an oxygen selective membrane is that the materials are capable of rapid oxygen exchange and diffusion of oxide ions, and maintain structural and chemical integrity under the conditions of the application. A 1000 MWe natural gas fired power plant, requires 15,000 t/d of pure oxygen. This means that with a target flux for economic viability of about 10 ml/cm2.min, a surface area of about 80000 m2 is needed, stable in all aspects, with no pinholes, no cracks, etc.. This is one big challenge in materials research, especially in reducing and CO2 rich environments!

FA-1.2:IL02 Commercially Reliable Oxygen Conducting Membranes for SOFC and Oxygen Generation Applications

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High temperature oxygen conducting membranes are poised to play a major role in reducing the carbon footprint from fossil fuels. The US Department of Energy's (DOE) Solid State Energy Conversion Alliance (SECA) is currently focused on the development and commercialization of solid oxide fuel cell (SOFC) technology for the generation of clean and affordable energy from fossil fuel energy sources. SOFC's are based on an all solid-state anode, cathode, and electrolyte. For commercialization, SOFC's electrolytes must posses: low resistivity, adequate separation of the fuel and air streams, and a reliable and economical fabrication method. The anode supported planar SOFC under development by Pacific Northwest National Laboratory (PNNL) is comprised of a thin (7- 20µm) yttria stabilized zirconia (YSZ) electrolyte co-sintered on a 500µm porous anode support. Reliable performance and fabrication of these cells is dependant on several factors including; consistency of electrolyte powder, impurities in the electrolyte powder and robustness of the fabrication process to powder variation. While YSZ is the preferred electrolyte material because of its excellent chemical and mechanical durability, other electrolytes such as; Scandia stabilized zirocnia (SSZ), acceptor-doped ceria's (Sm and Gd-doped CeO2), and lanthanum gallate (La1-xSrxGa1-yMgyO3) have also received significant attention because of their higher ionic conductivity. The DOE's Fossil Energy program has also made significant investments in ionic transport membranes to improve the efficiency and reduce the cost of oxygen generation applications for current coal gasification systems. These membranes are typically of the La1-xAExCo1-yFeyO3 perovskite family and are similar to current SOFC cathode materials. The impact of the powder fabrication process, impurities, and external contamination on material performance will also be discussed.

FA-1.2:IL03 Oxygen Carriers for Chemical-looping Combustion

T. Mattisson, A. Lyngfelt, M. Ryden*, Department of Energy and Environment, Chalmers University of Technology, Göteborg, Sweden

Chemical-looping combustion (CLC) is a combustion technology with inherent separation of the greenhouse gas CO2. The technique involves the use of a metal oxide as an oxygen carrier which transfers oxygen from combustion air to the fuel, and hence a direct contact between air and fuel is avoided. Considerable research has been conducted on CLC in the last decade with respect to oxygen carrier development. Most work has focused on oxygen carriers based on the metals Ni, Co, Fe, Cu and Mn using gaseous fuels, such as natural gas. A number of continuous prototype reactors based on interconnected fluidized beds with a thermal power of 0.3 - 120 kW have successfully been operated using different types of both natural and synthetic oxygen carrier particles. From these tests it can be established that almost complete conversion of the fuel can be obtained and 100% CO2 capture is possible at a low cost. The CLC process has also been adapted for solid fuels and Chalmers has successfully operated a 10 kW reactor using various solid fuels with the natural oxygen carrier ilmenite. Further, the technology has also been adapted for hydrogen production, i.e. CLR. The presentation will give an overview of the research performed on CLC and highlights the current status of the technology.

FA-1.2:L04 Supported Oxygen Transport Membranes for Oxyfuel Power Plants

Michael Betz*, Falk Schulze-Küppers, Stefan Baumann, Wilhelm A. Meulenberg, Detlev Stöver, Forschungszentrum Jülich, Institute of Energy Research IEF-1 Materials Synthesis and Processing, Jülich, Germany

The necessity of reducing CO2-emissions is evident and getting more and more social consensus all over the world. Therefore, carbon capture and storage (CCS) is an important option in order to achieve CO2 mitigation. One option for CCS is making use of oxyfuel technology, where pure oxygen is used for combustion forming primarily CO2 and H2O making CO2 capture much easier than by using air in the combustion. The required oxygen can be produced using ceramic membranes, which are associated with significantly lower efficiency losses compared to conventional separation techniques. The membranes consist of gastight mixed ionic electronic conductors, which allow oxygen diffusion through vacancies in the crystal lattice and simultaneous transport of electrons in the opposite direction at elevated temperatures. Their major advantage is infinite oxygen selectivity. Highest oxygen permeation is obtained using perovskite materials e.g. (Ba,Sr)(Co,Fe)O3 or (La,Sr)(Co,Fe)O3. In order to increase permeation rates, supported thin film membranes with activated surfaces are necessary. The preparation of supported multi-layered membrane assemblies as well as characterization results, e.g. SEM, porosimetry, permeation data, are presented and challenges and prospects are derived.

FA-1.2:IL07 High-temperature CO2 Sorbents for Pre-combustion CO2 Capture

R.W. van den Brink*, E.R. van Selow, P.D. Cobden, S. Walspurger, W.G. Haije, Energy Research Centre of the Netherlands (ECN), Petten, The Netherlands

Sorption-enhanced reactors combine catalytic reactions and CO2 separation in one reactor, and can improve CO2 capture efficiencies and reduce costs for pre-combustion CO2 capture. In sorption-enhanced reforming (SER) or water-gas shift (SEWGS) reactors, one of the products is extracted from the reaction zone, thus shifting the reaction equilibrium to the product side. In SER and SEWGS the SMR or WGS catalyst is mixed with a CO2 sorbent ("acceptor"). The CO2 produced during the reaction is adsorbed and the reverse reaction cannot occur. The two major sorbents examined for sorption-enhanced reforming are CaO-based materials and hydrotalcites, which will both be discussed in the presentation. Potassium-promoted hydrotalcite-based sorbents have been tested in the sorption-enhanced water-gas shift process. Experimental evidence shows that this sorbent can be regenerated by pressure-swing and is chemically stable for several thousand cycles. It was discovered that two CO2 adsorption process occur: a fast process possibly associated with a K-Al-carbonate active site and a slow process postulated to be caused by the formation of MgCO3. Strategies for sorbent improvement using these mechanistic insights will be highlighted.

FA-1.2:IL08 Designing New Microporous Framework Materials for CO2 Capture

Robert G. Bell*, Antonio Torrisi, Caroline Mellot-Draznieks, Department of Chemistry, University College London, London, UK

Microporous metal-organic framework (MOF) materials have attracted considerable interest due to their potential use in gas capture and separation technologies, as well as the huge variety of possible compositions and framework topologies. One method of enhancing the selectivity of a MOF towards CO2 is in incorporating organic linker molecules containing functional groups capable of specific interactions with CO2 molecules. In our work we have investigated the strength and nature of the intermolecular interactions between CO2 and a range of functionalised aromatic molecules using Density Functional Theory (DFT). Three classes of substituted benzene molecules were considered: (i) with halogen substituents, (ii) with methyl substituents and (iii) with polar substituents. The strongest interactions are with polar substituent groups, such as amino, nitro and sulphonate, where lone pair interactions and polarisation of CO2 dominate. With groups such as COOH and OH, cooperative hydrogen-bonding further enhances the binding energy. We have further proposed structural models for MOF materials containing such ligands, and characterised their behaviour towards CO2 sorption computationally using periodic DFT and Monte Carlo calculations.

FA-1.3 Thermal and Protective Coatings

FA-1.3:IL01 Self Diagnostic EB-PVD Thermal Barrier Coatings

John R. Nicholls[1]*, Richard G. Wellman[1], Remy Steenbakker[1], Joerg P. Feist[2], [1]Cranfield University, Cranfield, Bedford, UK; [2]STS Ltd, c/o Imperial College, London, UK

Thermal barrier coatings (TBCs) are an enabling materials technology to improve the efficiency and durability of gas turbines and thus through such efficiency improvements offer reduce fuel usage and an associated reduction in CO2 emission. This commercial drive is pushing both aero- and industrial turbines to be lifetime dependent on TBC performance - the TBC must be "prime reliant". However, the prediction of the durability of the TBC system has proved difficult, with lifetimes varying from sample to sample and component to component. One factor controlling this is the inability to measure accurately the bondcoat/ceramic interface temperature when buried under a TBC. In operating engines this is further exacerbated by the fact that such TBC systems operate in strong temperature gradients due to the need to cool aerofoil components. This research examines the design and manufacture of self diagnostic thermal barrier coatings capable of accurately measuring the interface temperature under the TBC, whilst providing the requisite thermal protection. Data on the temperature sensing capability of various rare earth doped EB-PVD thermal barrier coatings will be reported. It will be shown that systems exist capable of measuring temperatures in excess of 1300 °C. Details of the measurement method, the compositions and the thermal stability of such systems will be discussed in this paper. The ability to produce a sensing TBC capable of measuring interface temperature, surface temperature and heat flux will further be discussed permitting the design of thermal barrier protected components capable of in-situ performance monitoring.

FA-1.3:IL02 Development of Metallic and Ceramic Slurry Coatings for Materials in Severe Environments

B.L. Armstrong*, K.M. Cooley, J.J. Henry, L.R. Walker, B.A. Pint, Oak Ridge National Laboratory, Oak Ridge, TN, USA

Material loss caused by exposure to severe operating environments such as gasifiers, waste incinerators, and other advanced fossil power systems results in reduced service life and reliability and increased operating costs. This project aims to combine intelligent materials design with colloid science and coating technology to develop cost-effective materials and processes engineered for optimum performance and maximum service life. Lower cost and novel approaches of applying coatings to metals and ceramics are being explored to meet near-term goals. Thus, the development of coatings utilizing dip coating as a low-cost processing method is being pursued. Colloidal processing of material particles in suspension offers an economic and simple route to achieve uniform coatings on complex-shaped components. The issues of adhesion, uniformity, processing parameters on resulting phases, effective corrosion resistance in specified environments, and mechanical properties at use temperatures will be the technical challenges that must be addressed in order to prove feasibility. The ORNL process for the application of coatings on ferritic martensitic and austenitic alloys and ceramics will be discussed. This research was sponsored by US Department of Energy, Office of Fossil Energy.

FA-1.3:IL03 Inhibition of Interdiffusion in NiCrAlY Coated γ-TiAl by Introduction of a Yttria Partially Stabilized Zirconia(PYSZ) Layer

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γ-TiAl based alloys are candidate materials for many high-temperature structural applications. However their poor oxidation resistance at temperatures higher than 800 °C restrains their practical use. NiCrAlY can remarkably improve the oxidation resistance of TiAl by forming an external protective Al_2O_3 scale. The main disadvantage of NiCrAlY coatings is that the inward diffusion of Ni from NiCrAlY overlay coating to γ-TiAl substrate leads to the formation of brittle interlayers and then coating premature failure. This problem might be addressed by the introduction of a diffusion barrier between the coating and substrate to eliminate or greatly reduce the interdiffusion of alloying elements. However, a major problem in selecting a barrier is that the best adhesion is often obtained when there is some interdiffusion between the layers; this is what the barrier is trying to prevent. In this preliminary study, a thin 8wt% yttria partially stabilized zirconia(PYSZ) film was deposited by electron beam physical vapor deposition(EB-PVD) onto γ-TiAl substrates prior to depositing a NiCrAlY overlay coating. The effectiveness of the film in limiting interdiffusion was evaluated by oxidation at 1000 °C for various time in air. The results showed that the PYSZ film can induce the formation of two continuous Al-rich oxide layers at both the TiAl/PYSZ and PYSZ/NiCrAlY interfaces, providing a significant impediment to the inward diffusion of Ni from NiCrAlY overlay coating into the substrate.

FA-1.4 Long-term Creep and Fatigue

FA-1.4:IL01 Long-term Mechanical Stability in USC Steam Turbine Environments

J.A. Hawk, USDOE, NETL, Albany, OR, USA

In order to combat global warming, energy producers have looked towards USC and A-USC power plants to dramatically improve energy efficiency and reduce greenhouse gas emissions per unit of power delivered. This has required new materials be developed, such as the current generation of 9Cr steels, and in many cases the adaptation of other alloys, such as aerospace nickel alloys, for use in energy generation. This creates uncertainty in terms of long-term life of these materials as steam turbine components since experience with these alloys is limited, especially creep in excess of 100,000 hours at 620C. Current testing of 9Cr alloys show promise with laboratory tests reaching 100,000 hours. Nickel alloy testing at temperatures in excess of 700C, however, lag by comparison. The prospects of USC and A-USC turbines will be discussed with respect to potential alloys, strengthening potential and long-term microstructural stability. The potential for these alloys as steam turbine components will be assessed and representative results will be presented for the leading alloys in each instance.

FA-1.4:IL02 Degradation of Ni-Base Superalloys under High Temperature Creep Conditions

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During service in gas turbines the blade material microstructurally degrades under the influence of high temperatures and applied stresses. Therefore for reliable prediction of the blade lifetime this microstructural damage has to be considered. Improvement of lifetime prediction in turbine engineering was a target of European Action COST538 “High Temperature Plant Lifetime Extension” run in 2004-2008. The kinetics of microstructural degradation of the single-crystal nickel-base superalloy CMSX-4 was investigated under creep conditions in the temperature range 850-1100 °C. To cover a wide range of stress levels a new experimental technique was applied, namely repeated load annealing of flat wedge shaped specimens. The flat geometry allows non-destructive SEM investigations of the microstructure after each load annealing test, the wedge geometry to investigate the influence of stress in a single specimen. The results of metallographic investigation were introduced into the mechanical model, which consider the effect of microstructural degradation on the mechanical behaviour of CMSX-4.

FA-1.4:IL03 Creep Resistent Steels for Coal Power Plant Applications

R. Viswanathan, Electric Power Research Institute, Palo Alto, CA, USA

The world now faces the critical challenge of providing abundant, cheap electricity to meet the needs of a growing global population, while at the same time preserving the environment. Ultrasupercritical, high-efficiency coal-fired power plants could provide such electricity. Coal for electricity generation poses a unique set of challenges. On the one hand, coal is plentiful and available at low cost in much of the world, notably in the United States, China, and India. Countries with large coal reserves will want to develop them to foster economic growth and energy security. On the other hand, traditional methods of coal combustion emit pollutants and carbon dioxide at high levels relative to other generation options. Maintaining coal as an option will require methods for addressing these environmental issues. One of the options that has received great attention worldwide is the development of ultrasupercritical. high-efficiency coal-fired power plants. Their high efficiency reduces both fuel cost and emissions.) The efficiency of conventional boiler/steam turbine fossil power plants is a strong function of the steam temperature and pressure. Research to increase both has been pursued worldwide, since the energy crisis in the 1970s. The need to reduce CO_2 emissions has recently provided an additional incentive. The steam temperature of the most efficient fossil power plants are now in the 600 °C (1112°F) range, and is expected to each temperatures as high as 760C(1400F)within a decade. The key factor in achieving this goal is the availability of advanced materials that have adequate strength, fabricability and resistance to corrosion in steam and flue gas environments. This paper will review the state of the art with respect to materials related developments.

FA-1.5 Corrosion and Erosion

FA-1.5:IL01 Materials Performance in Advanced Steam Cycle and Oxy-fuel Combustion Systems

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The U.S. Department of Energy, Office of Fossil Energy is intensely promoting R&D of materials for advanced steam cycle systems and for oxy-fuel combustion systems. At Argonne National Laboratory, we have conducted studies to evaluate the corrosion performance of candidate structural alloys in coal-ash and in steam environments, in support of advanced steam cycle systems. The laboratory tests simulate the combustion atmosphere of advanced steam-cycle systems and three deposit chemistries that included ash constituents, alkali sulfates, and NaCl. Corrosion rate data will be presented for several Fe- and Ni-base alloys along with a mechanistic understanding of the corrosion processes. In the study on materials for oxy-fuel applications, we have evaluated the corrosion performance of the materials in CO2, steam, and in steam-CO2 mixtures. Information will be presented for materials exposed at temperatures between 650 and 950 °C for times up to 10,000 h. In the ongoing experiments, we have incorporated low levels of sulfur and chlorine compounds (in addition to CO2 and steam) in the exposure environment to establish the role of second/third reactant on the scaling, internal penetration, and long term performance of the structural alloys.

FA-1.5:IL02 **Modelling Solid Particle Erosion of Steels at Elevated Temperatures: A New Approach to CFD Modelling in 3-Dimensions**
M.M. Stack*, S.M. Abdelrahman, B.D Jana, Department of Mechanical Engineeering, University of Strathclyde, Glasgow, UK

Elevated temperature erosion of materials is a major issue in many energy conversion processes. In such cases, the wide range of variables and environments involved means that there are many possible regimes of interaction between the eroding particles and corrosive environment. Modelling such processes is thus approached with some difficulty. In studies of erosion-corrosion, a major advance has been the definition of various regimes of erosion-corrosion interaction. Such regimes may describe the mechanism of degradation and the extent to which a protective scale may enhance or inhibit the wastage rate. In aqueous environments, a further recent advance has been to superimpose such regimes on 3 dimensional components enabling in service piping experiencing erosion-corrosion to be mapped. In this work, a mathematical model for elevated temperature erosion in dry conditions has been developed for the Fe-Cr system. A CFD approach has been used used to map the erosion-corrosion regime transitions in dry conditions. The effects of the various erosion-corrosion parameters on the regime transitions, together with the advantages and limitations of such an approach, are described in this paper.

FA-1.5:IL03 **Important Compositional and Microstructural Factors Affecting the High-Temperature Degradation of Metallic Alloys and Coatings**
B. Gleeson, University of Pittsburgh, Dept. Mechanical Engineering & Materials Science, Pittsburgh, PA, USA

The surface of a material operating under aggressive, complex chemical environments tends to undergo reactions that scale with the severity of the environment.Protection of component surfaces against such reactions is crucial in many energy generation and storage technologies. Depending on exposure temperature and pressure, the necessary protective scales are typically Cr2O3, Al2O3 or SiO2.The rates at which these scales form are generally assumed to be parabolic (i.e., scale thickness is proportional to the square root of time); however, this is often an oversimplification that neglects the measurable contribution of the transient, initial oxidation stage and the evolution of the scale structure and phase constitution. As will be discussed in this presentation, it is well established that oxide formation on an alloy or coating surface is a function of numerous variables, including in particular the composition and microstructure (i.e., phase constitution, distribution and volume fractions) of the alloy or coating. This presentation will highlight some important subtleties of composition and microstructure on high-temperature degradation, with the aim of providing guidance on alloy and coating design.

FA-1.5:L04 **Electrochemical Investigation on Hot Corrosion of Inconel 740 Alloy in Simulated Coal Ash Environment**
Yinglu Jiang, Xingbo Liu*, Mechanical & Aerospace Engineering Department, West Virginia University, Morgantown, WV, USA

Increasing the temperature and pressure in a coal-based boiler/steam turbine system will increases the efficiency of the Rankine steam cycle used in power generation, which will also lead to the beneficial effects of reducing the amount of fossil fuel consumed and the emissions generated. However, hot corrosion of furnace boiler tubes, recuperator tubes, and other components has been one of major challenges to the development of next generation power systems. Although it has been well accepted that hot corrosion is electrochemical in nature because generally fused salts are electrolytic conductors and alloys are good electronic conductors, there has been very few electrochemical investigations on this topic. In this paper, we reported our high temperature electrochemical study on Inconel 740 alloy in simulated coal ash environments. The unique character of this research is the application of the high temperature stable reference electrode recently developed in our lab, which allows us to obtain reliable and repeatable electrochemical information of the corrosion reaction in the system. The results of polarization, CV and EIS will be presented and the mechanisms of hot corrosion will be discussed.

Session FA-2
Gasification and Gas Clean-up

FA-2.1 Catalysts for Water-gas Shift and for Fuel Production

FA-2.1:IL01 **New Ways of Understanding Site Structure and Function in Fuel Production Catalysts**
Jerry P.H. Li, Ibrahim Suleiman, Andrew Stafford, Michael Stockenhuber*, University of Newcastle, Chemical Engineering, Priority Research Centre for Energy, Callaghan, NSW, Australia

Despite the widespread use of zeolites and other solid catalysts in a number of chemical process applications relatively little is known of the fundamental changes that occur upon interaction of reactants with catalyst surfaces. These materials are widely used in fuel processing applications starting from fluid catalytic cracking to isomerisation to production of oxygenated additives. Small selectivity and activity improvements through rational catalyst design will result in significant cost savings and process improvements. Thus a good understanding of the influence of processes on materials is of extreme importance. In this paper we show some recent results on how to evaluate the changes of the catalytically active site under reaction conditions. The only current available method to determine the structure of irregular, little defined catalytically active sites under in situ conditions is X-ray absorption spectroscopy. A number of different systems have been investigated including solid acids and redox active catalysts. The catalytic activity of the catalysts is correlated with structural parameters that help us to understand structure function - relationships of currently used materials and catalytic systems which will enable a more rational design of new catalysts.

FA-2.1:IL02 **Water Gas Shift Reaction: From Conventional Catalytic Systems to Pd-based Membrane Reactors**
A. Basile*, A. Iulianelli, ITM-CNR, University of Calabria, Rende (CS), Italy

The water-gas shift reaction (WGSR) is conventionally performed in traditional reactors for upgrading carbon monoxide to hydrogen in the production of synthesis gas. In the last decades, a growing interest towards WGSR carried out in H2 perm-selective membrane reactors (MRs) has been observed owing to the use of PEM fuel cells, which need to be fed with high purity H2. Furthermore, MRs represent an alternative technology able to overcome the equilibrium conversion limitations of TRs. In particular, the MR combines two distinct scientific aspects: catalysis and membranes. The catalyst is certainly an important key factor for improving the performances of MRs, with particular reference to H2 production, e.g. fulfilling the requirements for the integration of fuel processors with PEM fuel cells. However, a large number of studies on water gas shift reaction performed in MRs is present in the specialized literature, but only few of them concern cost analysis of these devices. This could be due to the fact that MR technology still presents some deficiencies to be overcome before implementation at larger scales. An important issue concerning MRs consists of the effect of impurities on dense metallic membranes. In this presentation, the advantages in using MRs will be discussed.

FA-2.1:IL03 **Reactors with Integrated Separation by Membranes**
O. Görke, J. Thormann, P. Piermartini, P. Pfeifer, R. Dittmeyer*, Institute for Micro Process Engineering (IMVT), Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany

Membrane reactors for hydrocarbon reforming and water gas shift are complex in terms of the design of materials, components and their integration into one single unit. Harvesting the expected synergy from combining hydrogen generation with its in situ extraction requires a good match of the hydrogen production and permeation rates per volume. For microreactors, leak tight integration of metallic membranes in combination with catalyst coatings in the reaction zone is one of the big challenges. Microreactors on the other hand offer unique advantages such as very fast heat and mass transfer so that both reaction and separation may be significantly enhanced. And, due to the stacked planar design of microreactors and the small dimensions of the microchannels the required membrane area per unit volume is minimized and very compact reactors become possible. The contribution will summarize approaches to membrane reactors for hydrocarbon reforming and water gas shift followed in our own investigations in comparison to literature studies. It will give an overview and highlight important aspects of membrane fabrication, novel catalyst coatings based on techniques like sol-gel and nanoparticles integration, reactor design for e.g. diffusion bonding or laser welding and combined testing.

FA-2.2 Membranes for H_2 Separation and CO_2-selective Membranes

FA-2.2:IL01 **Carbon Molecular Sieve Membranes for H2 - CO2 Separation**

May-Britt Hägg*, Jon Arvid Lie, Qiang Yu, Dep. Chem. Eng., Norwegian University of Science and Technology, Trondheim, Norway

Carbon Molecular Sieve membranes (CMSM) are prepared from polymeric precursor material under controlled pyrolysis conditions such as final temperature, soak time, heating rate and type of inert gas for purge. By control of these variables and also type of precursor material, pores can be tailored to a very fine degree to be suitable for separation by molecular sieving. For the separation of H2 in a mixture with CO2, this means as a general rule that H2 will permeate from high pressure side to low pressure side while the larger molecule CO2 is being retained on the feed side of the membrane. Selectivities higher than 50 in favour of H2 have been documented at higher temperatures by using a CMS-membrane for such a gas mixture. The purity of the permeated H2 can easily be around 96%. For a fuel cell in need of high purity H2, a process solution with a Pd-membrane upgrading the H2 further to 100% may be suggested. The CMS-membrane is very stable and tolerant to other chemical impurities, but is vulnerable to high water vapour content in the gas mixture. By regeneration the membrane separation performance may, however, be recovered. The presentation will cover the preparation of CMS-membranes and report on obtained separation performance for H2-CO2 mixtures.

FA-2.2:IL02 **Synthesis and Characterization of Zeolite and Nanophase Ceramic Membranes for High Temperature Applications**

A. Julbe*, A. Ayral, V. Rouessac, S. Roualdes, Institut Européen des Membranes, Université Montpellier 2, Montpellier, France

Many emerging membrane applications are related to clean energy delivery technologies, e.g. for the separation, treatment and/or filtration of gases at high temperature. For these applications meso-, micro-porous or quasi-dense ceramic & composite membranes are typically required, with specific transport properties, with high thermal and chemical stability and sometimes with coupled functionalities such as separation & catalytic activity, adsorption or electrochemical properties. In this very challenging background, where industrial requirements are heavy, original membrane designs and new synthesis strategies could provide significant breakthrough. Several strategies are currently considered in our group. They are either related to the design of complex architectures or to the development of new reaction pathways influencing membrane material formation, such as those involving supercritical solvents, surfactant self-assembling, microwave-assisted methods or plasma-enhanced CVD. In this presentation examples will be given, related to the preparation and characterization of original zeolite, nanophase and plasma derived ceramic membranes designed for high temperature applications.

FA-2.2:IL03 **Non-Pd Alloy Membranes for H2/CO2 Separation**

Michael D. Dolan, CSIRO Energy Technology, Brisbane, QLD, Australia

For H2 separation from mixed gas streams produced by fossil fuel conversion (e.g., CO conversion and steam reforming), alloy membranes based on Pd are a reliable technology, but the high cost and limited reserves of Pd is driving the development of membranes that contain little or no Pd. In response, many groups are now developing membranes formed primarily from inexpensive transition metals. Body-centred cubic alloys, and amorphous alloys formed by rapid quenching, show promise as Pd-alternatives because the solubility of H2 in these materials is many times greater than that of Pd. As hydrogen embrittlement, however, is exacerbated by high concentrations of dissolved H, these materials are also less robust than Pd alloys under typical operating conditions. In order to meet future performance targets, non-Pd alloy membranes must balance the hydrogen flux and mechanical properties. Furthermore, given the scale on which membranes must be deployed for low-emissions power generation, consideration must be given to the methods by which these membranes will be mass-produced. The strategies being employed to achieve the balance between performance and durability will be discussed, which include alloying to reduce hydrogen solubility, multi-phase alloys and layered composites.

FA-2.2:IL04 **First Principles Calculations of Hydrogen Diffusion in Metal Hydrides, Metal Alloys, and Amorphous Metals**

David S. Sholl*, Shiqiang Hao, School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA, USA

The diffusion of hydrogen in solids plays a key role in both the storage and purification of hydrogen. First principles calculations continue to play a useful role in understanding the fundamental mechanisms of these diffusion processes. We will show that first principles calculations can be used to quantitatively describe hydrogen solubility and diffusion in amorphous metals, and that this information is being used to design high performance membranes for high temperature hydrogen purification. We will also discuss the mechanisms of hydrogen diffusion in light metal hydrides and borohydrides. In these wide band gap materials, charged states play an important role in diffusion, and understanding these states introduces interesting opportunities for enhancing hydrogen diffusion kinetics via doping.

FA-2.2:IL05 **Ceramic Membranes in Carbon Dioxide Capture: Applications and Potentialities**

Enrico Drioli[1, 2]*, Adele Brunetti[1], Giuseppe Barbieri[1], [1]ITM-CNR, c/o The University of Calabria, Rende (CS), Italy; [2]The University of Calabria, Department of Chemical Engineering and Materials, Rende (CS), Italy

Today, CO2 capture from flue gas has becoming an emerging opportunity for membrane gas separation. The flue gas coming out from power plants contains about 13% CO2, which should be separated before its sequestration. The most used membranes for this application are polymeric but they cannot be used at high temperature. The flue gas exits at ca. 200 °C, depending on the specific locations in the plant and, thus, it is highly desirable to separate it at high temperature[1]. An alternative class to polymeric membranes is represented by the ceramic one which comprise zeolites, carbons, silica, perovskites membranes[2, 3], that exhibit high fluxes and thermal resistance. However, a big challenge is to fabricate them as thin membranes, avoiding formation of cracks that compromise the separation. Today, new hybrid membranes able to combine the properties of different materials are proposed. Moreover, new works are done on mixed-matrix membranes, comprising of a molecular sieve guest phase dispersed in a polymer host matrix[3] which combine the advantage offered by the two materials.

[1]R.W. Baker, Ind. Eng. Chem. Res. 41 (2002) 1393; [2]W.J. Koros, R. Mahajan, J. Membr. Sci. 175 (2000) 181; [3]P. Bernardo, E. Drioli, G. Golemme, Ind. Eng. Chem. Res. DOI: 10.1021/ie8019032

FA-2.2:IL06 **High Temperature Polymer-based Membranes for Hydrogen Purification and Carbon Capture**

K.A. Berchtold*, K.W. Dudeck, R.P. Singh, D. Ortiz-Acosta, C.F. Welch, B.M. Patterson, Los Alamos National Laboratory, Los Alamos, NM, USA

Separation of H2 from shifted syngas is a highly utilized industrial unit operation with an ever growing demand for use and, correspondingly, an ever growing demand for a more energy efficient and technically viable means for conducting these separations. Syngas is used as a product fuel, a BTU source for power generation, or a chemical intermediate for chemicals/fuels production. To be technically and economically viable, a successful separation method must be applicable to industrially relevant gas streams at realistic temperatures and pressures as well as be compatible with large gas volumes. Our project team is developing polymer membranes based on polybenzimidazole (PBI) chemistries that can purify hydrogen and capture CO2 while meeting these demands. We are focused on developing and demonstrating membrane chemistries, structures, deployment platforms, and sealing technologies that achieve the critical combination of high selectivity, high permeability, chemical stability, and mechanical stability all at elevated temperatures (>150 °C) and all packaged in a scalable, economically viable, high area density system amenable to incorporation into processes such as an advanced Integrated Gasification Combined-Cycle (IGCC) plant for H2 purification and pre-combustion CO2 capture.

FA-2.2:IL07 **PdCu Membranes for Hydrogen Separation: Stability and Application Ranges**

A. Goldbach*, L.X. Yuan, H.Y. Xu, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, P.R. China

PdCu membranes attract much attention because of their low-temperature stability and sulfur tolerance, which renders them interesting for applications ranging from small-scale H2 purification for fuel cells to CO2 capture in industrial power plants. However, the PdCu phase diagram includes bcc and fcc structures below 600 °C that are separated by miscibility gaps. The optimum bcc Pd47Cu53 alloy is only stable up to 450 °C as it borders to a gap, and its H2 permeability declines fast, if the alloy composition deviates only by a few at%. Excursions into the gap due to overheating lead to structural and compositional heterogeneity[1]. This inhomogeneity is irreversible at practical membrane operation temperatures and it can trigger a loss of membrane integrity as a result of uneven expansion of fcc and bcc domains during charging and discharging of H2, because the H2 uptake of fcc and bcc PdCu phases varies by orders of magnitude. Eventually fissures appear between those domains, which can compromise the membranes permselectivity. This structure-related instability must be also taken into consideration if ultra-thin PdCu membranes are prepared by electroless plating[2].

[1]L. Yuan et al, J. Phys. Chem. B 111 (2007) 10952; [2]L. Yuan et al, J. Membr. Sci. 322 (2008) 39.

FA-2.2:IL08 **Computational Design of Pd-based Alloys for Membranes for Hydrogen Gas Separation**

A.J. Böttger*, D.E. Nanu, Delft University of Technology, Materials Science and Engineering, Delft, The Netherlands

The production of high-purity hydrogen requires membrane materials that can withstand elevated temperatures and pressures. Defect-free metal-based membranes are most suitable. However, the lifetime of existing metal-membranes is insufficient. Mechanical degradation is caused by the large (up to 10% in pure Pd) specific volume increase upon the alpha (low H content) to beta hydride phase transition. Adding alloying elements to Pd modifies the phase stability range, affects the volume differences between the alpha and beta phase and also could lead to order-disorder transitions. Recently, we developed a computational method that can predict the alpha/beta phase stability range and critical temperature as a function of the composition of the metal-matrix and the hydrogen content. The method is based on statistical thermodynamics and includes possible order-disorder transitions and volume changes. In this presentation we describe the principles of this method and illustrate its potential for application to design new, multi-component metal-based membrane materials of high thermal and mechanical stability that meet criteria such as: a critical temperature for hydride formation below operating conditions and high hydrogen solubility.

FA-2.3 High Temperature Seals

FA-2.3:IL01 **High Temperature Seals for Membrane Reactor Modules**

R. Donelson*, CSIRO, Melbourne, Victoria, Australia; M. Dolan, CSIRO Pullenvale, Queensland, Australia

Sealing of high temperature, metallic hydrogen-separation membranes can present a number of challenges. Amorphous metal membranes are especially problematic because of the performance degradation that occurs if the membranes are heated to the point where they become crystalline. This led us to conclude that a compression seal configuration would be preferred over thermal joining processes such as brazing and welding. The basis for this work was a membrane reactor where amorphous metal membranes were in close proximity to a reforming catalyst bed. Seal development included mechanical design and material selection. Furthermore, both gasket and O-ring were considered, and FEA was used to assess the uniformity of compression in candidate configurations. The seal materials under consideration included transition metals, noble metals and alloys. A number of promising results were obtained; the specifics of compression seal designs are described and the results of testing are presented.

FA-2.3:IL02 **Development of Friction Stir Welding Technology High-temperature Power Generation Applications**

K.S. Weil*, G.J. Grant, Y. Hovanski, J.T. Darsell, Pacific Northwest National Laboratory, Richland, WA, USA

Most ferritic/martensitic steels used in coal and nuclear plant applications are limited to operating temperatures of <600 °C due to an inevitable degradation in both tensile and creep strength. While the addition of insoluble, nanoscale oxide dispersoids greatly improves the high-temperature mechanical properties of these alloys, it can also make them more difficult to join into large-scale componentry, e.g. headers and pipes within the steam generator. Liquid phase methods of joining such as brazing and fusion welding lead to regions within the joints that are devoid of the dispersoids and the associated strengthening effects, making the joined components susceptible to failure by creep. Friction stir welding is a solid-state joining technique that has shown promise in joining hard-to-weld materials such as oxide dispersion strengthened alloys in coupon-size specimens. As will be discussed, our work is focused on translating the technology to larger scale plate and pipe joining, evaluating possible tools for thick section welds, and developing methods of weld qualification based on in-situ measurements of weld tool force.

Poster Presentations

FA:P01 **Comparison of High Temperature Mechanical Behaviour and Microstructure of the New Gamma-TiAl8Ta with Gamma-TiAl8Nb Alloy**

G. Angella, V. Lupinc, M. Maldini, G. Onofrio*, CNR-IENI, Milano, Italy

The high temperature mechanical properties of two gamma-TiAl base intermetallic alloys for gas turbine components, have been investigated within the Integrated European project IMPRESS. The alloys contain 8% at. Ta or Nb, respectively. The microstructure of both alloys was crossed convoluted lamellar rather than the well known conventional lamellar, typical of the usual gamma-TiAl. The microstructure of the Ta alloy was much more homogeneous than that of the Nb alloy. The creep properties of the alloys were investigated in the temperature range 700-850 °C with applied stresses in order to have times to rupture up to about 3000 h. The Ta alloy resulted more creep resistant than the Nb alloy. In low cycle fatigue at 650 and 700 °C the Ta gamma-TiAl showed longer lives than the Nb alloy, whilst the fatigue crack propagation behaviour did not show any significant influence of the chemical composition. The microstructures of the two alloys were analysed by scanning and transmission electron microscopy in order to rationalise the different mechanical behaviour.

FA:P02 **Elaboration and Characterization of the Properties of Refractory Cr Base Alloys**

Laurent Royer[1], Stéphane Mathieu[1], Pierre Steinmetz[1]*, Christophe Liebaut[2], [1]Institut Jean Lamour, Faculté Des Sciences et Techniques, Vandoeuvre Cedex, France; [2]SEVA, Chalon-Sur-Saone Cedex, France

For energy production and also for the glass industry, finding new Refractory alloys which could permit to increase the process temperatures to 1200 °C or more is a permanent challenge. Three main criteria must be satisfied for these alloys: to evidence a good resistance to HT oxidation and to corrosion by molten glass/salts and have good HT mechanical properties, especially for rotating parts. Chromium base alloys can be good candidates, considering the melting point of Cr itself, and also its low corrosion rate in molten glass. The main problem is however to find a good combination with alloying elements, which can limit catastrophic oxidation/nitridation of chromium by air, and also increase the mechanical properties up to values which could be compatible with an industrial use. Two families of alloys have been extensively studied for this purpose, Cr-Mo-W and Cr-Ta-X alloys (X= Mo, Si..). A finer selection of compositions has been done, to optimize their chemical and mechanical properties. Kinetics of HT oxidation by air, of corrosion by molten glass and also creep properties of several alloys have been measured up to 1250°C. The results obtained with the best alloys (Cr-Ta base) give positive indications as regards the possibility of their industrial use.

FA:P03 **Hydrogen Uptake and Hydrogen Profiles in Chromia Scales Formed in High and Low pO_2 Test Gases at 1000 °C**

L. Garcia-Fresnillo, S.L. Tobing, M. Hänsel*, V. Shemet, U. Breuer, L. Singheiser, W.J. Quadakkers, Forschungszentrum Jülich, IEF-2, Jülich, Germany

Various chromia forming materials have been exposed to different test gases with high and low pO_2. All the used test gases contained hydrogen species either in the form of molecular hydrogen and/or water vapour. To insure the validity of the measured H-profiles H_2 was replaced by with D_2 and H_2O by D_2O. The Deuterium profiles in the oxides formed were established using SIMS and GDOES techniques. The profiles were quantified and correlated with the growth rate and the microstructures of the chromia scales formed on the various materials in the high and low pO_2 test gases. A defect model is employed to explain the effect of hydrogen and/or water vapour on chromia growth in high and low pO_2 test gases.

This work has been sponsored by AMATECH (AMA Technological Solutions Ltd.), FAPEMIG and CNPq - Brazil.

FA:P06 **Effects of Firing Conditions on the Coal Ash Melting Behaviour**

D. Montinaro*, G. Di Salvia, M. Malavasi, ITEA SpA, Gioia del Colle, Italy; G. Amante, A. Chiechi, A. Licciulli, Università del Salento, Dipartimento Ingegneria dell'Innovazione, Lecce, Italy

Pressurized oxy-fuel combustion, provides a way of separating all of the CO2 emissions produced by coal combustion. Itea SpA, a start-up Italian company acquired by Sofinter group, developed the Isotherm Pwr® Flameless Oxy-Combustion technology which produces low-cost energy by a flexible use of different fuels such as waste, heavy oils, and coal. Main advantages of the Isotherm Pwr® with respect to older coal combustion technologies are the reduced particulate emissions and the production of an high quality CO2 stream, ready for sequestration. The high and homogenous temperature reached in the reactor allows the high efficient combustion of organics, while the inorganic species are converted into a vitrified slag. Knowledge of the coal ash melting behaviour under the typical oxy-combustion conditions is of key importance for process optimizations. In the present work, the melting behaviour of coal ashes with different compositions were investigated. Shape transformations of ash specimens heated under controlled gas atmospheres were monitored by a digital camera. Different conditions were observed to affect the determination of characteristic melting temperatures and such effects were correlated to the ash chemical composition and to the occurrence of different mineral phases.

FA:P07 **Viscosity Under Pressure Mixtures of Hydrocarbons: A Critical Model Reported Double Reference**
A. Ettahir[1]*, C. Boned[2], B. Lagourette[2], [1]Laboratoire de l'énergétique, des matériaux et de l'Environnement, EST Salé, Université Mohammed V Agdal, Rabat-Salé, Maroc; [2]LFC Université de Pau, France

The predictive model of viscosimetric behaviour we studied is that of K A. Petersen. The dominant idea of this method is to characterize the viscosity of a fluid from two others taken as a reference in passing through a reduced pressure, i.e. a method of corresponding states with twin references torque. This study shows that this method is dependent on the choice of reference torque and for each of the possibilities of double C10/C6H6 references C1/C10. We reviewed the results for four different weight ratios. Results show that the introduction of an adjusted coefficient does not improve results significantly compared with the method without adjustment factor, which appears to be the best choice. Regarding the influence of the choice of references, generally the two torque appears suitable but we note that the choice is not indifferent. In the case of mixtures containing at least one aromatic, the results are correct, especially if one takes the ratio with adjustment and our ratio without adjustment compared to that of K.A. Petersen. The viscosity calculated for some ternary, quaternary and mixed heavy component are close to the experimental values.

Symposium FB

MATERIALS AND PROCESS INNOVATIONS IN HYDROGEN PRODUCTION AND STORAGE

Oral Presentations

Session FB-1
Hydrogen Production

FB-1.1 Thermochemical H_2 Production

FB-1.1:IL01 **State-of-the-art of Thermo-chemical Hydrogen Production**
Jay Keller, Hydrogen and Combustion Technologies, Sandia National Laboratories, Livermore, CA, USA

Solar and nuclear power are sustainable long-term energy options and thermo-chemical water splitting hydrogen production is potentially an efficient approach for producing hydrogen. Thermo-chemical water splitting produces hydrogen using only water, heat from the sun or nuclear power, and chemicals that are completely re-cycled. Thermo-chemical water splitting is a technically feasible process with at least one demonstration project in operation in Japan based on the sulfur-iodine cycle and powered by a nuclear thermal source. This presentation will discuss the current state-of-the-art for thermo-chemical production of hydrogen using high temperature heat from concentrated solar or nuclear energy.

FB-1.1:IL02 **Hydrogen Production by the Thermochemical Cycle Based on Mixed Na-Mn Ferrites**
C. Alvani, A. La Barbera, F. Padella, F. Varsano*, ENEA - C.R. Casaccia, Rome, Italy

Water splitting thermochemical cycles (TC) are sequences of chemical reactions that are able to split water into its elemental constituents and successively to regenerate starting reactants without any supply of external matter. Feeding TC using renewable energy sources such as concentrated solar heat permits to hypothesize a way to produce a sustainable fuel and to implement a necessary tile toward the coming " hydrogen economy". The mixed sodium manganese ferrite cycle for hydrogen production is a metal-oxide based reaction sequence described according to the following schemes:

2MnFe2O4+3Na2CO3+H2O = 6Na(Mn1/3Fe2/3)O2+3CO2+H2 (1)
6Na(Mn1/3Fe2/3)O2+3CO2 = 2MnFe2O4+3Na2CO3+½O2 (2)

The cycle has been extensively studied by the authors and the obtained experimental results are here reported and discussed, outlining the influence of ceramic reactants on the reaction (1, 2) sequence. When properly processed, the mixed oxides are able to cyclically produce hydrogen and be regenerated at a constant temperature value as low as 750 °C, in contrast to other metal oxide-based TC operating in the 1000-1600 °C range.

FB-1.1:IL03 **Two-step Thermochemical Cycles for High-temperature Solar Hydrogen Production**
Tatsuya Kodama, Department of Chemistry & Chemical Engineering, Faculty of Engineering, Niigata University, Niigata, Japan

The greatly insolated "sun-belt" regions of the world include the South-western USA, southern Europe, north Africa, etc. The reflection and concentration of direct insolation can be achieved by sun-tracking mirrors called collectors or heliostats. The concentrated solar radiation is focused upon a solar receiver/reactor where maximum temperatures can reach 1500 °C. The concentrated solar high-temperature heat has the potential to produce hydrogen from water thermochemically. A two-step thermochemical water splitting by iron-oxide redox pair is one of the most promising cycles, and proceeds as follows:

Fe3O4 → 3FeO + 1/2O2
H2O + 3FeO → Fe3O4 + H2

However, the cycle requires heat above 1500K minimum. This provides a challenge to "windowed" solar reactor concepts, such as a monolithic type (Europe), a foam-type (Japan), a Rotating-Ring type (USA), and internally-circulating fluidized bed (Japan)reactors. In these reactors, the kinetics of the reactions must be an important key factor. Thus, further development of active redox materials will have a very large impact on the improvement of these reactors. The most active working materials of "zirconia-supported ferrites" are developed by Niigata University. This paper reviews the solar two-step thermochemical water-splitting cycles.

FB-1.1:L04 **Coupling a Biomass Gasification Plant with the NIS Thermochemical Cycle for Hydrogen Production**
Pier Paolo Prosini*, Giampaolo Caputo, Alberto Giaconia, Salvatore Sau, ENEA, Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Roma, Italy

Thermochemical water-splitting cycles (TWSC) are promising solution to the challenging objective of hydrogen production from water and renewable energy sources. Recently we patented a new thermochemical cycle (the NIS cycle) making use of Ni/NiI2/NiO/NiSO4 as recycling agents, where hydrogen is directly generated by the reaction of nickel metal with sulphuric acid. Originally developed to be powered with solar energy, the NIS cycle can be coupled with other heat sources. Waste heat from biomass gasification plant for electricity production can be used to power the cycle. The research activities are mainly focused on engineering issues regarding the coupling with the heat source, the equipment design and the efficiency improvements. In the talk the basic reactions of the cycle will be illustrated and its coupling with a biomass gasification plant for hydrogen and electric energy production discussed.

FB-1.2 Photoelectrochemical and Photobiological H_2 Production

FB-1.2:IL01 **Development of Photocatalysts for Water Splitting Under Visible Light**

Kazunari Domen, School of Engineering, The University of Tokyo, Tokyo, Japan

Hydrogen production on semiconductor photocatalyst by water splitting is an attractive method for the storage of sunlight energy. Although numerous studies have been performed, most of the results remain in the use of wide-gap materials requiring UV light irradiation. Various narrow gap semiconductors have been examined for the utilization of visible light in photocatalysis. The authors have developed some metal nitrides and oxynitrides as visible light-responsive photocatalysts. Visible light water photolysis was achieved based on two quaternary oxynitrides consisting of Zn-Ga-O-N and Zn-Ge-O-N. Although these materials decompose water under visible light irradiation, the usable wavelengths of light are limited to below ca. 500 nm because of their band gap energy. On the other hand, some transition metal nitrides based on Ti4+ and Ta5+ were found to have optical absorption edges around 600 nm with inherent potentials of H2 and O2 evolution. These are the next target group of photocatalysts which extend the usable wavelength of light. Various approaches to improve the photocatalytic performance of metal oxynitrides will be reported in the presentation.

FB-1.2:IL03 **Photoelectrochemistry of Complex Metal Oxides**

R. van de Krol, Department DelftChemTech / Materials for Energy Conversion and Storage, Delft University of Technology, Delft, The Netherlands

Solar water splitting with a monolithic device based on low-cost metal oxide semiconductors is an attractive route towards sustainable hydrogen production. The key challenge for such a photo-electrochemical device is to find semiconducting materials that combine good chemical stability with high visible light absorption. Research efforts in this area have recently started to shift from simple binary oxides towards more complex ternary oxides. We will discuss recent results on InVO4 and BiVO4. In contrast to previous reports, InVO4 is found to have a relatively large bandgap of 3.2 eV. The visible light absorption of InVO4 is due to the presence of deep donor states, which explains the large differences observed between powders and thin films of InVO4 (Enache et al. J. Phys. Chem. C, in press). For BiVO4, electron transport was found to limit the photoelectrochemical performance. By doping with W and tailoring the interface, the quantum efficiency of BiVO4 could be increased with a factor of 5. The role of ionic point defects in these materials will be discussed, and some guidelines for the design of efficient complex oxide photoelectrodes will be given.

FB-1.2:IL04 **Hybrid Assemblies for Solar-driven Hydrogen Production**

K. Brown, D. Svedruzic, J. Blackburn, S. Dayal, G. Rumbles, M.L. Ghirardi, P.W. King*, National Renewable Energy Laboratory, Golden, CO, USA; M. Heben, University of Toledo, Toledo, OH, USA

Photosynthetic conversion of solar energy into chemical bonds can be reproduced artificially by linking catalysts directly to photoactive nanomaterials. Higher conversion efficiencies are possible from materials with band-gap energies in the visible, and devices that avoid efficiency losses from multiple electrochemical reactions. Our investigations are examining hybrid molecular assemblies composed of hydrogenase and single-walled carbon nanotubes (SWNTs) or semiconducting nanocrystals (nc-CdTe). Hydrogenase mixed with SWNT or nc-CdTe results in self-assembly of functionally stable complexes. Charge-transfer in SWNT assemblies was observed as changes in SWNT PL and Raman spectra, and changes in the oxygen inactivation kinetics of the hydrogenase. These results are summarized in models of both SWNT electronic structure and hydrogenase redox state. For nc-CdTe-hydrogenase, charge-transfer was observed in the nc-CdTe PL spectra and the photocatalytic production of hydrogen. Under illumination, nc-CdTe-hydrogenase stabilities and photocatalytic activities were dependent on ionic strength, pH, donor redox levels and donor concentrations. Recent progress in these studies towards developing nanostructured electrodes and photocatalytic hybrid molecular assemblies will be discussed.

FB-1.2:IL05 **Bio-inspired Approaches to Solar Hydrogen Production**

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Photosynthesis begins with absorption of sunlight, transfer of excitation to a reaction center, and use of this energy to move an electron from a donor to an acceptor, creating a charge-separated state that preserves some of the photon energy as electrochemical potential. Later steps use the stored potential to synthesize fuels such as carbohydrate or hydrogen gas. Chemists can design and prepare artificial systems that use the basic chemistry of photosynthesis to harvest solar energy. Some of these rival natural photosynthesis in the ability to produce long-lived, energetic charge separated states with quantum yields of unity. In order to use this electrochemical energy for hydrogen production via water splitting, catalysts for water oxidation and hydrogen ion reduction must be found and interfaced to the artificial reaction centers. Ideal catalysts will have low overpotentials, be constructed from earth-abundant elements, and be stable enough for practical use. Biology produces such catalysts, and they can serve as inspiration for technological analogs.

FB-1.3 H_2 Production from Biomass Reforming, Electrolysis and Water-gas Shift in Advanced Coal Gasification

FB-1.3:IL01 **Materials Issues in High Temperature Solid-oxide Electrolyzers for Large-scale Efficient Hydrogen Production**

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The materials and fabrication technology that are used for high temperature solid oxide fuel cells (SOFC) are directly applicable to high temperature solid oxide electrolysis cells (SOEC). Ceramatec, in collaboration with Idaho National Laboratory under the DOE Nuclear Hydrogen Initiative has tested SOEC cells and stacks of various hydrogen production rates up to 5,700 NL/hr using SOFC materials set developed at Ceramatec. Long-term performance stability issues are found to be largely materials related. Some potential causes for degradation are common to SOFC device operation while others are unique to SOEC mode of operation. The dominant degradation mechanisms are related to electrolyte phase stability, interface delamination, in particular for the oxygen evolution electrode, deposition of species at electrochemical sites to cause electrode poisoning and phase instability, and oxidation of metallic components in high temperature, high steam conditions. Under a project funded by the Office of Naval Research, Sc-stabilized zirconia electrolyte, new electrode materials set (cobalt-ferrite in place of manganite) and spinel protective coatings on interconnects to reduce chromium evaporation are evaluated. These materials changes are found to improve stack stability significantly.

FB-1.3:IL02 **High Temperature Water Electrolysis Using Metal Supported Solid Oxide Electrolyzer Cells (SOEC)**

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Metal supported cells developed at DLR for use as solid oxide fuel cells by applying plasma deposition technologies were investigated in operation of high temperature steam electrolysis. The cells consisted of a porous ferritic steel support, a diffusion barrier layer, a Ni/YSZ fuel electrode, a YSZ electrolyte and a LSCF oxygen electrode. During fuel cell and electrolysis operation the cells were electrochemically characterized by means of i-V characteristics and electrochemical impedance spectroscopy including a long-term test over 2000 hours. During electrolysis operation at 850 °C a cell voltage of 1.28 V was achieved at a current density of -1.0 Acm-2; at 800 °C the cell voltage was 1.40 V at the same operating conditions. The impedance spectra revealed a significantly enhanced polarization resistance during electrolysis operation compared to fuel cell operation which was mainly attributed to the hydrogen electrode. During a long-term test run of a single cell over 2000 hours a degradation rate of 3.2%/1000 hours was observed for operation with steam content of 43% at 800 °C and a current density of -0.3 Acm-2. Testing of a single repeating unit proved that a good contacting of the cell and metallic interconnect is of major importance to achieve good performance.

FB-1.3:IL04 **Catalysts and Syngas Treatment for Water-gas Shift in Advanced Coal Gasification Cycles**

David L. King*, Liyu Li, Corinne Valkenburg, Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA, USA

Synthesis gas generated via coal gasification finds application in power generation, fuels and chemicals synthesis, and hydrogen production. Shifting the syngas (water-gas-shift) to obtain H2/CO ratios appropriate for a specific application, to minimize CO concentration, or to facilitate CO2 capture is a key element of syngas processing. Use of sulfur tolerant sour shift catalysts, based on sulfide supported cobalt-molybdenum oxides, is an important strategy for the cost-effective primary adjustment of CO when significant levels of H2S are present (such as with coal-derived syngas). Further treatment of CO, to fine tune the H2/CO ratio or minimize CO concentration, is then challenged by the reduced activity of sour shift catalysts at lower temperatures. In these cases, acid gas removal is employed to meet the stringent requirements of low temperature sweet shift catalysts. This approach comes with high energy cost. Improving the effectiveness of water gas shift is not simply a matter of improved catalyst compositions. Novel strategies are incorporating hot gas cleanup and sorbent-based hot CO2 capture to achieve desired synthesis gas compositions. This presentation will review syngas processing approaches including advanced concepts for the enhancement of water gas shift.

FB-1.3:IL05 **Combined Hydrogen and Power Production from Coal**

Giuseppe Spazzafumo, University of Cassino, Cassino, Italy

Most of the renewable energy sources, as well as nuclear energy, are more suitable to produce electrical power than fuels. On the other hand the final use of energy is mainly in the form of a fuel. Hydrogen can be produced both from electrical power and from fossil fuels, but the global conversion efficiency is higher when a fossil fuel is used as a primary energy source. While oil and natural gas are not very far from their peak of production, coal should last for a quite longer time. Therefore, coal could be the bridge between the current energy system and the future one, based maybe on renewable sources and nuclear fusion. Coal gasification allows to convert coal in a syngas and the syngas can be burned to generate heat and finally electric power. An interesting alternative is to clean syngas to obtain hydrogen which could be used for transportation and for residential heat and power cogeneration. At the same time the gasification process generates a significant amount of heat which can be recovered to generate electric power. Balancing the two final products (hydrogen and electric power) the energy demand could be satisfied with the best efficiency.

FB-1.3:L06 **Selection of Ceramics and Composites as Materials for a Supercritical Water Gasification (SCWG) Reactor**

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SCWG is a new way to convert humid biomass to energetic: methane and hydrogen. It has many advantages: (1) fast reaction; (2) high conversion rate (99.9%). But, it also presents technological problems that limit applications. In our work, thermochemical conversion of wastes from wine or sugar production is reached at temperatures and pressures up to 550°C and 250 bar. In these conditions, the durability of metals and alloys is limited by corrosion. Ceramics and ceramic composites are known to be stable under extreme conditions. For this reason, we have proceeded to an examination of a selection of ceramic materials that could be used as the thermal and anti-corrosive wall of the gasification reactor. As a conclusion, ultra-high temperature ceramics Si3N4, BN and SiC are strongly corroded by humid waste, but carbon-based materials and alumina are resistant. We outline the performance needed for carbon materials and discuss the role of composites based on graphite in improving the lifetime of SCWG reactors. In future applications, higher efficiencies of gasification process will be required. Ceramic composites based on oxide-graphite could be a solution to improving the thermal properties of carbon and shift its corrosion limit towards higher temperatures.

Session FB-2
Hydrogen Storage

FB-2.2 Metal Hydrides

FB-2.2:IL01 **Hydrogen Storage in Metastable Lightweight Hydrides**

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Light weight Mg has a long interest for hydrogen storage. Poor kinetics has prevented practical applications. Now we have a better understanding of how Mg interacts with different alloying metals in the presence of hydrogen. This can be used to find more practical metastable systems. If Mg is reacted with early transition metals (TM) in hydrogen, it is possible to stabilize a high pressure phase of a TM doped MgH2 having a CaF2 related structure. In this more open structure hydrogen diffusion is rapid. Hydrogen release pressure is only marginally increased but higher diffusion rates opens up for new high capacity battery electrodes. Mg does not alloy with early TMs and hydrogen is needed to keep the metal atoms from separating. If some hydrogen is left in the structure, the metastable metal combination can be prevented from separating, making reversible hydrogen storage possible. If Mg is reacted with TMs with more d-electrons, valence electrons from Mg can be used to form hydrogen rich TM hydrido complexes. Mainly sd-electrons are involved in the bonding, making 3d TMs complexes weak. Support from a polarizing Mg2+ ion is needed to keep them together. By reducing the amount of Mg2+ in favour of less polarizing counter ions; the hydrides will decompose at lower temperatures.

FB-2.2:IL02 **Developments in Magnesium-based Hydrides**

J. Huot*, Hydrogen Research Institute, Universite du Quebec a Trois-Rivieres, Trois-Rivieres, Quebec, Canada

Because of its high hydrogen storage capacity and low cost, magnesium has been intensively studied as a mean of hydrogen storage. Three basic problems prevent the utilization of magnesium for most commercial applications: long activation time (first hydrogenation), slow kinetics, and a temperature of operation that is too high. We will present some new ways to solve each of these problems. First, we will show that severe plastic deformation could have a beneficial effect on the activation properties of magnesium-based alloys. Secondly, we will discuss the addition of new catalysts as well as new technique (cold rolling) for catalysts addition. Finally, we will present synthesis by cold rolling of Mg-Ti and Mg-Sc compounds. For each system the crystal structure and hydrogen storage properties has been investigated. We will show how preferential orientation (texture) and defects induced by severe plastic deformation could have an effect on activation kinetics and hydrogen storage behaviour.

FB-2.2:IL03 **Hydrogen Storage in Destabilized Borohydride Materials**

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A study was done to see if a destabilized hydride system such as $CaH_2/LiBH_4$ would be suitable for hydrogen storage. When several additives, $TiCl_3$, V_2O_5, TiF_3 and TiO_2 were ball milled with the $CaH_2/LiBH_4$ mixture, TPD analysis showed that all of the mixtures released hydrogen reversibly in the 400-450 C range with the desorption temperatures being in the order $TiF_3 < TiO_2, \leq TiCl_3 < V_2O_5$. Kinetic modeling measurements showed that the reaction is controlled by diffusion. In an attempt to reduce the reaction temperature, a ternary system consisting of $CaH_2/LiBH_4/LiNH_2$ was tested for hydrogen desorption. TPD analyses showed that the ternary system released all of its hydrogen at a temperature that was about 100 C lower than the $CaH_2/LiBH_4$ mixture. However, the release of hydrogen from the ternary mixture occurs irreversibly. In a further attempt to lower reaction temperatures, double-cation borohydrides of general composition $MM'_{m-n}(BH_4)_m$ (M=Cu, Ni, Fe, Cd, Mn and Zr, M'=Li and Na) were synthesized by a mechanical milling process. The thermal desorption properties of $MM'_{m-n}(BH_4)_m$ were investigated by FTIR, TPD, TGA and RGA. The results indicate that the hydrogen desorption temperature T_d of $MM'_{m-n}(BH_4)_m$ correlates with the Pauling electronegativity X_p of M.

FB-2.2:IL04 **Computational Modelling of Destabilized Hydride Systems**

J. Karl Johnson*, Anant Kulkarni, University of Pittsburgh; Ki Chul Kim, David Sholl, Georgia Institute of Technology, USA

Light metal hydrides are promising materials for hydrogen storage because they can have both high gravimetric and volumetric hydrogen densities. However, there are two main problems associated with metal hydrides, namely unfavorable thermodynamics and slow kinetics. Development of new complex metal hydrides and destabilized hydrides offers the possibility of tuning the thermodynamics by combining different light elements. The number of possible reactions involving different species and compositions is enormous. Hence, there is a need to use modeling to quickly screen materials for acceptable thermodynamics in order to narrow the experimental search space. We present a method for screening the thermodynamics of a very large number of potential metal hydride materials with first-principles density functional theory. We have screened both single-step and multiple-step reactions over a wide range of materials, compositions, and temperatures. We have also investigated the formation of amorphous intermediates or products for select reactions. Experimental verification of selected predictions will be discussed.

FB-2.2:IL05 Destabilization of Mg Hydrides by Mechanical Constraint

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By means of a simple model, we show that the thermodynamic properties of hydrogen absorption in nanostructured metals can be tuned by means of elastic constraints. Large increases of plateau pressures can be reached by coating a soft H-absorbing metal with a thin hard material with a lower H affinity, e.g. a Mg layer capped by a transition metal such as Ni or Pd. At 333 K the plateau pressure of a 20 nm Mg film capped with 20 nm Pd is ~ 200 times higher than the plateau pressure of a free Mg layer. For 3D-nanoclusters the model predicts even stronger destabilization effects. For a Mg nanocluster of 10 nm radius covered with a MgO layer of only 1.7 nm thickness, we calculate an increase by a factor ~300 at 333 K. These predictions are quantitatively in agreement with p-c isotherms measured by hydrogenography[1] on bi-layers and multilayers of Mg and transition metals[2]. Our results open the door for the development of new hydrogen storage materials with attractive thermodynamic properties. They also show that the infinite range of the elastic H-H interaction in hydrides leads to a drastic influence of the imposed boundary conditions.

[1]R. Gremaud, et al, Advanced Materials 19 (2007) 2813-2817; [2]A. Baldi et al., Phys. Rev. Lett. 102 (2009) 226102

FB-2.2:L06 From Lab Scale Optimization of Mg-based Composites for H2 Storage to the Realization of a Portable Prototype

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In the frame of the Italian project “Nanostore”, focused on Mg-based composites prepared by ball milling, a wide range of composites were characterized concerning their kinetic and thermodynamic sorption performance. The best promising systems, i.e. Mg - Ni - C - TiO2 and Mg - C - MO (MO = TiO2, Nb2O5) composites, were optimized concerning stoichiometry, milling time and aggregation state (powders or pellets) for the use as H2 storage media in a portable 1 kW PEM-FC prototype. Concerning the lab scale tests, the samples (500 mg) were firstly activated by charging/discharging cycles at 350 °C and 35 bar/1 bar in a Sievert apparatus. The subsequent characterization was made by a multi-step procedure composed of thermal programmed absorption/desorption runs and subsequent kinetic runs at different working temperatures. At 350 °C, gravimetric capacities of 6.4% and 6.9% were obtained for the Mg - Ni - C - TiO2 and Mg - C - MO systems respectively. At the same T, the composites charged up to 90% of their filling up in 1.5 min maximum. Moreover, more than 98% of the full discharging, lasting 10 min, took place with a rate fully suitable to feed the 1 kW fuel cell. The first tests of the storage materials (about 1500 g) directly in the prototype are very promising.

FB-2.2:L07 In-situ Study of the Effect of Internal Stress on the Hydriding Kinetics of Pd-based Thin Film Systems

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The effect of pre-existing internal stresses on the hydriding kinetics of Pd thin films has been studied. An innovative way of increasing H-loading beyond the intrinsic thermodynamic and kinetic limits is to pre-strain the metallic alloy, allowing for more atomic H to find its way in the host crystal lattice. Our cantilevered thin film samples have been deposited using a PVD technique. The evolution of their curvature during the deposition process has been measured with a high resolution in-situ diagnostic tool, which continuously monitors the reflection of multiple laser beams coming off the sample surface[1]. The hydriding kinetics of the Pd films has also been studied by monitoring the evolution of their curvature in real time. The rate-limiting steps have been identified by comparing our results with a classical two-step hydriding model already developed in a previous study[2]. Relevant kinetic and thermodynamic parameters have been calculated from our experimental data. The effect of the internal stress on the hydriding kinetics will be discussed as well.

[1]J. Proost and F. Spaepen, J. Appl. Phys. 91 (2002) 204-216; [2]R. Delmelle et al, Proceedings of the 8th International Symposium on Hydrogen Power - Theoretical and Engineering Solutions, Lisbon (2009) 106-110.

FB-2.2:IL08 Size-selected Rare Earth and Palladium Nanoparticles for Hydrogen induced Switching and Sensing Devices

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A continuous and reversible “structural, optical and electronic” transition between reflecting metallic dihydride and transparent semiconducting trihydride states in rare earth (RE) metals on hydrogenation make these materials suitable for switchable mirror, sensing and other technologically important applications. In our laboratory, ‘nanoparticle route’ has been used for achieving an “all-round” improvement in the switching characteristics of a “new generation” of Gd and Pr nanoparticle based switchable mirrors in comparison to previously reported thin film, RE-Mg alloys and mutilayers. It has been shown that the observed improvements in color neutrality, response time, optical and electrical contrasts are a direct consequence of quantum confinement and enhanced surface area at nanodimensions. It has been shown that the changes in electrical and optical properties are directly linked to the H/RE ratio and H concentration profiles. A size selected nanoparticle synthesis set up consisting of spark generator for producing nano-agglomerates, UV charger for charging the particles, DMA set up for selecting the particles based on the electrical mobility and in-flight sintering furnace for converting the agglomerates to spherical and monocrystalline nanoparticles and particle deposition system for finally depositing particles onto substrates, has been fabricated for depositing Pd and rare earth nanoparticles. Gas sensing characteristics, electrical conductivity and crystal structure of Pd thin films, nanocrystalline layers, size-selected nanoparticle have been studied as a function of hydrogen concentration and measurement temperature. It has been observed that the pulsed response changes into slow saturation response at a threshold hydrogen concentration, which is a function of measurement temperature. The pulsed response is due to hydrogen induced geometrical and electronic effects. By controlling the nanoparticle size and separation, geometrical effects due to lattice expansion during hydride formation and electronic effects due to H incorporation can be controlled and separated. These results set the foundation for a new type of concentration specific H sensor having high sensitivity due to geometrical effect and fast response due to electronic effect.

FB-2.2:L10 Transmission Electron Microscopy of Materials for Hydrogen Storage

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Transmission electron microscope (TEM) is a powerful method for characterizing the atomic structure and microstructure of materials, as well as the interfaces resulting from phase transformation or phase growth. Since hydrogen storage process is basically a phase transformation process, in many cases involving multiple phases, diffusion of hydrogen and other atoms, interaction of hydrogen with surfaces, and often formation of metastable phases, use of TEM can be essential in understanding many critical questions. Nevertheless rather limited number of TEM studies can be found in literature. The main reason for that is in the specifics of hydrogen storage materials, which are in many cases very difficult to prepare for good quality TEM investigation: reactivity with air and moisture, instability of hydrides in a high-vacuum microscope column, morphology of ball-milled powders etc. In this paper we present a few examples of our TEM studies, which were essential for understanding materials, which were subjected for hydrogenation, hydrogenation processes and structures and morphologies of hydrides. The presented TEM studies were conducted in conjunction with other methods of characterizing hydrogenation, such as in-situ IR emissivity imaging, FTIR and Raman spectroscopy, and Sievert volumetric measurements. The studied materials include Y and Mg-transition metals films, selected borohydrides and Laves phases.

FB-2.2:L12 On the Nucleation Step in the Mg-MgH2 Phase Transformation

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The sorption reaction kinetics of Mg powder can be fastened by intensive plastic deformation and catalyst introduction, that have been shown to overtake the classical reaction rate limiting steps. The processing is generally performed by ball milling. In order to understand the different role that the different material features play in the MgH2 decomposition, we propose to integrate the traditional kinetics analysis based on the study of the reaction rate, with a metallographic approach able to provide information on the microstructure in partially decomposed samples. The method is based on low voltage Scanning Electron Microscopy observation of cross sectional samples. The catalyst particle distribution as well as hydrogen cycling can have important effects on the microstructure and so on the kinetic behaviour. This kind of analysis provides a new tool for a deeper and more precise interpretation of the kinetic behaviour in order to assist the processing toward optimum microstructure for hydrogen sorption and desorption.

FB-2.2:L13 Ball Milling in the Mg-Ti-H System

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This is the first report of a direct synthesis of ternary Ti-Mg-H hydride by direct combination of the binary hydrides by ball milling in 1 bar Ar. Magnesium hydride is a potential solid hydrogen store due to its hydrogen capacity of 7.6wt%, reversibility and low cost. Alas, MgH2 has problems as an H source for automobiles due to its poor kinetic performance at the low temperature (<373K) that fuel cells operate at. In this work a transition metal hydride TiH2 (0, 1, 3, 5, 10, 30 and 50 at%) has been milled with MgH2 under Ar atmosphere in an attempt to produce an improved kinetic performance. The samples have been examined by SEM, EDX, XRD, TEM, TGA and DSC and the kinetic behaviour examined by production of Kissenger plots. 5at% TiH2 shows >90% de/hydrogenation in 100s at 573K. XRD patterns of all were subject to Rietveld analysis. A rapid decrease in activation energy was observed upto 5at% TiH2. The samples with low TiH2 content (1-10 at%) consist of intimate mixtures of the two hydrides with crystals < 10 nm. The higher TiH2 content (30-50 at%) are homogeneous and consist of a solution of MgH2 in TiH2. TEM studies with EELs analysis show that the Ti and Mg are dispersed evenly throughout the sample. Rietveld refinement shows a TiH2 structure (Fm-3m), a = 4.5003(2)Å.

FB-2.2:L14 Pellets of MgH2-based Composites as Practical Material for Solid State Hydrogen Storage

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Hydrogen absorption/desorption (a/d) properties and mechanical stability of pellets made of compressed ball milled MgH2 powders mixed with catalysts (Nb2O5 and graphite) and a binding agent (aluminium powder) have been investigated. Structural characterization with X-ray diffraction and gas-solid reaction kinetic and thermodynamic tests with a Sievert's apparatus have been done on the samples up to 50 hydrogen a/d cycles. The best cycling behaviour and mechanical strength stability have been observed for pellets of catalysed MgH2 powders added with 5 wt% aluminium annealed in vacuum at 450 °C before starting the a/d cycles. This mechanical stability to cycles has been attributed to the formation of a solid solution of aluminium in magnesium.

FB-2.3 Complex Hydrides

FB-2.3:IL01 Achievements and Perspectives of the US National Program on Hydrogen Storage

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The U.S. DOE Hydrogen Program's mission is to reduce oil use and carbon emissions and to enable clean, reliable energy for stationary and portable power generation and transportation. Requirements for hydrogen storage continue to be some of the most technically challenging barriers to the widespread commercialization of hydrogen fuel cell products. The DOE-EERE hydrogen storage activities primarily focus on applied research and development of materials and engineering to provide low-pressure storage options that meet packaging, cost, safety and performance requirements to allow fuel cell systems to be competitive with current technologies. This presentation summarizes the status, recent accomplishments and current performance gaps of hydrogen storage technologies. The research is conducted under the framework of DOE's National Hydrogen Storage Project that includes independent projects and Centers of Excellence in both applied and basic hydrogen storage R&D. Material projects are focused in three main areas: metal hydrides; chemical hydrogen storage materials and hydrogen sorbents. New efforts include the Hydrogen Storage Engineering Center of Excellence, which will provide a coordinated approach to engineering research and development of hydrogen storage systems.

FB-2.3:IL02 Hydrogen Sorption Characteristics of Group I & II Borohydrides and Hydride Composites

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We have recently studied on group I and II metal borohydrides and composite hydrides containing at least one of these borohydrides with or without catalytic additives such as transition metal halides. In addition, theoretical studies based on the first principle and thermodynamic calculations have also been carried out on so-called mixed-anion borohydrides as well as binary hydrides. The results show that by careful control of both reaction temperature and hydrogen partial pressure, combined with a proper selection of catalytic additives, can make some of these high capacity metal hydrides quite reversible by improving the reaction kinetics through microstructure control during sorption cycles. Some of the preliminary results about the effect of the size confinement on both the thermodynamics and kinetics of the hydrogen sorption reaction will also be presented.

FB-2.3:IL03 LiBh4 - A Versatile Hydrogen Storage Compound

William I.F. David, ISIS Facility, Rutherford Appleton Laboratory, Chilton, UK

Lithium borohydride is a remarkable material. It is not only a candidate in its own right as a high wt% hydrogen store but also exhibits superionic conductivity. Moreover, it readily accommodates almost four times its own weight of ammonia and can intercalate other molecules such as methylamine. Combined with $LiNH_2$, it forms mixed lithium borohydride amide compounds with low melting points and promising hydrogen desorption profiles. This talk will present recent results on all these aspects of $LiBH_4$ that highlights the common theme of structural disorder and ionic conductivity.

FB-2.3:IL04 Microwave Absorption and Lithium Super-Ionic Conduction in Lithium Borohydride LiBH4

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LiBH4, one of metal borohydrides M(BH4)n, has been attracting great interest because of its various energy-related functions such as microwave absorption and lithium super-ionic conduction as well as hydrogen storage. By microwave irradiation, LiBH4 was heated rapidly above 380 K due to a large conductive loss, at which almost all hydrogen was desorbed [Appl. Phys. Lett., 88 (2006) 112104; 90 (2007) 232907]. As a result of clarifying the mechanism of the microwave absorption, we discovered lithium super-ionic conduction in LiBH4 [Appl. Phys. Lett., 91 (2007) 224103]. The lithium ionic conductivity of Li(BH4) jumps by three orders of magnitude at approximately 390 K due to its structural transition from orthorhombic to hexagonal phases, and the hexagonal phase exhibits a high conductivity of the order of 10-3 S/cm (lithium super-ionic conduction). The conduction can be the origin of the occurrence of the large conductive loss and also of the microwave-induced hydrogen desorption, as mentioned above. Just recently, the hexagonal, that is, lithium super-ionic conduction phase of LiBH4 was well stabilized even at room temperature by addition of lithium halides. [J. Am. Chem. Soc., 131 (2009) 894; Appl. Phys. Lett., 94 (2009) 084103; 94 (2009) 141912].

FB-2.3:IL05 Electrochemical Formation and Regeneration of Alane

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Aluminium hydride (alane, AlH_3) has been considered a potential hydrogen storage material because of its high hydrogen capacity (10wt%), high volumetric density (149g/L) and compatible discharge temperature with fuel cells. However, the main drawback to using aluminium hydride in hydrogen storage applications has been its unfavourable hydriding thermodynamics. The direct hydrogenation of aluminium to aluminium hydride requires over 105 bars of hydrogen pressure at room temperature. Aluminium hydride can be produce through the typical formation route of using chemical synthesis that typically produces stable metal halide such as LiCl. The impracticality of using such high hydriding pressure or the formation of stable by-products has precluded aluminium hydride from being used as a reversible hydrogen storage material. In this work we present a cycle that uses electrolysis and catalytic hydrogenation of spent aluminium to avoid either the impractical high hydrogen pressure needed for hydriding aluminium or the formation of stable by-products, using the chemical rout. A reversible cycle to form alane electrochemically using alanates such as NaAlH4 in polar solvent has been successfully demonstrated. To complete the cycle, the starting alanate can be regenerated by direct hydrogenation of the dehydrided alane and the alkali hydride (NaH). Alane produced by the electrochemical method was characterized using thermogravimetric analyzer, XRD and Raman spectroscopy.

FB-2.3:IL06 Hydrogen Storage Materials - Recent Development and Future Strategy of Japan

E. Akiba, AIST, Tsukuba, Ibaraki, Japan

Hydrogen storage on board is a critical issue to realize hydrogen fueled vehicle and finally the hydrogen economy. At present, high-pressure cylinder is used for on board hydrogen storage. However, when mass production of fuel cell vehicle starts, compact, light-weighted, energy efficient, recyclable, safe and economical on board hydrogen storage is indispensable. Hydrogen storage material is the most promising candidate. In 2007 Japanese national project for fundamental research on hydrogen storage materials (HYDRO-STAR) has been initiated. It includes materials characterization using synchrotron radiation and neutron, various in-situ measurement, and computational approach using both first principle and molecular dynamic calculation. Another hydrogen storage related national project (Development of Technologies for Hydrogen Production, Delivery and Storage Systems) was initiated in 2008. Under this project, the “hybrid tank” system that is combination of high pressure and hydrogen storage material has been developed. Both volume and weight hydrogen capacities are between high-pressure cylinder and low-pressure metal hydride tank. Japan simultaneously conducts variety of hydrogen storage materials research from fundamental research to applications for mass production.

FB-2.3:IL07 Evidence for Hydrogen Transport in Deuterated LiBH4 from Low-temperature Raman-scattering Measurements and First-principles Calculations

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By Raman spectroscopy we provide direct evidence for successive exchange of D atoms in the tetrahedral BH4 units of the molecular solid lithium borohydride. We prove the coexistence of all isotopomers by deconvolution of the D-stretching vibrations band of Raman spectra at 83K and 5K in partially D-exchanged LiBH4 and comparison with first-principles Raman intensity calculations. This implies net transport of atomic hydrogen in LiBH4 below the melting temperature.Tracer diffusion experiments of LiBH4/LiBD4 diffusion couples show a fast macroscopic diffusion of BH4 ions of D 6.8 x 10 ^ {-14} m ^ 2/s at 473 K. The direct exchange rate of hydrogen between BH4 units is 10 orders of magnitude slower, i.e. the relatively fast effective hydrogen diffusion has its origin in the fast diffusion of BH4 units.

FB-2.3:IL08 Approaches to Modify Complex Hydrides Towards Viable Onboard Hydrogen Storage

Rana Mohtadi*, PremKumar Sivasubramanian, Toyota Research Institute of North America; Tomoya Matsunaga, Toyota Motor Corporation; Joshua Gray, Doug Knight, Ragaiy Zidan, Savannah River National Laboratory, USA

Currently, hydrogen is being stored on board automobiles either using high pressure compressed hydrogen tanks at 350 or 700 bar, or using liquid hydrogen stored at 20 degrees Kelvin. These systems suffer from either low hydrogen volumetric storage density or hydrogen boil off, making them impractical for onboard storage. On the other hand, storage of chemically bonded hydrogen in complex metal hydrides would eliminate these issues. Currently, global research efforts are focused on creating new materials and enhancing the dehydrogenation thermodynamics, kinetics, and reversibility of promising known or new complex hydrides. While several progresses were made, the thermodynamic and the kinetic barriers of hydrogen charge and discharge still represent key challenges towards their utilization. In the work we will present, we will share our research efforts targeting the modification of complex hydrides thermal properties. We will show our concepts for altering the thermodynamic stability of both stable and unstable compounds. Methodologies to improve the safety of storing these materials onboard will also be shared. Achievements will be discussed and remaining challenges will be addressed.

FB-2.3:L09 Synthesis and Characterisation of Ca(BH4)2 for Solid State Hydrogen Storage

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Hydrogen storage technologies are gaining interest for the development of new sustainable energy carrier instead of fossil fuel and for reducing the release of greenhouse gases. Hydrogen is indeed a clean alternative carrier but safe and reliable storages are necessary. Metal borohydrides are potential materials for solid state hydrogen storage due to their high gravimetric and volumetric hydrogen densities. Among them, Ca(BH4)2 is interesting because of the predicted suitable thermodynamic properties, that should enable release of hydrogen within the operation range of PEM fuel cells. Simple synthesis route(s) and efficient catalyst(s) are therefore required for practical application. We investigate a new synthesis route using reactive ball milling of CaH2 and CaB6 under high hydrogen pressure (max 150 bar). The effectiveness of this new route and the yield of formation of Ca(BH4)2 have been examined by the combination of different techniques (in particular spectroscopy). The reversible decomposition/formation of Ca(BH4)2 is obtained using TiF3 as additive but not with TiCl3. The different influences of the additives on the decomposition pathway are discussed.

FB-2.3:L10 Thermochemical Transformations in 2Li(Na)NH2-3MgH2 Systems

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Thermochemical reactions in 2MNH2-3MgH2 systems (M = Li or Na) have been investigated using pressure-composition-temperature, x-ray powder diffraction and residual gas analyses. The thermally induced reactions in both systems proceed as reaction:
2MNH2 + 3MgH2 → Mg3N2 + 2MH + H2↑
A total of 6.45 and 5.1 wt.% of hydrogen is released beginning at 186 and 130 °C by the Li and Na containing systems, respectively. Combined structure/property investigations revealed that transformations in the 2LiNH2+3MgH2 system proceed as two step reaction:
Step 1: 2LiNH2+MgH2 ↔ Li2Mg(NH)2 + 2H2↑
Step 2: Li2Mg(NH)2 + 2MgH2 → Mg3N2 + 2LiH + 2H2↑
The transformations in the system with sodium proceed through a series of reactions and formation of different intermediates:
2NaNH2 + MgH2 → Mg(NH2)2 + 2NaH
NaH + MgH2 → NaMgH3
½Mg(NH2)2 + MgH2 → ½Mg3N2 + 2H2↑
½Mg(NH2)2 + NaMgH3 → ½Mg3N2 + NaH + 2H2↑
Partial rehydrogenation in 190 bar hydrogen pressure was observed in the 2NaNH2-3MgH2 system at 395 °C with formation of the MgNH imide.

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FB-2.3:L11 Proton Vibrations in Lithium Imide Studied Through Incoherent Inelastic Neutron Scattering

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Lithium imide (Li_2NH) and amide ($LiNH_2$) belong to the Li-H-N system, which has been recently considered for on-board hydrogen storage applications. However the imide low-temperature crystal structure is still highly controversial, with at least six options compatible with the diffraction experimental findings. A complementary study on low-temperature Li_2NH and $LiNH_2$ has been recently accomplished by the authors using neutron spectroscopy (with energy transfer in the 3-500 meV range). The rationale of these measurements was that the crystal structures (especially the proton arrangement) affect in a strong way the neutron scattering spectra, so that a combined use of computer ab-initio simulations and inelastic neutron scattering could be a stringent validation method for the various models. Accurate data analysis have pointed out large differences in the proton-projected phonon densities of states derived from forward scattering and backscattering detector banks. On the contrary, no discrepancy at all was found applying the same analytic procedure to lithium amide spectra. This Li$_2$2NH anomaly has been interpreted as clear effect of a fast proton jump diffusion among the available lattice sites, which smears out the lattice vibrational excitations in an angle-dependent way.

FB-2.3:L12 **Improved Cyclability of Titanium Catalysed Multicomponent LiBH4-LiAlH4 System for Hydrogen Storage**

M. Meggouh*, G.S. Walker, D.M. Grant, Engineering Faculty, University of Nottingham, Nottingham, UK

Due to its high hydrogen storage capacity of 18.5 wt%, LiBH4 has recently gained much attention as a potential onboard hydrogen storage medium for automotive applications. Unfortunately LiBH4 releases hydrogen above 600 °C, and hydrogenation does not occur below 600 °C and under hydrogen pressure of less than 350 bar. However, these conditions can be modified by thermodynamic destabilization. In this study, two different Al-sources (metallic Al and LiAlH4), in the presence of TiCl3 are used to investigate the improvement on the dehydrogenation/hydrogenation behaviour of LiBH4. Furthermore, continuous ball-milling compared to pre-milling of LiBH4 with an Al-source, was investigated also. It has been found that long ball-milling times for LiAlH4 in the presence of TiCl3 result in higher H2 release, than reported in the literature so far. In addition, a lower dehydrogenation temperature and better reversibility (350 °C, 85 bar) were achieved for the LiAlH4 containing samples than in the case of metallic Al. Whereas TiCl3 appears to accelerate the decomposition pathway of LiAlH4 during ball-milling, it shows a limited effect when used on its own. Continuous milling resulted in a lower dehydrogenation temperature than achieved with pre-milling with no decrease in the H2-release.

FB-2.3:L13 **Hydrogen Storage Research Activities in ENEA**

Pier Paolo Prosini, Paola Gislon*, Mario Conte, ENEA, Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Roma, Italy

Hydrogen storage is one of the key enabling technologies for the establishment of a new energy system, mostly based on hydrogen as energy vector in the transport and stationary applications. In the last 10 years, ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development) has extended its ongoing basic materials research to novel materials and methods specifically devoted to such new applications. The activities have been devoted to develop novel materials (e.g., metal, complex and chemical hydrides) with improved storage characteristics, the design and fabrication of fully engineered laboratory prototypes, the technological benchmarking in dedicated test rigs. Chief results of these activities are already interesting: modified alanates have been investigated showing an interesting 5.5%wt. hydrogen storage; chemical hydrides, such as NaBH4, have been deeply studied with some innovative solutions to get closer to the theoretical hydrogen content of 10%wt., by using solid powder instead of liquid mixtures and optimising the choice of catalysts; various laboratory scale tanks for hydrogen storage have been tested in dedicated test benches of different size. In the talk a survey of the main activities carried out in ENEA will be presented.

FB-2.3:L14 **Low Temperature Hydrogen Release from LiBH4-based Multicomponent Systems**

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Lithium borohydride is a promising candidate for hydrogen storage and fuel cell application due to its high hydrogen capacity, but has a high dehydrogenation temperature. In the present work, the dehydrogenation behaviour of (4LiBH4+5Mg-Ni-H) mixtures has been investigated. XRD has proved a novel destabilisation reaction with the mixture forming the ternary boride, MgNi2.5B2, after decomposing at 585 °C under Ar. It is demonstrated that the addition of 20h-milled (2MgH2+Ni) alloy has drastically lowered the dehydrogenation temperature for the mixture. LiBH4 now starts decomposing before the melting point and the majority of hydrogen is released below 300 °C, which is 170oC lower than the mixture of (2LiBH4+MgH2). There is about 4.5 wt.% hydrogen released from the mixture in the temperature range from 200 to 300 °C.

FB-2.3:L15 **Sorption Reactions of NaBH4-MgH2 Composite**

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Hydrogen storage in solid state has shown ever increasing research and development,compared with gaseous and liquid storage,due to economical and safety issues.Complex hydrides along with metal hydrides are considered promising classes of materials.Recently,an approach in mixing these two by ball milling,called reactive hydride composites,has been investigated,e.g.NaBH4-MgH2.Thermodynamic destabilization occur by new compounds formation,e.g.MgB2,which lowers overall reaction enthalpy.A comprehensive study of the reaction 2NaBH4+MgH2<>2NaH+MgB2+4H2 was conducted in this work.Sorption and kinetic studies were performed by in-situ X-ray diffraction,thermogravimetry and thermal desorption mass spectroscopy at different hydrogen pressures and heating rates.Desorption is established to begin at lower temperatures with destabilization of MgH2 by NaBH4,leading to dehydrogenation of the former into Mg and subsequent MgB2 formation.Reverse reaction is observed to give NaBH4 under moderate conditions(<50bar,<350 °C)together with NaMgH3.The results intend to stress understanding of interplay between thermodynamics and kinetics in destabilizing complex hydrides.A comparison of this system with others in the literature (i.e.LiBH4-MgH2)allows looking at suitable conditions for hydrogen storage.

FB-2.3:L16 **Ternary Phase Destabilized Complex Hydrides: LiBH4:MgH2:LiAlH4**

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This work presents investigation of a new quaternary complex hydride storage material, LiAlH4 : LiBH4 : MgH2. The system is based on destabilized LiBH4:MgH2, using LiAlH4 decomposition for fine distribution of Al particles. Results show a large reduction in the decomposition onset temperature to 250 °C, 70 °C lower than the previously reported 0.3LiBH4 : MgH2 system, whilst maintaining a storage capacity greater than 9 wt.%. This is extremely promising as a practical hydrogen storage device starts to become viable at these temperatures and with this capacity. MgAl and Li-Mg-Al ternary alloys are explored with reference to their improved cycling properties through in-situ neutron diffraction during pressure-composition-temperature analysis, allowing specific phases to be related to plateau pressures. Cycling experiments have shown that the 0.23LiBH4 : MgH2 : 0.05LiAlH4 system can be fully reversed by heating the decomposition products under 50 bar hydrogen at 400 °C with faster kinetics than the 2 LiBH4 : MgH2 system.

FB-2.3:L17 **Decomposition of Ammoniaborane (NH3BH3) at Sub-Ambient Pressures**

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NH3BH3 (AB) is attracting interest for its high hydrogen content (~19.4 wt%). Dehydrogenation of solid AB occurs rapidly upon melting (> 393 K); however partial release of H2 (6 wt%) is obtained from solid AB during isothermal aging at temperatures between 343 and 363 K. During decomposition, formation of volatile impurities is observed in the evolved gas, but their relative quantities and the final mass loss depend on the thermal history of the sample. In addition, no information about the influence of external pressure on the decomposition processes has been reported. More details about the role of external variables (p and T) on the decomposition mechanism are demanded in order to lower the dehydrogenation temperature and to avoid the formation of undesirable products. We report a systematic study of the isothermal decomposition of AB at 363 K as a function of Ar pressure ranging between 50 and 1040 mbar using TGA-DTA coupled with mass analysis of the volatile species. During thermal aging evolution of H2, aminoborane and borazine is monitored, with the relative mass loss depending on the pressure in the reaction chamber. It is also observed that the induction period required for H2 release decreases with decreasing pressure.

FB-2.4 Chemical Hydrides

FB-2.4:IL01 **Synthesis and Properties of Nanocomposites Based on Tetrahydroborates**

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An overview will be given on methods for the synthesis of pure tetrahydroborates including 11-B and D isotope labelled compounds which are needed for neutron studies. Selected properties of hydrogenated and dehydrogenated material will be reviewed and the stability and role of metal borides will be discussed. Full reversibility is a problem in a series of systems which may be due to the specific reaction path of the system. There have been numerous attempts to catalyse the transformation of borohydrides in order to reach lower operation temperatures and pressures. However, no breakthrough has been achieved yet, which would be comparable to the success of dopants for catalysis of tetrahydroaluminates. The role of intermediates will be discussed in this context and new approaches to gain thermodynamic control over the reaction path will be presented. Tetrahydroborates infiltrated in nanoporous scaffolds exhibit properties which may be different compared to the bulk materials. Encapsulating solid state reactions in nanocompartments may lead to interesting effects which will be discussed on the example of a hydride system with altered properties.

FB-2.4:IL02 Catalyzed Dehydrogenation of Amine-borane Fuel Blends

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With both protic N-H and hydridic B-H bonds as well as three hydrogen atoms per main group element, ammonia-borane (AB, H3NBH3) is a promising material for chemical hydrogen storage applications.[1] Selected metal complexes and supported metals have been shown to be effective catalysts for dehydrogenation of AB and substituted amine-boranes to afford oligomeric aminoborane (RHNBH2)n and iminoborane (RNBH)n products (R = H, alkyl). While AB has the highest storage capacity, preference for a “drop-in” liquid fuel has led to development of amine-borane fuel blends. For R = sec-Bu, for example, the amine-borane and its dehydrogenation products are liquids at operating temperatures and readily dissolve AB and its dehydrogenation products. Suitable catalysts and reaction conditions and performance will be discussed.

[1] *Stephens, F.H.; Pons, V.; Baker, R.T. Dalton Trans. 2007, 2613; Marder, T.B. Angew. Chem. Int. Ed. 2007, 46, 8116; Hamilton, C.H.; Baker, R.T.; Staubitz, A.; Manners, I. Chem. Soc. Rev. 2009, 38, 279.*

FB-2.4:IL03 Chemical Hydrogen Storage in NHXBHX Materials

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The NHxBHx class of materials may be classified as complex hydrides and/or a chemical hydrogen storage materials. Chemical hydrogen storage materials are of great interest for hydrogen storage because they are capable of providing large quantities of hydrogen with rapid kinetics at moderate temperatures. Our group has been working on developing an in-depth understanding of the chemical and physical properties of amine borane materials for solid state on-board hydrogen storage. Hydrogen is released at low temperatures through a series of moderate exothermic reactions. In this work we present experimental and computational studies designed to elucidate more details about how di-hydrogen bonding interactions affect the structure and dynamics of these hydrogen rich compounds. This approach provides insight into the mechanism for H2 formation from NHxBHx compounds in the solid state and in solution. Pacific Northwest National Laboratory is operated for the DOE by Battelle.

FB-2.5 Carbon Based Materials

FB-2.5:IL01 Hydrogen Storage in Nanoporous Structures

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Significant R&D efforts are being pursued globally to improve the efficiency and economics of onboard hydrogen storage systems for mobile applications. Hydrogen storage via physisorption on nanoporous materials, such as activated carbon, carbon nanostructures and metal organic frameworks (MOFs) is particularly enticing due to its inherent reversibility and cyclability. Moreover, these materials exhibit fast kinetics and operate at relatively low storage pressures. However, due to inherent low binding energy, hydrogen physisorption at ambient temperatures on currently available porous materials leads to unacceptably low hydrogen storage densities. Acceptable densities are only attainable at cryogenic temperatures. We will present the results of our evaluation of an adsorption-based hydrogen storage tank for vehicular application. We will discuss the net storage capacity of the system over wide temperature and pressure ranges, the thermal requirements to charge and discharge hydrogen at the desired flow rates, and dormancy.

FB-2.5:IL02 Neutron Scattering Studies of Hydrogen Storage Materials

D.K. Ross*, D.J. Bull, D. Moser, D. Roach, Z. Mileeva, I. Shabalin, W.A. Oates, Institute for Materials Research, University of Salford, Manchester, UK

Neutron scattering provides a very powerful way of studying the nature of the binding of hydrogen in solids because of the large incoherent scattering length of H, the predominantly coherent scattering length of D and the possibility of producing para-hydrogen or ortho/para mixtures. Examples described include in situ cycling of the Li3N system at different D2 pressures and contrast matching of H and D toluene to study the porosity of activated carbons for hydrogen adsorption. The use of polycrystalline Coherent Inelastic neutron Scattering as a way of studying the dynamics of carbons will also be discussed.

FB-2.5:IL03 Novel Catalytic Effects of Fullerene for Complex and Metal Hydrides

M.S. Wellons*, J. Teprovich, R. Zidan, Savannah River National Laboratory, Aiken, SC, USA

Carbonaceous nanomaterials utilized as scaffolds, catalysts, and additives in conjunction with complex and alkali metal hydrides have shown remarkable hydrogen sorption properties. Our studies have found fullerene-C60 is an excellent catalyst for the reversible hydrogen absorption/desorption with complex and metal hydrides. We will present on several novel fullerene-containing metal hydride composites comprised of fullerene-C60 and NaAlH4, LiBH4, or LiH which are capable of reversible hydrogen storage. These nanocomposites are synthesized with a ball-mill free approach comprised of solution-facilitated mixing of the reactants, solvent removal, and annealing. The prepared nanocomposite exhibit hydrogen desorption with reduced onset temperatures (ca.130 °C for C60-NaAlH4, 280 °C for C60-LiBH4, 260 °C for C60-LiH) as well as increased kinetics. Particular attention will be paid to the lithium fulleride nanocomponsite and includes the hydrogen cycling of various C60:Li stoichiometries, of which the most promising (Li6C60) can reversibly store a 3 wt% hydrogen content. The 6:1 lithium fulleride material stores approximately four hydrogen atoms in the rehydrided state per Li atom, indicative of the formation of a unique hydrogen storage matrix. Efforts to determine structural and mechanistic characteristics of the fullerene hydride composites are ongoing and will include computational modeling, MAS NMR, XRD, raman, PCT, and structural determination by neutron methods.

FB-2.5:IL04 High Pressure Hydrogen Storage in Zeolite Templated Carbon

Somlak Ittisanronnnachai, Li-Xiang Li, Hirotomo Nishihara*, Takashi Kyotani, Institute for Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; Masashi Ito, Nissan Research Center, Nissan Motor Co. Ltd., Japan

Microporous carbon prepared by using a zeolite template is characterized by a very uniform and ordered pore structure together with very large surface area and micropore volume. This carbon (zeolite-templated carbon, ZTC) is made up of buckybowl-like nanographenes assembled into a three-dimensional regular network. Due to the extremely unique structure, ZTC is quite promising for such applications as adsorbent for hydrogen storage. High pressure hydrogen storage of ZTC was investigated at room temperature (30 °C). Several types of ZTCs with different surface areas were prepared. The ZTC with the largest surface area (3370 m2 g-1) exhibited as high a hydrogen uptake as 2.2 wt% at 34 MPa. Moreover, only by loading a small amount of Pt nanoparticles (ca. 0.2 wt%) onto ZTC, hydrogen uptake capacity was increased from 0.87 wt % to 0.95 wt% at 10 MPa. One of the possible explanations for the increase of hydrogen uptake capacity by Pt-loading is the hydrogen spillover through the supported Pt nanoparticles to the carbon surface. Its detailed mechanism is now under investigation.

FB-2.5:IL05 Metal Loaded Carbons

Theodore Steriotis, Institute of Physical Chemistry, NCSR “Demokritos”, Athens, Greece

Nanostructured porous materials have been proclaimed as quite important candidate hydrogen stores and several structures are being continuously explored. Considerable attention has been given to carbon-based materials which are considered quite advantageous in view of their low cost, low densities, diverse bulk and pore structures, reasonably good chemical stability, and mainly amenability to synthesize a wide range of variants by post-treatment/functionalisation routes. In particular it has been shown, by numerous experimental and theoretical studies, that doping of a wide range of carbon substrates with small amounts of (e.g. transition) metals lead to a significant enhancement of their hydrogen storage capacity. Nevertheless, if nanostructured carbons are to become the base materials of a viable hydrogen-storage technology, many improvements remain to be achieved. The up to now results have shown that future research towards successful carbon materials has to focus on the enhanced understanding of key factors such as the pore and surface microstructure and topology, the effect of surface activity/functionality (e.g. defects, functionalisation, metal decoration), and the mechanism of H2 uptake-release (including the thermodynamic and kinetic behaviour).

FB-2.6 Other High Surface Area Adsorbents

FB-2.6:IL01 **Metal-Organic Frameworks for Hydrogen Adsorption**

Hong-Cai Zhou, Department of Chemistry, Texas A&M University, College Station, TX, USA

Physisorption-based hydrogen storage systems show fast kinetics with a charging time of minutes, due to the weak sorbent–sorbate interaction. However, the same weak interaction results in gravimetric hydrogen uptake of a sorbent at ambient temperature and applicable pressure of typically less than 2 wt%. In the past decade, there has been an escalation of interest in the study of metal-organic frameworks (MOFs), due to their fascinating structures and intriguing application potential. Their exceptionally high surface areas, uniform yet tunable pore sizes, and well-defined adsorbate-MOF interaction sites make them suitable for hydrogen storage. Various strategies to increase the hydrogen capacity of MOFs, such as using pore size comparable to hydrogen molecules, increasing surface area and pore volume utilizing catenation, and introducing coordinatively unsaturated metal centers (UMCs) have been widely explored to increase the hydrogen uptake of the MOFs. MOFs with hydrogen uptake approaching the DOE 2010 gravimetric storage goal under reasonable pressure but cryo-temperature (typically 77 K) were reported. However, the weak interaction between hydrogen molecules and MOFs has been the major hurdle limiting the hydrogen uptake of MOFs at ambient temperature. In the presentation, I will demonstrate the following strategies utilized to enhance H_2 uptake: (1) Prepared the catenation isomer pair to evaluate the contribution from catenation to the hydrogen uptake of a MOF material. Catenation can be utilized to reduce pore sizes in porous MOFs and has also been explored as an efficient method to improve the hydrogen uptake of MOFs. (2) Synthesized porous MOFs with high hydrogen adsorption capacities based on different coordinatively UMCs. The implementation of coordinatively UMCs into porous MOFs has been considered one of the most attractive ways to improve their affinities to hydrogen. (3) Hydrogen storage studies in MOFs containing nanoscopic cages based on double-bond-coupled di-isophthalate linkers. Those ligands containing phenyl rings in MOFs have been proved favorable for hydrogen adsorption. (4) Designed and synthesized porous MOFs based on an anthracene derivative which can provide additional hydrogen binding sites to increase the hydrogen uptake. (5) Obtained stable MOFs with high surface areas by the incorporation of mesocavities with microwindows. (6) Constructed MOFs with “close-packing” alignment of open metal sites, which can increase the number of nearest neighboring open metal sites of each H_2-hosting void in a 3-D framework so that they can interact directly with the guests (H_2 molecules) inside the void. (7) Built up porous lanthanide MOFs and studied their potential application in gas adsorption.

FB-2.6:IL02 **Investigating Hydrogen Storage Materials by In Situ Neutron Diffraction**

Gavin S Walker, Fuels and Power Technology Research Division, University of Nottingham, Nottingham, UK

In situ neutron diffraction is a powerful technique to probe the structural changes occurring during hydrogen sorption either in porous materials, such as metal organic frameworks (MOFs), metal hydrides and/or complex hydrides. The preferential adsorption sites for a series of copper-based MOFs have shown the importance of unsaturated metal centres and the trigonal windows that MOFs with similar copper-paddlewheel coordination centres have. For multicomponent hydride systems based on lithium borohydride, in situ neutron diffraction has also helped elucidate the reaction path involved in cycling such materials. It has been found that the stoichiometry of the system affects the cycling kinetics and the gas environment for the decomposition of the hydrides, not only controls the reaction path and but can lead to deactivation of the decomposition products, affecting cyclability.

FB-2.6:IL03 **Simple and Binary Hydrogen Clathrate Hydrates: Synthesis and Microscopic Characterization Through Neutron and Raman Scattering**

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Gas hydrates are solid inclusion compounds made of water and other molecular substances, which have a crystalline structure different from common ice (i.e. Ih). Cages of different size and geometries are present in the structure of the hydrate crystal, which hosts the guest molecules. The search for efficient hydrogen-storage materials has led to an increasing interest in these compounds, since it has been demonstrated that an appreciable amount of molecular hydrogen can be stored in the cages and released at melting. Different clathrate synthesis procedures are investigated in order to maximize the quantity of trapped hydrogen and to speed up the kinetic of formation. Moreover, understanding the interaction of H2 with the host material is a key issue for a rational design of clathrates as hydrogen storage materials. Here, we describe the synthesis technique and the microscopic structures (sII and sH) of hydrogen clathrates. Then we present the results of inelastic neutron scattering and Raman light scattering experiments on simple (i.e. with one guest molecule) and binary (i.e. with two guest molecules) hydrogen hydrates. For each type of clathrate we have obtained information on the motion of H2 inside the cages, on the occupancy of the cages by H2, and on lattice dynamics.

FB-2.6:IL04 **Hydrogen Storage in Metal-organic Frameworks**

M. Hirscher*, B. Panella, B. Schmitz, I. Krkljus, Max Planck Institute for Metals Research, Stuttgart, Germany

For hydrogen storage by cryo-adsorption, metal-organic frameworks (MOFs) are excellent materials due to their high specific surface area and their tunable porosity. The physisorption process is fast and fully reversible and, therefore, short refuelling times can be realized. For MOFs, the great variety of organic ligands and metal-ions, which can be used in the synthesis, offers the opportunity to design a wide range of networks possessing the desired pore dimensions and metal centres. Considering experimental results obtained by different techniques, the influence of these structural parameters on the hydrogen storage properties will be discussed. This lecture will give an overview on the progress achieved in the field of hydrogen physisorption on MOFs.

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FB-2.6:IL05 **Spillover Mechanism in Hydrogen Storage Materials**

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A great number of studies during the last five years have repeatedly reported a significant enhancement of hydrogen storage capacity as a result of doping various porous adsorbents, such as carbons, MOFs and other nanostructured materials, with small amounts of metals. The incorporation of transition metal adatoms with nearly completely-filled d-shells (e.g. Pd, Pt), has been believed to lead to dissociative chemisorption of hydrogen on the metal catalyst particles followed by diffusive cascading into various adsorption sites on the nanoporous support. This mechanism, collectively known as spillover, is considered an efficient option for significant enhancement of the absolute hydrogen capacity of nanostructured materials and comprises currently the hot topic of hydrogen related material research worldwide. However, despite the wide range of systems that have been studied and the quite encouraging developments, the mechanistic details of the spillover phenomenon are still poorly understood, significantly hampering the bottom-up design of efficient materials. The enhanced understanding of hydrogen storage by spillover also on the basis of a rationalised choice/combination of catalysts and receptors thus remains a front-line challenge.

FB-2.6:L06 **Effect of the Pore Structure Upon Coordinatively Unsaturated Cu Centres**

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Metal-organic frameworks are a challenging class of porous and crystalline materials exhibiting exceptional sorption properties. The growing interest in the community lies in the flexibility in structure design thanks to the wide range of organic ligands and metal clusters available facilitating the pore tuning compared to other porous materials. Herein inelastic neutron scattering (INS) and neutron powder diffraction (NPD) techniques were combined at ISIS-RAL and enabled the investigation of three Cu (II) - frameworks NOTT-102, NOTT-103, and NOTT-112 with various para-H2 and D2 gas loadings. It allowed us to better understand the effect of the pore topology upon the adsorption site distribution and the H2 interactions. Intriguingly, the INS work revealed unusual features at around 9-10 meV which were assigned by NPD study to para-H2 interactions with the unsaturated Cu centres. The fine structure in the INS spectra is a very exciting result as it has not been reported for H2 adsorbed on a MOF before. Moreover, the assymmetry of the Cu sites on NOTT-112 allowed us to preferentially populate the Cu within the spherical cage which was not possible with NOTT-102 and NOTT-103 samples. The data were also compared with similar study on other Cu (II) compounds.

FB-2.7 Theoretical Modeling

FB-2.7:IL01 First-Principles Studies of Phase Stability and Reaction Dynamics in Complex Metal Hydrides

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Complex metal hydrides are believed to be one of the promising materials for developing hydrogen storage systems that can operate under desirable conditions. At the same time, these are also a class of materials that exhibit intriguing properties. We have applied state-of-the-art computational techniques to study the structural, dynamic, and electronic properties of these materials. This talk will focus on the critical role played by the Ti catalyst in helping hydrogen cycling in the alanates, which remains a challenging topic for this hydrogen storage material. We have performed a series of calculations to address the hydrogen interaction on the aluminum surface in the presence of the Ti ”dopant,” focusing on the effect of near-surface alloying on the Al(100) surface. It is found that Ti occupies subsurface sites near the Al surface. This subsurface Ti arrangement not only enhances H binding with the Al surface layer, but also improves H mobility on the surface. Based on existing experimental data and our preliminary results, we propose a model in which the catalyst does not enter the bulk, but facilitates hydrogen dissociation-recombination near the surface. The implication of Ti as a catalyst for the hydrogenation reactions will be discussed.

FB-2.7:IL02 Computational Screening and Structural Design of Complex Hydrogen Storage Materials

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A three-step calculational procedure is applied to design new complex materials for hydrogen storage med favorable thermodynamic stability and enhanced mass transport kinetics. Step I combines density functional theory (DFT) calculations on representative model structures with database methods to perform fast, large-scale screening studies to identify a number of alloys or mixtures with favorable stabilities. In Step II, we apply path techniques and harmonic transition state theory (TST) to determine diffusion rates in the relevant candidate structures and design the alloying ratios to favor structures with fast kinetics. Finally, we seek to indentify the true ground state structure and perform a more detailed analysis of the harmonic TST diffusion rate by including an analysis of the effects of neighboring higher order saddle points. We present results from large-scale computational screening studies of ternary alkali-transition metal borohydrides, where both an- and cation substitution is performed, as well as results from studies of mixed metal ammines. Results from the modeling of pathways and rates of dynamical processes involved in the ab-/desorption mechanisms will also be presented and compared to quasi elastic neutron scattering data.

FB-2.7:IL03 Numerical Simulation of Hydrogen Dynamics at a Mg-MgH2 Interface

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The remarkable ability of magnesium to store significant quantities of hydrogen, in the form MgH2, has fostered intense research efforts in the last years in view of its future applications where light and safe hydrogen-storage media are needed. However, further research is needed since Mg has a high operation temperature and slow absorption/ desorption kinetics that prevent for the moment the use in practical applications. To improve and optimize the performances of this material a detailed knowledge of the hydrogen diffusion mechanism at the atomic level is needed. For these reasons a computational study of MgH2 has been performed to characterize the dynamics of hydrogen during desorption. Further insights are gained by characterizing the Mg-MgH2 interface with and without metallic catalysts which are supposed to play a major role in the hydrogen diffusion during absorption and desorption cycles. By means of accurate ab-initio molecular dynamics simulations based on the density-functional theory with norm-conserving pseudopotentials and plane-wave expansion (CPMD code) the Mg-MgH2 interface is studied. Extensive electronic structure calculations are used to characterize also the role of metallic catalysts near the Mg-MgH2 interface during hydrogen desorption.

FB-2.7:IL04 Nano-materials for Hydrogen Storage

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Materials capable of storing hydrogen with gravimetric density of about 10 wt% have to consist of elements lighter than Aluminum. Unfortunately, the bonding of hydrogen in these materials is either too strong or too weak and ways must be found to tune the hydrogen bond strength so that these materials can be used for mobile applications. This talk will discuss how the novel properties of materials at the nanoscale can improve the thermodynamics and kinetics of hydrogen. In particular, I will discuss how carbon based nanostructures such as nanotubes and fullerenes can not only be used as catalysts to improve hydrogen uptake and release in complex light metal hydrides such as alanates, borohydrides, and imides but also how they can be functionalized with metal and B and Ca atoms to adsorb hydrogen in a novel quasi-molecular form. I will also discuss the role of electric fields in hydrogen storage. These results, based upon density functional theory and quantum molecular dynamics, provide a fundamental understanding of the interaction of molecular hydrogen with hosts consisting of light elements. It is hoped that the understanding gained here can be useful in designing better materials for hydrogen storage. Results will be compared with available experimental data.

FB-2.7:L05 Thermodynamic Database for Hydrogen Storage Materials

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In order to be used for applications, the thermodynamic stability of a candidate hydrogen storage material should be suitable for hydrogen sorption at room conditions. By mixing different hydrides, it is possible to promote the hydrogenation/dehydrogenation processes. On the other hand, small changes in composition allow a tailoring of thermodynamic parameters. So, knowledge of thermodynamic stability of hydrides is fundamental to study the hydrogenation/dehydrogenation processes. Moreover, thermodynamics and phase diagrams are useful to rationalize synthesis reactions of these compounds and to suggest possible alternative reaction routes. The purpose of this work is to develop a consistent thermodynamic database for hydrogen storage systems by the CALPHAD approach. Experimental data have been collected form the literature. In absence of experimental information, an estimation of the energy of formation of hydrides has been obtained by ab-initio modelling. Calculations have been performed with the CRYSTAL program[1]. The La-H and La-Ni-H phase diagrams have been reviewed and thermodynamically assessed using the CALPHAD method. Al, Mg, Na, B-based compounds/systems of interest for hydrogen storage are also included. The effect on thermodynamic properties of fluorine-to-hydrogen substitution in simple hydrides is considered. A discussion on the thermodynamic properties of liquid hydrogen (lattice stability) is also provided. Calculated and experimental thermodynamic properties of various hydrides have been compared and a satisfactory agreement has been achieved.

[1] *www.crystal.unito.it*

FB-2.8 Storage Testing, Safety and Economic Issues

FB-2.8:IL01 Environmental Reactivity of Solid State Hydride Materials: Modeling and Testing for Air and Water Exposure

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To make commercially acceptable condensed phase hydrogen storage systems, it is important to understand quantitatively, the risks involved in using these materials. A rigorous set of environmental reactivity tests have been developed based on modified testing procedures codified by the United Nations for the transportation of dangerous goods. Potential hydrogen storage material, 2LiBH4·MgH2, NH3BH3, AlH3, and Mg(NH2)2·LiH have been tested using these modified procedures to evaluate the relative risks of these materials coming in contact with the environment in hypothetical accident scenarios. It is apparent that an ignition event will only occur if both a flammable concentration of hydrogen and sufficient thermal energy were available to ignite the hydrogen gas mixture. In order to predict hydride behavior for hypothesized accident scenarios an idealized finite element model was developed for dispersed hydride from a breached system. Empirical thermodynamic calculations based on precise calorimetric experiments were performed in order to quantify the energy and hydrogen release rates and to quantify the reaction products resulting from water and air exposure. Both thermal and compositional predictions were made with identification of potential ignition event scenarios.

FB-2.8:IL02 A New Technology for Hydrogen Storage: Theory and Applications for the Transportation and Gas Industries

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The storage of hydrogen poses inherent weight, volume and safety obstacles. Conventional storage methods are unable to meet US DOE future on-board storage goals. C.En Ltd's technology utilizes an array of thin sealed capillaries made of glass materials. The developed system ensures the safe infusion, storage, and controlled release of hydrogen gas, under pressures of up to 1200 bar. Pressure resistances of single & multiple capillaries have been determined through experimentation on capillary materials (quartz, borosilicate, alumosilicate and soda-lime glass) conducted at the German Institute for Materials Research and Testing (BAM). Borosilicate capillaries showed the highest pressure resistance. Storage tests at BAM have demonstrated that the C.En technology has a gravimetric storage capacity of 33% & a volumetric capacity of 45 g/L. Test results significantly exceed the published storage capacities and exceed the DOE 2010 storage targets. Calculations clearly demonstrate that all variables of the DOE 2015 storage targets are achievable. The various methods of refilling and releasing capillaries with compressed hydrogen, as well as the theoretical analysis and experimental results of the resistance of glass capillaries to hydrogen pressure, loading and release will be discussed

FB-2.8:IL03 Hydrogen Storage in Complex Hydride Tanks: Upscaling and Testing

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Hydrogen storage is one of the main hurdles for the use of hydrogen as an energy vector. Different storage methods are used, offering an array of advantages and disadvantages in respect of storage density, safety, working conditions, and costs. Complex hydrides can store hydrogen in a compact and safe way at a wide range of standard industrial pressures of a few up to several 100 bar and temperatures of 120 °C up to 380 °C depending on the selected material. However, since these materials have only been developed recently they have not been tested under application or application near conditions and only little experience exists in the construction and test of complex hydride based tanks and their usage. At GKSS, scale-up of such tanks has been underway for some time. The strategy of gradual scale up has been tried out with the best known complex hydride, sodium alanate, with good results, and is being pursued for other advanced materials. In the case of sodium alanate, the main driver towards good kinetics in the system has proven to be good heat transfer to the active material, since the intrinsic kinetics do not represent a limiting step. Moreover, investigation of the costs associated with complex hydride tanks have shown that they compare favourably with other alternatives.

Poster Presentations

FB:P01 Preparation of Metal Ion Doped Titanate Nanotube Thin Film for Hydrogen Production

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Various metal ions doped titanate nanotubes were hydrothermally prepared using TiO_2 nanopowders with additions of 5 wt% of Ni, Fe and W ions in strong basic solution at 130 °C for 48 hours. Multi-layered transparent titanate nanotube thin film were formed by alternative layer coating and dipping method. The prepared powders and coating films were fully characterized using SEM, EDX, TEM, AFM and UV-Vis. The SEM and TEM results of all prepared powders showed nanotube shape with approximately 10 nm in diameter. EDX results showed that doped metal content of Ni, Fe and W was measured 1.38, 1.47, and 0.9 wt%, respectively. UV-Vis result of all metal ion doped titanate nanotubes coating layer showed that the absorbance value in the visible light region is higher than pure titanate nanotubes coating layer. Photochemical water decomposition for the production of hydrogen was conducted using batch typed home made reactor equipped with solar simulator in 0.1 N H_2SO_4 aqueous solution. Hydrogen production amounts of metal ion doped titanate nanotubes were measured 0.03 to 0.1 mM/hour in accordance with their crystallinities and surface areas.

FB:P02 Photo-electrochemical Characterization of a Miniature PEC Cell with Non-immersion Type TiO_2 Photoanodes

Eui-Chol Shin*, Yong Kim, Hyun-Ho Seo, Jong-Sook Lee, Jong-Ho Kim, Dong-Ryun Cho, Chonnam National University, Gwangju, Korea; Eun-Young Jun, Kyung-Sik Oh, Tae-Joo Chung, Andong National University, Andong, Korea; Martin Lerch, Technical University of Berlin, Berlin, Germany

We successfully constructed a miniature photoelectrochemical (PEC) cell with TiO_2 photoanode in non-immersion type using a quartz cuvette with a drilled window. Measurements of the electromotive force (EMF) between the photoanode and Pt cathode or between the photoanode and Ag/AgCl reference electrode were made during the light-off and light-on cycles for various TiO_2 anode materials: as-sintered ceramic, reduced pellet in 5% hydrogen, ceramic derived from Ti-salt flocculated sludge, nitrided ceramic prepared by reaction of TiO_2 and TiN in a graphite furnace and TiO_xN_y films prepared from the powder from ammonolysis, and by plasma-enhanced chemical vapor deposition (PECVD). Among them PECVD thin film and reduced TiO_2 bulk ceramic exhibited reproducible photoresponse in OCV. As-sintered ceramic specimens from reagent chemical and from powders derived from sludge and nitrided ceramic specimens exhibited little photosensitivity or response in the opposite direction and the OCV values were not well defined.

FB:P05 The Rate Determinig Steps of Catalyzed Mg on Hydrogen Absorption and Desorption Reactions

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We have examined the kinetics of hydrogen ab/desorption reactions and the deuterium isotope effects for catalyzed Mg. MgH_2 was milled with a Nb_2O_5 catalyst and the sample was annealed under vacuum for a dehydrogenation, resulting that catalyzed Mg was obtained. The catalyzed Mg powder was hydrogenated/deuterated. For these samples, the thermal desorption mass spectroscopy experiments were performed at several heating rates. From the Kissinger plots, both the activation energies of the H_2/D_2 desorption processes for MgH_2 and MgD_2 were evaluated to be 70 kJ/mol. The fact of no isotopic effect indicated that the rate determining step of desorption process is related to the formations of H_2/D_2 molecules on a Mg surface, because enthalpy changes of both reactions should be essentially the same. Furthermore, the activation energies of the H_2/D_2 absorption processes were investigated using Sievert's method at several isothermal conditions. The Arrhenius plots of rate constants showed the activation energies for catalyzed Mg were 20 kJ/mol and 35 kJ/mol, respectively. This result agrees well with the activation energies of H/D atom diffusion reported by Nishimura et al. We conclude that the diffusion of the hydrogen atom is rate determining step in absorption process of catalyzed Mg.

FB:P07 Metal Hydride-based Composite Materials with Improved Thermal Conductivity and Dimensional Stability Properties

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Standing the metal hydrides (MH) interesting reversible H_2 absorption properties, relatively few efforts have been devoted to improve some properties of MH in view of their applications in H_2 storage devices. In particular, characteristics such as dimensional stability of MH particles during the charge-discharge cycles, thermal conductivity of the metal alloy powder and H_2 recharging kinetics, require a significant improvement in view of real applications. A decisive contribute in increasing MH properties can arise from a proper material engineering, particularly in the case of alloys exhibiting a high H_2 volumetric absorption capacity such as AB_5 alloys. At the aim of improving the MH hydrogen storage technology, ENEA and CNR groups are jointly carrying on a research activity on the development of an innovative composite storage material able to overcome the aforementioned main issues. Here, we present an innovative composite material able to strongly increase the performance of an AB5 based storage device, consisting in MH particles embedded in a micro-porous silica matrix. The composite material was added with different high thermal conductivity carbon based fillers and a set of consolidated samples was characterized as a function of both the types and the filler's amounts. The thermal conductivity was raised up to 30 times with respect to the MH value's. Significant samples were characterized in terms of their H2 adsorption properties by using both volumetric and gravimetric methods. Results were compared and discussed.

FB:P09 **Solid State NMR Investigation of LiAl(NH2)4 on Thermal Decomposition**

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Lithium aluminum amide LiAl(NH2)4 is an attractive material because it contains a large amount of hydrogen in the form of amide [NH2]- . It releases NH3 gas by 35 wt% with a peak temperature of about 140 °C, whereas a composite of LiAl(NH2)4 and LiH (1 : 4) releases 5.6 wt% H2 below 140 °C. LiAl(NH2)4 is known to decompose into an amorphous phase(s) on NH3 desorption, and some reaction models have been proposed. In this study, we investigated the structural changes on the amorphization of LiAl(NH2)4 during the thermal decomposition by using 6,7Li, 15N, and 27Al MAS and 27Al 3QMAS NMR techniques to clarify the reaction pathway. LiAl(NH2)4 was synthesized by milling LiH and Al mixture with liquid NH3 for 8 h and keeping it static for 7 days. The obtained LiAl(NH2)4 was characterized by thermogravimetry-mass spectroscopy (TG-MS), and in situ synchrotron radiation X-ray diffraction (XRD). Nuclear magnetic resonance (NMR) spectra were acquired at 14.1 and 21.8 T. TG-MS showed that the main gas phase released was NH3 with a peak temperature of 135 °C and a gradual release above 150 °C. XRD profile indicated the amorphization of LiAl(NH2)4 above 135 °C. 6Li and 27Al MAS NMR spectra suggested that the amorphous phase was different from the reaction products proposed previously.

FB:P11 **Preparation of Modified Carbon Nanostructures for Hydrogen Sorption Studies**

D. Mirabile Gattia*, M. Vittori Antisari, R. Marazzi, A. Montone, E. Piscopiello, C. Mingazzini, ENEA, Research Centre of Casaccia, Rome, Italy

Carbon nanostructures have been predicted to be suitable materials for gas storage, in particular hydrogen. Their high surface area, porosity and surface reactivity could be at the basis of gas adsorption. Theoretical calculations demonstrated that carbon nanostructures doped with alkaline earth metals, like Ca, could enhance hydrogen sorption properties even at low temperatures. A charge transfer mechanism and hydrogen molecule dipole-induced polarization due to the presence of the alkaline earth metals is supposed to be at the basis of the enhanced hydrogen adsorption. This work reports the efforts of synthesizing new forms of carbon nanostructures doped with Ca by an arc discharge. In previous results the synthesis of single wall carbon nanostructures, i.e. single wall carbon nanohorns (SWNH), has been optimized by the use of alternating current instead of direct current in order to supply power to the arc. In particular an AC arc discharge has the advantage of reducing the formation of the hard deposit and maximize the production of light soot containing SWNH. Instead of two pure graphite electrodes, in this work mixtures of graphite and Ca containing compounds have been arched changing voltage and frequency in the range 20-30 V and 35-1000 Hz respectively.

FB:P12 **Hydrogen Storage on Beryllium-Coated Toroidal Carbon Nanostructure C_{120} modeled with Density Functional Theory**

F de L. Castillo-Alvarado[1]*, J. Ortíz-López[1], J.S. Arellano[2], A. Cruz-Torres[1], [1]Escuela Superior de Física y Matemáticas, Instituto Politécnico Nacional, Unidad Profesional Adolfo López Mateos, Col. San Pedro Zacatenco, Delegación Gustavo A. Madero, México, D.F., México; [2]Universidad Autónoma Metropolitana Azcapotzalco, Departamento de Ciencias Básicas, México, D.F., México

In this work we present results for a DFT computational study of a C_{120} carbon nanotorus. The Dmol^3 module was used to calculate, among others, total and binding energies, charge density, HOMO-LUMO and Mulliken population analysis. First we probed the stability of the isolated C_{120} nanotorus and also for each one of the beryllium-coated nanotori with nH_2 molecules systems. As it occurs for carbon nanotubes, the nanotorus also has a peculiar texture and a large specific surface area. This characteristic suggested us to study the adsorption and storage of H_2 for this system. To build the nanotorus we used the initial structure with only 12 carbon atoms, proposed by Sigeo Ihara and coworkers[1]. The generated structure is composed by ten pentagonal, forty hexagonal and ten heptagonal rings. The weak van der Walls forces are taken into account in DFT using the generalized gradient approximation due to Perdew and Wang, (PW91). To calculate the interaction energies of the hydrogen molecules with the C_{120} nanotorus, the DFT is complemented with a double numerical plus polarization basis set, (DNP). In summary, we have studied the hydrogen adsorption capabilities of toroidal carbon C_{120} nanostructure as well as alkaline-earth metal (Be). Beryllium coated toroidal carbon C_{120} nanostructure is demonstrated to be good candidate with moderate adsorption energy of H_2.

[1] Sigeo Ihara and Satoshi Itoh, Phys. Rev. B 47, (19), (1993) 12908-12911.

FB:P17 **Innovative Systems for Hydrogen Storage**

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The main challenges in the perspective of a hydrogen economy is the development of storage systems safe and with high weight capacity. The most promising systems are the storage in innovative metal and chemical hydrides and the use of high pressure tanks built with composite materials. The present work deals with the results obtained in the frame of a cooperative Italian Project, whose objectives have been the development of innovative systems for hydrogen storage to use in specific technological applications: large scale energy storage coupled with renewable generation systems and automotive, with a particular attention to the fluvial and the sea transportation in protected area. Theoretical, modelling and experimental activities have been oriented to the development of innovative high capacity magnesium based hydrides, the definition of a regeneration method for chemical hydrides, the integration of intermediate pressure electrolysers coupled with advanced compressors and the development of thermomechanical models for executive design of storage systems. Prototypes has been realised and installed in a test facility in the Fusina (Venice) electric power plant. The activity has been completed with an executive feasibility study, in the perspective of industrial application.

Symposium FC

FUEL CELLS: MATERIALS AND TECHNOLOGY CHALLENGES

Oral Presentations

Session FC-1
Solid Oxide Fuel Cells (SOFCs)

FC-1:IL01 **Progress Towards Redox-stable Anode-supported Solid Oxide Fuel Cells**

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Besides several degradations mechanisms slowly reducing the cell voltage with time, there also exists the probability of spontaneous failure when the anode is unintentionally re-oxidised during operation. This so-called “redox stability” of anode-supported solid oxide fuel cells (SOFC) is still a major technological challenge although several ceramic materials have been proposed as redox-stable anode materials. For the development of an anode-supported cell, however, more challenging requirements are necessary to guarantee efficient electron transport and gas tightness of the electrolyte. Ceramics based on strontium titanate have been found to fulfil the ambitious demands for an SOFC anode substrate. Sr0.895Y0.07TiO3 was selected as the most appropriate composition and first fuel cells were manufactured with a size of 50 x 50 mm2. The test of gas tightness revealed no damage of the electrolyte layer after 20 cycles. After electrochemical performance test 200 redox cycles were carried out at 750 °C between H2/H2O fuel gas and air. The OCV remained nearly constant, thus providing superior redox behaviour compared to cells with Ni/YSZ anode substrates. Nevertheless, cell performance decreased by 35% indicating an increasing ohmic resistance of the cell.

FC-1:IL02 **Principle of Mixed Reactant Fuel Cells and Ways to Achieve the Required Catalytic Selectivity**

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In mixed reactant fuel cells (MR-FCs) air and fuel are mixed before being introduced into the fuel cell. The symmetry is broken using two electrodes with different catalytic properties, one catalyzing the electrochemical reduction of oxygen becoming the cathode, being inert towards the oxidation of fuel and the second electrode catalyzing the electrochemical oxidation of the fuel becoming the anode, being inert towards the reduction of oxygen from the gas phase. The direct chemical oxidation reaction of the reactants the gas phase is inhibited. A few MR-FCs have been demonstrated in recent years. However, all are operating at low temperatures (T < 100 °C). At elevated temperatures only single chamber fuel cells (SC-SOFCs) were prepared where the cathode is selective but the anode is not. If MR-FCs and in particular solid oxide ones (MR-SOFCs) could be made to function well they would have significant advantages over common fuel cells. We shall review the existing low temperature MR-FCs, then SC-SOFCs, the advantages of MR-FCs if realized and the possible ways to achieve the required selectivity at the electrode, which is the key problem in realizing MR-FCs. We shall pay special attention to high temperature MR-SOFCs.

FC-1:IL03 **Direct-fueled Solid Oxide Fuel Cells Using a Multi-layered Anode with Different Porosities**

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One of the major issues in solid oxide fuel cells (SOFC) is how to internally reform hydrocarbons directly, without the use of any pre-reforming fuel-processing steps. Internal reformation can potentially make the system very compact, as well as produce a higher overall system efficiency. However, few systems have successfully demonstrated internal reformation, since carbon deposits are formed within the gas channel and/or anode itself. To overcome this problem, a layered anode containing both a series of catalytic layers with different porosities and activities, as well as catalytic functional layers could be prepared, which could potentially allow for efficient internal reformation. In this preliminary work, multi-layered anodes (Mu-LA) were investigated. To characterize the performance of the Mu-LA, they were compared to standard mono-layered anodes (Mo-LA). The anodes for a Mu-LA and Mo-LA, consisted of 40 mol% NiO and 60 mol% YSZ. The Mu-LA had a porosity gradient, which was controlled using a pore-former, while the Mo-LA had a constant porosity throughout the anode structure. The anode supports were fabricated using a tape casting method; all green sheets for the anode and the electrolyte were hot-pressed at 80 °C, and sintered at 1350 °C. After the anode/electrolyte system was developed, the cathode was coated via a screen printing process. The 2 separate SOFC systems were electrochemically tested using hydrogen/steam and reformate. The preliminary results showed that the SOFCl with Mu-LA had lower overpotentials and resistances, and showed higher performance for both fuels. Initial results also showed no carbon formation on the anode. This paper will describe the results realized from the fuels tested, and will also show some FEA modeling of the anode to better understand the reasoning behind the improved performance.

FC-1:IL04 **Status of SOFC Cell Materials - Possibilities for Significant Improvements During the EU 7th Framework Programme**

Robert Steinberger-Wilckens, Forschungszentrum Jülich GmbH, Jülich, Germany

The performance of SOFC technology today is high and far surpasses any other type of fuel cell. Nevertheless, several issues still remain to be solved. Similar to the Molten Carbonate Fuel Cell (MCFC), the SOFC is discussed in the context of stationary power generation. Here, the target lifetime of systems is generally set around ten years, necessitating 100 000 hours of operation and more. Therefore, the durability of SOFC devices is a critical topic that needs to be addressed through improved materials that offer: - low corrosion and degradation of materials; - tolerance against gas impurities and temperature gradients; - high mechanical stability and stress tolerance. One approach in reducing detrimental effects on long-term performance is the lowering of the operating temperature. High-performance materials and thin functional layers lend themselves to this goal as well as, for instance, the development of new cell substrates. Nevertheless, not only the development of improved materials is an important issue, but also the understanding the influence of operating conditions on the materials, their interactions, their stability and kinetics. Although many materials have been used for a long time already, much of the information on long-term and stable performance is still missing.

FC-1:IL05 **Metal Supported SOFC Cells, Progress and Benefits**

N. Christiansen, Topsoe Fuel Cell A/S, Lyngby, Denmark

Considerable progress is being made in raising the performance of Solid Oxide Fuel Cells (SOFC). Today ceramic anode-supported SOFC cells represent the state-of-the-art. However the use of ceramic SOFC cells inherently impose limits in terms of reliability and ability to handle transients. The objective of the next generation SOFC technology is to develop a stack technology based on ductile metal-supported cells to improve robustness and general performance. In case of a metal supported cell concept, some new important challenges appear that must be overcome primarily concerning materials compatibility, materials processing and interaction, inter-diffusion and vaporisation of metallic alloy elements and finally hot corrosion/oxidation and high temperature creep of the metallic parts. Component development has to comprise fundamental studies concerning loss mechanisms and degradation phenomena in individual parts of cells and stacks. System-oriented cell and stack tests, with a special emphasis on cycling stability tests and robustness, has to prove the applicability of SOFC under demanding real operation conditions. The paper presents a review of the recent worldwide achievements within the field of metal based SOFC technology including electrochemical performance and durability of the novel metal-supported cells and stacks developed at TOFC and Risø-DTU. The results presented in the paper show that the novel cell and anode design has a promising performance and durability at a broad range of temperatures and is especially suitable for intermediate temperature operation.

FC-1:IL06 **Chromium Deposition and Poisoning at Solid Oxide Fuel Cell Cathodes - How Much do we Know?**

San Ping Jiang, Xingbin Chen, School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore, Republic of Singapore

For solid oxide fuel cells (SOFCs) using chromia-forming alloy as metallic interconnect, volatile Cr species are generated over the chromia scale, poisoning the SOFC cathodes such as (La,Sr)MnO3 (LSM) and (La,Sr)(Co,Fe)O3 (LSCF) and causing a rapid degradation of the fuel cell performance. Thus, a fundamental understanding of the interaction between the Fe-Cr metallic interconnet and SOFC cathode is essential for the development of SOFCs with high performance and high stability. In this presentation, the progress in the understanding of the mechanism and kinetics of the Cr deposition and poisoning at the SOFC cathodes in the last 10 years will be briefly reviewed. In particular, a systematic study on the chromium deposition and poisoning at the (La0.8Sr0.2)0.95(Mn1-xCox)O3±δ (LSMC, 0.0≤x≤1.0) cathodes will be presented. The result clearly demonstrated that there is no close correlation between the chromium deposition at the LSMC (0.0≤x≤1.0) cathodes and its electrocatalytic activity. Finally, a strategy to develop Cr-tolerant cathodes is proposed.

FC-1:IL07 **Low-temperature SOFC Development**

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The SOFC600 project is an EC funded Integrated Project, coordinated by the ECN. The 4-years project finished in February 2010. It joined virtually all major European groups on the development of planar stack components for low-temperature operation. In addition the consortium comprised organisations from China, Canada, Ukraine, Russia and Belarus. It concerned a generic technology development, with emphasis on stationary applications fuelled by natural gas. Degradation mechanisms that limit the lifetime of SOFC stacks are generally thermally activated. These mechanisms will be slowed down significantly by decreasing the operating temperature. Moreover, the lower operating temperature enables the use of cheap, conventional steels, not only for the stacks but also for the system components. The project addressed anodes, cathodes, electrolytes, seals, and interconnect materials and coatings. This presentation will give an overview of the main results obtained during the four years of development. Cell development was very successful meeting project targets on performance and degradation. Several combinations of standard steels and coatings have been identified that fulfil lifetime and electrical conductivity requirements. Long-term operation of single repeating units, combining the optimal components, demonstrated the achievement of final project targets on performance and degradation.

FC-1:IL08 **Electrochemical Processes Around three Phase Boundary Area in SOFC Electrodes**

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The three phase boundary among electrode, electrolyte, and gas phase is the stage of the electrochemical reaction for the solid oxide fuel cells (SOFCs). The microstructure around the three phase boundary and its morphological change directly affect the performance of SOFCs. Nickel-yttria stabilized zirconia (Ni-YSZ) cermet is a conventional anode for use in SOFC. The deterioration with steam can be expected in the downstream region of fuel cells at a deep discharge condition because of the concentrated steam produced by generation. Three-dimensional microstructure of a conventional Ni-YSZ anode is quantified by means of dual beam FIB-SEM system. The discharge in highly concentrated steam in fuel mixture accompanies the morphological change in Ni surface and TPB density. Internal reforming of hydrocarbons is attractive in deriving high conversion efficiency and simplified generation system. The present investigation focuses on the use of hydrocarbon fuel. The electrode cermets used were Ni-YSZ, Ni-ScSZ, and Ni-SDC. The rate of carbon deposition on these cermets was evaluated by generation characteristics, electrochemical analyses, gravimetric technique, and microstructural observation.

FC-1:L09 **Electrochemical Characteristics of Thin Film Electrodes of SOFC Grown by PLD**

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LaxSr1-xMnO (LSMO) and LaxSr1-x CoO (LSCO) have problem that they react with YSZ electrolyte to produce oxide ion insulator at high temperature. Gd0.5Sr0.5CoO3 (GSCO) is less reactive with YSZ at high temperature and has higher oxygen ion conductivity at low temperatures than LSMO or LSCO. So, GSCO has been suitable for material of cathode in Solid Oxide Fuel Cell (SOFC). GSCO film as cathode and NiO-YSZ film as anode have been fabricated on YSZ substrate by pulsed laser deposition (PLD). The film obtained has a columnar crystalline structure and so the active surface area contacted by gas increase. The PLD technique has been suitable for growing the film of complex composition, flatness. We searched optimum conditions of fabrication electrode film for performance of SOFC. The film has been studied for porosity, crystalline, electrical conductivity and power density. The GSCO film grown at high substrate temperature and high oxygen gas pressure have good crystalline and high electrical conductivity (820 Scm-1 at 973 K). This value is higher than it of the LSMO film. The power density of the cell with 3µm NiO-YSZ film grown by PLD became 10 times as high as the cell with 1µm NiO-YSZ film. In this way, optimization of fabrication conditions is important for SOFC cell performance.

FC-1:L10 **Long-Term Study of MIEC Cathodes for intermediate temperature Solid Oxide Fuel Cells**

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La0.58Sr0.4Co0.2Fe0.8O3-d (LSCF) as a mixed ionic and electronic conductor (MIEC) was reported as one of the best performing cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFC). Preliminary parameter studies of anode supported cell performance concluded that the overall degradation rate for ASC cells with composite LSM-YSZ cathode is significant less when compared to ASC cells with LSCF cathodes. In the meantime a high-sensitive long-term study of ASC cells with LSCF cathodes with special emphasis on the cathode degradation provided more details. Ohmic and polarization losses of electrolyte, anode and cathode were identified separately by high resolution impedance studies based on a combination of DRT-analysis (distribution of relaxation times) followed by a CNLS fitting approach. This method is highly valuable for a detailed examination of polarization losses in ASC cells. In the present contribution the time-related change of both anodic and cathodic polarization losses were recorded and evaluated for more than 700 hours of operation. The cathodic polarization resistance (0.018 Ω.cm2 at t = 11 h), by far the smallest part, could only be visualized in the relevant frequency range by well selected and adapted experimental parameters.

FC-1:L11 **High Performance and Long-term Stability of Ni/GDC Based SOFC Unit Cells Operated at Low Temperature Using CH4 Fuel**

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Present development of SOFCs has been focused on decreasing the operating temperature (~650 °C) and direct using of available fuels such as hydrocarbons. Gadolinium doped ceria (GDC) materials received much attention for their high ionic conductivity at low operating temperatures (500~700 °C). The NiO-GDC anode supported unit cells were composed with the GDC electrolyte that have the improved densification adding CuO 0.1 wt% as sintering aids. This unit cells were operated at direct use of methane under various conditions, temperature, ratio of fuels/air, and current loading. In this way, this work could develop the optimum operating condition in the Ni-GDC based SOFC unit cell without thermal degradation and retaining carbon deposition for a long period at 650 °C, CH4 atmosphere. Also, this operating condition showed high performance because carbon deposited from the methane improved Ni anode conductivity. The NiO-GDC based anodes showed the maximum power density of 0.58 Wcm-2 and almost no thermal stress (~0.15%/khr) until 1100 hours at 650 °C in dry CH4 atmosphere. Under the optimum operating conditions, the NiO-GDC anode supported unit cells showed great potential for direct utilization of hydrocarbon fuels.

FC-1:IL12 **Materials Challenges for Intermediate and Elevated Temperature Fuel Cells**

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Intermediate and high temperature using inorganic electrolytes fuel cells, spanning an operational temperature range between 300 and

750 °C, offer the possibility of using biofuels, hydrocarbons, and hydrogen with high efficiency. The technologies allowing for these developments continue to face important materials challenges to meet performance, durability, and cost targets. In this review, the trade-of between temperature of operation and performance are discussed as affected by materials requirements and choices. At lower temperatures, metallic interconnects can be used without the problems of oxidation that accompany high temperature operation. Nano-infiltrated catalysts can enhance performance without being limited by the coarsening. Alternative membranes, such as ultra-thin supported oxide ion and phosphate proton conductors may enable solutions to both cost and performance challenges.

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FC-1:IL13 **Feasibility of Liquid Fuels for SOFC with Ni-base Anode**

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One of the advantages of SOFCs is fuel flexibility. In principle, hydrocarbon can be used without external reformer and, as a result, highest efficiency can be expected. The reaction heats can be used most effectively for the internal reforming reaction, precious metal catalyst is not required, and the overall stack and system can be simplified. On the other hand, degradation and disintegration of nickel base cermet anode is a serious problem in direct utilization of hydrocarbon fuels, especially liquid fuels such as kerosene. In the present study, we tried to operate the SOFC with nickel - scandia stabilized zirconia (Ni-ScSZ) cermet anode by direct feeding of liquid hydrocarbons. SOFC operation tests were carried out at 800 °C with liquid hydrocarbons as n-dodecane (C12H26), toluene containing n-dodecane and desulfurized kerosene (sulfur content is lower than commercial kerosene) at S/C = 2. Nickel particles grew from about 1 micrometer to more than 3 micrometer in diameter after using the desulfurized kerosene. This nickel sintering seems to be enhanced by remaining minor impurities in the desulfurized kerosene such as sulfur. From thermodynamic consideration, it is suggested that Ni-S eutectics can be stably formed under some SOFC operation conditions.

FC-1:L17 **(Y0.08Sr0.92)(Ti1-xFex)O3-δ Perovskite for Solid Oxide Fuel Cell Anode**

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It is well known that Ni-YSZ cermet anodes of solid oxide fuel cells (SOFC) have outstanding catalytic activity for H2 oxidation, high electrical conductivity and good chemical/mechanical compatibility with an YSZ electrolyte. However, Ni-YSZ cermet anode suffers from long term performance degradation which was associated with the agglomeration of nickel particles, the deactivation of nickel under fuel with sulfur or hydrocarbon and microstructure change due to the oxidation of nickel and so on. Thus, along with the effort to overcome the problems mentioned above, an alternative perovskite-type anode material with excellent long term stability is being proposed recently. In this study, 8 mol% yttrium and iron co-doped SrTiO3-based anode, (Y0.08Sr0.92)(FexTi1-x)O3-δ (x = 0.05, 0.2, 0.25, 0.4 and 0.5) was fabricated by a solid state reaction method. Phase stability in air and reducing atmosphere, electrical conductivity and electrochemical property of the (Y0.08Sr0.92)(FexTi1-x)O3-d were investigated in terms of Fe doping content.

FC-1:L18 **The Study of Oxidation Resistance of Fe-Cr-Mn-X Alloys for Interconnector of Solid Oxide Electrolyte Fuel Cell (SOFC)**

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The iron chromium manganese alloy is a common material for metallic interconnector of solid oxide electrolyte fuel cell (SOFC). The oxidation resistance and high temperature properties still require elaborate work to improve its life time and performance. Different amounts of titanium, molybdenum, cobalt and lanthanum have been added into Fe-Cr-Mn alloys in order to improve their oxidation resistance and thermal property. The composition of alloy was designed to have bcc phase microstructure with aid of software thermal-calc and melted in argon gas protected electric arc furnace. It has been found that the Fe-Cr-Mn alloys tend to form chromium oxide (Cr2O3) in the inner layer, while manganese oxide will exist in the outer layer of oxide, which could relieve the harm evaporation of chromium oxide by preventing its exposure directly to the outside atmosphere. The phase diagram reveals that Fe-20Cr-2.2Mn alloy will generate Laves and mu phase with increase of Ti and Mo content, but it will maintain the bcc phase with proper increase of Co. It seems that addition of Co, La could have better effect than Ti and Mo on high-temperature oxidation resistance. In addition the influence of alloys elements on the thermal expansion and electrical resistance will also be examined.

FC-1:L20 **Structure and Ionic Conductivity of Apatite Type-lanthanum Silicates**

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Oxyapatite materials are generating considerable interest owing to their potential application as electrolytes in SOFCs operating at intermediate temperature. These materials, with the general formula $(Ln/A)_{10-x}(Si_{1-y}B_y)_6O_{2+\delta}$, where Ln is a lanthanide, A an alkaline earth (Ba^{2+} or Ca^{2+}) and B = Al^{3+} or Ge^{4+}, are chemically stable and exhibit good ionic conduction properties. The conduction mechanism of these materials is still a subject for controversy. An interstitial oxygen mechanism is admitted but the location of this oxygen and the migration pathways remain unclear. In this paper, the apatite structure was investigated by powder neutron diffraction at low temperature. The conduction properties and the microstructure of apatites doped on the Si-site were studied. $La_{9.67}Si_6O_{26.5}$, $La_{10}Si_{5.5}Mg_{0.5}O_{26.5}$, $La_{9.83}Si_{5.5}Al_{0.5}O_{26,5}$, $La_{9.67}Si_{5.5}Ge_{0.5}O_{26.5}$ powders and dense samples were prepared by high temperature solid state reaction. Neutron powder diffraction was carried out at 3K and room temperature. AC impedance spectroscopy was carried out in air between 200 °C and 900 °C. A maximum conductivity of 1.5 x 10^{-2} $S.cm^{-1}$ at 700 °C was obtained. Whatever the composition, the oxygen stoichiometry was the same ($\delta = 0.5$) and similar conductivities were measured. It seems that the nature of the dopant has little influence on the electrical properties. The existence of an interstitial oxygen site was proven. One interstitial site at [-0.01; 0.04; 0.06] was evidenced which allow to propose an oxygen diffusion pathway with realistic oxygen-oxygen bond lengths.

Session FC-2
Polymer Electrolyte Fuel Cells

FC-2:IL01 **High Temperature Polymer Electrolyte Fuel Cells: Prospects and Challenges**

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High temperature polymer electrolyte fuel cells (HT-PEMFCs) have drawn considerable attention during the past 10-15 years, from various industrial segments such as portable electronic devices, stationary combined heat and power (CHP), automotive and aviation. The CHP efficiencies they offer, together with the lower price of PBI based membranes compared to Nafion® based membranes and the possibilities that exist to use non-noble metal catalysts in these fuel cells which operate at around 180 °C, substantial (close to 70%) reduction in system size (when compared to LT PEMFCs) have been the major driving force. However, there remain some technical challenges to be addressed. Some of them are catalyst and catalyst support degradation, electrolyte (acid) management, both preventing it from being leached out and ensuring that it does not result in triggering other degradation phenomena in the total system, creep behaviour and the mechanical integrity of chemically stable gasket materials used in these high temperature cells. Overview of HTPEMFC component durability, degradation and possible ways to handle degradation, are discussed together with experimental results at the conference.

FC-2:IL02 **Status on New Materials Development for the ORR for PEM Fuel Cell Applications**

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The minimum Pt loading (sum of the anode and the cathode (optimistic scenario) is at least 0.6 mg/cm2. This leads at least 0.86 (e.g.0.9 g/kW-1 power). Assuming a stack power of 75 kWe as an average power for

Fuel Cell vehicle in North America, we will need 67.5 g/vehicle. This quantity is higher than 2 ounces (62.08 g) per vehicle. Even if we reduce the Pt loading to 0.4 mg/cm2 which will lead to 30g/vehicle, the Pt will be still high. In comparison the Pt loading of catalytic converters in current vehicles is 3 to 5 g per vehicle. This is one of the main reasons for the high cost of the PEMFC stack. Another reason is the availability of the Pt and will be analyzed during the presentation. Therefore, for mass production of PEMFC, it is necessary to find a better electro-catalyst and/or decrease the Pt amount used in PEMFC. Nevertheless to remove platinum from electro catalysts, researchers focused on new materials development for the ORR. This has triggered numerous studies on the ORR on various materials, ranging from Pt and Pt-alloys catalysts, to various following non-noble and metal catalysts which have introduced since few decades ago or during the last decade. The development of most of these various families of catalysts are in their earlier stage, and the various classes of these materials, their preparation, properties and performance will be presented. These materials include: Lighited ruthenium based chalcogenides; Catalyst based on pyrolysed Fe porphyrin; Metal carbides; Mo, Ir or Co based catalyst have been also studied; cobalt-polypyrrole or Pd-alloys materials which have been recently introduced by our group as ORR cathode electro catalysts for PEM Fuel Cells Applications. The stages of the development of the classes of non-noble catalysts will be presented and the improvements in their method of preparation and their characterization will be analyzed. The non-noble metal catalysts are dramatically less active than the Pt and Pt-alloys. Consequently, up to now, only Pt materials have been successfully considered as the efficient cathode for the ORR in PEMFC operating conditions. The presentation will discuss on the main parameters which make these various non noble catalysts very limited for the ORR for PEMFC applications. Palladium based bi metallic alloys which are less expensive than Pt-based electro catalysts. We will present the performance of the Pd-alloys as oxygen tolerant cathode for the alcohol fuel cells. We will correlate the variation of the intrinsic metal surface properties (lattice parameter, binding energy, work function (W_f), d-band filling and d-band center ε_d) and the O_2 and OH adsorption energies of on Pd-alloys surface using *ab initio* program to their electro catalytic properties. Why the decrease in the onset potential of the ORR on palladium alloys (18 mV) due to the presence of ethanol on the Pd-based catalysts is more than ten times smaller than those observed on bulk Pt and sputtered Pt (275 and 513 mV, respectively) will be presented. Fundamental interpretations of these results will be shown. How these results may allow the identification of new families of alcohol tolerant cathodes for the ORR will be indicated. How new non-Pt catalyst is a dream or reality will be discussed.

FC-2:L04 **Mesoporous Tungsten Oxide with Mixed Electron and Proton Conductivity**

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Mesoporous tungsten oxide powders were synthesized by a straightforward, non-hydrolytic sol-gel technique based on butylic alcohols as gelling agents. Surface area and pore size distribution were determined by nitrogen adsorption/desorption analysis. Transmission Electron Microscopy, Scanning Electron Microscopy and X-Ray Diffraction were employed for structural and morphological characterization. These materials have a hierarchical particulate structure with surface area up to 145 m^2/g and pore volume up to 0.57 cm^3/g. Electrical behaviour was investigated by Electrical Impedance Spectroscopy in anhydrous as well as wet conditions. Importantly, a simple “flash-sintering” treatment was successfully set up to ensure a mixed electron-proton conduction without reducing mesoporosity, what has implications for a variety of emerging technologies (e.g. fuel cells). Electron and proton conductivities of final products are strongly dependent on treatment conditions and at room temperature they exhibit typical values around 1 and 0.01 S/cm, respectively.

FC-2:IL05 **PEM Fuel Cells: Progresses and Challenges**

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Polymer electrolyte membrane (PEM) fuel cell has been aggressively developed worldwide as a clean power source for portable, mobile and stationary co-generation applications. Significant progresses have been made in terms of cost reduction, improvement in the durability and reliability, as well as in the performance and power density. For automotive applications, cold start capability has been demonstrated in real fuel cell vehicles. However, significant technical challenges remain to be resolved before widespread commercialization of PEM fuel cell technology. In this presentation, the progresses achieved will be reviewed in terms of the technology development and fundamental understanding, outstanding technical barriers to commercial applications of PEM fuel cells will be described, current efforts/understanding and possible resolutions to the technical challenges will be outlined. In addition, endeavor will be made to elucidate future prospects and research directions of PEM fuel cells.

FC-2:IL06 **Low Humidity Proton-conducting Membranes**

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Due to the considerable interest in PEM fuel cells as power sources for transportation purposes there has arisen a need to examine the feasibility of proton conducting membranes that do not depend on the presence of water or other free solvents for their performance. Elimination of the dependence on water as the solvent for proton conduction provides major system simplifications in water and heat management. The most attractive option involves a true solid-state material that contains no free solvent, is conductive at low temperatures as well as elevated temperatures, rejects rather than takes up product water and can be tailored to provide desired gas permeabilities for both the separator and the membrane-electrode assembly. Of course, the materials must be compatible with the electrode structures and catalysts so that the electrochemical reactions are supported with a minimum of overpotential. To accomplish this, proton solvating molecules must be selected to replace water and these molecules must also be tethered to the polymer backbones in an analogous fashion to the attachment of sulfonic acid groups to perfluorosufonic acid polymers such as Nafion®. Heterocyclic bases such as imidizole, benzimidazole and triazole have been selected as the candidate solvent molecules since it has been known for many years that these bases support proton transport. These molecules may be functionalized so that they can be covalently tethered to a polymer backbone so that they do not leach out of the membrane. However, in order to achieve practical conductivities (0.01-0.1S/cm), it is necessary to promote fast proton transport by mechanisms such as structure diffusion, sometime known as Grotthuss transport. To achieve this requires the appropriate choice of protogenic group in optimum relative concentration to the solvent molecules as well as control of the polymer morphology to provide pathways for the fast charge transport. The polymer morphology also plays a critical role in determining the gas diffusion through the material. This talk will describe studies on proton transport with imidazole based materials. Imidazole has been chosen due to its reported resistance to oxidation reactions. Model compound studies have been performed on proton conducting ionic liquids both in neat form, blended with polymer matrices and with polyelectrolyte blends to determine optimum conditions. It has been shown that block copolymer backbone structures are necessary to achieve high conductivities, particularly at lower temperatures. Conductivity results will be presented from materials that have fully tethered solvent and acid moieties as well as morphological properties and oxidative stability measurements. Compatibility tests with electrodes will also be discussed.

FC-2:IL07 **Synthesis of Novel Metallodendrimers and Their Applications**

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Dendrimers are highly branched organic macromolecules with successive layers or “generations” of branch units surrounding a central core. Organic inorganic hybrid versions have also been produced, by trapping metal ions or metal clusters within the voids of the dendrimers. We show that metalhalides, complex to the imines groups of a spherical polyphenylazomethine dendrimer in a stepwise fashion according to an electron gradient, with complexation in a more peripheral generation proceeding only after complexation in generations closer to the core has been completed. It should be possible to control the number and location of metal ions incorporated into dendrimer structures, which might and uses as tailored catalysts or building blocks for advanced materials. Using the template, a phenylazomethine dendrimer with the controlled number of Pt complexes, subsequent reduction of PtCl4 to Pt(0) results in the formation of platinum clusters composed of a defined number of atoms. As a result of exceptionally small particle size, the clusters exhibit very high catalytic activity for the four-electron reduction of oxygen molecules.

FC-2:L11 **Hybrid Materials for Proton Exchange Membrane Fuel Cell**

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Fuel cell technology has merged in recent years as a keystone for future energy supply. The proton exchange membrane fuel cell (PEMFC) is one of the most promising projects of this energy technology program;

the PEMFC is made of a conducting polymer that usually operates at temperatures in the range 20-80 °C. In order to reach high energy consumption application like transportation, the using temperatures need to be increased above 100 °C. Sol-gel organic/inorganic hybrids have been evaluated as materials for membranes to fulfill the high temperature using requirement. These new materials for membrane need to retain water content and therefore proton conductivity property with using temperature and time. The membranes also need to be chemical-resistant to strong acidic conditions and to keep their mechanical properties regarding stacking requirements. In order to answer all these specifications, the proposed hybrid membranes are based on nanoporous inorganic phase embedded in an organic polymer in which chemical grafting and conductivity network microstructure are optimized to preserve both water-uptake and proton conductivity at higher temperatures. Such very promising results on these new hybrids are presented and discussed regarding electrochemical properties/ microstructure.

Session FC-3
Solid-Polymer-Electrolyte Direct Methanol Fuel Cells (SPE-DMFCs)

FC-3:IL01 Membraneless Fuel Cells as Microscale Power Sources and Analytical Platforms

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A growing need for high energy density miniaturized power sources for portable applications has spurred the development of a variety of microscale fuel cells. For portable applications, membrane-based fuel cells using small organic fuels like methanol are among the most promising configurations as they benefit from high energy density and easy storage of liquid fuels. Unfortunately, their performance is often hindered by membrane-related issues such as water management and fuel crossover. Furthermore, lack of durability and high cost of catalysts and electrodes hinder commercialization. To address these challenges we have developed laminar flow-based fuel cells (LFFCs), which exploit microscale transport phenomena (laminar flow) to compartmentalize streams within a single microchannel. The performance of membraneless fuel and media flexible LFFCs, the scaling out to multichannel prototypes, as well as strategies to improve fuel utilization will be discussed. We have also developed a microfluidic fuel cell that serves as a powerful analytical platform to investigate and optimize the complex processes that govern the performance of catalysts and electrodes in an operating fuel cell while maintaining all capabilities of a traditional 3-electrode electrochemical cell.

FC-3:L03 Investigation of a Passive DMFC Mini-stack at Ambient Temperature

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Direct Methanol Fuel Cells (DMFCs) are promising candidates for portable electric power sources because of their high energy density, lightweight, compactness, simplicity as well as easy and fast recharging. Recently, the attention has been focused on portable applications with passive-feed DMFCs. Under this configuration, DMFCs operate without any external device for feeding methanol and blowing air into the cells. An investigation of properties and operating parameters of a passive DMFC monopolar mini-stack, such as catalyst loading and methanol concentration, was carried out. From this analysis, it was derived that a proper Pt loading is necessary to achieve the best compromise between electrode thickness and number of catalytic sites for the anode and cathode reactions to occurs at suitable rates. Methanol concentrations ranging from 1 M up to 10 M (40 vol%) and an air-breathing operation mode were investigated. A maximum power of 225 mW was obtained at ambient conditions for a three-cell stack, with an active single cell area of 4 cm2 corresponding to a power density of about 20 mWcm-2.

FC-3:L04 Novel PVA-SSA-HPA-Bridged-Mixed-Matrix-Membrane Electrolytes for DMFCs

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Stabilized forms of heteropolyacids (HPAs), namely phosphomolybdic acid (PMA) phosphotungstic acid (PTA) and silicotungstic acid (STA), are incorporated into polyvinyl alcohol (PVA) crosslinked with sulfosuccinic acid (SSA) to form a bridged- mixed-matrix membrane for application in direct methanol fuel cells (DMFCs). Bridging SSA between PVA molecules not only strengthens the network but also facilitates proton conduction in HPAs. The mixed-matrix membranes are characterized for their mechanical stability, sorption capability, ion-exchange capacity and wetting in conjunction with their proton conductivity, methanol permeability and DMFC performance. The methanol cross-over rate for PVA-SSA-HPA-bridged-mixed-matrix membranes decreased dramatically with increasing current density thereby rendering higher DMFC performance in relation to a DMFC using pristine PVA-SSA membrane. A peak power-density of 150 mW/cm2 at a load current density of 500 mA/cm2 is achieved for the DMFC using a PVA-SSA-STA-bridged-mixed-matrix-membrane electrolyte.

FC-3:L05 Pt alloys on Carbon Nanostructures as Electrocatalysts for Direct Methanol Fuel Cell

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Extensive efforts are focused on the development of Direct Methanol Fuel Cells, due to the intrinsic advantages of this type of devices for mobile power supply system. One of the major drawback of the DMFC resides in the easy poisoning of the anode electrocatalysyt (platinum) by CO-like reaction intermediates, which implies the need of high platinum load in order to obtain reasonable performances. The development of platinum alloys is considered one of the promising routes for overcoming this problem: the second metal in fact acts as inhibitor of the Pt poisoning. In this work we have combined the use of unconventional methods to deposit the electrocatalyst nanoparticles with unconventional carbon supports. PtAu and PtRu alloys have been deposited by sputtering and electrochemical techniques on carbon nanofibers with platelet morphology grown by plasma enhanced chemical vapour deposition on carbon paper. Cyclic voltammetry in H2SO4 was used to determine the electrochemical active surface and the electrocatalytic performance for methanol oxidation reaction. Even with lower Pt load, the innovative electrodes showed higher performance and stability respect to the ones prepared with commercial catalysts supported on carbon black.

FC-3:IL06 Tomographic Diagnostics of Electric Current Fluctuations in Fuel Cells

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We suggest two novel tomographic diagnostic methods for analyzing the electric currents in a fuel cell and a fuel cell stack. The first method is quite general and can be used for any tomographic procedure. It leads to an essential reduction of measuring points and at the same time to an increase of the precision. Applied to a single fuel cell the reduction amounts to 90% while the precision is increased by a factor of 3. The second method exploits the high electrical conductivity of slitted metallic (e.g. aluminum) plates to induce surface currents whenever the electric current density in the stack becomes inhomogeneous. These currents can be measured either directly or by measuring their magnetic field thus leading to a basic information about the state of every fuel cell in the stack.

FC-3:IL08 Small Direct Methanol Fuel Cells with Passive Supply of Reactants

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Small, stand-alone, direct methanol fuel cells (DMFCs) that have no auxiliary liquid pumps, and gas blowers/compressors, termed as passive DMFCs, are ideal for powering portable electronic devices, as this type of fuel cell uniquely has a simple and compact system and no parasitic power losses. This talk will give an overview of past experimental and numerical efforts of heat and mass transport in passive DMFCs. Emphasis is placed on the mechanisms and key issues of mass transport of each species through the fuel cell structure under the influence of passive forces. It is shown that the key issue regarding the methanol supply is how to feed high-concentration methanol solution but with minimum methanol crossover through the membrane so that both the system energy density and cell performance can be maximized. The key issue regarding the oxygen supply is how to enhance the removal of liquid water from the cathode under the air-breathing condition. For water transport, the key is to transport the water produced on the cathode through the membrane to the anode by optimizing the design of membrane electrode assembly so that the fuel cell can be operated with pure methanol and with minimum flooding on the cathode. With regard to heat transport, as the heat loss from a passive DMFC is usually large, it is critically important to reduce the heat loss so that the fuel cell can be operated at a sufficiently high temperature, which critically affects the cell performance.

Session FC-4
Molten Carbonate and Alkaline fuel Cells

FC-4:IL01 **Status and Challenges of Molten Carbonate Fuel Cells**

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The MCFC is standing at the end of several years' research and development, and is starting to establish itself as a validated technology. The strong potential of MCFCs is best brought to the fore by operating them on hydrocarbon fuels like natural gas, biogas and syngas. Unsurpassed efficiencies and ready implementation into today's fuel and energy supply infrastructure are the main drivers for this configuration. The stringent environmental requirements imposed by law in California and the determination to reduce dependence on fossil fuel imports in South Korea have provided the launching platform for a growing implementation of MCFC plants in these states. Maintaining its unique characteristics of high efficiency generation and premium quality power supply at the 100+ kW scale, developers have succeeded to bring down investment costs of the MCFC and increase their service lifetime. Large-scale factories are starting to step up the manufacturing process, hoping to achieve ulterior cost savings. In this context, it is interesting to see what the remaining challenges are that are to be tackled and solved in the coming years to maintain the advantage of high efficiency, high quality power supply in a changing society.

FC-4:IL02 **Critical Issues on MCFC Materials**

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MCFC technology is nowadays one of the most dynamic topics in the field of stationary fuel cells. Successful MCFC facilities are spread all over the world, mainly in the US, Europe and Asia, but molten carbonates are also investigated for new fuel cell devices such as solid oxide fuel cells and direct carbon fuel cells. A brief panorama of the advances in MCFC systems will be given at the beginning of this talk. Nevertheless, there is still a relatively long way towards mass commercialization, due to the actual costs, performance and lifetime. It is clear that important advances are still necessary in the heart of MCFC cells: new cathodes or the classical one including a protective layer, new anodes, more resistant bipolar plates, optimised electrolyte-matrix systems. Other topics are also of great interest: varied fuels, reforming processes, modelling. This presentation aims at showing what are the critical issues for improving electrode, electrolyte and interconnects materials. It will be focused most particularly on two aspects: - the molten carbonates physico-chemical properties and the way of optimising their composition and behaviour (conductivities, dissolution capabilities etc.) from thermodynamic and experimental viewpoints; - the interest of using thin layers technology as functional and/or protective layers. Some of the works going on in LECIME laboratory will be shown. Finally, the necessity of a sustained research effort and coordination will be analysed not only to improve MCFC systems, but also to combine them with other close-by technologies.

FC-4:IL03 **Solutions for Material Corrosion Problems in MCFC**

S. Frangini*, A. Moreno, ENEA CRE Casaccia, Dept. TER, S. Maria di Galeria, Rome, Italy

Despite the intensive developments of the past two decades, the success of Molten Carbonate Fuel Cell (MCFC) as advanced stationary power system in the challenging energy market is still uncertain due to high capital costs and to some unresolved lifetime issues, most of which arise from the use of a molten carbonate salt as a liquid electrolyte. In general, the carbonate liquid salt tends to degrade fuel cell endurance in various modes including evaporation, migration of salt constituents from one cell part to another and corrosion of system materials. Presently, the main lifetime problems derive from an insufficient chemical compatibility of both hardware and active cell materials with the molten carbonate salt, which has a definite corrosive acidic character under the typical fuel cell conditions. In detail, corrosion of the NiO cathode and of the stainless steel separator plates represent the two crucial problems that must be addressed by the MCFC developers for reaching the design target of a 40,000 h stack operation without maintenance stops. At the time of Symposium, the main lifetime-limiting corrosion failure modes occurring in MCFC systems will be illustrated along with various corrosion mitigation strategies, which are currently in use or being recently considered.

FC-4:L04 **Unraveling Oxygen Reduction Reaction Mechanisms on Carbon Supported Fe-Phthalocyanine and Co-Phthalocyanine Catalysts in Alkaline Media**

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Electrochemical measurements, such as the rotating disk electrode (RDE) and the rotating ring-disk electrode (RRDE) techniques, and density functional theory (DFT) calculations were employed to elucidate the mechanisms of the oxygen reduction reaction (ORR) on carbon supported Fe-phthalocyanine (FePc/C) and Co-phthalocyanine (CoPc/C) catalysts in 0.1 M NaOH solutions. The onset potential for ORR on FePc/C catalyst is found to be around 0.05 V vs. Hg/HgO in 0.1 M NaOH solutions, which is 100 mV more positive than that on CoPc/C. RDE and RRDE measurements show that the ORR mechanism is via a 4e- pathway on the FePc/C while is through a 2e- pathway on the CoPc/C catalyst. The catalyst stability tests reveal that FePc is much less stable than CoPc under fuel cell cathode working conditions. Moreover, DFT calculations were performed to study the adsorption of O2, H2O, OH, HOOH, and H2OO molecules on FePc and CoPc molecule catalysts. From our theoretical and experimental results for the ORR on FePc/C and CoPc/C catalysts, key factors to determine the activity and stability of the ORR were identified.

Session FC-5
State-of-the-art Application Engineering and Demonstrations

FC-5:IL01 **Towards Industrial Production of SOFC Stacks**

Mette Juhl Joergensen*, Soeren Primdahl, Topsoe Fuel Cell A/S, Lyngby, Denmark

Topsoe Fuel Cell develops, produces and markets solid oxide fuel cell stacks and subsystems. During spring 2009 a pre-commercial production facility for both planar SOFC cells and stacks was commissioned with support from EU-Life. The capacity of the plant layout is 5MW/year calculated as electrical output of produced stacks and fuel cells. The fuel cell plant is a scale up of a pre-pilot production facility situated at Risø DTU, Denmark. The facility serves to supply cells and stacks for the technology demonstration phase, and to generate decision data for scaling up to a fully industrial production facility as the next step. Conventional methods such as tape casting, screen printing and spraying are used for cell production. Sintering is performed in batch furnaces. Currently cells with a footprint of $12x12cm^2$ and $18x18cm^2$ are produced. Stacks of different design and power output in the range of 1-3kW are assembled by hand and conditioned in a batch process. The industrial stack production facility will include robotics for stack assembly and continuous stack conditioning. During the coming years the number of automated processes in the present production facility will increase to establish the background knowledge needed to make the stack production industrially viable.

FC-5:L02 **Demonstration of Polymeric Electrolyte Fuel Cell Systems for Future Power Distribution Grids**

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There are several opportunities for the future energy grids such as "smart grids" that require flexible "intelligent" generation systems, electrical storage, and high-level integration of all possible primary sources, traditional or innovative, fossil or renewable. PEFC systems, thanks to their quick start-up, user friendliness, and special features are already in the power-generation economy, taking significant niche market shares (APU, UPS, telecoms). Tests conducted have shown that the PEFC systems fed with hydrogen have the requirements to be commercialized already in short term also for residential applications, focus of the study. The present study aims to increase awareness in terms of performance of current fuel cell systems. As a matter of fact the tested PEFC system can be considered a plug and play pre-commercial product. Outputs of the paper highlighted both its limits and potential in the mid-to-long term for application of fuel cell systems in Distributed Generation applications in which RES are strongly exploited. In the paper, characteristics of a FC system and its performance operated in Microgrid configuration are described.

FC-5:L03 **Diagnostics and Effective Stabilization of Currents in a Fuel Cell Stack**

Julian Hirschfeld*, Forschungszentrum Jülich, IAS-1; Hans Lustfeld, Forschungszentrum Jülich, IFF-1; Martin Reißel, Fachhochschule Aachen; Bernhard Steffen, Forschungszentrum Jülich, JSC, Jülich, Germany

We suggest a novel scheme for detecting and stabilizing inhomogeneous internal currents in a fuel cell stack. In this paper the scheme is investigated for the case that the flow field plates in use consist of graphite. Then plates of high conductivity, e.g. aluminum between the flow field plates together with small slits in these plates have the effects: a) Whenever a local inhomogeneity of the electric current occurs at a particular cell in the stack this will induce a surface current close to that cell perpendicular to the averaged current. This current can be detected; b) The high conductivity of the small plates completely prevents the inhomogeneities from spreading to neighboring cells; c) Even at the particular cell the inhomogeneity is distributed equally over the MEA of that cell as far as possible. Thus this scheme leads to much better diagnostic possibilities and at the same time reduces electric instabilities. Slightly modified it can even prevent the breakdown of the fuel cell stack in many cases.

FC-5:L04 **Solide Oxide Fuel Cell System for Distributed Generation**

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Distributed energy generation are offering an increasing attractive alternative for power supply. The advantages include a short construction cycle as the supply can be located near to the demand, reducing transmission network losses, and contributing to reduction of emissions through clean combustion using innovative technologies such as natural gas co-generation, natural gas micro turbines, or fuel cells. Fuel Cells are now obtaining great interest from many research groups to aim at environment protection and energy saving. Among them, SOFCs show the advantage of working with more flexible gas feed than PEFCs. Moreover, under the system user point of view, SOFCs can reach high overall efficiency by performing heat recovery at high temperature. In this work, a SOFC micro-CHP system is analyzed. The aim is to evaluate its performance in the long run. The SOFC system is analysed in terms of response to start & stop cycles, power and heat production under different working conditions while assessing flexibility at the transient regime and several power to heat ratios. The decay is evaluated both in terms of catalyst poisoning (by EIS) and voltage stability over thermal cycles. The exhaust compositions (CO, CO2, O2, NO, NOx) have been measured during operations.

Poster Presentations

FC:P06 **Exploitation of the Conductivity Anistropy in Polycrystalline Apatite-type Solid Electrolytes Lanthanum Silicates**

Yong Kim,* Eui-Chol Shin, Jin-Sup Im, Jaekook Kim, Jong-Sook Lee, Chonnam National University, Gwangju, Korea; Dong-Ik Kim, Korea Institute of Science and Technology, Seoul, Korea

Recent reports have shown fast oxide ion conductivity in lanthanum silicates. Theoretical studies suggested that the silicates in hexagonal apatite structure should exhibit the conductivity anisotropy in contrast to other conventional electrolytes in cubic fluorite structure, although no experimental work has yet supported this aspect. We prepared the samples with different lanthanum composition La9.33+x(SiO4)6O2+3x/2 with x varying from -0.5 to 1.5 by the solid state reaction method and characterized the crystal structure, phase distribution, and microstructure using XRD, SEM, and AFM. The material exhibited abnormal grain growth of the elongated grains and the development of facets and anisotropic thermal grooving. The crystallographic orientation of these microstructural features was determined by EBSD (Electron Backscatter Diffraction). By using the controlled grain growth and the abnormal grain growth the conductivity anisotropy can be experimentally investigated.

FC:P08 **SrCo0.8Fe0.2O3-delta and Ba0.5Sr0.5Co0.8Fe0.2O3-delta Cathodes for LSGM Based SOFCs**

Y. Ekinci*, N. Solak, Istanbul Technical University, Turkey; O. Karakoc, R. Demiryurek, C. Oncel, M.A. Gulgun, Sabanci University, Turkey

SrCo0.8Fe0.2O3-δ (SCF) and Ba0.5Sr0.5Co0.8Fe0.2O3-δ (BSCF) are favorable candidates as the cathode material for LSGM based SOFC systems. In this study, the possible reactions are investigated between LSGM electrolyte material and BSCF or SCF cathode material. SCF and BSCF were synthesized by the combined EDTA-citrate method. SCF-LSGM and BSCF-LSGM powder mixtures were analyzed by the TGA/DTA, XRD and SEM to obtain the processing temperature range and to observe the undesired phases in the range of 800-1100 °C. The undesired phase which is 1.92% of total amount had started to form at 900 °C. Below that temperature, undesired phase formation was not observed. Therefore, there would be no chemical compatibility problem in the case of cathode coating (SCF or BSCF) on LSGM electrolyte below 900 °C. According to the XRD results, BaLaGa3O7 may be one of the undesired phases which was observed at 900 °C in the BSCF-LSGM mixture. In this manner, it is applicable for the case of SCF-LSGM mixture as having LaSrGaO4 phase. It may be necessary to work on the phase formation kinetics of the BSCF-LSGM and SCF-LSGM interactions at the service temperatures (<700 °C) to be able to understand long-term behavior of the system.

FC:P10 **High Temperature-FTIR Characterization of Gadolinia Doped Ceria**

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Doped ceria-based (DC) materials have recently been considered as the most promising solid electrolytes for intermediate temperature solid oxide fuel cell (IT-SOFC) applications. Doped ceria is usually prepared via thermal decomposition of its water soluble salts, especially, acetates and nitrates. The properties of the obtained product are directly influenced by the material and the decomposition products. Therefore, it is crucial to understand the decomposition steps and intermediate products. A number of experimental works have been reported using various in-situ and ex-situ techniques such as thermogravimetry with mass spectrometry (TG/DTA-MS), X-ray diffraction with differential scanning calorimeter (XRD-DSC). However, the available literature data is limited and not reasonably in agreement. In-situ high temperature infrared spectroscopy (HT-FTIR), TG/DTA and DSC, SEM techniques were used and results are compared with literature. A good agreement between the thermal analyses and FTIR results were obtained. A possible decomposition mechanism is discussed.

FC:P11 **Electrically Conductive CNT/PTFE Composite Film for Corrosion Resistant Coating on Bipolar Plate of Polymer Exchange Membrane Fuel Cells**

Yoshiyuki Show, Tokai University, Hiratsuka, Kanagawa, Japan

Carbon nanotube (CNT) is chemically stable and electrically conductive material. One of the applications of the CNT is filler into insulating materials for decreasing its electrical resistivity. In this study, composite film was formed from the carbon nanotube (CNT) and the polytetrafluoroethylene (PTFE). This composite film is electrically conductive (- 20S/cm) and highly corrosion resistance. Therefore, it is suitable material for corrosion resistant coating on bipolar plate of polymer exchange membrane fuel cells. The CNT/PTFE composite film was formed from dispersion fluids of the CNT and the PTFE. The CNT/PTFE dispersion was applied to stainless steel bipolar plate at the thickness 50 micron meter. The bipolar plates were dried under the atmosphere of 40 °C for 30 min, and then were heated at 350 °C for 10min. The fuel cell using the bare stainless steel bipolar plates showed the output power of 2.0W. The coating of composite film to the bipolar plates increased the output power up to 2.7W. Impedance analyzer measurement for these fuel cells indicated that the composite film coating decreased the contact resistance between the bipolar plate and the MEA, because the composite film prevents the bipolar plate surface from corroding.

FC:P12 **Low Pt Content Catalyst for PEM Fuel Cells Based on Water Insoluble Salts of Heteropolyacids**

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Salts of large cations (Cs+, K+, Rb+, NH4+) of heteropolyacids such as the H3PW12O40, H4SiW12O40, H3PMo12O40, H4SiMo12O40 have been used as zeolite type support to prepare low Pt content catalysts for PEM fuel cells. The present work describes the electrochemical behavior of MEA’s prepared using Cs2.5PW12O40 as support for Pt nanoparticles with a total Pt content as low as 0.1 mg/cm2 for Oxygen reduction and hydrogen oxidation. The Pt nanoparticles, trapped inside the micro-meso pores of the salt are be less prone to grow thus decreasing the degradation of the catalyst and the carbon catalyst support of conventional electrodes. The high acidity of the salts together with the high proton conductivity increase the oxygen reduction kinetics. The catalyst electrochemical properties studied either using rotating disk electrodes and single fuel cell will be described in details in comparison with those of commercial catalyst.

FC:P13 **Sulfonation of Polyaniline to be Used in Proton Exchange Membrane Fuel Cells**

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Recently, polyaniline (PAni) has been studied because of its low cost, easy preparation, good thermal and environmental stabilities, besides the fact that its electronic properties can be reversibly controlled by both protonic and redox doping. PAni is typically prepared by the oxidation of aniline with ammonium peroxydisulfate in acid medium. Polyaniline in the base form has three oxidation states: leucoemeraldine base (LEB, the most reduced), emeraldine base (EB, the intermediate state), and pernigraniline base (PNB, the most oxidized). The ideal emeraldine base oxidation state contains equal numbers of alternating amine and imine units. Proton exchange membrane fuel cells (PEMFC) are considered as promising alternatives to traditional internal combustion engines for submarines. Recently, the synthesis of sulfonated polyaniline (SPAni), the first self protonic doped polyaniline, has introduced aqueous processability and pH conductivity for values lower than 7.5. In this work, the sulfonation reaction used the fuming sulfuric acid at ambient temperature and was controlled by the spectroscopic techniques: Fourier Transform Infrared with Attenuated Total Reflection, Ultraviolet-visible and X-Ray Photoelectron Spectroscopy. The sulfonation of EB was performed successfully.

FC:P15 **Electrochemical Degradation of Gas Diffusion Layers in PEM Fuel Cells**

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The degradation of the main components of the membrane electrode assembly is a usual topic concerning the lifetime of fuel cells. Up to now however, one of the components has received less attention than the others: the gas diffusion layer (GDL). Although it is well-known that the control of the hydrophobic properties of the GDL can enhance the performances of the cell through a better water management, only little work has been published so far concerning the durability of GDLs. What if their surface properties were found to change during the lifetime of the device? Some studies have pointed out that a “Teflon wash out” could be observed in GDLs. Furthermore, carbon corrosion studies have shown that surface oxides can be formed on the corroded carbon. In this work, electrochemical degradation studies on commercial GDL samples have been performed and linked to a modification of the surface properties, as measured by X-ray Photo-electron Spectroscopy (XPS). Surface oxide formation and Teflon degradation have been studied at different temperatures and corrosion potentials. The results confirm that the surface properties of GDLs are significantly affected during such corrosion testing, which in turn is likely to affect the long-term performance and stability of PEM fuel cells.

FC:P16 **Synthesis of Pt-Mo-N Films and Their Catalytic Activity**

Akira Miura*, John M. Gregoire, Michele E. Tague, R. Bruce van Dover, Héctor D. Abruña, Francis J. DiSalvo, Cornell University, Ithaca, NY, USA

While Pt and Pt-based alloys have been studied as catalysts for proton exchange fuel cells for over decades, there has been no report of Pt-based nitride catalysts. Here we focus on synthesis and characterization of a Pt-based nitride, Pt2Mo3N, by using a composition spread thin film deposition technique. A Pt-Mo-N thin film was synthesized by co-deposition of Pt and Mo and further heat treatment in an ammonia flow at 800 °C for 6 h. The thin film was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) as well as electrocatalytic assessment for the oxidation of small molecule fuels under acidic conditions. The metal film was smooth and dense. After nitridation, it was 70-100 nm thick. XRD showed single-phase Pt2Mo3N in a well defined area of the film. XPS of the same region also showed a stoichiometric ratio of Pt:Mo:N of 2:3:1withen error. The Pt2Mo3N region showed negligible leaching of Mo in 0.1 M sulfuric acid solution between -0.2 and 0.6 V v.s. an AgCl reference electrode. It exhibited obvious oxidation currents for formic acid and methanol above 0.2 and 0.4 V, respectively.

Symposium FD

ELECTROCHEMICAL ENERGY STORAGE SYSTEMS: THE NEXT EVOLUTION

Oral Presentations

Session FD-1

Chemical Storage

FD-1:IL01 **Advances in Lithium Lithium-Air and Lithium-Water Batteries**
Steven J. Visco*, Eugene Nimon, Lutgard De Jonghe, PolyPlus Battery Company, Berkeley, CA, USA

The use of solid electrolyte membranes with high Li+ conductivity and stability towards aqueous media allows the construction of a new class of high energy density batteries based on lithium metal negative electrodes and aqueous electrolytes. These unique electrodes are termed protected lithium electrodes or PLEs and their development allows the construction of practical lithium-aqueous batteries having open circuit potentials above 3 volts. New systems include lithium semi-fuel cells such as Li-Air and Li-Water batteries, which are remarkably stable as evidenced by long-term testing of laboratory cells. Due to the use of a solid electrolyte membrane, the self-discharge rate for Li-Air and Li-Water batteries is effectively zero. Isolation of the oxidant from the battery housing is expected to yield benefits in terms of safety in that the energy for the cell reaction is not contained in the battery itself; this may be particularly important for large traction batteries. The unique advantages of these PLE cells offer step-change improvements in batteries on land, in the sea, and in medical devices. The state-of-the-art will be covered in the presentation.

FD-1:IL02 **Spinel Cathodes for Li-ion Cells**
Jaephil Cho, Ulsan National Inst. of Science & Technology, Ulsan, Korea

One of the important issues regarding the use of LiMn2O4 spinels as cathode materials is their large capacity loss observed during storage and cycling at elevated temperatures. Capacity fade upon cycling depends largely on Mn dissolution through the following reaction Mn3+ —>❑ Mn4+ + Mn2+ (with Mn2+ going into the solution), which occurs in presence of trace acids, especially HF. A solution to this problem is to trap HF as soon as it has been formed by means of HF scavengers. Because the Mn dissolution occurs where the electrolyte and manganese surface atoms are in contact (at the spinel/electrolyte interface), a possible solution is to minimize this contact area by creating a shell of inorganic material around each LiMn2O4 particle that will prevent contact with the electrolyte while still allowing the Li ions to pass through. In this regard, coated spinels have been reported. Although improved structural stability at elevated temperatures via metal oxide coatings have been reported, studies to improve both the rate capabilities of spinel and structural stability at elevated temperatures are rare. In this presentation, recent approaches for new coating method and morphology controls will be introduced for spinel cathodes.

FD-1:IL03 **Materials for Lithium Batteries**
P.G. Bruce, L. Hardwick*, University of St Andrews, St Andrews, Scotland

Performance of lithium-ion batteries remains limited by materials. New and improved lithium intercalation compounds are required as anodes and cathodes for new generations of lithium-ion batteries. Advances in solid polymer electrolytes are required to simplify cell construction and improve safety. Some examples of intercalation electrodes and recent developments in solid polymer electrolytes will be discussed.

FD-1:IL04 **Interfacial Phenomena in Solid-State Lithium Batteries with Sulfide Solid Electrolytes**
K. Takada, National Inst. for Materials Science, Tsukuba, Ibaraki, Japan

Lithium-ion batteries have been involving safety issue arising from combustible organic solvents used in the electrolytes. Replacement of the organic electrolytes with nonflammable solid electrolytes has been expected to be a fundamental solution to the problem; however, it lowers the power density. Highly-conductive solid electrolytes are key material to realize solid-state batteries. Some sulfides with ionic-conductivities as high as those of liquid electrolytes have been developed; however, even such highly-conductive electrolytes did not sufficiently improve power densities. We found that the reason for the poor high-rate capability, or the rate-determining step, is at the interface between the LiCoO2 cathode and the sulfide solid electrolyte. The different electrochemical potentials of lithium ions between the oxide and the sulfide and the electronic conduction in the LiCoO2 will form a Schottky-like interface, where a lithium-depletion layer, which should be resistive owing to the low mobile ion concentration, is highly-developed on the electrolyte side. We interposed an oxide solid electrolyte as a buffer layer at the interface. It drastically reduced the interfacial resistance and made the power density comparable to that of liquid electrolyte systems.

FD-1:IL05 **Multinuclear Solid State NMR Studies of Li Battery Electrode Materials**
Steve G. Greenbaum, Department of Physics & Astronomy, Hunter College of CUNY and CUNY Graduate Center, New York, NY, USA

Structural studies of materials utilized in lithium battery and fuel cell technology are often hampered by the lack of long-range order found only in well-defined crystalline phases. For example, powder x-ray diffraction yields only structural parameters that have been averaged over hundreds of lattice sites, and is unable to provide structural information about amorphous compounds. Our laboratory utilizes solid state nuclear magnetic resonance (NMR) methods to investigate structural and chemical aspects of lithium ion cathodes, anodes, electrolytes, interfaces and interphases. NMR is element- (nuclear-) specific and sensitive to small variations in the immediate environment of the ions being probed, for example Li+. A survey of several recent NMR investigations undertaken in our lab on materials provided by collaborating research groups will be presented, including 7Li and 31P studies of single crystals of LiMPO4 (M = Fe, Co, Ni), the nature of the charge storage mechanism in carbon-supported MnO2 nanofoam electrodes, and structural aspects of electrochemically lithiated CFx primary cathodes, BiF3 reversible conversion cathodes, and nanoscale Li4+xTi5O12 electrodes.

FD-1:IL06 **Printable Batteries for Smart Objects**
Reinhard R. Baumann, Chemnitz University of Technology, Institute for Print und Media Technology, Chemnitz, Germany

During the development of industrial printing technologies the printers gained a number of competences which will help to extend their scope beyond printed products addressing only the human visual sense. E.g. printing of an appropriate pattern with an ink which generates the functionality electrical conductivity gives the opportunity to print electrical wiring, circuitry or RFID antennas. These printed electronically active components can be supplemented by integrating silicon based systems, e.g. RFID chips. Thus printed smart objects will be able to communicate via computer networks either with humans or with other smart objects. Hence the internet of things will be entered by mass wise printed smart objects being the single item content of the big supply chains of the retailer giants. Additionally the printing technologies can be employed to manufacture components necessary to power-up electronic circuitry. These power sources are being integrated in the products and their energy content is balanced to the power consumption of the smart object during its lifetime. The paper will discuss opportunities, challenges and limitations to manufacture printed smart objects with functionalities beyond color.

FD-1:IL07 **An Approach to 12 V Lead-free Batteries Consisting of Lithium Insertion Materials for Automobile and Stationary Applications**
Tsutomu Ohzuku, Graduate School of Engineering, Osaka City University (OCU), Osaka, Japan

During the past 18 years, the lithium-ion batteries have been expanding their applications to portable electronic devices and have already reached a value over 550 Wh dm-3 or 220 Wh kg-1. Electrode materials used in lithium-ion batteries are lithium insertion materials for both negative and positive electrodes. Although a series of lithium insertion materials has been examined so far, many lithium insertion materials cannot find application to the lithium-ion batteries because of low energy density compared to the current lithium-ion batteries. To find the application of lithium insertion materials and to put the right insertion material in the right batteries, we have proposed two types of twelve-volt lead-free batteries. One consists of five cells connected in series and the other consists of four cells. We call the former the first generation of 12 V lead-free batteries consisting of LTO and LAMO, and the latter the second generation consisting of LTO and LiNiMO. The characteristic features of both 12 V batteries are a high rate capability, long life, and a high energy density compared to the 12 V lead-acid batteries, so that the stationary applications, such as solar & wind power generation systems on off-grid rural areas or electric vehicles in addition to the automobile applications seem to be appropriate. As were briefly described above, the lithium insertion materials for the 12 V lead-free batteries for sustainable developments with renewable and clean energies will be presented.

FD-1:IL08 Lithium Nitrides as New Anode Materials for Lithium-ion Batteries

Duncan H. Gregory*, WestCHEM, Department of Chemistry, University of Glasgow, Glasgow, UK

Light metal nitrides are emerging as potential materials for energy storage and towards energy conversion (e.g. as H2 stores for fuel cells). Perhaps uniquely, lithium nitrides can perform functions both as electrodes (anodes) in secondary batteries and as high capacity hydrogen stores. It is a powerful combination of simple, yet remarkably flexible, structural and chemical characteristics that allows Li3N derivatives to perform these dual roles. In the former context, we have demonstrated how lithium nitrides can be modified for applications as negative electrodes and sought to explain the underpinning behaviour. Li+ ion transport and charge carrier (vacancy) concentration can be modified dramatically by substitution of late transition metals for Li. By similar substitutions, one can transform undoped Li3N from an indirect band gap semiconductor to an anisotropic metal (LiNiN) and in the process change the magnetic properties of the materials. A combination of X-ray and neutron diffraction, solid state NMR and DFT calculations has been essential in understanding defect and electronic structure and in characterising the dynamics in these materials. It is thus possible to begin to correlate structure, composition, physical properties with electrochemical behaviour and performance.

FD-1:L09 A Safe, High-rate and High-energy Polymer Lithium-ion Battery Based on Gelled Membrane Prepared by Electrospinning

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In this presentation we report the characteristics of a polymer Li-ion battery based on a unique combination of innovative electrode and electrolyte materials. In particular, the electrolytic separator of this system is based on gelled membranes that were prepared by electrospinning technique. Electrospinning of polymer fibers is usually realized by applying a strong electric field to a polymer solution in an appropriate solvent. Typical membranes (mats) consist of nanometer size fiber and have porosities of 56-85%. Here we describe the fabrication, the physical chemistry and electrochemical properties of PVdF (Poly vinylidene di-fluoride)-based electrospun membranes and their use as gelled electrolyte in Li-ion battery. Moreover, we describe the performances of a battery formed by sandwiching a gelled membrane by a nanoscale engineered Sn-C based anode and a lithium nickel manganese oxide spinel cathode. The battery so obtained has appealing performances in terms of energy density, power capability, cycle life and safety.

FD-1:L10 Study of Carbon Nanotubes for Lithium-ion Batteries Applications

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Since they have been discovered, the interest around Carbon Nanotubes (CNTs) is continuously growing. Particularly in the last decade, their properties became interesting for Li-ion batteries applications. The high electrical conductivity compared to carbon blacks makes them suitable as conductive agents for cathodes. In the same time their ability of inserting Li ions might allow the use as anode active materials. In spite of the flexible properties of these compounds, there are still some limitations and difficulties in preparing electrodes containing CNTs. In the present work we investigated the influence of CNTs addition to composite electrodes based on different anode and cathode materials. The results might suggest some guidelines for a really suitable application of CNTs in commercial batteries.

This work was done in the frame of the Innovation Alliance Carbon Nanotubes with the support of Germany's Federal Ministry for Education and Research (BMBF).

FD-1:IL11 On the Road Towards 3D-integrated All-solid-state Batteries

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Micro-batteries are expected to become more and more important in numerous small-sized devices, like medical implants, biosensors, hearing aids and autonomous network devices. Characteristic for these electronic applications is that they have to operate autonomously and reliably without any risk of electrolyte leakage. Hence they need to be rechargeable and have an extremely long cycle life. As the average energy consumption of these future devices will be rather small, this opens up the possibility to integrate all-solid-state rechargeable batteries. Current state-of-the art thin-film batteries are planarly structured, unfortunately resulting in a relatively low energy density. By depositing the complete battery stack in a 3D etched substrate obtained by, for example, physical or wet-chemical etching of mono-crystalline Silicon-wafers, the effective energy and power density can be tremendously increased. Moreover, utilizing novel battery electrode materials with high storage capacity are highly beneficial. In this presentation the concept of the 3D-integrated batteries will be outlined. Electrochemical characterization of the various active and passive battery layers will be addressed.

FD-1:IL12 Materials for Aqueous Rocking-chair Batteries

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The present power sources are encountering still unresolved problems to meet the demands for energy storage in large scale. Consequently, exploring new energy storage and conversion systems has evolved as a major challenge. In 1994, it was proposed that rechargeable lithium battery can use aqueous solution as electrolyte. The used aqueous solution, whose ionic conductivity is about 1-2 orders of magnitude higher than that of organic electrolytes, is quite suitable for high rate charge and discharge. In addition it is inherently safer. Our lab has been doing research work on aqueous rechargeable power sources based on rocking-chair mechanism. The investigated materials for aqueous rocking-chair batteries include positive electrode materials such as LiCoO2, LiMn2O4 and LiFePO4, NaxMnO2 and KxMnO2 and anode materials such as LiV3O8, polyaniline, polypyrrole and activated carbon. Based on our latest results, the aqueous rechargeable lithium batteries provide great promise for applications no matter in terms of safety, rate capability, costs or cycling life. This paves new ways to explore new kinds green power sources based on rocking-chair mechanism.

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FD-1:L13 Solid State and Aqueous Li-ion Batteries with Polyanionic Electrode Active Materials

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Polyanionic cathode/anode active materials such as olivine and NASICON-type phosphates with the high thermal stability and low environmental impact have been expected for next generation Li-ion battery. In addition, we have also focused on the other characters such as 3D framework and the flat charge/discharge voltage profiles, because they should be also suitable for solid-state and aqueous Li-ion batteries, respectively. In this presentation, the cell performances of Li3V2(PO4)3/Li1.5Al0.5Ge1.5(PO4)3/Li3V2(PO4)3 and Na3V2(PO4)3/Na3Zr2(SiO4)2PO4/Na3V2(PO4)3 are demonstrated as all NASICON phosphate symmetric solid-state lithium ion and sodium ion battery, respectively. In addition, LiFePO4/1M Li2SO4 aqueous electrolyte/LiTi2(PO4)3 is also introduced as a aqueous Li-ion battery with olivine cathode and NASICON anode. They are two prototypes of the next generation safe secondary batteries with polyanionic cathode/anode active materials.

FD-1:L14 Activation of Phosphate Olivines LiMPO4 (M = Fe, Mn) by Functionalized Carbon Nanotubes: Application for Cathode Materials of Li-Ion Battery

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The nanotube-mediated redox wiring is based on synergic action of adsorbed redox-active molecule, which provides the interfacial charge transfer to the surface and the single-walled carbon nanotube (SWNT), which transports charge to longer distances in the material. A Ru-bipyridine complex Z-907Na, turned to be particularly suitable for this purpose, because of its amphiphilic character enabling solubilization of SWNT. Electrodes fabricated from optimized composite materials containing LiFePO4 (olivine) exhibit a greatly enhanced activity for electrochemical Li+ storage compared to electrodes from commercial carbon-coated LiFePO4 or from LiFePO4 derivatized either by adsorption of sole redox-mediator molecules or by pristine SWNT. Multi-walled carbon nanotubes (MWNT) functionalized by carboxylic groups, exhibit better affinity towards LiMPO4 (M - Fe, Mn) as compared to that of pristine MWNT. The surface functionalization of MWNT enhances charge storage capacity and reversibility of a composite with LiMnPO4 (olivine), but mediates also the electrolyte breakdown at potentials >4.2 V. Whereas the electrochemical activation of LiMnPO4 (olivine) by functionalized MWNT is quite modest, excellent performance was found for LiFePO4 (olivine) in the composite with 2% MWNT.

FD-1:L15 Sago Based Gel Polymer Electrolyte for Zinc-Air Battery

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Sago gel electrolyte as a new polymer gel electrolyte candidate was introduced in zinc-air (Zn-air) using porous Zn electrode as the anode. Sago gel electrolyte has been prepared by mixing the native sago solution with potassium hydroxide solution. The highest conductivity of sago gel electrolyte is achieved with 6 M KOH with the conductivity value of 4.45 x 10-1 S cm-1. The viscosity for sago + 6 M KOH gel electrolytes is 0.19 Pa s. Meanwhile, window stability of sago + 6 M KOH gel electrolytes is ~1.0 V (vs. stainless steel). The Zn-air battery demonstrated voltage of open circuit of 1.46 V during 48 h of storage, discharge capacity of 488 mA h g-1, power density of 20.24 mW cm-2. The failure of the cells was dominated by degradation of Zn anode due to the formation of a zinc oxide insulating layer.

FD-1:IL16 Modified Graphite Anodes for Lithium-ion Batteries Optimized for Low Temperature

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Different ways to modify graphite electrodes for improving the low temperature electrochemical properties will be presented. Composite electrodes prepared mixing partial oxidized graphite and metal nanoparticles or cast electrodes covered by metal layers using vapor deposition will be described. The effect of the different modification on the graphite electrochemical properties will be illustrated with particular attention to the low temperature lithium intercalation/deintercalation abilities. The variation induced by the different methods on the relevant electrochemical properties such as charge transfer resistance and intercalation/deintercaltion mechanism will also be discussed together with a tentative explanation of the physical reasons of the improved low temperature behavior.

FD-1:IL17 Gel-polymer Composite Electrolyte for Perspective Li-metal Secondary Battery Systems

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To achieve the drastic CO2 reduction in the world, the realization of electric vehicles and energy network systems are essential. These systems require large-scale batteries with high energy density, cycle durability, and safeness. For attainment of these requirements, gel polymer electrolytes for lithium secondary batteries are widely investigated. For these electrolytes, both high ionic conductivity and mechanical strength are required mainly. Thus we have investigated the polymer gel electrolytes composed of polyethylene oxide (PEO), which serves high ionic conductivity when plasticized and poly styrene (PS), which serves mechanical strength without being plasticized. In this presentation, we will introduce a polymer blend gel electrolyte prepared by simple hot-blending PEO and PS and a diblock copolymer gel electrolyte prepared by casting PEO-PS diblock copolymer. In addition, feasibility of ionic liquid as a candidate of a plasticizer and interface improvements by an experimental atmosphere or additives will be mentioned.

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FD-1:L18 Ionic Liquid Electrolyte Mixtures for Low Temperature Applications

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Room Temperature Ionic Liquids (RTILs) are excellent candidate as electrolyte components in the place of volatile and hazardous organic solvents for fabricating high safety, lithium battery systems. Sub-ambient temperature applications require, also, low melting point electrolytes with poor viscosity, this allowing fast ionic conduction at low temperatures. In order to match this target, the characteristics of two or more ionic liquids may be favorably combined to obtain mixtures with improved physical-chemical properties. In fact, the association and ordering of the ions may be more complicate in ionic liquid mixtures. Particularly, the interactions among cations and anions may be modified, thus affecting their short-range aggregation motives and, therefore, the physical-chemical properties of the mixtures. In the present work is presented and discussed the beneficial synergic effect on chemical-physical properties due to the combination of two different ionic liquids. Various binary mixture sets, based on N-alkyl-N-methyl Pyrrolidinium RTILs (synthesized at ENEA) having different (perfluoroalkylsulfonyl)imide anions, were prepared and investigated. In particular, binary RTIL mixtures exhibited better low temperature performance than the starting materials.

FD-1:L19 New Synthesis Method for Conversion Materials with High Cyclic Stability

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Conversion materials offer high theoretical capacities for electrochemical storage. However, segregation of the active materials may occur during their phase transformation leading to a loss of capacity and cyclic instability. In this context, we have developed a new simple and scalable synthesis procedure for conversion systems which are based on transition metal fluorides. In a battery, iron fluoride reacts reversibly with lithium to Fe and LiF, with a theoret. capacity of 712 mAh/g. Nanocomposites consisting of LiF, Fe, and nanocarbon were prepared by mechanical mixing of LiF and a metal organic precursor and subsequent pyrolysis of the mixture. The resulting composite material consists of iron nanoparticles which are intimately embedded in a porous nanocarbon structure, and LiF dispersed through out the matrix. As a result, the cathode material shows a very stable cycling behaviour, after an initial degradation. The specific capacity is in the order of 280 mAh/g as determined between 0.5 V and 4.5 V. Electrochemical characterization and structural investigations based on HR-TEM, Mössbauer spectroscopy, and XRD will be presented.

Session FD-2

Capacitive Storage

FD-2:IL01 Emerging New Materials for Electrochemical Capacitors

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There have been many efforts devoted to improve the properties of electrochemical capacitors (ECs). Our main focus of this presentation to elucidate the anomalous behavior centered the new intermetallic transition metal silicide, Ni_2Si and arrive a conclusive explanation of the increasing columbic efficiency upon extended cycling. We report both bulk and cavity micro electrode (CME) performance in the context of analyzing the pseudo capacitance and compare it with nano NiO, NiO/Ni nano-composite and NiM'$_2$O$_4$ (M'=Co, Ni and Fe). We also report our recent work in nanodots of NiM'$_2$O$_4$ (M'=Co, Ni and Fe) spinels impregnated into mesoporous carbon structures. The electrochemistry of these new hybrid electrodes are discussed in the light of electrochemical capacitance and in this manner a new paradigm is being introduced to increase the capacitance of any given electrode materials for Electrochemical capacitors.

FD-2:IL02 Graphene Supercapacitors

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Exfoliated nanosheets have potential for use in various applications due to the high surface/bulk ratio that can be achieved from such material. Graphene, a single layer of graphite, is a two-dimensional crystallite with an ultimate thickness of one carbon atom and has attracted great interest from many researchers in recent years as a new-type of nanocarbon. In this study, graphite oxide nanosheets with thickness of approximately 1 nm were and varying lateral size was synthesized via exfoliation of various graphitic materials. The lateral size of nanosheets could be controlled by using different carbon precursors as well as ultrasonic treatment. Graphene electrodes with smaller lateral size exhibited larger specific capacitance, which is discussed based on the edge/basal plane ratio of the graphene nanosheets.

FD-2:L03 Self-assembled Synthesis of Graphene Nanosheets for Supercapacitors

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Graphene nanosheets have been intensively explored because they exhibit very excellent mechanical and electrical properties. For example, graphene materials have been intensively investigated for electronic, optoelectronic, sensing nanoelectronics, batteries, and hydrogen storage applications. Although many methods, including the scotch tape (peel off) method, epitaxial growth, noncovalent functionalization of reduced graphene oxide, and chemical reduction of suspensions of graphene oxide, and so on, were reported to prepare graphene nanomaterials, some of these are very complicated. In this study, we have described a novel way to directly prepare few-layers (< 3 layers) graphene nanosheets. Highly crystalline lattice of single-layer and few-layers graphene were clear observed from the TEM images, whose graphene structure was confirmed from Raman and XPS results. The growth mechanism of graphene nanosheets is also proposed. Finally, graphene-based supercapacitors with high capacitive performances were reported due to their high electronic conductivity, porous structure, and specific surface area. Graphene nanomaterials prepared in this work were tested as highly promising electrode materials of next generation supercapacitors.

FD-2:L04 Flexible Supercapacitors Consisting of Polyaniline and RuO2/Graphene Nanocomposite

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Because flexible electronics exhibit novel properties of lightweight, rollable and potentially foldable, they are developed for many portable products such as roll-up displays, sensor, integrated circuits and electronic paper. Therefore, various kinds of flexible power devices are highly desirable as a energy storage system in these portable flexible electronics. To fabricate flexible power devices, conducting polymers and carbon nanomaterials are considered as the best promising materials due to their excellent flexibility. Recently, we have successfully prepared polyaniline nanofibers and RuO2/graphene nanocomposites via simple chemical methods. The highly porous polyaniline nanofibers and well-dispersed RuO2 nanoparticles on graphene will significantly improve the electronic and ionic pathways, and enhance the utilization of electron materials. Therefore, a flexible supercapacitor with high performances, such as high power property, high energy density, and long cycle life, has been fabricated in this work.

FD-2:IL05 3D-integrated All-solid-state Capacitors

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Passive devices integrated in Si attract great interest for applications in portable communication where heterogeneous System-in-Package integration imposes cost-effective die-to-die (e.g. passive-to-active) stacking. Roadmaps target capacitance densities >1 µF/mm2 within a few years. Such densities enable new applications beyond decoupling, like local DC-DC conversion. In the past decade we studied novel material and capacitance improvement schemes. The 1st-generation trench capacitors of the high-density (25 nF/mm2) MOS type contained ONO dielectrics and poly-Si top electrodes, mainly deposited with LPCVD in high-aspect ratio (20:1) macropores. Next-generation trench capacitors require MIM stacks of high-k dielectrics and metallic films. Here, Atomic Layer Deposition is considered as key for conformal layer-by-layer growth. We start with multiple TiN/Al2O3/TiN MIM stack capacitors, yielding 440 nF/mm2 records. Rare-earth doped ZrO2 and HfO2 follow. O2 plasma-assisted ALD of SrTiO3 was developed from the constituent ALD processes of TiO2 and SrO allowing film composition control by adapting [TiO2]/[SrO] cycle ratios. As-deposited planar films were amorphous regardless composition, but crystallized upon PDA (600 °C, N2) yielding k >80 for 50 nm thick films with Ebd~1 MV/cm.

FD-2:IL06 Design of Nanostructured Oxides for Advanced Electrochemical Supercapacitors

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We briefly review the development of oxide-based materials for supercapacitors and address the key factors determining the capacitive performances of oxides. We try to design ideal nanostructures of typical oxides or composites for the application of advanced electrochemical supercapacitors. In the first example, anodic composite deposition of RuO2xH2O-TiO2 is employed to reach the desirable porous architectures due to its simplicity, one-step process, reliability, and hydrous nature of RuO2xH2O. In the second example, a 3-D a-MnO2/Mn3O4/MnOOH nanocomposite is constructed to improve Mn utilization and depress a-MnO2 degradation. In the third example, 3-D porous vanadium oxides were anodically deposited onto graphite substrates (denoted as VOx?nH2O/G) at various potentials from an aqueous solution containing 25 mM VOSO4 and 5 mM H2O2. All the above nanostructured oxides were demonstrated to show excellent capacitive performances based on the understanding of bottlenecks for the charge-discharge process of oxide-based electrode materials.

FD-2:L07 Printed Supercapacitor as Hybrid Device with Enzymatic Power Source

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Low cost printable power sources are needed e.g. in sensors and RFID applications. As manufacturing method printing techniques are preferred in order to keep the costs low. The materials should also be easily disposable. Enzymatic bio-fuel cells are an alternative for printable primary batteries. Since one drawback of bio-fuel cells is their low power, we have developed supercapacitors that can be applied with enzymatic bio-fuel cells to provide the power peaks necessary in the applications. The materials for the supercapacitors have been chosen to be compatible with the fuel cell and with printing methods, e.g. the activated carbon powder in the electrodes was bound with chitosan. As substrates we have used paper boards. The current collectors have been made of graphite and metal inks. Since the voltage requirement is limited to slightly over 1 V, aqueous electrolytes have been used. Printed supercapacitors of various sizes have been prepared. Geometrical electrode areas have been 0.5 - 2 cm2. The maximum feasible output current has been of the order of 50 mA corresponding about 50 mW power. When the capacitor is used together with enzymatic power source, the leakage current must be as low as possible. Typical leakage current values have been of the order of 10 µA.

FD-2:L08 Electrochemical Deposition of Vanadium Oxides for Supercapacitors: The Key Factor of Determining the V^{5+}/V^{4+} Ratio

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This work demonstrates that accumulation of V^{5+} species at the vicinity of electrode surface is the key factor for successful anodic deposition of vanadium oxide (denoted as $VO_x \cdot nH_2O$) at a potential much more negative than the equilibrium potential of the oxygen evolution reaction (OER). The results of *in-situ* UV-VIS spectra show that the V^{4+}/V^{5+} ratio near the electrode surface can be controlled by varying applied potentials, leading to different, three-dimensional (3-D) nanostructures of $VO_x{\cdot}nH_2O$. The accumulation of V^{5+} species due to V^{4+} oxidation at potentials ≥0.4 V (vs. Ag/AgCl) has been found to be very similar to the phenomenon by adding H_2O_2 in the deposition solution. The X-ray photoelectron spectroscopic (XPS) results show that all $VO_x{\cdot}nH_2O$ deposits can be considered as aggregates consisting of mixed V^{5+} and V^{4+} oxy-/hydroxyl species with the mean oxidation state slightly increasing with the applied electrode potential. This semester we will continue our study in supercapacitor category, to figure out what's the effect of different potential to capacitor properties.

FD-2:IL09 **Mesostructured Materials for Electrochemical Capacitors**

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Capacitive energy storage is distinguished from other types of electrochemical energy storage by short charging times and the ability to deliver significantly more power than batteries. A key limitation to this technology is its low energy density and for this reason there is considerable interest in exploring pseudocapacitive charge storage mechanisms in which fast and reversible redox reactions are used to achieve higher levels of charge storage. In this paper we review our recent studies on mesoporous TiO2 and MoO3 films in which increased levels of pseudocapacitance and enhanced energy storage are obtained. The advantage of the interconnected mesoporous network is that it enables greater electrolyte access to the oxide framework than occurs with dense films. The mesoporous architecture is attractive for the design of electrochemical capacitor materials because of the prospect of achieving increased energy density while still maintaining high power density.

FD-2:IL10 **Electrode Materials for Hybrid Supercapacitors**

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The combination of supercapacitors (SC) and batteries (BAT) gained significant interest because of the hope to combine high power and high energy within one device. Such hybrid devices were proposed using a battery electrode and a capacitor electrode in one device, which could be looked at as a series combination of SC and BAT. A parallel combination of SC and BAT was frequently investigated by an external interconnection of a capacitor and a battery. A Matlab Simulink model was used to compare the performance of a parallel and a serial connection of SC and BAT in terms of Ragone plots for constant power or pulsed loads. The parallel connection provides the highest benefit for pulsed load due to the power sharing between SC and BAT. According to the results of the simulations, electrodes based on SC and BAT materials were developed and characterized with a particular electrochemical cell allowing measuring the currents delivered by the individual electrode materials. The behavior of such bi-material electrodes is in good agreement with the results of the simulations. The bi-material electrodes exhibit a "battery like" behavior at slow discharge rate and a "capacitor like" behavior at high discharge rate and are a promising approach for high-power, high-energy SC/BAT hybrids.

FD-2:IL11 **Tailoring of Mesoporous Carbons for Advanced Electric Double Layer Capacitors**

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Activated carbons with various degrees of micro- and mesoporosity were prepared by zinc chloride activation of spent coffee grounds at different temperatures. These carbons exhibited excellent electrochemical double-layer capacitance of up to 368 F g-1 in aqueous 1 M H2SO4 and 140 F g-1 in organic 1 M TEATFB/AN. The electrochemical evaluation and empirical analysis using improved model for evaluation of micropores and mesopores surface area contributions to the capacitance showed that in the case of aqueous electrolyte, the contribution of micropores to the double-layer capacitance is dominant at low current loads. On the other hand activated carbons with greater mesopore content retained higher specific capacitance at fast charge-discharge rates as the mesopores acts as channels or reservoirs for electrolyte transport. In an organic electrolyte, carbons with a greater volume of mesopores performed better than microporous carbons with 100 F g-1 capacitance retained at the current load of 20 A g-1. It was confirmed that chemical activation can be used to control the carbon meso/micropores ratios, with increased ZnCl2 ratio producing larger pores, and this activation process can be tailored to produce carbon pore size distributions suitable for specific electrolyte.

FD-2:IL12 **Recent Advances in Understanding the Capacitive Storage in Microporous Carbons**

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We will present a review of our recent work on capacitance of carbide-derived carbons. Specific capacitance as high as 14 μF/cm² or 160 F/g was achieved using carbide-derived carbons with tailored subnanometer pore size, which is significantly higher than 6 μF/cm² or 100 F/g) for conventional activated carbons. Such high capacitance was obtained in several types of organic electrolytes with or without solvent. A maximum is obtained for the carbons with the mean pore size close to the bare ion size, ruling out the traditional point of view that mesoporosity is highly required for maximum capacitance. Surprisingly, carbons with subnanometer porosity exhibit high capacitance retention, since only a 10% loss is measured when 6 A/g discharge is drawn. These findings show the importance of fitting the ion size with the mean pore size. The double layer theory falls short to explain such charge storage mechanisms at the nanometer scale, thus atomistic modeling is required to find out an alternative charge storage model.

FD-2:IL13 **Nanohybrid Capacitor: A New Hybrid Capacitor System, Triply Enhanced Energy Density by Use of nc-Li4Ti5O12/CNF**

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There is presently a major effort to increase the energy density of EDLCs up to a target value in the vicinity of 20 Wh kg-1. One important alternative approach to meet this goal that is under serious investigation is to develop "Li-ion capacitors". This approach can overcome the energy density limitation of the conventional EDLC because it employs a hybrid system of a battery-like (faradic) electrode and an EDLC-like (non-faradic) electrode, producing higher working voltage and capacitance. However, the Li-ion capacitors based on a carbonaceous Li intercalation negative electrode have some possible disadvantages, such as long-term stability and safety. Here we suggest a novel hybrid system that certainly achieves a high energy density (triple of conventional EDLCs), high stability and high safety at the same time. This is the new lithium-ion based hybrid capacitor using the lithium titanate Li4Ti5O12 negative intercalation electrode that can operate at unusually high current densities. The high-rate Li4Ti5O12 negative electrode has a unique nano-structure consisting of unusually small single nano-crystalline Li4Ti5O12 nucleated and grafted onto carbon nano-fiber anchors (nc-LTO/CNF).

Session FD-3

Application Engineering

FD-3:IL01 **Electrochemical Storage for Multi-source Hybrid Renewable Energy Systems**

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Distributed Energy Resources (DER) are attracting attention due to the increasing exploitation and in particular to issues linked to the dispatch at very large scale, as for Renewable Energy Systems (RES) intermittency can impact on grids affecting them in terms of power quality and of security of supply. Multi-source hybrid alternative energy systems have great potential to provide higher quality and more reliable power than a system based on a single resource. In this study different innovative micro-storage devices are evaluated both at experimental and theoretical level exploiting both an hybrid system as demonstrator and a simulation model aimed to design and analyze the overall system performance of a possible small rated power hybrid system for residential use. The multi-source hybrid system consists of a thin film PV roof-top plant, a vertical axis wind generator, a micro-storage device, and a suitable management system. Three different innovative key-technologies were compared (Li-ion and Ni-NaCl batteries, and Regenerative Fuel Cell with hydrogen storage) under different boundary conditions such as stand alone or grid connection operations, different tariffs and COE, different loads and whether data, to meet the best solution in terms of cost-benefits analysis.

FD-3:IL02 Energy Conservation and Management Strategies for Commercial Li-ion Batteries in Telecommunication Applications

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A number of problems have arisen to the use of lead-acid batteries as backup power sources for communications facilities. Sufficient floor space occasionally cannot be secured when additional batteries are needed to accommodate the provisions of new services in urban areas. Moreover, unlike communications equipment, batteries used as backup power supplies do not generate revenue, so they should be as small as possible to save space. As a result, Li-ion batteries, which possess a high energy density and have the potential for saving space and reducing weight, are promising as batteries that can significantly contribute to downsizing telecommunications power supply. To utilize Li-ion batteries, two key factors are constant discharging voltage and safety. Up until now, from the standpoints of constant discharging voltage and thermal stability of batteries during internal short-circuits and overcharge, we have been pushing ahead with research on Li-ion batteries using manganese-spinel compounds as their positive materials. First of all, self-extinguishing was achieved by adding a phosphazene flame retardant to the electrolyte. In addition, we are confident that we can prolong the battery life by substituting part of the positive electrode material with other metallic elements.

FD-3:IL03 Real-time Impedance Monitoring of Electrode/ Electrolyte Interfaces

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Prior to the presentation of the real-time impedance monitoring technique developed in our laboratory, a brief account of various efforts that had been made to carry out real-time impedance measurements in many electrochemistry laboratories across the world will be presented as a background; concepts involved, advantages, and disadvantages of these methods will be summarized. This will then be followed by the description of what is called Fourier transform electrochemical impedance spectroscopy (FTEIS), which has been developed in our laboratory over the years based on entirely different concept from those employed in earlier studies. Following the brief description of the theory involved and the implemented methodology, we will go on to present how the real-time impedance experiments are conducted by combining the FTEIS with staircase voltammetry and the applications thereof to various electrochemical problems. Finally, we will take a few examples of the real-time impedance measurements on various systems and their interpretations.

Poster Presentations

FD:P01 Nanostructured Anode and Cathode Materials for Li-ion Batteries

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In the field of batteries, the use of nanostructured materials can play a fundamental role owing to their high specific surface enhancing the electrocatalytic performance. Consequently, extended investigations are necessary in order to find potentially cheap and scalable fabrication process, and to correlate the electrochemical behavior to structural and morphological parameters. In this paper, we present some results relative to the development of advanced materials for Li-ion batteries. In particular, the attention was focused on fabrication of LiFePO4 and SnCo alloys by using nanostructured anodic alumina membrane as template. LiFePO4 was obtained by impregnation of the membrane with the precursor solution in two different ways: immersion and vacuum permeation. It was found that it was possible to control the filling of the membrane pores, by adjusting the impregnation time. In the case of the alloy, an electrochemical procedure was investigated in order to simultaneously deposit both Sn and Co. This objective was reached by investigating baths with different precursors, buffers, complexing agents and SnCo molar ratio. Electrochemical results on lithiation-delithiation of the developed SnCo anode materials in conventional organic electrolyte are also presented.

FD:P02 Validity of MgFe2O4 Normal Spinel as a Cathode Material for Rechargeable Battery

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Magnesium based Spinel oxides, MgM2O4 (M = Fe), prepared by the solid state reaction is an inverse Spinel, being not ideal for an electrode for rechargeable battery. A normal Spinel is expected to be better because of its ionic conduction paths. A normal Spinel is synthesized by the ion-exchange method from alpha-NaFeO2, precursor material, synthesized from Na2O2 and alpha-Fe2O3. alpha-NaFeO2 and Mg(NO3)2.6H2O powders were mixed and heated at 310 °C for 48h in air. During heating, sodium ions were exchanged with magnesium ions due to the difference in their ionicity. X-ray diffraction pattern taken after the ion-exchange reaction demonstrates successful synthesis of normal Spinel phase. Eelectrochemical measurement (cyclic voltammetry) was performed between 0V and 2.5V in a three-electrode beaker-type cell set up with a platinum counter electrode, a magnesium reference electrode and electrolyte of 1M Mg(ClO4)2 diluted in acetonitrile. A well defined cyclic voltammetric curve was observed, indicating that the ion-exchanged MgFe2O4 can be used as a cathode material.

FD:P03 A Molecular Dynamics Study on Pressure Dependence of Ag Diffusion in Ag3SI

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The study of materials properties at different temperatures and pressures, provide much information to understand the microscopic mechanism that originate the observed behaviors. In the present study, the pressure dependence of the Ag diffusion coefficient in Ag3SI has been investigated by molecular dynamics simulations. Ag3SI is a well known superionic conducting material that at ambient pressure exhibits two structural phase transitions. With the increase in temperature, the first transition occurs at T = 157 K (from γ- to β-phases) and the second occurs at T = 519 K (from β- to α-phases). Concerning the pressure effect, only few studies have been done in the past. In our study, we have found that in the high temperature superionic α-phase, the Ag diffusion coefficient decreases with the application of pressure. On the other hand, in the intermediate temperature superionic β-phase, the Ag diffusion coefficient exhibit a peaked behavior at around 2.8 GPa. The origin of the behavior has been studied by analyzing the pair distribution function. The analyses indicate that the peaked behavior is related with the pressure induced disordering of the immobile ion sublattice.

FD:P04 A Chemical Bonding Approach to Ionic Conduction and Thermal Expansion in Oxide Ion Conductors

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In complex perovskite-type oxides, which have been studied as cathode materials, the thermal expansion coefficient (TEC) increases with the increase in the oxygen ionic conductivity. The present study aims at explaining such a behavior from a chemical bond point of view. A theoretical study has been carried out on oxides of perovskite structure that contain oxygen anion O and two cations, A and B, or more elements. The ionicity of the individual bond, A-O and B-O, and the thermal expansion coefficient of the mixed oxides were estimated by using semiempirical methods. The oxygen defects are introduced by partial substitution of metal atom A and/or B, or by adjusting the oxidation state. It is found that the thermal expansion coefficient decreases as a function of the difference in the ionicity Δfi, between A-O and B-O bonds. The values of TEC calculated are consistent with those found experimentally. It is also shown that the measured oxygen ionic conductivity decreases with Δfi. The result suggests that the ionic conduction mechanism could be understood from a point of view of materials bonding.

Symposium FE

ADVANCES IN MATERIALS AND TECHNOLOGIES FOR EFFICIENT DIRECT THERMAL-TO-ELECTRICAL ENERGY CONVERSION

Oral Presentations

Session FE-1
Theoretical Concepts and Basic Approaches

FE-1:IL01 **Thermoionic and Thermoelectric Energy Conversion**
Ali Shakouri, Baskin School of Engineering, University of California, Santa Cruz, CA, USA

In this talk we review the direct conversion of heat into electricity using ballistic or diffusive motion of electrons in a single or multi barrier heterostructure device. The transition between thermionic and thermoelectric energy conversion is studied theoretically and experimentally. We then describe the trade offs in the thermoelectric figure-of-merit between electrical conductivity, Seebeck coefficient and thermal conductivity. We describe how these parameters are related to the bandstructure and the transport of various phonon modes. Theoretical calculations show that superlattices and embedded nanoparticles can improve the energy conversion and efficiencies in excess of 20% can be achieved. Theory and experiment are compared for a series of samples based on rare-earth nanoparticles in III-V semiconductor matrix as well in nitride metal/semiconductor multilayer films.

FE-1:IL03 **Ab Initio Studies of Impurities, Defects and Defect Complexes in PbTe Based Thermoelectric Materials***
S.D. Mahanti, Department of Physics and Astronomy, Michigan State University, East Lansing, MI, USA

Although there is no fundamental theoretical limit on the value of thermoelectric figure of merit ZT, increasing it beyond 1 has been experimentally (and theoretically) challenging. Recently, a class of PbTe based ternary and quaternary systems, denoted as APb_mBTe_m + 2 (A = Ag, Na, K and B = Sb, Bi) have been discovered which show great promise for high-temperature thermoelectric applications[1]. A thorough understanding of the electronic and atomic structure of these materials is crucial for explaining, predicting, and optimizing their properties, and to suggest new materials for improved performance. In this talk I will discuss theoretical studies of two aspects relating to the electronic and atomic structures of these fascinating systems. The first is the nature of deep defect states associated with group III (In, Ga, Tl) substitutional impurities in PbTe, addressing the validity of mixed valence impurity models. The second is the energetics of structural ordering of A and B atoms in a PbTe matrix and the associated electronic structure near the band gap region. In particular I will address how the electronic structure impacts the thermoelectric properties.

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[1]Hsu et al., Science 303, 818 (2004).

FE-1:IL04 **Multi-layered Thermoelectric Power Generator**
Ryosuke O. Suzuki, Dept. of Materials Science, Hokkaido University, Japan; also JST-CREST

Thermal fluids such as hot air and cold water are served to give the greater DeltaT to the thermoelectric (TE) junctions. For the larger power generation using a limited number of modules and the limited amounts of thermal fluids, the multi-layered TE panels can save the occupied space effectively. Because the temperatures of the fluids vary along the planer TE panels due to heat exchange through the panels, the directions of fluids is important to obtain the larger output power, P, from a TE power generator. The methods stacking a few long planer TE panels and the fluid directions are mathematically studied from the steady-state heat exchange. P for 128 kinds of fluid directions is evaluated when two panels are exposed to the two fluids. P commonly shows the maximum against the panel length because of the internal resistance and DeltaT. This maximum of P can be further maximized by choosing the counter flow for the two fluids. The non-dimensional analysis predicts that two fluids should flow in counterwise, and that the branched flow system can generate the larger DeltaT with a short generator length. When two series of fluids are used, the circulation method is another issue for TE design. The multi-tubing or roll-cake type generators are evaluated.

FE-1:IL05 **Nanostructured Thermoelectric Materials and Their Potential Applications**
G. Chen*, M.S. Dresselhaus, Massachusetts Institute of Technology Cambridge, MA, USA; Z.F. Ren, Boston College, Chestnut Hill, MA, USA

Seebeck effect can be exploited to generate power when there is a temperature difference. The efficiency of thermoelectric power generation systems depends on the materials thermoelectric figure of merit, heat source temperatures, and heat transfer in and out of the devices. This paper reports recent progresses in improving materials' figure-of-merits based on nanostructured bulk materials and understanding transport processes in nanostructured thermoelectric materials, and examines a few potential applications of thermoelectric devices.

FE-1:IL06 **Thermoelectric Energy Conversion Near Carnot Efficiency**
Heiner Linke, The Nanometer Structure Consortium and Division of Solid State Physics, Lund University, Lund, Sweden

One approach to high-efficiency thermoelectrics uses nanowires, which are predicted to suppress phonon heat flow due to enhanced surface scattering, and which offer a modified electronic density of states, which can be further customized using heterostructures in nanowires. Here I will present our efforts to use heterostructure, group III/V nanowires as model systems to understand how electronic properties and phonon flow in such designed structures can be used to optimize thermoelectric behavior. Specifically, I will review the theory underlying concepts for highly efficient thermal-to-electric energy conversion using sharp features of the electronic density of states, and will report the near-Carnot efficient energy conversion using a quantum dot embedded into a nanowire, as demonstrated by an electronic ZT > > 1 (neglecting phonon-mediated heat flow). I will also discuss evidence for an unusual phonon-mediated heat flow mechanism past energy barriers in nanowires that would otherwise be expected to block electronic heat flow.

FE-1:IL07 **Theory of Nanostructured Thermoelectrics**
Gerald D. Mahan, Penn State University, University Park, PA, USA

The best thermoelectric materials are mostly semiconductors. Growth technologies can be used to grow semiconductors with quantum wells, superlattices, arrays of quantum dots, or arrays of quantum rods. Do these nanostructured materials improve the figure of merit ZT of thermoelectric devices? The figure of merit depends upon ZT = sTS2/K, where s is the electrical conductivity, S is the Seebeck coefficient, T is temperature, and K is the electrical conductivity. We review the history of this field. Several reports of increased ZT for superlattices have not been duplicated in other laboratories. Although the initial hope was that the nanostructure would increase the power factor P = sS2, that has not happened. Instead, the nanostructure tends to reduce the thermal conductivity, due to the thermal boundary resistance at interfaces. Our recent work on thermal boundary resistance will be reviewed.

FE-1:IL08 **Large Thermopower Driven by "Pudding-mold"-type Bands**
Kazuhiko Kuroki, Department of Applied Physics and Chemistry, The University of Electro-Communications, Tokyo, Japan

The discovery of large thermopower in a sodium cobaltate Na_xCoO_2 by Terasaki et al has brought up a new direction for searching good thermoelectric materials, i.e., those exhibiting metallic conductivity with high carrier concentration. In the present study, we first propose that the coexistence of large thermopower and metallic conductivity in the cobaltate is due to its peculiar band structure which we call the “pudding mold” type. Namely, the relevant band has a nearly flat portion at the top, bending into a dispersive portion, and this type of band, when the Fermi level lies near the bending point, can give rise to a large Seebeck coefficient while also giving large conductivity. Next we show that related materials that exhibit large thermopower, such as Li_2RhO_4, CuRhO_2 and LaRhO_3, have the pudding mold type band, and the calculated Seebeck coefficient shows good agreement with the experiments. Finally, we move to a totally different kind of material, a molecular solid called the tau-type conductors, which exhibits large thermopower and metallic conductivity. There again we show that a pudding mold type band (an inverted one) plays an essential role in the occurrence of the large thermopower.

FE-1:IL09 Zintl Chemistry for Designing High Efficiency Thermoelectric Materials

G. Jeffrey Snyder, California Institute of Technology, Pasadena, CA, USA

Zintl phases and related compounds are promising thermoelectric materials, for instance high zT has been found in Yb14MnSb11, Ge-clathrates and the filled Sb-skutterudites. The rich solid-state chemistry of Zintl phases enables numerous possibilities for chemical substitution and structural modifications that allow the fundamental transport parameters (carrier concentration, mobility, effective mass, and lattice thermal conductivity) to be modified for improved thermoelectric performance. For example, free carrier concentration is determined by the valence imbalance using Zintl chemistry, thereby enabling the rational optimization of zT. The low lattice thermal conductivity found in complex structures with large unit cell volumes is generally due to the high fraction of low velocity optical phonon modes. Despite their complex structures and chemistry, the transport properties of many modern thermoelectrics can be understood using traditional models for heavily doped semiconductors.

FE-1:IL10 Strategy for Thermoelectric Application

Ryoji Funahashi*, Saori Urata, Yoko Matsumura, Kanako Iwasaki, Atsuko Kosuga, National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan; Tomoyuki Urata, CREST, Japan Science and Technology Agency, Chiyoda, Tokyo, Japan

Thermoelectric modules composed of 135 pairs of p-type Ca2.7Bi0.3Co4O9 and n-type CaMn0.98Mo0.02O3 legs were constructed using Ag electrodes and Ag paste including the p-type powder. Dimensions of both oxide legs were 7 mm wide and 3.5 mm thick and 5 mm high. There was a substrate on the one side (hot-side) of the module, namely a half-skeleton type module. The module can generate up to 20 V and 27 W of open circuit voltage and maximum power, respectively, at a hot-side temperature of 963 K and a temperature differential of 515 K in air. The maximum density of power generation reaches 4.2 kW/m2 by decrease in space between oxide devices so far. Thermoelectric arrays consisting with four modules, heat collection fins, and a water jacket have been fabricated. The arrays were installed into an industrial refuse incinerator. Tests of power generation and durability of the arrays were carried out. 1 kW/m2 of power density has been obtained from one array with 30x30cm surface area.

FE-1:L11 Development of Nanocrystalline Thermoelectric Films of p-type Bi2Te3 Based Compound

S. Jarby, R. Bar, V. Ezersky, V. Kasiyan, Z. Dashevsky*, Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel

The Bi2Te3 compound is a well known as p- and n-type semiconductors for thermoelectric applications up to 550 K. They posses high value of figure of merit ($Z = \alpha 2\sigma/k$), where a is the Seebeck coefficient, s is the electrical conductivity and k is the thermal conductivity. These compounds are characterized by a remarkable anisotropy linked to the crystal structure. The structure of these compounds belongs to space group R3m, and consists of atomic layers stacked in the order of Te(1) - Bi - Te(2) - Bi - Te(1) along the c-axis that are called quintets. Inside each quintet strong covalent bonds prevail, while the quintets are bond by weak Van der Waals bonds. This crystal anisotropy lies at the basis of the anisotropy of the thermoelectric conversion efficiency. While the Seebeck coefficient is isotropic, the electrical and the thermal conductivities have an anisotropic behavior demonstrating higher values of s and k perpendicular to the c-axis thus figure of merit, Z is about 1.5 times higher than the one parallel to it with values in the vicinity of 3×10-3 K-1. Enhancing thermoelectric figure of merit linked to the nanoscale phenomena- decreasing the dimensionally of a material cause dramatic differences in the density of electronic states allowing new opportunities to vary α, σ and k independently. Reducing k is carried out by introducing numerous interfaces that scatter phonons more effectively than electrons, while enhancing a is achieved by “filtering process”- higher energy carriers with scattering parameter >1 are more efficiently separated from lower energy carriers. It is demonstrated that nanocrystalline nucleation and the generation of a nanostructure having a high concentration of grain boundaries occur in thin Bi2Te3 based films deposited at low temperature. In such films it was observed the thermally activated conductivity dependence on temperature and a higher value of Seebeck coefficient, α (up to 350 ?V/K) in comparison with a value of a for the bulk crystals.

FE-1:L12 Thermoelectric Iron Oxides

T. Kajitani*, T. Nozaki, K. Hayashi, Department of Applied Physics, Graduate School of Engineering, Tohoku University, Sendai, Japan

P-type and N-type thermoelectric iron oxides, based on Delafossite CuFeO2 and Spinel Fe3O4 ,respectively,are developed. Dimensionless figure of merit, ZT, of the bulk P- and N-type iron oxides become 0.15 and 0.10 at 1200K, respectively. These values were doubled by the introduction of nano-voids. Physical properties of these iron oxides are structurally unique, because of their triangular or Kagome arrangement of FeO6 octahedrons. The Delafossite CuFeO2 becomes antiferromagnet at temperatures less than 20K and the Spinel Fe3O4 is a ferrimagnet at room temperature. In both crystals, iron ions are conceivably at the high-spin state. We found enhanced dynamic spin frustration at about TN in CuFeO2 by the cold neutron scattering measurement. Thermoelectric performance of the P- and N-type iron oxides will be discussed with the light of spin dynamics and entropy of spin arrangements[1].

[1] *K. Hayashi, T. Nozaki, R. Fukatsu, Y. Miyazaki, and T. Kajitani; PRB (accepted in Sept.2009).*

FE-1:L13 Macro to Micro Derivation of the Thermoelectric Thermo-dynamics

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According to the linear response theory we derive the principal contributions to energy and entropy fluxes in a thermoelectric material using a force-flux description of the particles transport. The introduction of the so-called thermoelectric potential gives a direct estimate of the best working condition for practical applications. Moreover we show that this thermodynamical approach is strongly linked with microscopical descriptions of the electronic transport. In particular, it is shown that the so-called relative current can be derived form the expression of the cross-correlation between the heat and particles fluxes. Practical conclusions are drawn for thin film thermoelectric devices design and working conditions.

FE-1:L14 Theoretical Performance Characteristics of Wearable Thermoelectric Generators

Vladimir Leonov, IMEC, Leuven, Belgium

Wearable service-free electronics, including health monitoring wireless sensors, requires a lifetime thermoelectric power supply working on a wasted human body heat. In this work, its theoretical performance characteristics have been calculated based on thermal matching of a TEG with the human body. The characteristics have been obtained for a range of ambient temperatures by using new experimental data collected in this work (i) on the heat exchange in wearable TEGs, (ii) on the location-dependent thermal resistance in humans, and (iii) on the acceptance-related limit for a heat flow at different ambient conditions. Comparison of calculated performance characteristics with those practically obtained in existing devices is then performed. Then, a comparison with wearable photovoltaic cells is performed showing advantages of thermoelectric converters. Technological requirements are discussed for thermopiles to become successful on the market of autonomous wearable electronics. The practical design-related power generation limits for a wearable TEG are then discussed based on the power consumption of existing prototypes of both self-powered wireless medical devices and smart power management systems. This allows prediction of the application areas.

Session FE-2

New and Improved Materials and Low Dimensionality Structures

FE-2:IL01 Materials and Devices for Thermal-to-Electric Energy Conversion

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Theoretical prediction of drastic improvement in thermoelectric (TE) performance by means of the quantum confinement effect proposed by Dresselhaus et al. in 1993 triggered the development of high-efficiency materials by constructing low-dimensional nanostructures such as 2D superlattices, 1D quantum wires, and 0D quantum dots. The concept of "low-dimensional nanostructure" is indeed helpful to achieve high ZT in thin films, short fibers, etc. However, these small materials cannot be directly applied to large-scale conversion of heat into electricity which is expected now to contribute to reducing CO2 emission, so that bulk materials embedded with quantum nanostructures which could enhance the power factor through quantum confinement of charge carriers as well as reduce thermal conductivity through phonon scattering at nanointerfaces are strongly required to achieve our goal to develop thermoelectrics as one of the innovative technologies to solve global warming and climate change issues. The current status of the bulk nanomaterials development and the future prospects for applications will be presented and discussed.

FE-2:IL02 Thermoelectric Perspectives of Transition Metal Oxides

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The possibility to recover the high temperature waste heat (e.g. gas-engine, combustion furnace,..) opens the way to increase the efficiency of thermoelectric generator. Consequently serious need for the search of new chemically stable high temperature thermoelectric material exists. Transition metal oxides are of the prime interest as these offer, in principle, high chemical stability, low toxicity, high thermoelectric power and low thermal conductivity; factors, which predestinate them as perspective high temperature thermoelectrics. In our presentation we will focus namely on the thermoelectric appraisal of a family of mixed valent oxides in which electron-phonon/magnon interactions are large enough for trapping carriers forcing them to hop from site to site thanks to a thermal activation. The thermoelectric power of these hopping conductors is, at high temperature limit, expressed as the configurational entropy of charge carriers presented often using the well-known Heikes formula. Among all, we will discuss the perovskites with Mn3+/Mn4+, Co3+/Co4+, Cr3+/Cr4+, Fe2+/Fe3+/Fe4+ and Ru4+/Ru5+ mixed valency systems and focus on the role of spin and orbital degeneracy in thermoelectric power and magnetic excitations in the thermal and electric conductivities, respectively.

FE-2:L03 Search for n-type Thermoelectric Oxides: the Case of the Hollandite

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To realize all-oxides thermoelectric generators performing n-type legs are still missing.Best candidates at 1000K are doped In2O3 or ZnO with ZT=0.30[1] and 0.47[2], respectively. As shown by Ohta *et al*[3] from the study of the SrTiO3/Nb-SrTiO3 intergrowth, the dimension reduction for the electron gas enhances the Seebeck coefficients. This originates from the shape change in the density of states at the Fermi level.In order to look for other candidates, we have investigated the properties of the hollandites AxV8O16. The distorted 1D hollandite framework consists in double rutile ribbons of edge shared VO6 octahedra, which interconnections via the corner sharing of these ribbons delimit square channels.In the latter, the heavy masses A counter cations limit the phonon propagation. Depending on the oxidation state and content of the A cations, the vanadium mixed valency can be tuned in between V3+(d2) and V4+(d1).S values are found to be always negative with increasing with T, reaching S=40 V.K-1 at 1000K for Pb1.5V8O16. The relationship between S and the V oxidation state together with the results of densification by the SPS technique will be presented.

[1]D.D. Berardan et al, Solid State Comm. 146, 97 (2008); [2]M. Othaki et al JEM 38, 1234-2009; [3]H.Ohta et al.Nat Mat6 129-2007.

FE-2:L04 Effect of Co-substitution on the Structure and Thermoelectric Properties of Chimney-ladder Solid Solution (Mn1-xCox)Siγ (γ~1.7)

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A partially cobalt-substituted solid solution of Nowotny chimney-ladder phase, (Mn1-xCox)Siγ, has been prepared using a tetra-arc-type furnace and a subsequent annealing process. The compounds consist of two tetragonal subsystems of [Mn1-xCox] and [Si], with an irrational c-axis ratio γ = cMn/cSi ~1.7. The crystal structure and thermoelectric properties of (Mn1-xCox)Siγ solid solution were compared with those of the Fe-substituted solid solution, (Mn1-xFex)Siγ. In the case of Co-series, extra valence electrons are introduced relative to Fe-series, since the valence electron counts are 3d74s2 for Co but 3d64s2 for Fe, respectively. It was naturally expected that the Fe- and Co-substituted MnSiγ becomes n-type conductor from the p-type one at x > 0.23(5) and x > 0.10(5), respectively. Experimentally, the Fe-substituted samples become n-type at x > 0.28 but it is not the case for the Co-substituted ones. It is thus evident that there is an unknown factor which controls the thermoelectric properties of Co-substituted samples.

FE-2:IL05 Recent Advances in High Temperature Thermoelectric Generating Technology

Jean-Pierre Fleurial*, Thierry Caillat, Erik Brandon, Jay Pak, Vilupanur Ravi, Pawan Gogna, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA

Thermoelectric power sources have consistently demonstrated their extraordinary reliability and longevity for deep space missions as well as terrestrial applications where unattended operation in remote locations is required. There are very significant large scale opportunities for producing electricity from waste heat recovered from a variety of energy intensive industrial processes and the exhaust of transportation vehicles. The development of new, more efficient materials and rugged modular devices is the key to improving existing space power technology and expanding the range of terrestrial applications. For high grade heat sources, achieving high ZT values over a wide temperature range requires the development of cascading and segmenting thermoelectric technology. To that effect, refractory rare earth tellurides and antimonides, and bulk nanostructured Si-Ge alloys have been selected as high temperature elements. Recent experimental results on the development of power generating couples capable of operating up to 1275 K will be compared to that of state-of-practice Si-Ge alloys. Progress in transitioning thermoelectric technology to a more flexible, lower cost modular array configuration suitable for various high temperature application opportunities will be discussed.

FE-2:IL06 Clathrates: A Challenge for Thermoelectricity?

Peter Rogl, Institute of Physical Chemistry, University of Vienna, Vienna, Austria

Automotive applications of thermoelectric generators (TEGs) for the conversion of the waste heat of combustion engines into electricity is a most timely issue. Among the manifold of "intermetallic" clathrates, hitherto two series of clathrate type I compounds have shown interesting thermoelectric properties: EA8M16Ge30 and EA8MxGe46-x-y•y (EA=earth alkaline metal, • stands for a vacancy). The paper focuses on a systematic study of clathrate formation (phase equilibria in isothermal sections, isopleths, liquidus projections), clathrate structures, bonding and structure-property relation in multicomponent clathrate type I materials EA8Mx{Si,Ge}46-x-y•y with M being one or a combination of transition elements. The present analysis will evaluate the difficulties in preparation and design of clathrate compounds at a given electron/atom concentration. Validity and shortcomings of the Zintl concept for clathrates will be outlined. The correlations obtained, although not complete for many systems, may provide useful in defining compositional regions of interest for further optimization of clathrate materials with high thermoelectric efficiency in energy conversion.

FE-2:L07 Effect of Annealing on High Temperature Thermoelectric Performance of ZrNiSn Half-Heusler Compounds

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The ZrNiSn half-Heusler compounds have been prepared by the combination of arc melting and spark plasma sintering technique. The ingots were annealed under vacuum at 1073 K for 1, 3, and 7days. The thermoelectric properties of all the samples were measured in the temperature range of 300-850 K. With increasing annealing time, both the Seebeck coefficient and electrical resistively increase on account of the decrease of Hall carrier concentration. The highest power factor of 37μW/cmK2 has been achieved for the as prepared sample. Thermal conductivity for all samples increases with increasing annealing time. The as prepared sample exhibits the lowest thermal conductivity due to the extra mass fluctuation scattering caused by the interchange of Zr and Sn sublattice. The maximum dimensionless figure of merit ZT of 0.64 was obtained at 800 K for the as prepared sample. The electronic structure for ZrNiSn with different degree of interchange between Zr and Sn sublattice was also calculated. Besides the shrink of band gap caused by the disorder, larger density of states near the Fermi lever was observed compared with perfectly ordered ZrNiSn, which could be responsible for the excellent electrical transport properties for the as prepared sample.

FE-2:L08 **Non-contact Optical Method for Measuring Thin Film Lattice Temperatures**

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Thin film IV-VI semiconductors are direct gap materials that have recently received significant interest for thermal-to-electrical energy conversion applications. Ability to measure localized lattice temperatures in thin films is important for the determination of fundamental materials parameters such as thermal conductivity. IV-VI semiconductor band gap energies vary strongly with lattice temperature. This makes it possible to determine absolute lattice temperature with relatively good precision by using mid-IR photoluminescence (PL) to measure band gap energy, which varies positively with temperature at the nominal rate of 0.4 meV/K. This presentation will describe PL techniques involving diode laser pumping and FTIR spectral analysis. With an FTIR spectral resolution of 0.5 cm-1, the accuracy of this lattice temperature measurement method is better than 0.16 degrees. Results will be presented showing significant PL peak blue shifting corresponding to measured lattice heating of more than 30 degrees as pump laser injection currents are increased from 1 amp to 3 amps. Finite element thermal modeling results and prospects for using this PL method to measure thermal conductivities of various IV-VI semiconductor thin film structures will also be discussed.

FE-2:IL09 **Thermoelectric Properties of Cobalt Oxides Improved by Spin State Control**

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The spin state is a fundamental concept in transition-metal compounds. Especially the spin state of a trivalent Co ion is degenerate among the low, intermediate and high spin states. Since the entropy is different for different spin states, the thermopower, the entropy per charge, can be dependent on spin state. In this talk, by properly designing the Co/Rh oxides, we show that (i) the thermopower can be enhanced by 150 micro V/K with remaining resistivity intact, (ii) the thermopower continues to increase at 800 K by blocking the spin state transition, and (iii) the disorder in the spin state enhances the low temperature thermopower and modifies the magnetic properties as well.

FE-2:IL10 **Layered Thermoelectric Oxides**

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It was shown in 1997 that a metallic behaviour coexists with a large thermopower in the layered cobalt oxide NaxCoO2 [*I. Terasaki et al, PRB56, R12685 (1997)*]. Since then, this family of oxides has been investigated and the complex phase diagram of these materials has been established [*G. Lang et al, PRB78, 155116 (2008)*]. The peculiar properties of these materials originate from the presence of CdI2 type CoO2 layers, made of edge shared CoO6 octahedra, in which Co3+ and Co4+ should coexist in low spin states. The importance of the electrostatic potential generated by Na+ on the transport and magnetic properties has also been shown [*C.A. Marianetti et al, PRL98, 176405(2007)*]. In this talk, the results obtained in the misfit family and related compounds, made with similar CoO2 type layers will be presented. The origin of the large thermopower in these metallic oxides will be discussed emphasizing the importance of doping, and spin and orbital degeneracy of low spin states Co3+ and Co4+. The peculiar properties generated by these CdI2 type layers will be compared to other oxides, with a more classical behaviour. Also, the influence of the separating block layers on the transport properties will be detailed.

FE-2:L11 **Epitaxial Growth of Nanostructured Bismuth Films on Si Through a Chemical Solution Route**

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Thermoelectric bismuth films have been prepared through a chemical solution at low temperature (~70 °C) using single silicon as substrate. The prepared films are composed of compacted nanoparticles ranging 10-50 nm in size. The growth process of the films was also monitored by SEM. The maximum Seebeck value of 105mVK-1 at 180K has been achieved from the quantum size effect, implying the potential application in miniature thermoelectric device.

FE-2:L12 **Electrical and Thermal Transport Properties of ZnO Thermo-electric Oxide Doped with Al and Ga**

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Co-doping of Al-doped ZnO with another group 13 elements resulted in a drastic decrease in the thermal conductivity, κ, from 40 W/m K down to ~5 W/m K at room temperature and 8 to ~3 W/m K at 1073 K. Although the electrical conductivity, σ, of the samples co-doped with In was much lower than that of Al-doped ZnO, the samples co-doped with Ga maintained significantly high s values with a metallic temperature dependence. The absolute values of the negative Seebeck coefficient of the samples also somewhat increased with the co-doping of Ga. As a consequence, the power factor of the co-doped samples showed an improvement of 25-35% over the whole temperature range. These results led to maximum ZT values of 0.47 at 1000 K and 0.65 at 1247 K, being the highest values so far reported for bulk n-type oxides. The amount of a Ga-related impurity phase giving a peak at around $2\theta = 35°$ in XRD showed an excellent agreement with the decrease in the thermal diffusivity. Analyses of the carrier mobility and the phonon thermal conductivity revealed that a selective reduction of the phonon thermal conductivity (selective phonon scattering) would be operative in the co-doped samples. The phonon scattering will be discussed in terms of the mean free path and microstructure in the oxide.

FE-2:IL13 **Synthesis, Structure and Thermoelectric Properties of Complex Rare Earth Antimonides**

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Always in quest for more efficient thermoelectric materials, we have focused our investigation on complex antimonides crystallizing in the Th3P4 structure type. More particularly, we targeted to improve the properties of Yb4Sb3 by the substitution of the divalent Yb, by a trivalent rare earth, or by substituting Sb atoms by electron richer Se, Te or I atoms. The compounds are made by classical high temperature synthesis in niobium tubes, characterized by x-ray powder diffraction and electron microscopy. The polycrystalline samples are densified by spark plasma sintering and their thermal and electronic transport properties measured up to 1000°C. The substitutions on the cationic site have led to several compounds that exhibit rather promising figure of merit, for instance Yb3.5La0.5Sb3 has a ZT of about 0.75 at 1000K. Substitutions on the anionic site, when possible, show interesting results. We will also discuss the limit of the synthetic method we have used and present the undergoing work dedicated to either increase the substitution rate by using mechanical alloying synthesis or by trying to fill the vacancies present in the structure.

FE-2:IL14 **Functions of Key Structural Unit and Performance Optimization in Novel Thermoelectric Compounds**

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After understanding the filling fraction limits for both single- and multiple-filling in filled CoSb3 skutterudite compounds, we are stepping forward to maximize their TE performance. The first part of this talk will focus on how to realize the phonon glass behavior. we tried to reveal some special properties of skutterudites due to the intrinsic cages, incoherent localized rattling behavior, rattling-frequency-dependent resonant phonon scattering, and the limited but universal range of the optimum electron concentration for n-type filled CoSb3. In the second part of this talk, I will talk about the diamond-based semiconductors as promising thermoelectric materials, where the key structural unit is the tetrahedral blocks. While the perfect or undeformed compounds such as diamond and silicon always show high lattice thermal conductivities, the multi-component compounds, such as the Cu2ZnSnSe4-based materials, always give very low thermal conductivity primarily due to the large deformation of the tetrahedrons and randomness of multi atoms. Our work also hinted that there might exist an electron transport network, and it should not be disturbed for obtaining good electrical transport properties.

FE-2:L15 Effect of Strontium and Europium Substitutions on Thermoelectric Properties in Silicon-Based Clathrate Compounds

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Silicon-based clathrate compounds are of growing interest as potential thermoelectric materials at high temperatures because of advantages in the thermal stability, economical and environmental points. The low thermal conductivity of clathrate compounds is due to the weak guest-host interactions whereby the localized guest vibrations interact strongly with the host acoustic modes. In addition, the guest-host interactions through the overlap between guest and host wave functions are expected to have a significant influence on the electronic properties of clathrate compounds. Thus, we have investigated into the modification of the electronic structure caused by guest substitutions and the effect on the electronic transport properties as well as the thermal properties of silicon-based clathrate compounds. The composition, microstructure, and thermoelectric properties are examined on polycrystalline strontium- and europium-substituted barium-silicon-based clathrate compounds prepared using a spark plasma sintering technique. We discuss the effect of guest substitutions on the Seebeck coefficient, density-of-states effective mass, carrier mobility, carrier relaxation time, and lattice thermal conductivity.

This work was supported by KAKENHI (19560713) and JST, CREST.

FE-2:L16 Thermal Expansion of Clathrate Compounds Ba8Mx{Si,Ge}46-x (M = Cu, Zn, Pd, Ag, Cd, Pt, Au)

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Thermal expansion is one of the mechanical properties, which plays a key role for the fabrication of thermoelectric generators. N- and p-legs should exhibit similar thermal expansion coefficients to ensure a proper lifetime of these devices. Thus the thermal expansion of a series of multicomponent clathrate type I compounds Ba8Mx{Si,Ge}46-x where M is one of or a mixture of the following elements Cu, Zn, Pd, Ag, Cd, Pt, Au, was measured in the temperature range 4-300 K using a highly sensitive tilted plate capacitance dilatometer[1]. At higher temperatures a pushrod dilatometer was used for the measurement. The data were analysed using a semiclassical treatment of thermal expansion[2] and Debye- and Einstein-temperature were extracted. Thermal expansion coefficients were compared to data available in literature to provide a comprehensive compilation on thermal expansion data for thermoelectric clathrates including inverse clathrates.

[1]M. Rotter, H. Müller, E. Gratz, M. Doerr and M. Loewenhaupt, Rev. Sci. Instruments (7), 2742-45 (1998); [2]G.D. Mukherjee, C. Bansal, A. Chatterjee, Phys. Rev. Lett. 76(11), 1876-1879 (1996)

FE-2:IL17 High Temperature Thermoelectric Properties of a Homologous Series of n-type Boron Icosahedra Compounds: a Possible Counterpart to p-type Boron Carbide

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The useful energy conversion of waste heat is a large incentive to find viable thermoelectric (TE) materials which can function at high temperature. Boron-rich compounds are attractive materials for their stability, exhibiting melting points above 2200 K. Furthermore, they also possess intrinsic low thermal conductivity, an inherent advantage for TE application. As a synthesis method we have discovered that small amounts of third elements like C, N, and Si can function as bridging sites and result in the formation of novel and varied boron cluster structures[1]. REB44Si2 exhibit large Seebeck coefficients and unlike most compounds, ZT shows a steep increase at T > 1000 K. A series of homologous RE-B-C(N) compounds; REB17CN, REB22C2N, and REB28.5C4, was recently discovered to be the long awaited n-type counterpart to p-type boron carbide, which is one of the few TE materials which has been commercialized. I will give an overview on synthesis methods and present advancements in research (e.g. doping, densification) for the application of RE-B-C(N) compounds as high temperature TE materials. The mechanism of the anomalous n-type behavior will also be discussed.

[1]T. Mori, in Handbook on the Physics and Chemistry of Rare Earths, Vol. 38 (North-Holland, Amsterdam) p. 105-173 (2008)

FE-2:IL18 Synthesis, Structural and Chemical Characterizations, and Transport Properties of $Mo_{3-x}Ru_xSb_{7-y}Te_y$

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The metallic Mo_3Sb_7 compound has recently received great attention due to its intriguing properties such as superconductivity and low-dimensional magnetism. Apart from its unique physical properties observed at low temperature, it was also shown that this material is attractive for thermoelectric power generation at moderated temperature when properly alloyed. After a detailed description of the physical and chemical properties of Mo_3Sb_7 including the crystallography, the electronic band structure and the magnetic and thermoelectric properties in a broad range of temperature (2 - 1000 K), we shall show how one can modify the metallic nature of Mo_3Sb_7 to substantially improve its thermoelectric properties through judicious partial substitution either on the Mo, the Sb or both sites. The transport properties of the ternary and quaternary compounds, namely $Mo_{3-x}Ru_xSb_{7-y}Te_y$, will be presented and discussed with a special emphasis on the evolution of the magnetic interactions displayed by Mo_3Sb_7.

FE-2:L19 Tuning of Thermoelectric Properties in Double Doped Skutterudites from Electronic Structure Calculations

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Partially filled skutterudites appear more attracting thermoelectric materials than unfilled ones, since they offer more possibilities of modification their electron and phonon characteristics. We present electronic structure features in double doped InyCo4-xFexSb12 solid solutions as resulted from ab initio calculations using the self-consistent Korringa-Kohn-Rostoker technique with coherent potential approximation (KKR-CPA). We show that the position of the Fermi level can be smartly controlled by filling the void with In on one hand and diluting Fe on Co site on the other one. The critical concentrations of both dopants have been well established, where a crossover from hole-like to electron-like type of electrical conductivity is expected. Our KKR-CPA results are discussed in view of recent electron transport experiments. The electronic transport behaviours in InyCo4-xFexSb12 are compared to those recently observed in CayCo1-xNixSb12[1]. It seems that electronic properties of InyCo4-xFexSb12 are similar to those detected in Fe1-xNixTiSb half-Heusler alloy[2], where the composition induced metal-semiconductor-metal accompanied by the change of thermopower sign, was found.

[1]Puyet et al, Phys. Rev. B 75, 245110 (2007); [2]Tobola et al, Phys. Rev. B 64, 155103 (2001).

FE-2:L20 Thermoelectric Properties of the Heavy Element Doped Heusler Fe2VAl Alloy Prepared by Powder Metallurgy Technique

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A Heusler alloy, Fe2VAl, is a promising candidate for thermoelectric power generation near room temperature because of its high thermoelectric power factor comparable to a Bi-Te system. The thermoelectric figure of merit of this alloy is poor, however, because of its high thermal conductivity: ca. 26 W/mK. Reduction of thermal conductivity is therefore required for practical applications. In this study, we investigated the effect of heavy element doping on thermal conductivity of the Heusler alloy. For the sample preparation, a pulse-current sintering technique with fine powder prepared by mechanical alloying was used. By using the powder metallurgy technique, a heavy element with a low melting point can be stably doped, compared to the melting process. Then a Heusler Fe2VAl1-xSbx sintered alloy was synthesized to evaluate the effect of Sb substitution on thermoelectric properties. Thermal conductivity was effectively-reduced by a small amount of the substitution because of the large atomic mass of Sb compared to the constituent elements of Fe2VAl alloy. Since the Seebeck coefficient and electrical conductivity can be enhanced by controlling the valence electron density, thermoelectric figure of merit was improved.

FE-2:IL21 Misfit Layered Compounds - Nanocomposite Thermoelectric Materials

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We have discovered a broad class of new materials with ultra-low thermal conductivity, on the order of 0.1 WM-1K-1 or less for fully dense solids, that is a consequence of turbosratic disorder - a rotational disorder between crystalline layers. Misfit layered compounds are one example of a class of compounds where this disorder can be trapped and TEM, XRD and thermal conductivity data on misfit compounds will be presented demonstrating the link between turbostratic disorder and ultra-low thermal conductivity. A kinetic synthesis route based on controlling diffusion distances allows us to prepare particular [(MSe)1+d]n(TSe2)m compounds and determine the relationship between structure, properties, the thickness of the constituent layers (n and m) and the ratio between the constituents (n/m). Charge transfer between the constituents leads to structural changes that vary with position relative to the interface between the components. To make these compounds useful thermoelectric materials, the electrical properties are controlled and optimized by annealing in a controlled atmosphere of selenium resulting in reproducible carrier concentrations.

FE-2:IL22 Recent Advances in In2O3 Based Thermoelectrics

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Indium oxide, a wide band gap semiconductor, has attracted considerable attention due to its great potential for gas sensing, optical transparency and optoelectronics. Numerous studies have been carried out on thin films of this material as a transparent conductor (TCO). They have shown that the doping with tin increases dramatically the electrical conductivity, as illustrated by the well know Indium Tin Oxide (ITO). In the last years, the doping of In2O3 thin films with titanium, zirconium, molybdenium or tungsten has shown the possibility to reach very high carrier mobility with carrier density higher than 1020 cm-3. However, very few studies have been reported regarding the transport properties of In2O3 bulk ceramics for other applications. Recently, we published that metal doped In2O and cosubstituted In2-2xSnxMxO bulk ceramics exhibited a great potential as n-type elements for thermoelectric generators. Recent advances in the processing and characterizations of In2O3-based bulk thermoelectrics are presented and discussed.

FE-2:L23 Thermoelectric Generating Properties of Perovskite Like Materials

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Research and development of thermoelectric generators have been actively carried out to use waste heat. It is well known some p-type oxides show high thermoelectric performance. However, the high performance n-type oxide has not been found. N-type CaMnO3 is a promising material because of its high Seebeck coefficient. The electrical resistivity of this oxide is, however, too high to use it practically. Not only high Seebeck coefficient but also low electrical resistivity is required for practical use. At first, we investigated the effects of element substitution in order to decrease the resistivity. N-type CaMn0.9M0.1O3(M=Cu, In) compounds were prepared by solid-state reaction and hot pressing. Relative density of n-type CaMnO3 (HP) was over 99%. The maximum value of power factor for CaMn0.9In0.1O3 was 0.204 mWm-1K-2, which was the largest of all specimens at 673 K. This value was, however, not enough to use it practically. Secondly, we focus attention on the Aurivillius compounds. Aurivillius compounds consist of Perovskite layers and Bi-O layers. We expect that this crystal structure shows large Seebeck coefficient due to the quantum confinement of electron in Perovskite layer. Thermoelectric properties of Aurivillius compounds will be reported in the presentation.

FE-2:L24 Thermoelectric Properties of Spark Plasma Sintered (SPS) Fully Dense Silicon Carbide Nanoensembles

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We have undertaken a systematic study of the interrelationship between thermopower, electrical and thermal conductivity initially using nanocarbon ensembles with a view to controlling, insofar as possible, these three parameters separately[1, 2]. Here we present recent work on fully dense SPS processed nanostructured alpha and beta SiC containing ensembles which shows that partial substitution of SiC for nanographite raises the thermopower from 40 to about 400 microWatt/K. We will present data and discuss our approaches to increase the electrical/thermal conductivity ratios. The overall goal of the study is to develop high ZT materials for efficient energy conversion. Suitable materials for this purpose must resist recrystallization at high temperatures and must not be resource limited so as to qualify for large scale power generation applications.

[1] D.M. Gruen, P. Bruno, R. Arenal, J. Routbort, D. Singh, M. Xie, "Thermoelectric Power Factors of Nanocarbon Ensembles as a Function of Temperature", J. Appl. Phys. 105, 073710, (2009); [2] P. Redfern, D. Gruen, L. Curtiss, "Effect of Boron Substitution on the Electronic Structure of Nanographene: Thermoelectric Transport Properties of Nanocarbon Ensembles", Chem. Phys. Lett. 471, 264, (2009).

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FE-2:L25 Enhanced Thermoelectric Performance of Carbon Nanotube/Polyaniline Composites

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During the last few years great interest has been attracted by thermoelectric materials because of their great potentials for applications such as energy conversion of waste heat into electricity and solid state heating and cooling. Nowadays, most of the studies have been limited on the traditional inorganic materials. Comparing with inorganic thermoelectric materials, conducting polymers possess several attractive features for use as thermoelectric materials because of low cost due to rich resources, easy synthesis and easy processing into versatile form. Furthermore, Polymers are intrinsically low thermal conductors, which are ideal for thermoelectric materials. However, their poor electrical transport properties, including low electrical conductivity and Seebeck coefficient, have excluded them as feasible candidates for thermoelectric materials in the past. Thus it is necessary to find an effective way to improve the power factor of conducting polymers. In this communication, ordered carbon nanotube/polyaniline nanocable composites were synthesized. A strong interaction between polyaniline and CNTs promotes the electrical conductivity and Seebeck coefficient by constructing ordered microstructure. The maximum power factor of composites reaches 2*10-5 Wm-1K-2and the maximum ZT value of composite reaches 0.004, that are the highest values among bulk polymer thermoelectric materials ever reported.

FE-2:IL26 High Figure of Merit Superlattice Thermoelectric Materials and Devices

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Nanoscale material approaches - superlattices (SL), nano dots and second phase nano-inclusions - have become the dominant approach to enhancing the figure of merit (ZT) in thermoelectric materials for energy conversion. There has been considerable progress in ZT at 300K in p-type Bi_2Te_3/Sb_2Te_3 SLs (ZT~2.4) and recently, in delta-doped n-type $Bi_2Te_{3-x}Se_x$ thin-films (ZT>1). We will describe SL structural characterization by X-ray absorption spectroscopy, X-ray diffraction, coherent optical phonon measurements, thermal conductivity by 3-omega and ZT enhancement in Bi_2Te_3-based SL material systems. These studies have led to thicker films (~15 microns) to extract larger cooling differentials and higher power conversion efficiency in devices. The Bi_2Te_3-SL films have been used to create advanced chip-scale cooling modules for Si microelectronics. The work in low-temperature Bi_2Te_3-based SL thin-films has motivated us to develop 2-D and nano-dot superlattices (NDSL) in the mid-temperature PbTe-based and high-temperature SiGe-based materials. PbTe-GeTe SL have been developed with exceptionally good power factors. Thermal conductivity measurements of Si/Ge NDSLs indicate low values for lattice contribution. The modeling of cross-plane carrier transport will be discussed as well.

FE-2:IL27 Rapid Solidification Methods for Fabrication of Novel Thermoelectric Materials

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The development of novel preparation technique about high-performance thermoelectric materials with nanostructure is of great significance to the commercial applications. In this research, we developed a new synthesis route that is melt spinning combined with spark plasma sintering technique (MS-SPS) to rapidly prepare nanostructured thermoelectric materials. Using this synthesis route, we have prepared nanostructured n-type Yb0.3Co4Sb12+y bulk materials and InxCeyCo4Sb12 compounds with evenly dispersed nano-InSb (10~80 nm) second phase on the boundaries. More importantly, compared with traditional method, the preparation time of filled Skutterudite by using MS-SPS can be notably reduced from 10 days to less than 40 hours. The ZTmax reaches 1.45 at 800 K for n-type In0.15Ce0.15Co4Sb12 compound prepared by MS-SPS technique. Moreover, we also prepared p-type Bi-Sb-Te bulk materials with some special nanostructures (such as amorphous structure, fine nano-crystalline, quasi-coherent structure and so on) by MS-SPS. This system show very low thermal conductivity while they possess good electrical transport properties, and therefore ZTmax reaches 1.56 at 300 K. The nanostructured Bi-Sb-Te bulk materials show a very high compressive strength which is double of zone-melting samples.

FE-2:L28 Thermal Expansion and Mechanical Properties of Skutterudites

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With a worldwide energy shortage and decreasing supplies of primary energy, thermoelectric devices are becoming very important. For high thermoelectric energy conversion efficiency, materials constraints request high ZT for both legs but also thermal expansion a and mechanical properties are important features. We compared the thermal expansion coefficient for Sb-, Ge-, and P- based skutterudites determined from (i) a capacitance method (LT) (ii) a zero force method (HT) or (iii) a temperature dependent measurement of the lattice parameter. For high ZT didymium, mischmetal (DDy/MmyCox/NixFe4-xSb12) and triple filled skutterudites we elucidated the dependency of a on the filling level, a difference between p- and n-type alloys and insignificant differences in micro and nano structured alloys. The semiclassical model of Mukherjee has been successfully used to quantitatively describe a in terms of Debye and Einstein temperatures, which compare well with corresponding results from specific heat, resistivity or x-ray measurements. We calculated porosity,measured Vickers hardness, finding solid solution hardening. Young's modulus (ultrasound resonant method)and Poisson´s ratio showed dependencies on hardness and porosity. We made compression tests to define yield strength.

FE-2:L30 Low-temperature Properties of Layered g-CaxCoO2 Compound

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Layered compound g-NaxCoO2 with promising thermoelectric properties has being intensively studied since 1997. It was widely recognized that the transport properties are closely related to the two-dimensional crystal structure consisting of conducting CoO2 layer and poorly conducting block layer. As an isostructural to g-NaxCoO2, the systematic investigation for g-Ca0.35CoO2 compound is also highly required in order to further reveal the relevant intrinsic behaviors, including thermoelectric properties and magnetic properties. The g-Ca0.35CoO2 samples, including polycrystal and single crystal, were prepared by a low-temperature ion exchange of the corresponding g-Na0.35CoO2 precursor. Electrical resistance, Seebeck coefficient, thermal conductivity, susceptibility and specific heat were measured. The susceptibility shows an antiferromagnetic behavior at low temperature and Curie-Weiss behavior above 50 K. The in-plane resistivity of g-Ca0.35CoO2 single crystal shows a metallic behavior above 15 K, with only 0.9mohmcm at 300 K, which is about 5 times larger than that of g-NaxCoO2 single crystal, implying that Ca0.35CoO2 is also a candidate of good oxide thermoelectric materials.

Session FE-3

Progress in Devices and Applications

FE-3:IL01 Solar Thermoelectric Generation

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Historically, thermoelectric generators have been used for deep-space exploration and waste heat recovery. Direct solar to electrical energy conversion is possible with a solar thermoelectric generator (STG). Utilizing low-cost optics, selective surfaces, and commodity modules, solar thermoelectrics are a cost-effective (less than 0.3 $/kWhr)alternative to solar photovoltaics for micro-power generation. A prototype STG has been constructed in our lab. Fresnel optics are used to concentrate AM 1.5 radiation to 66x suns. A selective surface is applied directly to the thermoelectric module - the coating has high absorption in the visible and low emissivity in the infrared thereby suppressing radiation loss. A system efficiency of 3% was measured for a commercial Bi2Te3 module with the output power of 1.8W, which is to our best knowledge the highest efficiency for solar thermoelectrics using a module. The early prototypes have been deployed in three separate field trials during the last 15 months. The field trials have been conducted in collaboration with One Earth Designs under the project name SolSource; the project was awarded both the St. Andrews Prize for Energy and the Environment and the Clinton Global Initiative in 2009.

FE-3:IL02 Thermoelectric Application for Power Generation in Japan

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Thermoelectric power generation technology has been recognized to contribute to the realization of environment-friendly society all over the world in the future. Present status and future prospects on the thermoelectric power generation technology in Japan are overviewed. The thermoelectric applications for power generation have been mainly considered to be one of the waste heat recovery systems from industrial, private, and transportation sectors in the Japanese energy system. The demonstration system tests have been achieved using practical heat sources such as hot springs, incinerators, motorcycles, diesel engine co-generation, etc. Several topics of experimental results on advanced materials such as layered oxides, half-Heusler compounds for power generation from the view points from environment-friendly and nanostrucuture approach are introduced. In the future prospects the recent R&D projects for thermoelectric power generation technology and the commercialization of thermoelectric power generation applications are discussed.

FE-3:L04 Modular Combustor-radiator for Micro-TPV System Application

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We report an experimental study on a modular planar combustor-radiator for micro-TPV system application. Compared to the typical cylindrical structure, a modular planar combustion facilitates fabrication and assembly for increased power output and improved system efficiency when integrated with a recuperation stage. The micro combustor is a key component of a micro-TPV system. To maximize the power output, the combustor needs to achieve the highest possible wall temperature with a uniform temperature distribution along the radiating combustor wall. Micro combustors with channel width of 1.0 mm, 1.5 mm and 2.0 mm have been studied. Results indicate that the wall temperature decreases with an increase in the channel width due to the reduced heat transfer between the wall and the hot gases. Among a number of parameters studied, the use of porous media inserts shows a marked increase in system performance. Porous media inserts enhance both the preheating of the inlet fuel mixture and the heat transfer between the hot gases and the wall, thereby contributing to the increased combustor-radiator wall temperature. An increase of 80-90 °C has been obtained along the wall of the micro planar combustor with SiC as porous media, projecting an increase of 33% in radiation energy density.

FE-3:L05 Vehicular Thermoelectric and Air Conditioner/Heater Development

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Thermoelectric generators (TEG's) directly converting engine exhaust gas energy to electricity will be commercially introduced in the 2013-

2015 timeframe. The Dept of Energy is supportin work at BSST developing TEG's for BMW, X-6 and 531 and for Ford's Escape Hybrid. GM is working on TEG's for the Chevy Suburban and Michigan State University is working with Cummings and Navistar for converting the heavy duty truck diesel engine exhaust to electricity. Teams headed by Ford and GM have just been competively selected to develop Automotive Thermoelectric Heating, Ventilation and Air Conditioning (TE HVAC). These teams will use the Zonal or Disbursed concept wherein only the occupants are cooled not the whole cabin. This approach will reduce the fuel consumption for vehicle air conditioning by > 50 per cent. Reversing the DC current converts the TE HVAC to a heater. Each year through refrigerant gas compressor seal leakage and frontal collisions 43 million metric tons of CO2 equivalents are relased into the atmosphere in the United States. TE HVAC is refrigerant gas free with no moving parts other than a small fans and a cooling loop pump. Therefore it should have a low maintenance cost. Thermoelectrics generate power without releasing carbon and greatly reduce "Greenhouse Gases".

FE-3:IL06 **Micro Peltier Devices for Cooling and for Power Generation**

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Due to their unique properties thermoelectric microdevices, thermogenerators as well as Peltier coolers are of high demand for different applications namely for cooling of high heat densities like in microprocessors generated or to drive with microthermogenerators stand alone sensor system with wireless data transmission using everywhere existing small temperature differences. Thus worldwide efforts are undertaken to expand the technology for thermoelectric devices into the field of typical microsystem technologies including aspects of advanced low dimensional high ZT materials. The favourite thermoelectric material system is up to now based on bismuthtelluride (V2-VI3) compounds. Recent results proof the capability to implement also low dimensional materials into microsystem devices and show different wafer based microelectronic technologies for the fabrication of thermoelectric devices even for the non CMOS related materials based on bismuthtelluride related compounds. Thus this survey will present the state of the art, a summary of recent results together with the intended applications, as well as technological aspects for microsystems fabrication. An attempt will be made to compare strength and weakness of the different technological concepts.

FE-3:L08 **Development of Thermoelectric Modules Based on Bulk Oxide Materials**

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New high-performance thermoelectric materials will play a key role in the current challenge to develop alternative energy technologies, reduce our dependence on fossil fuels and minimize greenhouse gas emissions. The performance of thermoelectric materials is given by the figure of merit ZT = (C*S ^ 2*T)/k where C, S and k are the electrical conductivity, Seebeck coefficient, and thermal conductivity, respectively. Bulk oxides have been recognized as good candidates to develop modules for thermoelectric power generation, since they are thermally and electrically stable, easy to manipulate and low-cost. Pure and Al2O3 doped ZnO and pure Ca3Co4O9 (Ca349) sintered pellets were prepared by conventional solid state synthesis starting from the oxides[1]. The best doped sample was 2% Al2O3-ZnO with S=-180 mV/K and C=8 S/cm at 400C, while k=1.8 W/m*K at 600C. For Ca349 S=82.5 mV/K and C=125 S/cm at 800C, while k=1.01 W/m×K at 600C. Several Al2O3-ZnO/Ca349 modules obtained by elements cut from sintered pellets were tested. The best performance was obtained in a module constituted by six 2% Al2O3-ZnO/Ca349 couples with an output power P=300 mV at 500 °C. Progresses in the module development will be discussed at the meeting.

[1] P. Mele et al Mater. Res. Soc. Symp. Proc. 2009 1166-N03-2

FE-3:L09 **Design and Fabrication of Filled Skutterudite Device**

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Filled skutterudites are high performance thermoelectric materials. The reported ZT value exceeds 1.3 for the n-type filled skutterudite and 1.1 for the p-type one, which can greatly increase energy conversion efficiency of thermoelectric device. However, reports on filled skutterudite device are rare. In this paper we will report design, fabrication and testing results of filled skutterudites device, including performance of p/n type filled skutterudites, process of the device fabrication and calculating and testing properties of device.

FE-3:L10 **Recovery of Waste Heat from the Exhaust of Small Automotive Engines**

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This work presents a design and new results on the performance measurements of a prototype thermoelectric generators TEG mounted both on a spark ignition engine and a self ignition engine. Using the prototype generator TEG as a tool, benchmark studies were performed in order to compare its parameters in terms of the heat recovery from exhaust gases of both engine types. The test bed study was performed with the Automex AMX - 210/100 eddy-current brake dynamometer. To provide the comprehensive overview of the TEG generator operating conditions the characterisation of its parameters such as temperature distribution, heat flux density and efficiency was done at the engine speeds and loads similar to these within the range in operation in the real road conditions.

Poster Presentations

FE:P02 **Preparation of Multiphase Composites Including Sr, Ti and Nb Oxides, and Their Thermoelectric Properties**

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Multi-phase oxide composites including metallic cations, Sr, Ti and Nb were prepared by a combination of a wet processing and a SPS sintering. The microscopic structure and chemical composition were examined by using scanning electron microscope attached with an x-ray spectroscopy. The crystallographic structure was determined with a high power x-ray diffractometer. The composites obtained here were found to be constructed of fine oxide phases, such as SrTiO3 (STO), TiO2, Sr6Ti7Nb9O42 (STNO) and SrNb2O6 (SNO). The distribution of these phases varied depending on the atomic composition of the metallic cations. The electrical conductivities and the Seebeck coefficients were measured simultaneously using an ULVAC ZEM-1 instrument in helium atmosphere. The thermal conductivity was measured by a laser flash method. By inspecting the correlation between the microstructure and the TE properties, we found two different tendencies affecting the thermoelectric performance, (1) the thermal conductivity reduction is associated with the occurrence of the STNO or SNO phases and (2) the higher power factor appears as the fraction of the STO phase increases.

FE:P03 **Improved Thermoelectrics Based on Bismuth and Antimony Chalcogenides for Temperatures Below 240 K**

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Solid solutions based on bismuth and antimony chalcogenides n-type (Bi, Sb)2(Te, Se, S)3 with various atomic substitutions in sublattices of bismuth telluride are the most effective thermoelectrics, providing cooling to temperatures down to 100 K. Samples of the solid solutions were prepared by the directed crystallization method with high-precision temperature control during crystallization. Thermoelectric and galvanomagnetic properties were studied. Average values of the figure-of-merit through the temperature interval 100 -240 K are equal to (2.5 - 2.65) 10-3 K 1 for nominal compositions and carrier concentration. Galvanomagnetic properties were analyzed in frameworks of the many -valley- model of energy spectrum with isotropic scattering of charge carries, and the changes of scattering of charge carriers were estimated in dependence on composition and carrier concentration for solid solutions. The figure-of-merit is shown to be determined with optimal relations between the values of the effective mass, the mobility of charge carriers and the lattice thermal conductivity and connected with the anisotropy of the constant energy surface.

FE:P04 Characterization and Properties of Nano-crystalline Mg2Si Prepared by the Ball Milling Process

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Most recent trends on thermoelectrics have shown that the existence of structural nano-features in promising thermoelectric materials enhances their performance through the decrease of the thermal conductivity and the increase thermopower without much of reduction in electrical conductivity. Mg2Si-based materials are promising intermetallic compounds for TE energy conversion applications with several important advantages. They have a rather high melting point, low density, they consist of elements in the earth's crust and their non-toxicity makes them environmentally friendly. In this work, nano-crystalline Mg2Si powder was prepared by mechanical alloying using a planetary ball milling procedure. Milling parameters and conditions, with emphasis on milling media and ball size, were explored in order to investigate their effect on the structural features of the material. Crystallite evolution during ball milling was followed by powder X-ray diffraction (PXRD) measurements as well as TEM studies. The broadened PXRD peaks were analyzed by Voigt functions indicating small crystalline size and stress introduced during the mechanical alloying process. Thermoelectric properties are also discussed in terms of Seebeck coefficient and the thermal conductivity.

FE:P06 Heat Treatment on Ball-Milled K2Bi8Se13 Thermoelectric Materials

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Research on complex bismuth chalcogenide compounds has shown that K2Bi8Se13 has many attractive features that make it promising for thermoelectric applications. Nanocomposite K2Bi8Se13 materials recently fabricated by powder technology show enhanced Seebeck coefficient as well as reduced thermal conductivity. These materials consist of nano and micro-crystalline phases as well as amorphous phase. In this work, various conditions for heat treatment were applied on the K2Bi8Se13-based nanocomposites in order to study the reversibility of the amorphization process that takes place during the nanocomposite fabrication. The reversibility of such process is important for the application of sintering process that is necessary for the development of thermoelectric modules. The recrystallization process was also investigated with respect to the structural features, thermal analysis, morphology as well as thermoelectric properties.

FE:P07 PbTe-Sb2Te3 Nanocomposites Prepared by Mechanical Alloying: Microstructure and Thermoelectric Properties

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Recent research on thermoelectrics focuses on the ability to improve the properties of existing materials with good performance by exploiting the nanoscale dimension. The thermoelectric performance of PbTe-based materials has been enhanced through this approach. Typical example is LAST materials for which ZT values ranging from 1.5 to 2 have been reported. In addition, powder techniques such as ball milling process are being extensively investigated as low cost for obtaining nano-materials. In this work PbTe-based nanocomposites are investigated. Nano-crystalline powders of PbTe and Sb2Te3 were obtained by mechanical alloying using a planetary ball mill. Mixtures of various concentrations were used to fabricate the PbTe-Sb2Te3 samples via cold-pressing and sintering. The composition dependence of microstructures and phases were studied by scanning electron microscopy and powder X-ray diffraction. Thermoelectric measurements were performed on pressed pellets over a wide temperature range from 5 to 300K. The thermal conductivity decreases with increasing Sb2Te3 concentration showing significant suppression of the low temperature phonon-drag peak. The Seebeck coefficient and electrical conductivity changes are also discussed.

FE:P08 Mg2Si Thin Film Preparation for Thermoelectric Applications

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Magnesium based compounds have been proposed as good thermoelectric materials for higher temperature range. Mg2Si is a prospective material due to its thermophysical properties such as high melting point, elevated compression strength and Young modulus. The formation of thin Mg2Si films is restricted because of the low condensation coefficient and of the high vapor pressure of Mg. Although the growth of polycrystalline Mg2Si films has been realized either by the co-deposition of Mg and Si atoms by molecular beam epitaxy or by the reactive deposition of Mg onto Si, the synthesis of single crystalline Mg2Si film still remains an open subject. In this work, the preparation of Mg2Si thin films by e-beam evaporation under UHV conditions is reported. The Mg2Si thin films are deposited either directly by evaporation of proper stoichiometry commercial target on Si substrates or at Mg/Si multilayer form and subsequent annealing at 380oC, that facilitates Mg2Si formation within the bilayers. To study the film morphology and verify proper stoichiometry along thin film area SEM is employed. X-ray diffraction is used to verify the Mg2Si formation. The optical properties of films are also studied, while the Mg2Si phase is, additionally, proved by studying of the infrared spectra.

FE:P09 Raman Spectroscopy Study on Na2/3Mn1-xFexO2 Oxides

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After the discovery of thermoelectric properties of layered sodium-cobalt oxides by Terasaki, the structural characterization of low-dimensional sodium transition metal oxides became one of the most widely studied topics in materials chemistry. Several experimental techniques have been employed for their structural characterization. Raman scattering spectroscopy is often suitable for examination of the degree and type of cation ordering in complex oxide systems. In this contribution, the structural characterization of layered sodium manganese-iron oxides with Na2/3Mn1-xFexO2 compositions (where x=0, 1/3, 2/3) is reported using Raman spectroscopy. Raman spectroscopy allows distinguishing between layered phases with orthorhombic and trigonal distortion. It has been found that the crystal structure and the composition of Na2/3Mn1-xFexO2 display a strong dependence on the history of the thermal treatment. The orthorhombic distorted modification is stabilized at high temperatures (1000 °C). At lower quenching temperature, there is a phase separation into an orthorhombic and a hexagonal modification, concomitant with an increase in the oxidation state of Mn. The hexagonal modification is able to accommodate the over-stoichiometric Mn4+ ions by creation of vacancies in the MnO2-layers.

Symposium FF

MATERIALS CHALLENGES FOR FUTURE NUCLEAR FISSION AND FUSION TECHNOLOGIES

Oral Presentations

Keynote Lecture

FF:KL **Crosscutting Materials Issues for Next-generation Fission and Fusion Energy Systems**
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Structural and functional materials for fission and fusion energy systems must perform satisfactorily in a hostile operating environment, incorporating intense neutron and gamma radiation fluxes, high temperatures, corrosive coolants, and high mechanical stresses. The requirements for structural materials for fission and fusion reactors share several common features, including high strength at elevated temperatures and good resistance to neutron irradiation for the in-core components. The high heat flux components in fusion (plasma facing components) and fission (fuel cladding, steam generator tubing) systems also share common requirements of coolant compatibility and good thermal conductivity, along with the requirement of radiation resistance for in-core components. Finally, the materials used for plasma diagnostic and reactor instrumentation components in many cases require special consideration of physical property changes associated with ionizing and displacive irradiation. An overview of the similarities and differences of materials issues in next-generation fission and fusion energy systems will be presented. Coordination of research activities may enhance the rate of discovery of new high-performance materials for these important next-generation energy systems.

Session FF-1

Structural Components for Fission and Fusion Applications

FF-1:IL01 **Material Development for GFR Core Components**
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The material development for GFR core components deals both with fundamental research and technological worries. The challenge is not only to find appropriate materials to work in severe conditions but also to insure compatibility between all the constituents. The challenge is noticeable for slender fuel assemblies which should work under high irradiation flux from 400 °C (lower part) up to at least 800 °C (upper part). Above all, the cladding must be robust and reliable in terms of geometric stability and fuel containment. That is why the reference SiC/SiC cladding tube should deal with a multi-material object constituted of SiC component and inner/outer liners, diffusion barriers, buffers... According to technological issues related to the use of damageable but still brittle SiC/SiC as structural component, metallic fuel cladding have been considered as back up solution. The main difficulty is to balance the neutronic penalty induced by refractory metals and good thermomechanical properties at high temperature. An overview of basic research and technological work lead at CEA to develop GFR core components will be presented. This includes investigation of monolithic carbides, SiC/SiC composites, damageable MAX phases and also investigation of metals such as W, Nb and V.

FF-1:IL02 **Structural Materials Development and Characterisation for Innovative Reactor and Transmutation Systems: The EU Project GETMAT**
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Advanced nuclear fission systems are under development to address important goals as e.g. sustainability, economical competitiveness, safety and reliability. To reach these goals, design options as e.g. high temperature and high thermal gradients, high fuel burn-up and different coolant technologies are under consideration, entailing relevant requirements on structural materials. Within this framework the European Commission is supporting the FP7 project, "Generation IV and Transmutation Materials (GETMAT)" that has the aim to address cross-cutting R&D items on two classes of materials i.e. the high Cr ODS and the high Cr ferritic-martensitic steels. The R&D activities are focussed on ODS development, assessment of join and weld techniques and on qualification of the two classes of materials in terms of mechanical, corrosion and irradiation resistance in a wide parameter range and within liquid metals and gas environment, and on a fundamental approach to understand the behaviour of Fe-Cr alloys under irradiation. This contribution will describe the rationale and the structure of the GETMAT project and will give a summary of relevant results.

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FF-1:IL04 **Tungsten as a Structural Divertor Material**
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Present helium cooled divertor design studies make use of the high temperature strength and good heat conductivity of tungsten. In such outlines, refractory materials are used for structural parts. The most critical issue of tungsten materials in connection with structural applications is the ductile-to-brittle transition (DBT) which is already at rather high temperatures for tungsten materials. But depending on irradiation and dynamic load conditions, the DBT level could be even higher. A systematic study of microstructure, thermal conductivity and impact bending properties was performed on different tungsten rod and plate materials provided by PLANSEE. Compared to the typical behaviour of bcc metals, the Charpy results of the tungsten materials look quite different. Most plate materials show worse properties than the rod materials. There are three types of fracture behaviour (brittle, ductile, and delamination) which is closer correlated to the materials microstructure than to the materials composition. A combination with other material testing results allowed for a reasonable explanation of this unique fracture behaviour. In summary, this paper reviews the relevant properties of tungsten materials with respect to a possible application for structural divertor parts.

FF-1:L05 **Development of Structural Materials for a High Temperature Gas Cooled Reactor in KAERI**
Ji Yeon Park*, Dong Jin Kim, Dae Hwan Kim, Woo Gon Kim, Sung Ho Kim, Choong Hwan Jung, Se Hwan Chi, Korea Atomic Energy Research Institute, Daejeon, Korea

A project called "Development of Key Technologies for a Nuclear Hydrogen using a very high temperature gas cooled reactor (VHTR)" which includes a selection and modification and property evaluations of structural materials for very high temperatures and a coupled thermo-chemical process has been being performed from 2006. The major areas of work on these materials development covered by this project, are as follows: (1) material screening/selection and qualification for a RPV, an IHX, core structures, and process heat exchanger materials for a SI system based on their high temperature properties, irradiation behaviors, a corrosion resistance and a manufacturability; (2) codifications of the relevant high temperature structural design rules; (3) material characterizations and a database establishment. Candidate materials are 1) 9Cr-1Mo for a RPV, 2) alloy 617 for an IHX and hot gas duct, 3) Cf/C and SiCf/SiC composite for a control rod and core components, 4) graphite for a reflector and support structures in the core region and 5) Fe-Si, SiC, Hastelloy, novel metals etc. for the SI process reactor. In this presentation, the on-going activities on structural materials R&D for a VHTR in KAERI will be reviewed briefly.

Session FF-2
Low Activation Structural Materials for Nuclear Fusion Systems

FF-2:IL01 RAFM Steel Materials for DEMO: Properties After Irradiation

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Fusion power and innovative fission reactor systems require high performance materials as inevitable requirement for economical and environmentally acceptable operation. While for ITER or the first generation fission reactor designs the maximum damage level accumulated by any structural material over its lifetime is on the order of a few displacements per atom (dpa), the structural materials of DEMO reactors will operate up to damage levels approaching 150-200 dpa. In addition, compared to fission reactors, up to 30 times more Helium will be produced by inelastic collisions that can contribute substantially to additional irradiation embrittlement. In order to provide structural materials design data for short term needs of the ITER Test Blanket Modules and for a Fusion Demonstration Reactor, the international fusion materials community is concentrating their R&D work besides W alloys and SiC_f/SiC mainly on the reduced-activation ferritic-martensitic (RAFM) steels of type 8-9 CrWVTa. The systematic and successful development of the European RAFM steel EUROFER includes a broad based irradiation programme: A variety of EUROFER-type steels have been irradiated with mixed spectrum neutrons between 250 and 450 °C up to 15 dpa, with fast breeder neutrons at ~330 °C up to ~70, and with spallation neutrons at different temperatures up to ~19 dpa. The presentation will give an overview on more recent European results, both on mechanical properties like tensile, dynamic fracture toughness or fatigue, and on microstructural evolution under neutron irradiation. Special emphasis will be put on the Helium embrittlement by showing structure property correlations in the range 0.3 - 330 appm He/dpa. Finally, tensile and TEM results will be shown that highlight the potential of nano-scaled oxide dispersion strengthened RAF(M) steels steels for superior irradiation resistance.

FF-2:IL02 Super ODS Steels R&D for Cladding Material of Next Generation Nuclear Systems

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The development of high performance fuel cladding is essential for the realization of Gen-IV systems. The 9Cr-ODS martensitic steel was developed as the cladding material for sodium-cooled first breeder reactor in Japan, and the steel showed a good performance in sodium, while the corrosion resistance is poor in supercritical water (SCW) and lead-bismuth eutectics (LBE). High-Cr ODS steels added with Al showed a drastic improvement in the corrosion resistance in SCW and LBE. High-temperature strength, however, was reduced by Al addition because of the characteristic changes in the dispersion morphology of oxide particles. Recently, "super ODS steels" have been developed by means of the third element alloying method, that is, a small addition of Zr, which results in the improvement of high-temperature strength with maintaining high-resistance to corrosion in SCW and LBE. High performance of the super ODS steels stems from the fine nano-scaled (Y, Zr)-oxide particle dispersion. Dispersion morphology of the oxide particles, such as size, number density, chemical compositions, coherency between matrix and particles, are characterized by FE-TEM/EDS observations, high temperature XRD measurements and analyses by FE-EPMA and FE-AES. Chemical compositions of the main particles were influenced by addition of small amount of Zr, which were (Y, Zr) oxide particles rather than (Y, Al) oxide particles. The size and the number density of Zr-added steel was reduced and increased. The coherency of the (Zr, Y) oxide particles depended on the size of the particle. Characteristic features of the oxide particles for strengthening mechanism will be summarized for the super ODS steels. Present study includes the result of "R&D of corrosion resistant super ODS steel for highly efficient nuclear systems" entrusted to Kyoto University by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

FF-2:IL03 Development of Nanostructured Ferritic Alloys

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Recent advances in dispersion strengthened steels have resulted in the development of nano-structured ferritic alloys (NFA) that contain a high concentration of oxygen-enriched nanoclusters (NC) and possess very attractive high temperature strength and creep properties. The NC show remarkable stability at high temperatures and stresses and recent studies indicate they are stable during neutron and ion irradiations. The NFA 14YWT was developed by mechanical alloying to possess nano-size grains and Ti-, Y-, and O-enriched NC. The 14YWT has superior tensile strengths compared to conventional ODS ferritic alloys and a ductile-to-brittle fracture transition temperature below room temperature. This presentation will highlight advances that have been made in understanding the formation and stability of NC and cover the scientific and technical issues with regard to the processing and properties of NFA including the 14YWT alloy that make them attractive for high temperature nuclear applications.

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FF-2:IL04 Metallic and Ceramic Low Activation Structural Materials For In-vessel Components of Future Fusion Reactors

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Manufacture, broad characterization and testing of low activation materials is essential for fusion nuclear reactor technology. The efforts in R&D are focused on the selection and test production of in-vessel materials and then components to be exposed to high heat loads and neutron fluxes. At present carbon fibre composites (CFC), beryllium and tungsten have been selected for ITER. However, the erosion characteristic limits the possibility of using beryllium and CFC a steady-state machine. Therefore, for a future device (e.g. DEMO) with high n-flux several categories of materials are considered: (i) tungsten and its alloys for the plasma-facing components (PFC) and (ii) steel, various silicon carbide and vanadium-titanium alloys as structural materials. The aim of this contribution is to provide a critical overview on advantages and limitations in the application of tungsten and its alloys or mixtures with oxides of rare earth elements and silicon carbide composites (SiC and Si-C mixtures) for in-vessel components. Two issues will be addressed: (i) impact of material composition and structure on fuel retention (tritium inventory) and (ii) activation of major constituents and impurity species originating from the material production process.

FF-2:IL05 Ceramic Composites for Fission and Fusion Applications

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The use of ceramic composite materials is considered in advanced fission and fusion energy systems because of their exceptional stability in harsh radiation environment, the favorable high temperature and nuclear properties, and the recent advancement in the application technology. In the U.S. and international fusion material programs, fundamental research are undertaken for silicon carbide (SiC) composites as promising materials for both blanket structures and insulating functions. For advanced fission energy, qualification of ceramic composites for use in high temperature helium-cooled reactors is being pursued in the U.S. Generation IV R&D program. Currently, both carbon fiber composites and SiC composites are being developed for in-vessel application. Critical feasibility issues have been positively addressed for both materials. This paper provides an overview of recent effort and future prospect of ceramic composites for these energy applications.

FF-2:IL06 Development of Low Activation Vanadium-based Alloys for Nuclear Fusion Applications

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Vanadium alloys are candidate structural materials for fusion reactors because of its low activation properties, high temperature strength, radiation resistance and so on. Especially, self-cooled liquid lithium blanket with vanadium alloy structure is a quite attractive concept because of its high heat extraction efficiency and Be-free tritium breeding processes. V-4Cr-4Ti has been regarded as the leading candidate. Fabrication technology including joining and coating has been enhanced significantly for V-4Cr-4Ti in recent years. Efforts are being made to enhance high temperature creep strength by (1) applying a new TMT by which high density of Ti-CON precipitate coupled with cold-work induced dislocations are introduced, (2) changing the alloy composition e.g. increasing Cr level, and (3) by applying Mechanical Alloying method for high density particle dispersion and fine grain structures. As to the compatibility with lithium, recent tests with a mono-metallic vanadium alloy loop confirmed high compatibility of vanadium alloys with Li once impurity in Li is highly controlled. Remaining issues and roadmap toward the development of vanadium-based alloys for fusion reactors will be discussed.

FF-2:IL07 SiCf/SiC Composites Irradiation Behaviour in Fusion Reactor Environment Conditions

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Silicon carbide fiber-reinforced Silicon carbide composite is one of the major candidates as the advanced structural materials for fusion reactor due to its low induced radioactivity, high specific strength, and high temperature strength. One of the main concerns to use these materials in the fusion environment is the radiation stability of the microstructure in advanced SiC/SiC composites which in turn will affect the high temperature mechanical properties and the lifetime of these materials. In fusion reactor, cavity related gas atoms production rate was estimated to be about 2000 appm He/(MW/m2) and 800 appm H/(MW/m2) corresponding to a gas/dpa ratio of 150appm He/dpa and 60appm H/dpa. Helium atoms are almost insoluble in SiC and trapped by vacancy clusters produced by neutron cascade easily. The solubility of hydrogen in the SiC is also low. Hydrogen is always trapped at both Si- and C-sites. But the mobility of hydrogen is much higher at elevated temperatures, because the bonding of Si- and C- were broken. Previous studies show that hydrogen may enhance the cavity formation. We have studied two types of uni-directionally silicon carbide fiber-reinforced silicon carbide matrix composites (SiCf/PyC/SiC) provided by the Oak Ridge Nation Laboratory and the Kyoto University. The reinforcement is the advanced silicon carbide fibers with low oxygen, highly-crystalline and near-stoichiometric composition namely Hi-Nicalon Type-S fibers (HNS) and Tyranno-SA (TSA). The specimens were irradiated by using dual-ion beam (6 MeV Si3+ and 1.13 MeV He+) and triple-ion beam (6 MeV Si3+ ,800keV He+ ,and 280keV H+) at various temperatures to simulate the fusion reactor environment conditions. The JEOL 2010F transmission electron microscope, operated at 200 kV and equipped with Schottky-type field emission gun and a Gatan imaging filter (GIF 863 Tridiem), is employed to analyze the microstructure of SiCf/SiC composites and to measure the densities of helium atoms. The detector in this equipment is Gatan 2K x 2K CCD-camera and the dynamic range is from 0 to 60000 counts per channel. It is found that the smaller grain size (both matrix and fiber) gives better resistance to the bubble formation both in dual-beam and triple-beam irradiations. This can attribute to the much more nucleation sites for smaller grain size materials than the larger ones which increases the number of nucleus formation and suppress the growth rate of the average bubble diameter and in turn decrease the total volume of the cavities. Hydrogen atoms in the SiC/SiC composites will enhance the nucleation rate of cavity in the beginning stage of irradiation due to its high diffusivity which increases the number density of bubbles and later on may also contribute to the growth of the bubbles. We have also developed a new method to quantify the amount of He atoms in the cavities by measuring the energy shift of the He K-edge of the electron energy loss spectrum which is a function of the density of He atoms inside the measured bubble. Combine with the number density and the average diameter of the cavities, we are able to measure the amount of He atoms that are retained in the cavities and those are still in the matrix of materials. It is found that small bubbles contain much higher density of He atoms than the larger ones. At irradiation temperature above 1000 °C, all the He atoms will be trapped inside of the bubbles but it may not be the case for the lower irradiation temperature conditions. It is also concluded that the triple-ion-beam irradiation facility in National Tsing Hua University is a very powerful equipment to study the structural materials in fusion reactor environment conditions.

FF-2:L08 Thermo-mechanical and Electrical Behaviours of Ion-irradiated SiC Fibers for Nuclear Applications

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Advanced SiC fibers, which are high purity, stoichiometric composition and highly crystalline, have been expected to have good resistance to neutron irradiation. To improve irradiation resistance of SiC/SiC composites, advanced fibers, such as Hi-Nicalon TypeS and Tyranno-SA, are used as reinforcing fibers. The fundamental research of in-situ thermo-mechanical/-electrical behaviours during irradiation is essential for design of the composites. A specific tensile device, named MecaSiC, has been developed to be couple with JANNUS facility at CEA-Saclay in order to study in-situ irradiation effects. In this study, as a first trial, the in-situ thermo-mechanical/-electrical behaviours of ion-irradiated SiC fibers were investigated by MecaSiC. Tyranno-SA fibers were irradiated at GANIL under high vacuum with 95 MeV Xe ions at room-temperature. The irradiation was performed at room temperature. To prevent damage gradient in fiber, the fibers were irradiated on two sides (0.05 or 0.2 dpa per side). Electrical and elastic behaviours of the ion-irradiated fibers at high-temperature were compared with those of non-irradiated fibers. In addition, the correlation between microstructural evolution and thermo-mechanical/-electrical behaviours will be presented in details.

FF-2:L09 Experimental Development at a Pilot Plant Scale of a Reduced Activation Ferritic/Martensitic RAFM Steel

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Ferritic/Martensitic steels, with chromium contents ranging between 9 and 12%, were introduced into fusion material programmes due to the better creep resistance and excellent thermal properties comparing to austenitic stainless steels. Reduced activation ferritic/martensitic (RAFM) steels are considered promising candidates for the test blanket modules of the future *International Thermonuclear Experimental Reactor* (ITER). EUROFER steel is the EU reference material. It is a 9Cr RAFM steel which exhibits a tempered martensitic microstructure and presently allows operation up to 550 °C. This paper shows the work carried out to develop at a pilot plant scale a Reduced Activation Ferritic/Martensitic (RAFM) steel with chemical composition and metallurgical properties very close to EUROFER steel. A experimental grade of RAFM steel was obtained in a Melting Pilot Plant. A High Vacuum Induction Melting Furnace was used in order to control and avoid possible impurities and atmospheric pollution. The melting process undertaken as well as the evaluation of the microstructural and mechanical properties is described in this paper in detail. Deformation and Quench Dilatometry has also been used to select the appropriate parameters for the thermo-mechanical and thermal treatments and the obtained results are also analyzed.

This work has been supported by the Spanish Ministry of Science and Innovation under the CONSOLIDER TECNO-FUS INGENIO 2010.

FF-2:L10 Corrosion Analysis of the Candidate Structural Materials for Fusion Reactor in DRAGON Series LiPb Loops and Static Capsules

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The fusion energy is under wide research in the world, such as in Europe, USA and China, because of its many attractive advantages compared with other energies. As the core component of fusion reactor, the blanket has the functions of tritium production, and nuclear heat production and transfer. One of the blanket concepts, liquid lithium-lead (LiPb) blanket, has been studied by FDS Team for many years. Based on the development strategy for fusion reactors and liquid LiPb blankets in China, series of liquid LiPb experimental loops and static capsules named DRAGON have been designed and built to investigate the feasibility of the candidate materials for the application in fusion reactor. The corrosion experiment of candidate structural materials such as CLAM (China Low Activation Martensitic) steel, refractory metals and SiCf/SiC composites for fusion reactor have been performed in these liquid LiPb experimental facilities at the temperatures ranging from 480 °C to 1000 °C for thousands of hours both. The compositions, micro-structures and mechanical properties of the tested materials were analyzed to investigate the corrosion behavior and evaluate the compatibility of those materials with liquid LiPb at different temperatures levels and flow velocities. The results shown that CLAM has good compatibility with LiPb, and others metal materials, except for SiCf/SiC have a higher corrosion rate with the exposure time. The results will promote the R&D of the LiPb blanket for Chinese ITET DFLL-TBM design.

Session FF-3

Materials for First Wall Components of Nuclear Fusion Systems

FF-3:IL02 Radiation Effects on First Wall Components for Fusion Power Reactors

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In fusion power reactors, the plasma facing (first wall, divertor) and breeding-blanket components will suffer from an intense irradiation by 14 MeV neutrons that are the product, together with energy and helium nuclei, of the envisaged fusion reactions between deuterium and tritium nuclei. The high-energy fusion neutrons will produce atomic displacement cascades and nuclear transmutation reactions, i.e., important radiation damage and effects, in the irradiated materials. The first wall will consist of a structural material attached to a plasma facing (or armour) material. Bulk tungsten and tungsten-base coatings are considered as the main candidate plasma facing materials for the first wall. Candidate structural materials for the first wall include Reduced Activation Ferritic/Martensitic (RAFM) steels, Oxide Dispersion Strengthened (ODS) RAFM and ODS Reduced Activation Ferritic (RAF) steels, tungsten-base materials, vanadium-base alloys and fibre reinforced SiC/SiCf ceramic composites. Each alternative alloy class exhibits specific problems arising from their intrinsic properties and from their resistance to fusion-relevant environmental conditions. Radiation effects on candidate plasma facing and structural materials for the first wall in fusion power reactors will be reviewed.

FF-3:IL05 Effect of Plasma-facing Materials on the Tritium Inventory in Fusion Devices

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Plasma-wall interactions determine the choice of the plasma-facing materials for next step fusion devices, such as ITER. A prominent issue is the tritium inventory build-up in the vessel which must be limited for safety reasons. The initial material selection, i.e. beryllium (Be) on the main vessel walls, tungsten (W) on the divertor upper baffle and dome, and carbon fibre composite (CFC) around the strike points on the divertor plates, results from the attempt to reduce the tritium inventory. Resulting from the use of different materials in different areas of the vessel wall, compounds and alloys formed by the intermixing of the three materials must also be considered as plasma-facing surfaces. Material mixing processes depend on erosion and plasma transport which is discussed for the example of beryllium. Tritium inventory build-up includes processes such as implantation, trapping and diffusion in plasma facing materials as well as surface erosion and co-deposition of tritium with eroded material. The effect of neutron irradiation creating additional traps for diffusing tritium must be taken into account in fusion reactors beyond ITER. Estimates for the tritium inventory build up are given for the initial choice of ITER materials, as well as for alternative material options.

FF-3:IL06 Materials Challenges for Plasma-facing Materials in Future Fusion Reactors

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To conceive and to develop suitable plasam-facing materials for fusion reactors is a major endeavour on the way towards economic and sustainable fusion power production. During reactor operation these materials have to fulfil very complex and sometimes contradicting requirements which have to be reconciled by materials science and engineering. These requirements span from plasma compatibility, low erosion and the related long lifetime, controllable tritium inventory, from thermomechanical stability and good heat transfer properties to stability under neutron irradiation and, possibly, to low neutron activation. At present, tungsten-based materials show the highest promise as plasma-facing material for use in fusion reactors. Experiments in the ASDEX Upgrade tokamak demonstrate that plasma operation is feasible with wall and divertor surfaces covered with tungsten. Calculations of the erosion lifetime and experiments indicate that continued reactor operation for several years may be possible. Heat sink materials to remove very high heat fluxes from the plasma have to operate at temperatures well beyond those accessible with existing copper-based materials. New SiC- and W-fibre reinforced copper composites which are presently being developed for this purpose.

FF-3:L07 Fabrication and Characterization of Magnetron Sputtered Tungsten/EUROFER 97 Coatings

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A specific topic of R&D on components of the helium cooled divertor developed at the Karlsruhe Institute of Technology addresses the thermal mismatch between the ferritic martensitic steel EUROFER97 and tungsten. Previous FE-simulations showed that a functionally graded joint between these two materials should result in a reduction of the thermally induced stresses and strains. In this work materials science based aspects of the development of new functionally graded tungsten/EUROFER97 joining layers will be presented and critically discussed. W-Fe-Cr-Mn-C coatings were deposited by magnetron sputtering of a segmented tungsten/EUROFER97 target. The substrate samples were placed in various, stationary positions opposite to this target. For each substrate position, a W-Fe-Cr-Mn-C coating with individual elemental composition, microstructure and properties were deposited. These coatings were characterized before and after heat treatment at 700°C by XRD methods to determine their crystal structure and a possible appearance of intermetallic phases. Porosity and morphology of the coatings were analysed by scanning electron microscopy. Additionally, nano-indentation tests were performed providing preliminary knowledge about the mechanical behaviour of the deposited layers.

Session FF-4

Functional Materials

FF-4:IL02 Study of Radioluminescence on Functional Ceramics for Nuclear Fusion Application

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Radioluminescence, which is optical emission induced by the electronic excitation of radiation effects, has several attractive features. As a radiation induced phenomenon, itself is interesting for detailed study. Also, it can be utilized for the characterization of ceramics, as spectra of radioluminescence are sometimes sensitive to chemical stoichiometry, nanostructures, and other material parameters. For nuclear application of ceramic materials, on-line monitoring of material parameters is sometimes crucial. One example will be the chemical stoichiometric change and the tritium retention behavior. The paper will describe behaviors of radioluminescence on several ceramic materials for nuclear fusion applications, such as lithium containing tritium breeding oxides, proton conductive oxides, and silicon carbide based composites, and will show some possibility of applying radioluminescence as a monitoring tool for property changes of functional ceramics in service.

FF-4:IL03 Performance Assessment of Ceramic Breeder Materials and Their Testing

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The technological feasibility of nuclear fusion for power generation will be demonstrated in the ITER project, currently under construction in southern France. The establishment of technologies for a closed fuel cycle using tritium breeding from lithium compounds is the essential step towards commercialisation of fusion power. The overview will start with a review of requirements for solid breeder materials for fusion blankets and the main ceramic systems studied to date. The key properties and manufacturing technologies of lithium oxides, and ternary compounds like zirconates, titanates and silicates, will be discussed. Testing of ceramic breeders comprises of the mechanical and physico-chemical properties and their evolution with increasing lithium burn-up, irradiation damage and other ageing phenomena. Ongoing R&D and recent results will be highlighted. This includes discussion of advances pebble-bed thermo-mechanics, and nuclear performance tests at the High Flux Reactor at Petten, the Netherlands, in support of the European programme. The paper concludes with a discussion of the performance assessments and testing methodologies that are envisaged for further development and qualification of ceramic breeder materials towards the realisation of fusion power.

FF-4:IL04 Utilization of Hybride Materials in Nuclear Reactors

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Metal hydrides have high hydrogen atom density, which is equivalent to that of liquid water. Fast neutrons are efficiently moderated by hydrogen in metal hydrides. Metal hydrides have been studied for their potential application as a moderator, a reflector and shield components for nuclear reactors. In this study, an application of the Hf hydride and Gd-Zr hydride has been investigated as neutron absorber in FBR (Fast Breeder Reactor). The core design has been performed to examine its characteristics and to evaluate the cost reduction effect. Demonstration of fabrication of hydride pin has been done with hydride pellets and stainless steel cladding. Coating technique of inner cladding surface has been also developed to reduce the permeation of hydrogen through stainless steel cladding. Physical and chemical properties of the pellet have been measured for designing the hydride pin. The integrity of the pellets at high temperature has been tested and their compatibility with sodium have also been tested. Irradiation test of hydrides has been performed in the fast experimental reactor. The hydride fuel is an excellent integral fuel-moderator system. Hydride fuel containing 237Np, 241Am and 243Am has also been studied as a candidate transmutation target to reduce the radioactiviy.

Session FF-5
Nuclear Fuel Materials

FF-5:IL02 From High Enriched to Low Enriched Uranium Fuel in Research Reactors

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Since the 1970's, global efforts have been going on to replace the high-enriched (>95% 235U), low-density UAlx research reactor fuel with high-density, low enriched (<20% 235U) replacements. This search is driven by the attempt to reduce the civil use of high-enriched material because of proliferation risks and terrorist threats. American initiatives, such as the Global Threat Reduction Initiative (GTRI) and the Reduced Enrichment for Research and Test Reactors (RERTR) program have triggered the development of reliable low-enriched fuel types for these reactors, which can replace the high enriched ones without loss of performance. Most success has presently been obtained with U3Si2 dispersion fuel, which is currently used in many research reactors in the world. However, efforts to search for a better replacement, which will also allow the conversion of some high performance research reactors (HPRR), including the Belgian reactor BR2, that currently cannot change to U3Si2, have continued and are for the moment mainly directed towards the U(Mo) alloy fuel (7-10 w% Mo). This talk will provide an overview on the results obtained with U3Si2 and outline the current status of the U(Mo) qualification pathways and materials properties and challenges.

FF-5:L03 Preparation and Characterisation of UyAm1-yO2-x for Transmutation in Fast Neutrons Reactor

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CEA is currently assessing transmutation and more specifically minor actinides (MA) recycling in nuclear fuels for reducing nuclear wastes radiotoxicity. Heterogeneous recycling, where large amounts of MA are added to UO2 fuel, is one of the most studied options. The first part of this work is devoted to the fabrication and the characterisation of both dense and tailored porosity pellets containing up to 30 wt% of americium. UyAm1-yO2-x compounds were characterised and the influence of the sintering temperature and atmosphere were studied using a thermochemical modelling approach. As a result, the required oxygen potential and the sintering temperature to fabricate such type of compounds were determined. In addition to their specific thermo-dynamical behaviour, americium compounds also exhibit a very high alpha activity inducing structural defects formation and the swelling of pellets. To prevent any risk of interaction between the pellets and the cladding material, the study of the geometrical stability with time of UyAm1-yO2-x due to ❑self-irradiation was performed. For 2.2.1017 alpha particles/g, a 0.6% increase of diameter was observed. This study will be continued under larger doses to characterize to characterize the swelling behaviour of pellets versus long time.

FF-5:L05 Simulation and Modelling the Heterogeneous Effects of the Microstructure MOX Fuels on their Effective Properties in Nominal Pressure Water Reactor Conditions

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The experimental analyses of the MOX fuel before and after irradiation made conspitious a partly different behaviour compared to UO2 fuel: the heterogeneous character of the material must be considered. The macroscopic models implemented in the industrial codes need to be fed in a relevant way to better simulate the effective properties. Multi-scales approaches are good alternatives to allow extrapolating these properties. This study conducted in the "Laboratoire d'Études et de Simulation des Combustibles" at CEA Cadarache within the framework of a PhD work, aims at contributing to the development of a numerical multi-scale simulation tool, able to describe the heterogeneousness of the MOX fuels microstructure. The first works of this PhD, presented here, concern exclusively the numerical representation of the microstructure MOX. Three points will be present. The first one will show the acquisition and the treatment of the experimental pictures. The second will deal with the stereological domain and will enlighten the model used to go back up the two dimensional statistical information in three-dimensional. Finally the last point will present the innovative tool providing with the numerical representation of the MOX microstructure.

FF-5:IL06 Fabrication of Fuel and Recycling of Minor Actinides in Fast Reactors

Joseph Somers, JRC-ITU Karsruhe, Germany

Fuels for future fast reactors will not only produce energy, but they must also actively contribute to the minimisation of long lived wastes produced by these, and other reactor systems. The fuels must incorporate minor actinides (MA = Np, Am, Cm) for neutron transmutation into short lived species. Within Europe oxide fuels are favoured. Transmutation can be considered in homogeneous or heterogeneous reactor recycle modes (i.e. in fuels or targets, respectively). Fabrication of such fuels can be made by advanced liquid processing methods, enabling property determination and screening irradiation experiments. This paper will describe these fabrication processes, and discuss properties and fuel irradiation experiments made to date. Both fertile and inert matrix fuel types are considered.

FF-5:IL07 Metallic Liners for SiCf/SiC Fuel Cladding

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In the frame of gas-cooled fast neutron fission reactor (GFR), the use of refractory compounds as silicon carbide is evaluated. However SiC is a brittle ceramic, so the cladding applications likely involve SiC fiber-reinforced ceramics as SiCf/SiC. Nevertheless, it appeared necessary to add a leak-tight barrier to prevent the fission products and He diffusion through the clad. The current reference choice for the internal and external liners is refractory metals as W-xRe or Mo-xRe. On this way, the contacts between reactive elements and/or compounds must be taking into account. All analyses reveal that SiC reacts with metallic substrates. The kinetics laws allow us to define the thickness of reaction zone whatever thermal conditions. For example, for the system SiC/W-5Re, the thickness of reaction zone is around 1 µm at 1000 °C during 3 years. The effect of irradiation has to be evaluated, as well as the consequences of these reactions on the thermo-mechanical properties of the clad. The addition of an interlayer in order to prevent all reaction has been studied. The use of TiC allows us to reduce the reaction extent at any temperature but not to stop the diffusion, whereas the use of TiN can totally prevent Si and C diffusion in the system SiC/W.

FF-5:IL08 Advanced Measurement Techniques for Highly Radioactive Materials

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In the realm of radioactive materials, a major challenge to the development of materials is the measurement of the properties for which the material is being developed. For example, the phenomenon of microstructure evolution of a nuclear fuel in reactor is well known but the details of the effects of the change on the behavior of such important subjects as thermal conductivity, mechanical properties, and phase formation have not been quantified at the grain size level. There is a strong need to develop or adapt advanced instrumentation for measurements on radioactive materials. Idaho National Laboratory has an ongoing effort to develop or adapt a variety of measurement techniques to highly radioactive materials. A laser based device called the Scanning Thermal Diffusivity Microscope, conceived and developed over the past few years, has recently been installed in a hot cell where examinations of fresh and irradiated fuel samples have begun in order to profile the thermal diffusivity of fuels and materials at 50µm spatial resolution. Further development effort is the unique application of dual-beam focused ion beam (FIB) microscopy to highly radioactive materials, which will be an exceedingly useful tool to prepare samples for study by nano/micro indentation or compression testing (also under development), transmission electron microscopy, or even atom probe tomography. Finally, the application of micro-focus X-ray diffraction will allow crystal phase identification at spatial resolution of 10-100 µm. This contribution will present the current state of the implementation plan of these instruments to highly radioactive materials. Material study examples will be given and the challenges met to implementing these measurement techniques to highly radioactive materials will be discussed.

Session FF-6
Radiation Effects

FF-6:IL01 **Computer Simulation of Primary Radiation Damage**

Kai Nordlund, Department of Physics, University of Helsinki, Helsinki, Finland

Molecular dynamics (MD) computer simulations have during the last 20 years proven to be a highly useful method for providing insight into the primary state of radiation damage in materials. With the use of appropriate interatomic potentials, MD can be used to simulate all classes of materials relevant in nuclear reactors, ranging from carbon tiles in the fusion reactor first wall to metals in the vacuum and pressure vessels, and glasses in diagnostic windows. In my talk, I will first present a historical overview of how MD entered the study of radiation damage, then give examples of recent results on damage in reactor materials such as BeC, FeCr and SiO2.

FF-6:IL02 **Radiation-induced Segregation in Austenitic and Ferritic-martensitic Steels**

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Radiation-induced segregation (RIS) is an important factor affecting the integrity of light water reactor core materials, as it has been linked to irradiation assisted stress corrosion cracking. RIS in austenitic steels occurs in the temperature and dose ranges relevant to light water reactors. Of the major alloying elements, Cr depletes and Fe and Ni enrich at grain boundaries. The behavior of these elements under irradiation can be explained by the inverse Kirkendall mechanism. However, minor elements such as Si, P, B, are also observed to segregate. They are not as easy to detect experimentally, and our understanding of the segregation mechanism is not well developed. Ferritic-martensitic alloys are candidates for fast reactor and supercritical water reactor core materials. RIS also occurs in these alloys, however, the data is very sparse and internally inconsistent as Cr has been observed to enrich and also to deplete. Enrichment of Cr creates the potential for the formation of brittle, Cr-rich phases. This paper will review our understanding of RIS of major elements, and the outstanding issues of minor element segregation in austenitic alloys, and also segregation behavior in ferritic-martensitic alloys.

FF-6:IL03 **Direct In-situ Electron Microscope Observations of Dynamics of Radiation Defects in Irradiated Materials**

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In-situ transmission electron microscopy (TEM) is useful for examining the variation processes in local structures within solids in response to various stimuli. We have been applying this technique to lattice defects such as prismatic dislocation loops in crystalline materials produced by energetic particle irradiation. It is believed that dynamic behaviors of loops in metals play key roles in microstructural evolution under irradiation. Molecular statics/dynamics calculations and our in-situ TEM studies in alpha-iron have revealed that almost isolated nanoscale loops can undergo one-dimensional glide diffusion. In this lecture, we will show some modification factors of the loop diffusion, as follows. (1) Solute atoms: Static solute atoms trap loops, and dynamic solute atoms also decelerate loops via the atmosphere locking or dragging. (2) Interaction among loops: Elastic interaction among loops modifies the loop diffusion, and often causes the collision among loops. (3) High-energy particle irradiation: Energetic particle irradiation enhances the loop diffusion via the enhancement of the de-trapping of loops from trapping centers.

FF-6:L04 **On the Origin of Large Interstitial Clusters in Displacement Cascades in Iron**

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Displacement cascades with wide ranges of primary knock-on atom (PKA) energy and mass in iron have been simulated by MD. New visualisation techniques show how the shock-front dynamics and internal structure of a cascade develop over time. These reveal that the nature of the final damage is determined early on before the onset of the thermal spike phase of the cascade process. A zone (termed ‘spaghetti’) in which atoms are moved to new lattice sites is created by a supersonic shock front expanding from the primary recoil event. A large cluster of self-interstitial atoms can form on the periphery of the spaghetti if a hypersonic recoil creates damage with a supersonic shock ahead of the main supersonic front. When the two fronts meet, the main one injects atoms into the low-density core of the other and they become interstitial atoms during the rapid recovery of the surrounding crystal. The hypersonic recoil that gives rise to an interstitial cluster occurs in less than 0.1 ps after the primary recoil event. The equivalent number of vacancies forms at times one to two orders of magnitude longer in the spaghetti core as the crystal cools. By using the spaghetti zone to define cascade volume, the energy density of a cascade is shown to be almost independent of the PKA mass. This throws into doubt the conventional energy-density interpretation of an increased defect yield with increasing PKA mass in ion irradiation.

FF-6:IL05 **Radiation Damage in Ferritic High-Cr Alloys for Nuclear Applications**

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High-Cr ferritic/martensitic steels (containing 7-14%Cr) are being considered as structural materials for a large number of future nuclear applications, from fusion to fission accelerator-driven systems and GenIV reactors; hence the importance of understanding the basic mechanisms governing their behaviour under neutron irradiation. The performance of these steels and their base (Fe-Cr alloys) under irradiation is largely determined by the Cr content. For example, the addition of Cr significantly reduces void swelling, reaching a minimum at ~5 ÷12% Cr, depending on temperature and dose. The origin of these and other Cr-dependent effects is most likely to be attributed to the magnetic nature of high-Cr steels, as a consequence of which Cr has an extraordinary high solubility limit in Fe (~10% at temperatures of technological interest). Below it, Cr atoms tend to order; above, to precipitate. Such a dual behaviour apparently has an influence also on the nanostructure evolution under irradiation and on the corresponding response of the material to mechanical load. Interestingly, the best performance is usually observed for steels and Fe-Cr alloys with Cr composition close to 10%.

FF-6:IL06 **Evolution of Nano-structures in Pressure Vessel Steels in the Course of Irradiation**

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Nano-structural change by neutron irradiation causes degradation of materials. Embrittlement of nuclear reactor pressure vessel (RPV) steels by neutron irradiation is one of the examples; precipitation of impurity/solute atoms such as Cu, Ni, Mn, Si etc., defect clusters such as interstitial loops, vacancy clusters and vacancy-impurity/solute complexes, and grain boundary segregation of P, As etc. are the candidates of the nano-structural change to affect the mechanical properties of the RPV steels. During the last decade, understanding of the embrittlement mechanism has progressed considerably. In this lecture, we would like to introduce the recent progress of the study of

RPV steels focused in the following two points of view: 1) nano-structural changes in surveillance test specimens of real power reactors (as well as the model alloys) are studying and making clear the effect of neutron flux experimentally, 2) developments and improvements of techniques to observe the nano-structure, such as positron annihilation and laser-assisted 3D atom probe tomography, and the combination of these state-of-the-art techniques are contributing to understand the embrittlement mechanism.

FF-6:L07 The Influence of Interaction Geometry on the Obstacle Strength of Voids and Copper Precipitates in Iron

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Extensive atomic-scale computer simulations have shown that nanoscale voids and copper precipitates can be strong obstacles to the glide of dislocations in neutron-irradiated iron. In the case of voids, an edge dislocation climbs by absorbing vacancies at it breaks away. The obstacle strength of copper precipitates, on the other hand, is associated with a dislocation-induced structural transformation of the copper if they are large enough and the temperature is low enough. Most of the reported simulations have placed the centre of a spherical void or precipitate on the slip plane of an edge dislocation. The present work has been undertaken to investigate how the obstacle strength of 2 and 4 nm voids and precipitates varies with the distance of their centre from the slip plane at temperatures across the range 0 to 450 K. The strength of voids is highest when their centre coincides with the slip plane, but this is not the case for small precipitates, which do not transform from the BCC structure. The strength of both types of obstacle, and the extent of climb at voids and transformation of large precipitates are not symmetric with respect to distance of their centre above or below the slip plane. These results are discussed in terms of the atomic mechanisms involved and the consequences for continuum treatment of irradiation hardening.

FF-6:L08 Residual Stress Analysis of SiC/SiC Composites Following Irradiation

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The residual stress at fiber/matrix interface in Silicon Carbide (SiC) fiber reinforced SiC matrix (SiC/SiC) composites is originally introduced due to the difference of CTE•@between fiber, matrix and carbon interface, which primarily governs the mechanical properties of the composites. Irradiation-induced differential swelling of the constituents is suspected to introduce the significant modification of the residual stress.•@The purpose of this study is to clarify the effect of irradiation-induced residual stress modification on mechanical property changes after self-ion irradiation. The materials used were SiC/SiC composites reinforced with near-stoichiometric SiC fibers (Hi-Nicalon™ Type-S and Tyranno™-SA). They were fabricated by chemical vapor infiltration (CVI) or nano-infiltrated and transient eutectic phase (NITE) method. After ion irradiation, volumetric swelling was determined by means of atomic force microscopy. The residual stress in ion-irradiated composite system was estimated considering thermal residual stress and swelling of the constituents. Higher swelling rates and/or saturated swelling values of a matrix comparing to those of a fiber was observed on CVI SiC/SiC at 1273 K, indicating several % of reduction of misfit stress at the fiber/matrix interface.

FF-6:L09 Atomic-scale Mechanisms of Strengthening Due to Localized Obstacles in Irradiated Metals

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Accumulation of radiation-induced microstructure leads to specific behavior of irradiated materials under deformation such as hardening, strengthening, loss of ductility, etc. In addition, significant microstructure modification may occur during deformation. Many of these phenomena are controlled by atomic-scale mechanisms of interactions involving moving dislocations and radiation-induced defects. The reactions between dislocations and lattice defects also affect microstructure accumulation at a particular level of plastic deformation during irradiation. We present here a review of results of extensive atomic-scale modeling devoted to the study of the interaction between moving screw and edge dislocations in bcc and fcc metals and irradiation-specific defects such as voids, He-filled bubbles, stacking fault tetrahedra, interstitial dislocation loops and soft and rigid particles/precipitates. We consider reactions between dislocations and individual defects as well as with groups of different defects. Microstructure changes due to these reactions involve a spectrum of effects, including complete elimination or restoration of defects, their mutual recombination, and change of size and/or structure (shear, Burgers vector change, etc.). We show how the reactions may be classified and discuss them in the light of experimental observations.

FF-6:L10 Quantitative TEM Investigations on EUROFER 97 Irradiated up to 32 dpa

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The intention of this work is to evaluate the microstructure of the neutron-irradiated reduced activation ferritic/martensitic (RAFM) steel EUROFER 97. For this purpose irradiation induced defects like defect clusters, dislocation loops, voids/bubbles and precipitates are identified by transmission electron microscopy (TEM) and quantified in size and volume density. Emphasis is put on analyzing the influence of the irradiation dose and different neutron fluxes on the evolution of size and density of the defects at a constant irradiation temperature of 300-330 °C. To study the dose dependence, samples irradiated to 15 and 31.8 dpa are analyzed. In order to investigate the influence of the neutron flux at a constant dose of 15 dpa, the microstructures of samples which were exposed to a flux of 1.8x10 ^ 19 m ^ -2s ^ -1 (>0.1 MeV) in the BOR 60 fast reactor of SSC RF RIAR in Dimitrovgrad are compared to the microstructures of samples which were irradiated with a lower flux of 4.0x10 ^ 18 m ^ -2s ^ -1 (>0.1 MeV) in the Petten High Flux Reactor (HFR). The obtained quantitative data will be used for correlation of the changes in the microstructure to the changes in the mechanical properties and will serve as an input for models describing this correlation.

FF-6:L11 Microstructure Change of Ti3(Si,Al)C2 After Ion Irradiation

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In the frame of material development for the future Gas Fast nuclear Reactors (GFR), Ti3SiC2 based compounds have been recently considered as candidate materials. In particular they could be used in some parts of core components e.g. in cladding tubes or reflectors. Resistance to irradiation of this compound is then a new worry focused on the stability of the MAX specific nano-layered structure. In parallel to neutron irradiations, CEA launched in 2006 irradiations with ions to specify the evolution of several Ti3SiC2 grades. In this work, Ti3(Si,Al)C2 fabricated by IMR, Shenyang, China (collaboration) was irradiated by 74 MeV Kr and 92 MeV Xe at 20 °C, 300 °C and 500 °C. The effect of dose and temperature on microstructure was investigated by SEM, TEM and XRD. The resulting hardness change was determined by nanoindentation. This work showed that Ti3SiC2 exhibits limited evolution up to 1E13ions/cm2. Above this dose, lattice swelling, micro-strains and atomic disorder were highlighted. In spite of the resulting increase in hardness, the damage tolerance was preserved at 2E15ions/cm2. Finally, annealing of irradiation defects with temperature was observed. Additional investigations are in progress to highlight beta-Ti3SiC2 formation under irradiation suggested by XRD analysis.

FF-6:IL13 The Change of Thermo-mechanical Properties Resulting from Irradiation

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The neutron induced degradation of plasma facing materials such as carbon fibre composites, tungsten, and beryllium are among the most critical issues in the field of nuclear fusion research. This material degradation with respect to thermo-mechanical and thermo-physical properties reduces the maximum applicable heat flux and shortens the lifetime of a component which has been verified in thermal fatigue tests of irradiated and reference divertor test modules performed in the electron beam facility JUDITH at Forschungszentrum Juelich. The decreasing operational performance of these modules is caused by radiation effects on the plasma facing materials, e.g. reduction of thermal conductivity, especially for carbon fibre composites, an embrittlement of tungsten based materials, and the agglomeration of gaseous transmutation products in beryllium. Hence, for the development and construction of ITER, the evaluation of the high heat flux performance under quasi-stationary thermal loads and under short transient events such as edge localised modes (ELMs) and plasma disruptions has become an important issue, especially in combination with the neutron induced deterioration of the material properties.

FF-6:IL14 Irradiation-induced Nanoscale Self-organization: Simulations, Experiments, and Application to Radiation-resistance

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The continuous irradiation of materials in nuclear reactors often drives and maintains these materials into non-equilibrium states. These non-equilibrium dissipative material systems display a tendency to self-organize. Using atomistic simulations and continuum modeling, we will show that this self-organization results from the competition of dynamical processes acting at different length scales. Furthermore, the characteristic length scale of these self-organized structures, which is typically in the range of 1 to 100 nm, varies continuously as the irradiation-induced displacement rate and the temperature are varied. These predictions are tested using experiments on Cu-base alloys using transmission electron microscopy, magnetic measurements, and atom probe tomography. Irradiation-induced self-organization opens a new route for the synthesis of nanostructured materials intrinsically stable under irradiation. It is proposed to take advantage of this property to design materials with high and stable density of sinks for point defects, thus suppressing detrimental phenomena such as radiation-induced segregation and precipitation, and creep.

FF-6:L16 SANS Investigation of Phase Precipitation in HT-9 at High Neutron Irradiation Dose Levels

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The Advanced Fuel Cycle Initiative is investigating methods of burning minor actinides in a transmutation fuel. To achieve this goal, the fast reactor core materials (cladding and duct) must be able to withstand very high doses (>200 dpa design goal) while in contact with the coolant and the fuel. Thus, these materials must withstand radiation effects that promote low temperature embrittlement, high temperature helium embrittlement, swelling, accelerated creep, corrosion with the coolant, and chemical interaction with the fuel (FCCI). Phase precipitation caused by neutron irradiation is known to strongly influence the mechanical properties of the structural materials and forms one of the lifetime limiting factors for high Cr cladding. Therefore, specimens of ferritic-martensitic alloy HT-9 were taken from a duct irradiated in the FFTF reactor up to 155 dpa at a temperature of 350-510 °C. In this presentation we will discuss the Small Angle Neutron Scattering (SANS) results from 5 different locations along the length of the duct and relate them to the microstructure and mechanical properties of the material.

FF-6:IL18 Interaction of Twin Boundaries with Radiation Damage in hcp Metals

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The interaction of twin boundaries (TB) with crystal defects is of particular interest for metals in which twinning is an important deformation mode. When the material suffers radiation damage in the form of point defects and their clusters, the interaction of these defects with TB contributes to changes in the mechanical properties. In this presentation, relevant processes that occur at atomic level in twin interfaces, such as interfacial defect mobility associated with boundary motion and boundary interactions with defects, are described. Atomic-scale computer simulation has been used to model alpha-Ti and alpha-Zr. Topological theory has been used to identify possible interfacial defects and a method to simulate the motion of twinning disconnections, i.e. defects with both step and dislocation character, over large distance has been developed. The method has been used to investigate the interaction of a moving (10-12) TB with vacancy and self-interstitial clusters. It has been shown that point defect clusters can act as obstacles and cause strengthening by pinning the twinning disconnections and restricting TB motion. Moving boundaries can also act as sinks or recombination centres for defects, thereby providing a means for removing defects from regions of radiation damage.

FF-6:IL19 An Atomic-based Mesoscale Model of Radiation Induced Segregation

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Modelling the evolution of the concentration fields of point defects and solute elements in non equilibrium systems is a long standing tradition. It follows the approach of the Thermodynamic of Irreversible Processes. The resulting mesoscale models have been applied to simulating the segregation of a second phase in unstable solid solutions but also to studying the formation of concentration heterogeneities at point defect sinks, such as grain boundaries, produced by the Inverse Kirkendall (IK) effect in alloys under irradiation. However, a Self-Consistent Mean Field (SCMF) theory starting from a detailed description of the diffusion mechanism via point defects leads to mesoscale kinetic equations which can be in contradiction with the phenomenological laws. A SCMF kinetic model includes the coupling between the short range order and the concentration field kinetics and leads to a structure factor which does not follow the Cahn’s theory of spinodal decomposition. Starting from an atomic jump frequency the SCMF theory yields the fluxes with a complete Onsager matrix. In opposition to the previous diffusion models of concentrated alloys, the sign of the off-diagonal terms of the matrix may change and then lead to a solute drag by the vacancy to the sinks induced by an IK effect.

FF-6:L20 Non-equilibrium Thermodynamics of Irradiated Alloy Fuels

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A non-equilibrium thermodynamics theory of defect dynamics and microstructure evolution in irradiated materials will be presented, with applications intended for alloy nuclear fuels. Derived from thermodynamics and statistical mechanics principles, this theory consists of a set of balance laws of defect concentrations, stress and energy, augmented by all closure constitutive laws. The defect balance laws describe the evolution of vacancy, interstitial, gas atom and solute element densities in space and time. Phase changes and microstructure evolution are also incorporated in the current theoretical framework by including the physics of nucleation and interface dynamics via non-conserved thermodynamic variables representing the long-range order in the irradiated fuel. Two forms of the final equations will be discussed; the first is suitable for phase-field simulation of defect and microstructure evolution in fuels while the second describes the same processes in the corresponding sharp interface limit. Numerical examples will be presented to demonstrate the applicability of the current theory with respect to the concurrent void formation and solute segregation, where the interaction of these two processes will be demonstrated.

FF-6:L21 Microchemical Evolution Under Irradiation of Fe Dilute Alloys Representative of RPV Steels by Atomic Kinetic Monte Carlo

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The evolution of the microstructure of dilute Fe alloys (Fe-CuNiMnNiSiP-C) under irradiation has been modelled using a multiscale approach based on ab initio and atomistic kinetic Monte Carlo simulations. In these simulations, both self interstitials and vacancies, isolated or in clusters, as well as carbon atoms are modelled. The parameterisation has been improved to take into account in a more proper way interstitial clusters and more specifically the interstitial cluster diffusion as well as the carbon interactions with solutes and intrinsic defects. Isochronal annealing after electron irradiation experiments have been simulated in pure Fe, and dilute Fe-X alloys, focussing on stage I and II. Most of the phenomena observed experimentally are reproduced and their interpretation is discussed. The model has been used to simulate the medium evolution of different Fe dilute alloys under electron or neutron irradiations. The irradiation is modelled by introducing cascade debris of MD cascade as well as a flux of Frenkel pair. Some results about these irradiations will also be presented and discussed.

FF-6:L23 Nucleation Free Energy of Copper-vacancy Clusters in bcc-Fe: An Atomistic Study

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Copper-rich precipitates are assumed to be the main cause of hardening and embrittlement of Cu-bearing reactor pressure vessel steels since they act as obstacles to dislocation motion within the grains of polycrystalline bcc-Fe. Multiscale modeling contributes to a better understanding of point-defect-induced formation of these clusters during reactor operation. Rate theory is an efficient tool to simulate the cluster evolution on realistic time and length scales. However, many parameters used in rate theory, such as the diffusion coefficients of mobile species and the free binding energies of clusters, are not very well known from experimental investigations. Atomic-level computer simulations can provide these data. In the present work the free binding energies are determined for small and medium-sized copper-vacancy clusters in bcc-Fe. The most recent Fe-Cu interatomic potential by Pasianot and Malerba[1] is used. Enthalpy and entropy contributions are calculated using combinations of on-lattice Monte Carlo simulations and off-lattice molecular dynamics calculations.

[1] *R.C. Pasianot and L. Malerba, J. Nucl. Mater. 360, 118 (2007).*

Session FF-7
Materials Modeling and Dabase

FF-7:IL01 A Material Data Base and Properties Handbook for ITER

V. Barabash*, M. Merola, K. Ioki, N. Mitchell, G. Sannazzaro, N. Taylor, on behalf of the ITER Organization and the ITER Parties, ITER Organization, St Paul Lez Durance Cedex, France

ITER is the first experimental fusion facility under construction at Cadarache Site, France, which brings together the key material and technological issues related to development of fusion reactors. During design activities the specific ITER requirements have been identified and the materials for various components have been selected based on a comprehensive assessment. The current status of the materials data organization will be presented in the paper. One of the main document is the ITER Materials Properties Handbook (MPH). The goal of the MPH document is to provide ITER Organization and the Parties with a single reference source of material data. The MPH includes physical and mechanical properties of materials which are needed for the design assessment. For standard materials (e.g. austenitic steels type 316L, 304) data from existing international Codes (ASME, EN standards, RCC-MR etc.) are proposed for use. For other materials, or for operational conditions which are not included in the Codes, property data have been collected from open literature and from the ITER R&D reports. The recommended property data are being produced in accordance with internationally accepted procedures described in the relevant Codes and specified for the different components. Examples of specific recommendations for materials properties and assessment of the materials performance will be presented. Further materials activity during the ITER construction phase is briefly discussed.

FF-7:IL02 Multiscale Modelling of Radiation Effects in Fusion Materials

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Interest in modelling radiation effects is driven by the realization of the fact that the expected range of irradiation, thermal, and mechanical loading conditions in a fusion power plant is too diverse to be tractable by purely empirical methods. Analysis based on a combination of density functional theory and model Hamiltonians shows that the origin of unusual features in the zero-Kelvin concentration versus enthalpy-of-formation phase diagram is associated with electron exchange and correlation effects. The development of the Magnetic Cluster Expansion model for iron-chromium alloys, and the need to treat vector magnetic moment variables on equal footing with atomic coordinates, have led to the development of time-dependent algorithms for integrating spin-lattice dynamics equations for iron and iron-chromium alloys. Modelling the real-time dynamics of microstructural evolution requires developing algorithms describing diffusion of defects on the timescales many orders of magnitudes longer than those accessible to atomistic simulations. Presently it appears possible to perform simulations of thermally activated Brownian motion of interacting radiation defects on the timescales matching those of in-situ electron microscope observations.

Work supported by UK EPSRC and EURATOM.

FF-7:L04 Modelling Steels Used in Nuclear Energy Applications

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Materials under the extreme conditions present in nuclear energy facilities are degraded by their exposure to conditions such as high temperatures and irradiation. Life-time assessments of these materials have traditionally been performed using physically based lifetime assessments of materials which follow simple concepts. A more indepth understanding of the materials' expected service behaviour would be extremely advantageous for the future development of new materials. This entails knowledge on the materials' long term damage evolution and requires an understanding on the microscopic level of single defect damage effects all the way up to macroscopic effects, as can be performed with multiscale modelling. Model validation through experiments is a parallel area of research that needs to be included in any modelling scheme to accurately describe materials phenomena. The multiscale modelling strategies implemented at PSI to study high temperature materials with a focus on ODS ferritic steels are presented. Within this framework issues which are found to be highly important at each scale will be addressed.

FF-7:L05 Multiscale Modelling of the Influence of Damage on Thermal Properties During Tensile Loading of Ceramic Matrix Composites

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Ceramic matrix composites (CMC) are very attractive materials for structural applications at high temperatures. They are designed to be used in various systems, including aerojet engines, stationary gas turbines and in nuclear power plants. Not only must CMC be damage tolerant, but they must also allow thermal management. For this purpose heat transfers must be controlled even in the presence of damage. Damage consists in multiple cracks that form in the matrix and ultimately in the fibers, when the stresses exceed the proportional limit. Therefore the thermal conductivity dependence on applied load is a factor of primary importance for the design of CMC components. The present paper proposes a model of heat transfer in the presence of matrix cracks in a woven CMC under uniaxial tension. Multiscale finite element analysis of stresses and heat transfers in cells with matrix cracks and debonded fibers was developed. This approach allowed predictions of thermal conductivity with respect to applied tensile stress. The predictions are compared to measurements during tensile tests on SiC/SiC composites. Finally, important trends in thermal/mechanical properties relationships are anticipated.

FF-7:L06 From Point Defect Clusters to Threshold Displacement Energies in Iron by Ab Initio Methods

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In the past decade, ab initio predictions have provided new insights about defect properties in iron and iron based alloys, relevant for studies of radiation damage and microstructural evolution. Detailed information about the properties of point defects and point defect clusters has been shown to be well described using ab initio methods such as Density Functional Theory (DFT). Firstly, a DFT study of point defect cluster properties in bcc iron is presented. The canonical parallel self-interstitial clusters are shown to be less stable than their non-parallel counterparts. The stability with respect to cluster size and Burgers vector has been studied. The implications for the evolution of the microstructure is discussed in the framework of parameterizations of larger scale models, such as kinetic Monte-Carlo. Secondly, due to the recent progress in computation speed which renders even ab initio molecular dynamics feasible, a study of the threshold displacement energy surface in iron has been performed and is here presented. This basic materials property has previously largely been estimated using semi-empirical potentials and to a smaller degree using experiments. The implications of a fully dynamic Born-Oppenheimer ab initio treatment are presented and discussed.

FF-7:IL08 Experiments and Modelling for Evaluation of Neutron Irradiation Embrittlement of Reactor Pressure Vessel Steels in Fission Reactors

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Ductile-to-brittle transition temperature shift of fracture toughness property is the parameter that determines the operation conditions and the structural integrity of reactor pressure vessels (RPVs) of fission reactors. Changes in mechanical properties are caused by the microstructural changes in the materials in nano-meter scale due to irradiation, and thus the understandings on the mechanisms of microstructure formation as well as the correlation between the microstructure and mechanical property strongly help us to predict the future embrittlement at long term operation conditions. In this paper, we will describe how we could utilize state-of-the-art experimental and computational tools as well as the materials database for the prediction of the irradiation embrittlement of RPVs. The characterization of the behavior of solute atom clusters are performed using 3D atom probe tomography, and the underlying mechanism of the solute atom behavior is further studied by the atomistic-level computer simulation techniques.

Then all the knowledge on the formation of microstructural changes as well as corresponding mechanical property changes are formulated using rate equations, whose coefficients are optimized to reproduce the transition temperature shift of the real commercial RPVs.

FF-7:IL09 **Multi-scale Modeling of Irradiation Effects on Nuclear Fuel Microstructure**

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The critical ingredient needed for the development of a predictive, materials-physics based nuclear fuel modeling capability lies in a better understanding of microstructural processes. However, in spite of the well-known existence of microstructural phenomena in nuclear materials, such as void swelling, fission-gas release and crack development, a comprehensive understanding of how microstructural processes control the thermo-mechanical behavior of nuclear materials remains to be developed. This lecture will provide an overview and vision on how a predictive nuclear fuel modeling capability can be developed by an atomistically-informed mesoscale approach that, in turn, is linked to the continuum level. Three critical elements of this hierarchical modeling approach are: - capturing irradiation effects within a mesoscale modeling framework; - development of a comprehensive theoretical and computational mesoscale approach that considers all the various, simultaneously occurring and highly coupled microstructural process within a unified framework; and - linking these microstructural simulations with continuum fuels-performance simulations via a scale-bridging approach. The critical need for experiments for both materials input parameters and validation will be emphasized.

FF-7:IL10 **Demented Rabbits, or the Complexity and Stability of Materials Under Extreme Irradiation Environments**

P.M. Derlet*, S.L. Dudarev. Condensed Matter Theory Group, Paul Scherrer Institute, PSI-Villigen, Switzerland; Culham Centre for Fusion Energy, Abingdon, Oxfordshire, UK

Materials in extreme radiation environments exhibit a complex and dynamic behaviour strongly influenced by their initial as-prepared microstructure, and at the same time show fundamental generic features - radiation defects are mobile, interact with each other via long range elastic forces and when sufficiently close, react and transform to micro-structures characterized by quite different mobility and interaction laws. Such a scenario suggests that the traditional mechanistic viewpoint may not be sufficient to understand and predict the related materials properties. The present talk considers this issue through the review of work which strongly borrows from complexity and stability analysis methodologies used for the study of naturally occurring eco-systems. Particular materials-related illustrations will be given that, in part, demonstrate the paradigm that the more complex a material is, the more stable it might be under extreme conditions. We conclude by discussing the dilemma between general understanding and quantitative prediction that necessarily arises when such a Darwinian approach is taken to the problem of materials development.

S.G. Roberts, Public Communication, CEA Saclay, Paris, 2009.

FF-7:IL11 **Defect Clusters and Helium-vacancy Clusters in Iron and Other bcc Metals from First Principles**

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Body centered cubic metals is an important class of materials for nuclear applications, from ferritic steels to refractory metals in particular tungsten for fusion applications. The structure and mobility of radiation defects in these materials have been revisited in the past few years on the basis of first principles electronic structure calculations, evidencing a dependence of these properties on the filling of the valence band. Concerning self-interstitials, the specificity of iron, in agreement with experiment, is a strong stability of <110> dumbbells. Small interstitial clusters are made of <110> dumbbells, with a multiplicity of competing low energy configurations, where the dumbbells are not necessarily aligned, as revealed by simulations using the Activation Relaxation Technique and the Mendelev potential. As expected from empirical potentials, DFT calculations in iron confirmed that vacancies are attractive at first and second nearest neighbours, with a larger binding energy for the latter. The same tendency is observed in Nb and Ta but not in other bcc transition metals (V, Cr, Mo and W), where the next nearest neighbour configuration can even be strongly repulsive. This result suggests that the clustering tendency of vacancies is quite different among these metals. Finally, the fate of helium, produced by transmutation reactions, is governed by its energetics in interstitial configuration or in small vacancy clusters. The metal dependence obtained from DFT calculations will be discussed.

Session FF-8

Crosscutting Materials Issues for Nuclear Fission and Fusion Systems

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FF-8:IL01 **Cross-cutting Issues Related to Structural Materials in Fission and Fusion**

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After a brief recall of the past interactions between fission and fusion materials development work, 6 types of structural materials are retained for cross-cutting detailed examinations and future perspectives. For each type of material important issues regarding their application in fission GEN-IV and ITER, DEMO and fusion power reactors are discussed. It is noted that the austenitic stainless steels will continue to be favoured for main vessel and other critical structural components in either system. Likewise, conventional Mod 9Cr-1Mo steel and its equivalent low activation derivatives, such as Eurofer and F82H steels, should continue to be the preferred choice for internal structures exposed to high irradiation doses, and steam generators of sodium cooled fast reactors (SFR). In the immediate future, ODS grades of these steels and in the not so long future, ODS ferritic steels, could be considered in support or in replacement to increase their service temperature window. Development of higher temperature materials, such as SiCf/SiC composites and refractory alloys (tungsten and vanadium alloys) will need more time and in the long term could allow more efficient high temperature fission and fusion designs.

FF-8:IL04 **From Model-alloys to Ferritic-Martensitic and Ferritic Oxide Dispersion Strengthened Steels: The Fusion-fission Synergies**

Jean-Louis Boutard, Materials Consultant, DEN/RB CEA/Saclay, Gif sur Yvette, France

Structural applications for the core of the Generation IV fast neutron nuclear plants and the in-vessel components of the fusion nuclear reactors require steels with improved heat and radiation resistance. Structures withstanding operating temperatures up to ~750°C significantly improve reactor thermal efficiency. Structural materials maintaining dimension stability up to ~100 dpa under a high production of He and H caused by transmutation reactions due to the 14 MeV neutrons of the Deuterium-Tritium fusion are mandatory for improving component lifetimes and thus economical attractiveness of fusion. In addition, Low Activation materials should improve the environment friendliness of fusion systems. The main steps of the development of radiation resistant austenitic and ferritic steels for fast neutron reactors will be recalled. Conventional and Low Activation (LA) 9%Cr Ferritic-Martensitic (F-M) steels show high radiation resistance due to their Body Centered Cubic (bcc) crystalline structure and their martensitic microstructure, which remain stable up to high dose ~150 dpa in the temperature range from 380 to 550 °C. Their maximum allowable temperature is ~550 °C due to modest creep resistance. In addition, they present possible He-embrittlement above ~500appm, which promotes low energy intergranular failures along prior austenitic grains. Their swelling resistance might be modest under triple beam irradiation (simultaneous dpa production and He & H implantation). The Oxide Dispersion Strengthened (ODS) ferritic steels are a route to improve or mitigate these deficiencies. The first development of ODS ferritic steels for fuel cladding has started in the early 70's. These steels, reinforced by oxide particles but also by intermetallic phases, exhibit unacceptable brittleness when irradiated in Phenix as fuel cladding. ODS 9%Cr FM steels were then developed and irradiated with some success. More recently 12-14% Cr ODS ferritic steels are being developed using high energy Mechanical Alloying (MA). Some of these steels with high density (~10^{23} 10^{24} m^{-3}) of nano-clusters enriched in Ti, Y and O exhibit excellent creep strength up to 750 °C and very promising radiation resistance versus hardening. In addition the nano-clusters have been shown to be effective He traps, which could mitigate He embrittlement and swelling. These results will be discussed, especially Mechanical Alloying, which forces the alloys far from their thermal equilibrium, opening possible achievement a large range of steady states and microstructures, which cannot be obtained using metallurgical processes close to thermal equilibrium.

FF-8:IL05 An Overview of Life Limiting Irradiation Damage Degradation Phenomena in Reduced Activation 9Cr Steels

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The major life limiting irradiation induced degradation phenomena in reduced activation tempered martensitic 9Cr steels for service in advanced fission and fusion energy systems are reviewed. These phenomena include degradation of fracture toughness and ductility loss at lower temperatures, void swelling at intermediate temperatures and thermal creep, strength limits and helium embrittlement at high temperatures. Corrosion, irradiation creep and fatigue related phenomena are also important over a wide range of temperatures. In combination, these phenomena set neutron dose, temperature, and stress limits for specific structural applications. In this presentation three issues are addressed in some depth. A quantitative model is used to assess both the magnitude and impact of fracture toughness degradation with particular emphases on the synergistic effects of high levels of helium produced in the fusion nuclear environment. The effects of high helium levels on void swelling are also explored based on a combination of models and experiments, including *in situ* helium injection studies in mixed spectrum reactors. Dimensional stability limits are also assessed including the effects of both irradiation and primary creep. The potential for 14Cr nanostructured ferritic alloys to enormously extend these limits is briefly discussed.

Session FF-9
System Integration and Interface Design

FF-9:IL01 Joining SiC Ceramics and Composites for Fusion and Nuclear Applications

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Joining of silicon carbide based ceramics and composites for nuclear applications should be seen today both for future thermo-nuclear fusion reactors (DEMO) and for new generation fission reactors components: in particular SiC/SiC are candidates for fusion blanket structures and flow channel inserts and their use is proposed in various advanced fission systems. In both cases, in addition to extreme thermo-mechanical loads on the joined components, not completely known service conditions and requirements including high temperatures, neutron irradiation, harsh chemical environment, and low induced activation are to be taken into account. Considering that the design of these components is constantly reviewed, that one suitable widely accepted mechanical test for joined ceramic matrix components is still unavailable and the influence of neutrons on new materials is mostly unknown, the required R&D is far from being completed. Some joining techniques and joining materials for SiC and SiC/SiC will be described with particular reference to their radiation-resistance, compatibility of process conditions, chemical compatibility with specific coolant, fuel, and fission products. The mechanical characterization of the joints before and after neutron irradiation.

FF-9:IL02 Design and Integration of ITER Divertor Components

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The ITER Divertor is located at the bottom of the plasma chamber and is aimed at exhausting the major part of the plasma thermal power including alpha power and at minimizing the helium and impurity content in the plasma. It consists of assembly of 54 divertor cassettes. Each divertor cassette has three plasma-facing components (PFCs) and cassette body that accommodates these PFCs. The PFCs consist of the inner and outer vertical targets and the dome. The vertical targets directly intercept the magnetic field lines and are designed to withstand heat fluxes as high as 20 MW/m2. After an intensive R&D effort and successful completion of the qualification program, the three Parties (Japan, Europe and Russia) are qualified and they are in charge of procurement of the first set of Divertor. The divertor cassettes are replaced and refurbished by off-line in hot cell facility by remote handling. The replacements are foreseen three times during the twenty years of the ITER operation. In the presentation, the integration of the system as well as the detail component design shall be addressed.

Poster Presentations

FF:P01 General Corrosion Properties of Modified PNC1520 Austenitic Stainless Steel in Supercritical Water as a Fuel Cladding Candidate Material for Supercritical Water Reactor

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The Super-Critical Water-cooled Reactor (SCWR) has been designed and investigated because of its high thermal efficiency and plant simplification. There are some advantages including the use of a single phase coolant with high enthalpy but there are numerous potential problems, particularly with materials. As the operating temperature of supercritical water reactor will be between 280 °C and 620 °C with a pressure of 25MPa, the selection of materials is difficult and important. Austenitic stainless steels were selected for possible use in supercritical water systems because of their corrosion resistance and radiation resistance. The PNC1520 austenitic stainless steel developed by Japan Atomic Energy Agency (JAEA) as a nuclear fuel cladding material for a Na-cooled fast breeder reactor. The corrosion data of PNC1520 in supercritical water (SCW) is required but does not exist. The purpose of the present study is to research the corrosion properties for PNC1520 austenitic stainless steel in supercritical water. The supercritical water corrosion test was performed for the standard PNC1520 (1520S) and the Zr-additional type of PNC1520 (1520Zr) by using a supercritical water autoclave.

FF:P03 Development of Fe-base and Ni-base ODS Alloys for Advanced Nuclear Fission Application

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The oxide dispersion strengthening (ODS), through the addition of thermally-stable yttria (Y2O3) particles dispersed into the matrix, is an attractive way for strengthening materials at high-temperatures. For Fe-base ODS alloys, martensitic 9CrODS steels and ferritic 12-16CrODS steels were developed on the basis of superior radiation resistance in both bcc type steels. The martensitic 9CrODS steels are a promising fuel cladding materials for sodium-cooled fast reactors (SFR). The ferritic 12-16CrODS steels have great advantage for utilization at higher temperature of 800-1,000 °C without phase transformation. In this paper, we focus on the ferritic 12-16CrODS steels, and it was shown that the primary to secondary recrystallization was controlled through crystalline rotation by 35° around <011> axis. The effect of grain-boundary sliding on high-temperature strength was quantitatively clarified by means of electron backscattering diffraction (EBSD). The new Ni-base ODS superalloys were also developed by dispersing nano-sized oxides, Y2Hf2O7, through addition of hafnium element. Directionally recrystallized structure was created by means of zone-annealing technique. The developed Ni-base ODS superalloys have adequate strength at higher temperature over 1,000 °C.

FF:P06 The Influence of Helium and ODS on the Irradiation-induced Hardening of Eurofer97 at 300 °C

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The influence of Helium on the mechanical properties of RAFM steels under fusion-relevant irradiation conditions is still a concern. While the fact that Helium can affect the mechanical properties is well established[1, 2], the underlying mechanisms are not fully understood[1, 2]. In this work ion-irradiation was used to simulate the effects of He and displacements per atom (dpa) on the irradiation-induced hardening of Eurofer97 at 300 °C. To separate these effects different irradiation modes were applied: 1) Fe+ irradiation up to 1 and 10 dpa; 2) He+ irradiation up to 10 appmHe; 3) dual-beam irradiation, pre- and post-implantation of He up to 1 dpa and 10 appmHe each. Additionally, ODS-Eurofer was irradiated with Fe ions up to 1 and 10 dpa. A multi-step irradiation with different energies was performed to produce a roughly rectangular damage profile and He-distribution. The characterization of the damage layer was carried out using nanoindentation with maximum loads ranging from 1 to 500 mN. It was observed that the hardening increases in the following order: pre-implantation < dual-beam irradiation < post-implantation. We conclude that there is a significant interaction between dpa and He implantation at 300 °C under the present conditions.

[1]*H. Trinkaus, B.N. Singh, J. Nucl. Mater. 323 (2003) 229;* [2]*R. Schäublin, Y.L. Chiu, J. Nucl. Mater. 362 (2007) 152*

FF:P07 **Progressive Development for Structural Integrity Quantification of Nuclear Grade Graphite in Very High Temperature Gas Cooled Reactor Core Environments**
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Nuclear grade graphite, served as reflector and moderator in very high temperature gas -cooled reactor (VHTGR), have attracted great attentions to the fundamental and applied research due to their potential use in nuclear applications. Graphite is known will store defect energy (wigner energy), resulted from the displacement of atoms accumulation inside the crystalline lattice during high-doses radiation. However, a thermal transient would cause enormous amounts of defect energy released and result in a temperature spike. The unexpected, sudden temperature spike would raise the core environmental temperature over the design limit.Therefore, it is a potential disaster to reactor safety. In order to investigate the stored energy, a progressive method is developed and used to quantify the structural integrity of nuclear grade graphite by using High-Resolution Transmission Electron Microscopy (HRTEM). In our study, the nuclear grade graphite was first carried out ion implantation with 3 MeV C2+ ions (0.6, 3, 5, and 10 dpa doses) to simulate the material in VHTGR core environment. Here, the implanting temperatures are 500, 600, 700, and 800 °C, respectively. After irradiation, HRTEM analyses was proceeded to quantify the microstructure evolution and calculate the Energy storage in nuclear grade graphite crystalline lattice by use of Fast Fourier Transform of HRTEM images. Finally, we use the elastic deformation model to evaluate the possible raising temperature. Accordingly, in 600 °C, 10 dpa, it would store 764 (cal/g) and cause temperature raise about 2000 °C . The detailed results will present in the conference.

Focused Session FF-10

MATERIALS TECHNOLOGY FOR NUCLEAR WASTE TREATMENT AND DISPOSAL

Oral Presentations

Session FF-10.1

Waste Form Development

FF-10.1:IL01 **Advantages Hot Isostatically Pressed Ceramic and Glass-ceramic Waste Forms Bring to the Immobilization of Challenging Intermediate- and High-level Nuclear Wastes**
E.R. Vance*, S. Moricca, B.D. Begg, M.W.A. Stewart, Y. Zhang, M.L. Carter, Australian Nuclear Science and Technology Organisation, Menai, NSW, Australia

Hot isostatic pressing (HIP) is a technology with wide applicability in consolidating calcined intermediate-level and high-level waste, especially with wastes that are not readily processable by vitrification at reasonable waste loadings. The essential process steps during the HIP cycle will be outlined. We have demonstrated the effective consolidation via HIP technology of a wide variety of tailored glass-ceramic and ceramic waste forms, notably simulated ICPP waste calcines, I sorbed upon zeolite beads, Pu-bearing wastes, inactive Cs/Sr/Rb/Ba mixtures, simulated waste pyroprocessing salts from spent nuclear fuel recycling, Tc, U-rich isotope production waste, and simulated K-basin (Hanford, WA, USA) and Magnox sludges (UK). Can-ceramic interactions have been carefully studied. The principal advantages of the HIP technology include: negligible offgas during the high temperature consolidation step, relatively small footprint, and high waste loadings. As a batch process, the wasteform chemistry can be readily adjusted on a given process line, to deliver wastes into different end states (e.g. direct HIP versus chemically tailored). This flexibility allows the treatment of multiple waste streams on the one process line.

FF-10.1:IL02 **Overview of Nuclear Waste Treatment Research Activities at Forschungszentrum Jülich**
D. Bosbach, Institute for Energy Research (IEF-6), Forschungszentrum Jülich GmbH, Jülich, Germany

The presentation is intended to provide an overview of research activities on material science aspects of nuclear waste management in the Institute for Energy Research at Forschungszentrum Jülich. The research programme covers a range of basic and applied topics focusing on solid state aspects. Applied aspects include waste characterisation and the development of new characterisation techniques such as prompt gamma neutron activation analysis (as one of the latest developments) for characterising chemotoxic components in waste packages. Waste qualification as implemented by two quality control groups, who advise the German federal office of radiation protection. Basic science regarding the long-term safety of nuclear disposal is focused on spent fuel corrosion and near field retention of radionuclides by secondary phases under repository conditions. New disposal strategies on partitioning & conditioning include studies on zirconia based pyrochlore-type and monazite-type compounds. Key questions are focused on radiation effects and their consequences on chemical durability under repository relevant conditions. Research is aiming at a molecular level system understanding using state of the art spectroscopic/diffraction (Raman, EXAFS, TRLFS) and microscopic (TEM, SEM) techniques.

FF-10.1:L03 **"DuraLith" - A Geopolymer Radioactive Waste Form**
W.L. Gong*, W. Lutze, I.L. Pegg, The Catholic University of America, Washington, DC, USA

Conversion of certain low activity liquid waste streams into solid waste forms can be advantageously effected at temperatures near ambient to minimize loss of volatile species. One example would be waste containing organic compounds such as alkali tetra-phenylborate (Savannah River Site, SC, USA), which releases benzene at >50 °C, a challenge for cementitious waste forms. Geopolymers do not release heat during curing. We developed a geopolymer (DuraLith), for which the benzene gas release is <0.005 µg/kg/h during and after production, compared to the limit of concern of 0.9 µg/kg/h. The solid waste form releases <0.05 mg/L into water. Briefly, alkali hydroxide and silica were dissolved in simulated waste without cooling, and certain chemicals were added to enhance the immobilization of Tc-99, I-129, and Cs137. The liquid was then mixed with meta-kaolin, blast furnace slag, and silica fume. In another application, simulated low activity waste with high contents of salts from the US-Department of Energy’s sites in Idaho (sodium-bearing waste) and Hanford, Washington (a secondary waste stream) were converted into DuraLith. Geopolymer compositions were optimized using statistical experimental design techniques. Compositions and properties of these new waste forms will be reported.

FF-10.1:L04 **Synthesis and Properties of Reaction-bonded SiC Ceramic with Embedded UO2 - TRISO Coated Particles**
A.A. Bukaemskiy*, J. Fachinger, D. Bosbach, Forschungszentrum Jülich GmbH - IEF-6, Jülich, Germany

Ceramics based on SiC are characterized by extreme hardness, high thermal conductivity, relatively low thermal expansion and chemical durability. In principle, SiC ceramics can be considered as a long-term stable matrix for final disposal of radioactive waste, such as coated fuel particles (CP) separated from the graphite matrix from spent HTR (high-temperature gas-cooled reactor) fuel pebbles. In the present work, SiC-based ceramic with the embedded UO2 - TRISO (tristructural-isotropic) coated particles was synthesized by the reaction-bonding process. The synthesis was performed in standard SiC crucible. Several physico-mechanical properties of the synthesized samples were investigated. It was shown that the coated particles in the reaction-bonded silicon carbide (RBSiC) matrix are distributed homogeneously. The amount of pores is insignificant and the crippling of the coated particles is not observed. Besides, the junction between CP and RBSiC matrix and between RBSiC matrix and the SiC crucible is very good. For all ceramic components of the synthesized samples, namely, for the UO2-kernels, SiC-layers, SiC crucible wall and for the synthesized RBSiC ceramics, the values of microhardness and fracture toughness were measured and compared with the reference data. The strength properties, such as tensile strength of the synthesized samples, failure mechanism of the reaction-bonded SiC ceramic with embedded UO2 - TRISO coated particles, microstructure of the fracture surfaces, the peculiarities of the coated particles fracture were investigated in detail. Moreover, the diffusion of radioactive tracers (137Cs, 241Am, 36Cl, 3H) across synthesized ceramic was studied and the high safety characteristics of the synthesized ceramic were demonstrated.

FF-10.1:IL05 **Actinide-REE Host Phases with Fluorite-related Structures**

S.V. Yudintsev, IGEM RAS, Moscow, Russia

Among the phases suggested for actinide rich waste immobilization oxides with fluorite-type structure: cubic (Zr,REE,An)O2-x, pyrochlore, zirconolite, and murataite are of the highest interest. The largest attention was paid to pyrochlore-composed matrices due to its rather simple structure, huge amount of synthetic phases and radioactive mineral analogs, high capacity in respect of actinides and good corrosion durability, and existence of different routes for synthesis, including industrial scale fabrication. Due to these reasons, pyrochlore is the reference actinide waste form and properties of any other material should be thoroughly compared with this type of confinement matrix. The most complete review on pyrochlore as form for high-level waste immobilization is a paper of Ewing *et al* (J. Appl. Phys. 2004. Vol. 95. N11. P.5949-5971). New data on this problem and approaches to pyrochlore applications have been recently appeared. In this presentation some of the results are discussed. Relationships between pyrochlore and the other compounds with close structure (zirconia, zirconolite, and murataite) were also analyzed.

FF-10.1:IL06 **Zirconia-based Waste Forms from Spent Fuel Rod Treatment**

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We are investigating the potential use of Light Water Reactor cladding elements as precursor materials in zirconia-based host matrices for conditioning, transmutation, and burning of actinides. Fuel claddings in LWRs are made of zirconium-rich alloys (Zr>98 wt%), the other alloying elements being, for example, Sn, Fe and Cr for the zircaloy-4 alloy and Nb, Fe, Cr for the M5 alloy. When fuels are reprocessed, these cladding elements are currently treated as technological wastes. They are chopped during reprocessing operations, cleaned in hot nitric acid, rinsed, compacted in disks and then introduced in special stainless-steel containers to be disposed in a dedicated repository. The recycling of these cladding elements would be extremely interesting and valuable in terms of nuclear waste minimisation. The approach envisaged in the present studies is to convert the cladding into stable zirconia-based matrices and to optimize the process taking into account various technological aspects and radiological constraints. Our presentation will describe the waste minimisation strategy and consequences for the back-end of the fuel cycle as well as the results of our most recent scientific investigations.

FF-10.1:L08 **New Actinide Waste Forms with Pyrochlore and Garnet Structures**

T.S. Livshits*, S.V. Yudintsev, IGEM RAS, Moscow, Russia; S.V. Stefanovsky, SIA Radon, Moscow, Russia; R.C. Ewing, University of Michigan, Ann Arbor, MI, USA

Cubic oxides with pyrochlore (space group Fd3m, ideally A2B2O7) and garnet (Ia3d, A3B2T3O12) structures, where "A" = Ca, Ln, An; "B" = (Ti, Sn, Hf, Zr) - in pyrochlore and (Al, Ga, Fe) - in garnet only; "T" = (Al, Ga, Fe) - are promising matrices for long-lived actinides immobilization. At selection of the phase compositions their isomorphic capacity with respect to actinides and REE was determined. To predict the long-term behavior of these waste forms in potential underground repository radiation stability of pyrochlores and garnets was studied. Most of the samples studied have the critical amorphization doses close to 0.2 displacements per atom (at 298 K). For the pyrochlore-structure phases these values significantly increased for Sn- and Zr-rich specimens. Corrosion behavior of the waste forms was investigated. The lowest actinides leach rates from the matrices were observed in neutral and alkaline water solutions most typical of sites of their ultimate disposal. Amorphization of the matrices has a low influence on their corrosion behavior, resulting in only slight increase of leach rates of the elements (less than 5 times in comparison with as-prepared specimens). Possibility for joint incorporation of actinides and Tc into zirconate- and titanate-based matrices with the pyrochlore structure is discussed.

Session FF-10.2

Methods of Processing Challenging Waste Constituents, Such as Actinides and Noble Metals

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FF-10.2:IL01 **Advanced ORIENT Cycle for Turning Radioactive Waste into Resource**

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Nuclear Rare Metals, a Copernican Revolution

Fission reaction of U-235 will generate more than 40 elements and 400 nuclides. Among them, 31 elements are categorized as rare metals (*i.e.,* NRM: Nuclear Rare Metal). In particular, Ru, Pd (light PGM), Zr, Mo, Cs, Ce, Nd (Ln) are highly enriched in FBR spent fuel. By close investigation, *exit strategy* can be drawn in their the utilization. The most significant strategy change is, NRM should no longer be the wastes but the product in the fuel cycle.

Adv.-ORIENT Cycle, with a Multi-functional Reprocessing

A new fuel cycle concept, Advanced ORIENT Cycle, was proposed, toward simultaneous realization of utilization of elements/nuclides and minimization of the rad.wastes/risks ultimately. To realize, several tactics are set up in reprocessing, for instance; 1) Higher purity on NRM for utilization, but allowed lower DF on actinides for burning in FBR; 2) For reduction of the secondary rad. wastes, adopt *soft*, but non-SX, separation process and *salt-free* reagents; 3) To sharpen the separability, hydrochloric acid (HCl) is allowed in combination with nitric acid (HNO_3) media; 4) Chose hydrometallurgical separation processes. A catalytic electrolytic extraction (CEE) method, utilizing under potential deposition (UPD) by Pd_{adatom}/Rh_{adatom}, is advantageous for separation and utilization (and/or stockpile) of light PGM and Tc. To separate all *f*-elements, tertiary pyridine resin (TPR), composing a nitrogen atom in six-membered ring, characterized as weakly basic anion-exchanger and soft donor ligand, is employed as a vital tool of ion exchange chromatography.

The scheme was preliminary demonstrated using MOX spent fuel irradiated (143.8GWd/t) at the fast experimental reactor "Joyo", and pure Am(III) and Cm(III) products were successfully recovered.

FF-10.2:IL02 **The Role of Noble Metals in HLLW Vitrification**

Guenther Roth, Karlsruhe Institute of Technology, Institut für Nukleare Entsorgung, Eggenstein-Leopoldshafen, Germany

Vitrification of highly noble metals-containing waste solutions by Joule-heated ceramic melting systems requires special melter design and operational modes. Noble metals are insoluble in borosilicate glass melts and tend to form highly electrically conductive and viscous sediments on the melter bottom. If not discharged during routine glass pouring, accumulation of the sediments entails distortion of the electric field and, hence undesired power distribution in the melt. With increasing retention time noble metals are predisposed to change their morphology, resulting in a high-viscous, non-Newtonian flow behavior of the noble metals-rich glass layers. These layers are immobile and cannot be discharged from the melter. At the Institut fuer Nukleare Entsorgung (INE) of the Karlsruhe Institute of Technology (KIT) noble metals-compatible melter designs has been developed and tested in nonradioactive prototype test facilities. Recently the Karlsruhe Vitrification (VEK) Plant has started hot operation using the new melter design. Mission of this plant is to immobilize 60 m3 of highly noble metals-containing HLLW solution stored on site. The paper will describe the noble metals problem in detail, the melter design and results of testing. Also the actual results from hot VEK operation will be given.

FF-10.2:IL03 On Nanostructured Hydrogen Catalysts, Fission-product Alloy Particles Extracted from Spent Nuclear Fuel

Daqing Cui, Studsvik AB, Nyköping, Sweden, and Stockholm University, Dept. of Material and Environmental Science, Stockholm, Sweden

Nanostructured 4d-transition metal catalysts play important roles in energy and environmental science, but are expensive and difficult to synthesize. This work presents results on the characterization of 4d-metal alloy particles extracted from spent nuclear fuel by using a non-destructive method. Composition (26.5Mo-32.7Ru-7.6Tc-6.3Rh-23.2Pd-3.9Te), nanostructure (atomic level homogeneity, diffraction pattern), aggregation tendency, and hydrogen catalytic effect will be described. The latter was investigated in a dedicated experiment: oxidized forms Se(IV), Tc(VII), U(VI), Np(V) and Pu(VI) were found to be stable in a solution saturated with a gas mixture Ar + 10% H2 + 0.03% CO2, but could be reductively immobilized in the same solution when contacted with the extracted alloy particles. It was also observed that in presence of a beta-radiation field the hydrogen catalytic effect of a piece of synthetic alloy (with stable elements and similar composition as the extracted particles) could be enhanced. The 4d metal alloy particles contained in spent nuclear fuel may contribute to ensure reducing local environment in the deep geological repository, thus protecting UO2 matrices from oxidative corrosion, and immobilizing redox sensitive radionuclides by catalysis of the hydrogen generated from water corrosion of iron waste canister. Other potential applications of the fission product alloy particles, e.g. for production of hydrogen from water, will be mentioned.

FF-10.2:L04 Co-conversion of Actinides into a Uranium Matrix

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An alternative to the direct disposal of long-lived radionuclides is their separation (partitioning) from the original waste in connection with a subsequent special treatment. The general aim is to lower the risk potential coming along with the radioactivity (radiotoxicity). A promising concept after the partitioning step is the embedding of Am, Cm & Cf, the “Minor Actinides” (MA), in uranium-based nuclear fuel (co-conversion). Through this the MAs can be eliminated by nuclear reactions with fast neutrons (transmutation) in upcoming reactor concepts. One way to obtain such fuel is the Sol-Gel-Process: An amorphous gel is created and crystallised at low temperatures. The main advantages are the high automation potential as well as the co-conversion being carried out predominantly in aqueous solutions without dust-creation. The formulation of appropriate sols for this gelation process is one important step towards a working process as the chemistry of U/MA-Systems is quite complex. Therefore actinide surrogates are utilised for basic research on reaction mechanisms. Additionally the ceramics obtained through thermal treatment of the gels are characterised to optimise the calcination and sintering process.

FF-10.2:IL06 Sulfur Incorporation in Borosilicate Glass - A Challenge for Vitrification Facilities Processing High Sulfur Bearing HLLW

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Sulfur belongs to the set of troublesome elements in High Level Liquid Waste (HLLW) which can pro-vide severe problems during conversion of the waste to glass. Sulfur respectively its compounds have a limited solubility in borosilicate glass and tend to form separated molten phases which accumulate in the glass melting system and have highly undesirable properties. The achieveable sulfur loading of the waste glass can therefore directly impact the overall economics of a vitrification plant including HLLW throughput capacity, operation time, amount of glass to be produced and finally disposed. Therefore methods to enhance the sulfur loading of the waste glass are of considerable importance. The paper will present fundamental aspects of sulfur incorporation in a borosilicate glass structure as well as experimental results obtained by various methods. Recent lab-scale results related to the impact of additives like vanadium pentoxide, antimony pentoxide and barium oxide to the HLLW or to the glass matrix will be given. The paper contains also a short literature review about the sulfur problem as well as results obtained from large-scale technical test facilities and from a hot operation plant.

FF-10.2:IL07 An Innovative Hybrid Process Involving Plasma in a Cold Crucible Melter Devoted to the Future Intermediate Level Waste Treatment: The SHIVA Technology

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The cold crucible technology first developed for the treatment of the high level fission products can also be used for the direct treatment of intermediate level wastes. The first experiments carried out for the direct treatment of ionic exchange resins emphasised the requirement of very high temperature on the glass. When the surface is to cold, the unperfected oxidation lead to produce inclusion such as metallic compounds coming from the reduction of species contained in the waste. Thus, the quality of the glass could be not enough to meet with specific requirements for long term storage. For few years, the CEA has been studied the capability of a cold crucible to involved plasma torches ensuring the high temperature required for a complete oxidation. The developments and the assessment of different technological ways lead to build a cold crucible fitted with a bottom inductor together with twin plasma torches. This is the SHIVA process. The researches carried out on this technology have shown the high efficiency of the combination for the treatment of a large variety of wastes. The oxidation is complete and the produced glass can be easily poured in a canister. This innovative process provides new perspective of treatment for a large variety of intermediate level waste.

FF-10.2:L08 Recovery of Long-lived Minor Actinides from High Active Waste Solutions Using Innovative Partitioning Processes

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The selective recovery of long-lived minor actinides from high active waste solutions and separate treatment by transmutation (P&T) or conditioning in tailored- ceramics (P&C) can considerably improve long-term safety of nuclear disposal. The present paper will give a summary about the ongoing research activities at Forschungszentrum Jülich on the field of actinide (III) partitioning by innovative hydrometallurgical solvent extraction processes. However, partitioning of the trivalent actinides (Am, Cm) is not possible with the present reprocessing technique according to the PUREX process. This additionally requires more complex partitioning steps and is the subject matter of our investigations. These are based on the co-separation of trivalent actinides and lanthanides (e.g. TODGA/TBP process) from the PUREX raffinate, followed by the subsequent actinide(III)/lanthanide(III) group separation in the SANEX process. The main objectives of our research are on the one hand fundamental research on partitioning, to improve the knowledge of the chemistry of actinides and the extraction agents and on the other hand process development involving testing of extraction devices with cold and genuine radioactive waste solutions.

Session FF-10.3

Waste Form Modeling, Performance and Characterisation

FF-10.3:IL01 Development of New Waste Forms to Immobilize Iodine-129 Released from Spent Fuel Reprocessing Plant

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I-129 is released to an off-gas stream at a reprocessing plant when spent fuel is dissolved and is captured by a silver adsorbent as AgI. I-129 is a very long-lived radionuclide and is a mobile fission product because AgI is unstable under reduction condition of a geological repository. Because of these characteristics, I-129 is one of the key radionuclides in a safety assessment of the geological disposal of radioactive wastes which are generated from the reprocessing plant. To improve safety of disposal, several new waste forms have been developed to confine I-129 for a very long-term to reduce the leaching rate of I-129 from the waste. The objects of the new waste form are to solidify more than 95% of I-129 into the waste form and to attain the leaching rate less than 10^{-5}/y. Typical iodine immobilization techniques are as follows. -Hot Isostatic Pressing treatment of spent silver-adsorbent -Low temperature vitrification with BiPbO$_2$I; -High performance cement solidification with IO$_3$. The paper presents the experimental results in regard to the treatment process, leaching behavior, modeling, etc.

FF-10.3:L03 Is the Aqueous Corrosion of Borosilicate Glass Really Controlled by Diffusion Processes?

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Understanding the mechanism of aqueous corrosion of nuclear waste borosilicate glasses is essential to reliably predict their long-term performance in a geologic repository. Here we report the results of corrosion experiments with polished cuboids of borosilicate glasses under different physico-chemical conditions, including experiments with O, Mg, and Si isotope tracers. Several observations were made in this study such as (1) the occurrence of silica corrosion rims while the overall shape of the cuboids was retained, (2) chemical oscillations in the rim, (3) an enrichment of all stable isotopes in the rim without observable diffusion profiles, (3) a sharp phase boundary between the corrosion rim and the pristine glass, and (5) a high porosity in the corrosion rim. These features are not at all compatible with classical theories about the formation of the corrosion or “gel” layer that are based on diffusion-controlled hydration and ion exchange reactions and subsequent solid-state re-condensation of the hydrolyzed glass network. We propose a new mechanistic corrosion model that is based on congruent dissolution of the glass that is spatially and temporally coupled to the precipitation of amorphous silica at an inward moving reaction interface.

FF-10.3:IL05 **The GRAAL Model: a Tool for Predicting Long-term Nuclear Glass Dissolution Kinetics**

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A new model called GRAAL has been developed to simulate nuclear glass dissolution kinetics in geological disposal conditions. The model is based on some key mechanisms required for describing the different kinetic regimes as a function of chemical and hydraulic boundary conditions. These mechanisms are the following: (1) the glass hydration, (2) the formation of a passivating layer limiting the water reactive transport towards the pristine glass surface, (3) the dissolution of this layer from its external surface up to chemical equilibration with the bulk solution and (4) the precipitation of secondary crystalline phases. Experimental data obtained in various conditions (static or dynamic tests in initially pure water) are compared with model predictions. A good agreement is observed despite the small number of model internal parameters, determined independently. Applying the model to a simplified geological disposal layout enables to discuss the influence of each of those parameters on the glass long-term behaviour: the fate of silicon in the near field, either diluted by diffusion or consumed by Si-rich secondary phases precipitation, appears to control the final rate and consequently the long-term glass durability.

FF-10.3:IL06 **Characterization and Modelling of Materials for Advanced Nuclear Systems**

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A number of oxide, silicate, and phosphate compounds are of interest in the development of materials for encapsulation of fission products, minor actinides, and plutonium in advanced fuel cycles. These materials must exhibit robust performance in response to radiation damage and chemical attack by aqueous fluids. Thus it is necessary to conduct multidisciplinary experimental and modelling studies of the kinetics and mechanisms of radiation damage, geochemical alteration, and synergistic effects between the two. Following a brief summary of criteria for waste form performance, we illustrate some of the problems of radiation damage and aqueous alteration that can be studied via a combined experimental and modelling approach. Examples of this methodology include the application of static and dynamic atomistic simulations, ion irradiation, actinide-doping experiments and studies of natural samples in order to develop a more complete picture of radiation response from picosecond to million year time scales. Similarly, investigations of aqueous alteration benefit from a combination of modelling, laboratory experiments, and studies of natural samples. Selected examples will be presented together with suggestions regarding advanced characterization techniques.

FF-10.3:L07 **Synthesis and Hydrothermal Stability of Ce-doped Zirconolite Ceramics**

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Zirconolite CaZrTi2O7 is a promising candidate for the safe immobilization of actinides. To study its chemical stability, corrosion experiments on powders of Ca1-xCexZrTi2O7 (with Ce as inactive stand-in for actinides) under hydrothermal conditions were performed in six aqueous solutions: 1M HCl, 2M NaCl, 1M NaOH, 35% H2O2, 1M NH3, deionized H2O. Zirconolite proved to be extremely stable in a broad range of cases, since the alteration rate was undetectable in all solutions other than 1M HCl. 1M HCl was used in four additional experimental series, varying the following quantities: (1) composition (XCe = 0-0.225 apfu); (2) surface area-to-fluid volume ratio S/V (0.005-0.02 m2/ml); (3) temperature (T = 100-300°C); (4) reactor material (Teflon©, Ni, Ag). The experimental results can be summarized as follows: (a) zirconolite dissolution was incongruent (TiO2 and m-ZrO2 replaced zirconolite grains to varying extent during the tests); no clear effect on the degree of alteration (b) of Ce-content and (c) of S/V were observed; (d) the degree of alteration increased slightly with increasing temperature; (e) if compared to the case of Teflon reactors, in the Ag vessels the alteration rate increased dramatically, while in Ni reactors the concentration of Ti and Zr in solution was lower.

FF-10.3:IL10 **The Methodology of SCK.CEN to Evaluate the Long-term Performance in Geological Disposal Conditions of Immobilized High-level Radioactive Waste**

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Belgium is considering both vitrified high-level radioactive waste and spent fuel as waste forms resulting from the irradiation of nuclear fuel in its nuclear power plants, which are providing about 55% of the nation’s electricity. This double approach is due to an earlier governmental moratorium on reprocessing of spent fuel. These high-level waste forms are planned to be disposed of in a stable geological formation. Belgium is considering a Boom Clay formation as potential geological disposal rock. Long-term running R&D programmes have been launched in order to determine the chemical durability and compatibility of the HLW forms in and with the potential disposal environment. This R&D includes laboratory studies using simulated (inactive in case of glass, unirradiated UO2 in case of spent fuel) samples, radioactive samples, in-situ tests in the underground laboratory in clay (SCK.CEN site), and geochemical and analytical modelling. Participation to international R&D projects provides additional information and validation of the R&D. This integral approach is expected to provide the necessary basic understanding of the HLW waste form dissolution processes and the requested input data into the safety assessment studies for geological disposal. Our R&D is also taking into account the geological disposal designs considered by the Belgian radioactive waste management agency (NIRAS/ONDRAF). Until a few years ago the R&D was focused on the SAFIR 2 design, considering essentially stainless steel overpacks and bentonite clay backfills as engineered barriers in addition to the immobilized high-level waste, emplaced in a Boom Clay formation. Recently the supercontainer design has been selected, which uses C-steel overpacks inside of a concrete backfill as main engineered barriers, for disposal in the Boom Clay formation. The study of the waste form behaviour takes into account the potential environments that might interact with the HLW forms in the reference disposal conditions in the short, medium and long term - covering up to thousands or hundreds of thousands of years. The paper will discuss the following issues: - the approach used in the Safety Case, and the geological disposal designs considered; - the methodology used in the R&D; - some typical results.

This work is performed as part of the programme of ONDRAF/NIRAS (the Belgian Agency for Radioactive Waste and Fissile Materials) on the geological disposal of high-level/long-lived radioactive waste. The authors also gratefully acknowledge financial support of the EC for part of the R&D reported in this paper.

Session FF-10.4

Design and Operation of Waste Immobilisation Facilities

FF-10.4:IL01 **Commercial-scale Immobilization of Nuclear Waste via Cold Crucible Melter**

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The application of cold-crucible melting (CCIM) to nuclear waste has been studied for more than 20 years now. The interest of this technique, which had been initially developed for metallurgical applications, was rapidly perceived by those who had to tackle with the corrosive nature of nuclear waste glass, and with the limits of more traditional melters. The potential for higher temperatures, and the perspective of improved melter life, were the major drivers for these developments. During those 20 years, the technology has matured, mainly in France and Russia. The French technology has been demonstrated on industrial scale pilots, and exported to South Korea for processing low activity waste. Effluents representing typical US HLW have been studied, demonstrating excellent performance during the recent ART demonstrations. The CCIM has been adapted to highly radioactive environments; a first-of-a-kind, fully "nuclearized" CCIM has been designed, qualified, and is being retrofitted in an existing La Hague cell. With the start-up of this facility, the CCIM technology will reach the stage of full industrial maturity for nuclear environments.

FF-10.4:IL03 Studies on Helium Accumulation, Behaviour and Release from Nuclear Spent Fuel and Waste Forms

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Spent UO2 fuel contains Pu and some amounts of the minor actinides Np, Am and Cm. It is therefore subjected to ❑-decay damage and ingrowth of helium during long term storage. Among the different options considered for the back end of the nuclear fuel cycle some include reprocessing of the fuel and immobilization of the highly radioactive actinides in waste glass or in other confinement matrices. Also in these materials large quantities of helium will be generated by decay in conjunction with alpha-damage build up. If the helium generated in spent fuel will be released it could overpressurize the fuel rod possibly causing clad creep. If the helium stays in the fuel, helium bubbles might form causing swelling and possibly embrittlement of the fuel. These aspects have to be well understood to be able to predict the long term behaviour of any material envisaged for actinide confinement. 238Pu-doped UO2 with different Pu content, aged 238PuO2, synthetic zirconolite (CaZrTi2O7) doped with 238Pu, 239Pu or with 244Cm have been investigated by helium desorption spectrometry, transmission electron microscopy and X-ray diffraction. The helium release profiles were interpreted in conjunction with other radiation damage and previous annealing behaviour studies.

FF-10.4:IL04 Using the Vitrification Test Rig for process Improvements on the Waste Vitrification Plants

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The Vitrification Test Rig (VTR) is a full scale non-active waste vitrification plant (WVP), that replicates the lines used for immobilising highly active reprocessing waste at Sellafield in the UK. In the high level waste (HLW) vitrification process, liquid HLW is dried in a rotating tube furnace then mixed with an alkali borosilicate glass frit. This mixture is heated to form a homogeneous product glass that is poured, cooled and stored in steel canisters. The primary function of the VTR is to trial and develop methods to increase the efficiency of high level waste processing at the active WVP. Efficiency gains are mainly achieved by increasing the rate at which the immobilised product is created and by increasing the ratio of HLW to glass frit in the product. The VTR has also been used to investigate the chemistry of various process additions and conditions, the effects of potential fault scenarios, and the processing of dilute waste streams that will be received by WVP in the future. All of these areas have the potential to improve processing efficiency through the optimisation of process conditions and the minimisation of unplanned plant outages. This paper discusses several VTR campaigns that have lead to overall improvements of WVP operation.

FF-10.4:IL05 Cold Crucible Inductive Melting Technology - Application to Vitrification and Ceramization of High Level and Actinide Wastes

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Cold crucible inductive melting (CCIM) is a promising method for production of high-temperature materials. The method is based on direct heating of conductive materials by high-frequency (105-107 Hz) electromagnetic field from external source. Electromagnetic field penetrates through the gaps between the water-cooled pipes or sections of the melter - cold crucible into the melt thus heating it. Whirl currents induced in the melt create active hydrodynamic regime providing for high specific productivity and absence of refractories and electrodes contacting with melt elongates lifetime of the cold crucible. Thin layer of partly melted material ("skull") between the high-temperature melt and pipes or sections forming the cold crucible walls protects them from corrosion. CCIM is used for production of high-fusible materials such as optical glasses, stone cast, single crystals for science, technical and jewelery applications. In early 1980s CCIM process was proposed for vitrification of high level waste (HLW) and the cold crucible was being considered as an alternative to Joule heated ceramic melter and inductively heated hot crucible. In Russia first bench-scale unit for HLW vitrification was constructed at spent fuel reprocessing plant at Production Association "Mayak" in late 1980s.

Session FF-10.5

Repository Design and Requirements

FF-10.5:IL02 Lessons Learned from the Yucca Mountain and WIPP Projects

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For more than 30 years Sandia National Laboratories (SNL) has played a key role in the development and implementation of total system analyses of waste management systems in the United States. Two very important applications have been the total system analysis of long-term performance that supported the Compliance Certification Application for the Waste Isolation Pilot Plant (WIPP) in 1996 and the License Application for the Yucca Mountain (YM) Repository in 2008. Our work at WIPP and YM supports the conclusion that deep geologic disposal remains a viable option for the long-term isolation of radioactive waste. This conclusion is consistent with observations from repository programs in other countries. Key technical lessons learned from WIPP and YM include: the development and conduct of a site characterization program that allows the understanding of the expected and potentially disturbed performance of the disposal system; the translation of that understanding into mathematical and computational models; and the use of the models to technically assess the long-term performance of a disposal system in a manner that is suitable for informing regulatory decisions about deep geologic disposal of radioactive wastes.

FF-10.5:IL03 Uncertainty in Radionuclide Retention Processes for Crystalline Rock Repository Far-field

Gunnar Buckau, Karlsruhe Institute of Technology, Institute for Radioactive Waste Management, Eggenstein-Leopoldshafen, Germany

The safety of a repository for radioactive waste in crystalline rock is built around the multi-barrier system approach. One of these barriers is the far-field, i.e. the part of the host-rock beyond where the properties are altered significantly by the repository. Retention of highly sorbing radionuclides is associated with considerable uncertainty, with respect to both the detailed retention processes and the associated data. Amongst the highly sorbing radionuclides are the actinides, some of the isotopes with long half-life and are a emitters with high specific radiotoxicity. The present paper deals with the retention of such radionuclides. The radionuclide retention in the far-field is the result of both chemical and physical processes. The chemical processes include redox reactions determining the chemical state and ionic charge of the actinides, a key parameter in governing the geochemical behavior. The chemical retention processes include reversible sorption, formation of surface complexes with slow dissociation kinetics, frequently in combination with change in the redox state of the concerned radionuclide, and formation of new phases of varying stability, including mixed phases/solid solutions. The chemical retention processes are subject to high spatial variation, with specific minerals dominating the retention, where these minerals can be distributed over the rock material down to the nm scale. The physical retention processes are governed by residence of the radionuclides in flow-stagnant regions ("matrix diffusion"). For obvious reasons the physical retention is also a very inhomogeneous process, including retention by residence in distinct micro-fractures and structures. A considerable effort is made in order to delineate different processes on the different lateral and time scales involved. For this purpose, a broad spectrum of methods is used, covering the relevant lateral and time scales. Such methods include real system analysis for determination of diffusion of natural tracers into the micro-fracture network and analytical methods determining the chemical state of actinide ions on a micro-resolution scale. The implications for lowering the uncertainty in radionuclide transport modeling are discussed.

Poster Presentations

FF-10:P02 **Synthesis and Characterization of ZrO2 Based Pyrochlore-type Ceramics for Nuclear Waste Conditioning**

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Safe disposal of radioactive waste is an exigent challenge of scientific and social interest that has to be solved within the following decades. Radioactive waste partly consists of highly radiotoxic nuclides that are planned to be disposed in geological repositories. Therefore innovative strategies of disposal and concepts of final storage have to be developed to ensure safety efforts over a period of a few hundred thousands of years. Pyrochlore-type ceramics based on ZrO2 are promising materials that meet these demands because actinides will be integrated on the atomic scale into the crystal lattice of the matrices. ZrO2 based ceramics can be prepared by several methods e.g. coprecipitation, sol-gel route and solid state reactions. Hydrothermal reactions offer a number of advantages in contrast to conventional chemical reactions such as precipitation of crystalline low-temperature precursors, improvements in sintering capabilities as well as in homogeneity of cation distribution in the structure. This poster presents our recent investigations focused on synthesis of zirconia based pyrochlore-type ceramics by hydrothermal synthesis depending on pH, temperature and time. The morphological and structural characterizations were carried out by SEM and XRD measurements respectively.

FF-10:P03 **Conditioning of Actinides in Monazite-type Ceramics**

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The research on crystalline ceramic waste forms as host for high level nuclear waste has induced great interest in recent years. These should be able to condition specific fission products or minor actinides after their partitioning. Owing to its good properties, e.g. irradiative and chemical durability, monazite-type ceramics have been chosen as promising host matrix for conditioning of tri- and tetravalent actinides. To avoid radioactive dust formation, synthesis routes like conventional solid state reaction are impracticable. Thus wet chemical routes such as hydrothermal synthesis and precipitation have been chosen within our recent research. XRD patterns demonstrate that crystalline structures of the resulting products can be identified as monazite and its hydrated form respectively, which have been obtained without any thermal treatment. In order to simulate actinide integration into the lattice structure of the monazite-type matrix, lanthanides doped monazite matrices, La(1-x)LnxPO4 (Ln = Ce, Nd, Eu, Gd, Lu, x = 0.10 to 1.00) have been prepared. First structural and morphological results applying XRD and SEM are presented combined with thermal behavior, aqueous durability and radiation tolerance tests.

FF-10:P06 **Effect of Temperature on Glass Leach Kinetics**

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90Nd/10-simulated Chinese HLW glass was analyzed after 2.5years static leaching test. During the period, two temperatures (90 °C, 150 °C) were used as main effected parameters to be studied. As to the results of SEM and XRD, it was found that more secondary phases formed in 150 °C than in 90 °C; at same time, the NR of glass was more in 150 °C than in 90 °C. It should be controlled by silicon solubility following the first order law if the glass alteration was under classic corrosion procedure. However, the mechanism in 150 °C was found to be changed compared with the first order law from the results of normalized leaching rate of main elements. And, it was also found that glass alteration resumption was happened in 150 °C.

Symposium FG

PHOTOVOLTAIC SOLAR ENERGY CONVERSION: MATERIALS AND TECHNOLOGY CHALLENGES

Oral Presentations

Keynote Lecture

FG:KL **Sustainable Energy by Mesoscopic Solar Cells**

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The field of photovoltaic cells has been dominated so far by solid state p-n junction devices made of crystalline or amorphous silicon, CdTe and copper indium gallium diselenide (CIGS) profiting from the experience and material availability of the semiconductor industry. However, there is an increasing awareness of the possible advantages of devices based on mesoscopic inorganic or organic semiconductors commonly referred to as “bulk” junctions due to their interconnected three-dimensional structure. Their embodiment depart completely from the conventional flat p-n junction solid-state cells, replacing them by interpenetrating network junctions, their mesoscopic morphology producing an interface with huge huge contact area. These cells are formed, for example, from nanocrystalline inorganic oxides, ionic liquids and organic hole conductor or conducting polymer devices, which offer the prospect of very low cost fabrication without expensive and energy intensive high temperature and high vacuum processes. They can feasibly be produced employing flexible substrates and are compatible with a variety of embodiments and appearances to facilitate market entry, both for use in domestic devices as well as in architectural or decorative applications. Materials used for mesoscopic solar cells are abundantly available so that the technology can be scaled up to the terawatt scale without running into feedstock supply problems, in contrast to several competing thin film photovoltaic converters that use highly toxic materials of low natural abundance. However, a drawback of the current embodiment of mesoscopic solar cells is that their efficiency is significantly lower than that for single and multi-crystalline silicon as well as for CdTe and CuIn(As)Se. This lecture focuses on dye sensitized mesoscopic solar cells (DSCs), which are the only photovoltaic system that accomplishes the separation of the optical absorption from the charge separation and carrier transport processes by associating a sensitizer as light-absorbing material with a wide band gap semiconductor, of nanocrystalline morphology[1-3]. The DSC has made phenomenal progress since its discovery was announced in the scientific literature only 18 years ago. The efficiency problem is being tackled using molecular science and nanotechnology. Currently there is a quest for sensitizers with enhance harnessing of the red and near IR part of sunlight. Progress in this area has been significant over the last few years resulting in a boost in the conversion efficiency of the DSC to over 12 percent for single junction and 16 percent for tandem cells rendering the DSC a credible alternative to conventional p-n junction devices. Commercial production of DSC has started in several countries. Mesoscopic solar cells have become viable contenders for large-scale future solar energy conversion systems on the bases of cost, efficiency, stability and availability as well as environmental compatibility.

[1]B. O’Regan and M. Gratzel, Nature 335, 1991, 7377; [2]U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissortel, J. Salbeck, H. Spreitzert and M. Gratzel, Nature, 395, 1998, 550; [3]M. Gratzel, Nature, 414 , 2001, 338.

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Session FG-1
Crystalline Cells

FG-1:IL01 Challenges for High Efficiency Amorphous/Crystalline (a-Si:H/c-Si) Silicon Heterojunction Solar Cells

L. Korte*, T. Schulze, C. Leendertz, R. Stangl, E. Conrad, H. Angermann, M. Schmidt, B. Rech, Helmholtz-Zentrum Berlin, Berlin, Germany

Solar cells based on amorphous/crystalline silicon heterojunctions have gained much attention due to their high efficiency as demonstrated by the so-called "HIT cell"[1], recently reaching 23% efficiency on 100cm^2. Rapid industrial application was particularly enabled by the simplified preparation comprising only low-temperature thin-film deposition techniques. To realize the Voc potential >700mV of such cells, it is crucial to minimize recombination at the a-Si:H/c-Si heterojunction. Based on our latest results, we will review the challenges on the way towards this objective: Wet chemical pre-treatment of the c-Si surface prior to a-Si:H deposition; a-Si:H doping; thermal post-treatments of the a-Si:H/c-Si stack[2]. The link between these technological steps and the physics governing recombination and charge transport in the device will be discussed. Finally, rear emitter a Si:H/c Si cells[3] are candidates for further improvements in cell efficiency. Their potential will be assessed by simulations and demonstrated in the device.

[1]Tsunomura et al. Sol. En. Mat. Sol. C. 93 ('09) 670 ; [2]Korte et al. Sol. En. Mat. Sol. Cells 93 ('09) 905; Schulze et al., Appl. Phys. Lett., accepted; [3]Tucci et al. Proc. IEEE COMMAD ('08) 242; Stangl et al. Sol. En. Mat. Sol. C. 93 ('09) 1900

FG-1:IL02 Advanced Material and Technological Concepts for Photovoltaic Solar Cells Based on Thin Silicon Wafers

Frederic Dross*, Ivan Gordon, Giovanni Flamand, Joachim John, Niels Posthuma, Jan Van Hoeymissen, Emmanuel Van Kerschaver, Jef Poortmans, IMEC, Leuven, Belgium

Providing clean and renewable energy for the future is one of the main and most interesting challenges that the world faces today. Photovoltaics is the most promising candidate to achieve this objective. Today, the material accounts for a large part in the final cost of the PV systems. Therefore the development of new PV materials is a natural path for cost reduction. On the other hand, the material dominating the PV market is the relatively cheap, very abundant, non toxic silicon which has properties incredibly well suited to PV applications. As a consequence, in order to fulfill the stringent requirements of the PV industry, this new material should be consisting of silicon! How to engineer "new" materials made of Si? By changing the shape of the silicon material (for instance ultra-thin wafers, or Si nano-features which induce quantum effects), or by adapting the synthesis method (using CVD, or very innovative mechanical cleavage techniques), the "new" Si material acquires specific properties (bandgap, crystallinity, shape.) that can be used advantageously for PV applications, but that require new concepts to be used as a base material for solar cell. This presentation highlights some of the opportunities and challenges that these new Si-based materials offer us.

FG-1:IL03 Ultrapurification of Silicon for Photovoltaic Applications

C. del Canizo*, A. Luque, Universidad Politecnica de Madrid, Spain; A. Rodriguez, G. Ovejero, Universidad Complutense de Madrid, Spain

The recent explosive growth of Photovoltaics (PV) and the relative avidity for silicon of the predominant solar cell technology have resulted in a dramatic change of the polysilicon industry structure. While in the past the polysilicon was manufactured almost exclusively for the semiconductor industry, in 2008 67% of the market was devoted to the solar industry. The different alternative routes to purify silicon for PV applications will be presented, analysing their advantages and drawbacks. Emphasis will be made on the CENTESIL initiative, a new private-public partnership promoting a pilot plant that is in an advanced state of construction. The goal is to allow the PV companies worldwide to count with an independent research centre to help them to establish their own polysilicon plant. The development contains four areas of activity, that will be presented and discussed: (1) synthesis of chlorosilanes, with the silicon tetrachloride as the main source of chlorine, and purification based on fractional distillation but with additional processes to remove lifetime-killing impurities; (2) development of a chemical vapor deposition reactor aiming at low energy consumption; (3) recycling of the byproducts for optimal use and sustainability; and (4) material characterisation.

FG-1:L04 Organolanthanide Down-shifters to Improve Si-based Solar Cell Efficiency

Alessia Le Donne*, Maurizio Acciarri, Simona Binetti, University of Milano-Bicocca, Department of Material Science, Milano, Italy

It is widely known that an increase of the energy conversion efficiency of first generation solar cells could be obtained exploiting the solar spectrum region below 450 nm, this high energy tail being not efficiently converted from silicon. This work reports the optical and electrical characterization of commercial c-Si solar cells coated with layers doped with different Eu3+ organic complexes. Such Eu3+-doped layers are able to realize down-shifting of photons with wavelength lower than 400 nm without introducing strong modifications of the industrial process leading to the fabrication of the PV modules. In a previous work an increase of 2.8% of the total delivered power has been observed by encapsulating solar cells with Eu3+-doped PVA. Other host matrixes compatible with PV module fabrication such as silica will be tested. A further enhancement of the cell conversion efficiency could be obtained exploiting a wider portion of the solar spectrum. However, the excitation window of Eu3+ organic complexes is limited to the near-UV due to the energetic constraints defined by the physics of sensitised lanthanide luminescence. To overcome this problem, Eu3+ organic complexes whose absorption is shifted towards the visible through the presence of a co-ligand will be studied.

Session FG-2
Thin-film Photovoltaics

FG-2:IL01 Materials Challenge of Polycrystalline Silicon Based Thin Film Solar Cells Prepared by High-rate Electron Beam Evaporation on ZnO Coated Glass Substrates

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This paper discusses the materials challenge of a new approach to realize highly-efficient and cost-effective poly-crystalline silicon based thin film solar cells on ZnO:Al coated glass substrates. The poly-Si cell preparation comprises the deposition of amorphous silicon by electron evaporation at very high deposition rates of typically 600 nm/min, a subsequent solid phase crystallization step at 600 °C, followed by rapid thermal annealing at 900-1000 °C, and, finally, a defect passivation step using hydrogen plasma treatments. Very recent results achieved in cooperation with CSG-Solar, Sydney, proved the high quality of our e-beam prepared poly-Si by showing small area module efficiencies as high as 6,7% on SiN coated glass substrates. By studying the crystallization behavior of amorphous silicon on ZnO coated glass we observed two important features: firstly, the kinetics of crystallization is apparently different on ZnO coated glass as compared to SiN, and, secondly, the ZnO:Al films protected by the silicon films significantly improve in their opto-electronic properties (e.g. yielding a carrier mobility as high as 67 cm2/Vs) due to the high process temperatures applied during crystallization.

FG-2:IL02 Thin Film Silicon Solar Cell with Advanced Light Trapping

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We have proposed the high performance tandem solar cell with Advanced Super Light Trapping structure (ASLT) consisting of well designed texture, super-thin amorphous silicon top cell and interlayer of very low refractive index. We have been engaged in this interlayer with multi-stacked materials of very low refractive index. Superior optical properties for refractive index of 1.5 at a wavelength of 600nm was obtained. The 30 percent current increase of top cell for a-Si/ µc-Si tandem solar cell by applying this ASLT structure has been performed. Calculated results of optical scattering and absorption on the ASLT structure showed a significant enhancement of the spectral response of the top cell by lowering the refractive index of the interlayer and optimizing the surface texture of TCO. Threfore, we can conclude that our developed ASLT structure will enhance much more the efficiency of the thin film Si solar cells

FG-2:L03 Triple Silicon-carbon-nitride Alloy Films for Silicon Solar Cells

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Amorphous silicon-carbon-nitride a-SiCN:H films were deposited by PECVD (80 Pa)at 13.56 MHz (power density 0.1 W/cm2) from silane-methane-ammonia gaseous mixture at 180 °C. Optical and structural properties were in correlation with PECVD parameters. The films were smooth, homogeneous, chemically inert and wear resistive. The growth rate of films was influenced mainly by the presence of ammonia and silane in PECVD process. The refractive index decreases with increasing nitrogen and carbon contents in a-SiCN:H films. Tauc energy gap revealed the dependence on nitrogen and carbon content in films. The technological conditions were chosen to obtain the a-SiCN:H with optical properties suitable for applications in photovoltaics (PV) as antireflective coatings. Total reflectivity as a function of wavelength is minimal in the range from 400 nm to 1100 nm. Silicon substrates covered by these films exhibit the apparent decrease in total reflectivity, which indicates that a-SiCN:H might be good candidate for PV applications. Hydrogen effectively passivates structural defects in multicrystalline silicon solar cells with a-SiCN:H films which improves device properties.

FG-2:IL04 Thin Film Full Spectrum Solar Cells with Low Concentration Ratios

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In Japan, the NEDO program named “Innovative PV Technology” was initiated in June, 2008 aiming at very exciting efficiency target of 40% including thin-film solar cells toward 2050. Tokyo Tech proposed a program “Thin Film Full Spectrum Solar Cells with Low Concentration Ratios” in collaboration with 8 Universities and 6 companies. The research consortium consists of three research teams, Band Engineering, Thin Film Full Spectrum Solar Cells, and Light Management and TCO. In order to realize thin-film solar cells that are capable for large area application with the conversion efficiency of 40%, we are developing novel absorber materials with a wide range of bandgap, from wide-gap to narrow-gap materials including Si-based and chalcopyrite-based thin-film absorbers. Moreover, we are also developing a light management technology to effectively capture more photons in a wide wavelength area. Employing these element technologies, we then are going to fabricate 5-to-6-junction thin film solar cells with low concentration ratios of sunlight. We attempt to achieve a conversion efficiency of 30% by March 2014.

FG-2:IL05 Crystalline Silicon Thin Films Solar Cells on Foreign Substrates: Potential and Challenges

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Crystalline silicon thin films, free standing or deposited on foreign substrates are considered as a very promising alternative approach to bulk silicon based cells. Cost reductions can be accomplished through the processing and the amount of silicon used. The carrier collection can be improved by light confinement provided by the highly reflective substrates or back contacts. The presentation will briefly give the present status of research on free standing crystalline silicon films based silicon solar cells, including advanced concepts such as rear contact cells and heterojunctions. Then, the different methods used to form thin silicon layers on foreign substrates by direct chemical vapor deposition (CVD) process or by crystallization of amorphous silicon will be reviewed. A more particular attention will be put on metal and laser assisted crystallization processes. The structural and electronic quality of the crystalline silicon layers will be reported and potential and limiting factors towards high efficiency solar cells will be discussed.

FG-2:L06 Broadband Absorption Enhancement Using Unique Nanostructures

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Thin film solar cells have attracted much attention because of the potential to provide virtually unlimited clean energy at relatively low cost. Currently, their performances are limited by poor light absorption. In this research, large, broadband, and polarization-insensitive light absorption enhancement was realized via integrating with unique metallic nanostructures. A test shows up to ~30% broadband absorption enhancement when comparing to bare Si thin film solar cells, and up to ~10% improvement at certain wavelengths when compared to bulk Si solar cells. Three possible mechanisms, the Fabry-Perot resonance, surface plasmonic resonance, and planar waveguide coupling, were indentified to be responsible for such an enormous enhancement. Potential integration with other approaches will be discussed as well.

FG-2:L07 In-situ Internal Stress Measurements During Sputter Deposition of Metallic Oxide Thin Films for Photovoltaic Applications

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Internal growth stresses are intrinsically related to the growth of thin films and multilayers on a substrate, and can therefore not be avoided. However, numerous possibilities exist to engineer these stresses by choosing the appropriate deposition parameters. Indeed, as these growth stresses originate from multiple microstructural phenomena (like nucleation, growth, diffusion) interacting during the deposition process, it is exactly this intricate link with underlying microstructural stress generation mechanisms that allows to fine-tune the critical deposition parameters in order to arrive at a “desired” internal stress state. We will illustrate this statement based on selected but sufficiently generic results that we recently obtained on a number of energy-related thin films and multilayers, vacuum deposited in a custom designed (reactive) sputter deposition tool, equipped with several in-situ diagnostic probes. In particular, we will focus on some representative metallic oxide layers such as those used as anti-reflection coating or in the window layer of PV thin film solar cells. In addition, some specific features related to stoichiometry control of these layers will be presented, based on the in-situ monitoring of the internal stress evolution during their growth.

FG-2:IL08 CdTe Thin Film Photovoltaics - Challenges in Materials Science

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The challenges and research needs for advanced CdTe solar cells are discussed from a material science point of view. It is possible to define optimized device structures from physical considerations. As promising thin film device concepts a p-i-n heterostructure is suggested which will avoid a defined doping of the absorber. CdTe solar cells consist of layer sequences of dissimilar materials. The front and back contact properties will be presented based on surface science results. Efficient contacts are only obtained after interdiffusion processes at all heterointerfaces. Interdiffused or graded heterointerfaces are evidently needed for efficient thin film solar cells using dissimilar and lattice mismatched heterointerfaces. The performance also strongly depends on cell inhomogeneities as given by the structure and morphology of the polycristalline films. CSS deposited CdTe films tend to grow in columnar layers with (111) orientation. If the sample temperature is strongly increased the (111) texture is lost and large 3D grains of nearly statistical orientation are formed similar as after the activation process using e.g. CdCl2 treatment. Strategies to overcome the given limitations are presented in order to approach the physical limits of CdTe cells.

FG-2:IL09 Advances in Low Temperature Grown CdTe Solar Cells on Glass and Polymer Films

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Amongst all the existing thin film solar cells lowest manufacturing cost has been achieved with CdTe based thin film solar cells on glass substrates. High efficiency CdTe solar cells are commonly grown in a “superstrate” configuration while the solar cells in “substrate” configuration exhibit very low photovoltaic conversion efficiencies. The CdTe solar cell processing can be categorised in two categories: low temperature (<450 °C) suitable for thermally sensitive polymer films or soda-lime glass substrates and high temperature (>550 °C) suitable for achieving >15-16% high efficiency solar cells on thigh temperature stable borosilicate white glass substrates. We have developed a simple evaporation processes suitable for in-line as well as roll-to-roll manufacturing. The CdS/CdTe layers and the CdCl2 layer for annealing treatment are grown with vacuum evaporation processes. Solar cells were developed on different types of transparent-conducting-oxide (TCO) layers, while application of high resistivity ZnO layer helped to reduce the CdS layer thickness which contributed to yield high current density in solar cells. Properties of the solar cell layers and influence of various deposition parameters have been investigated. CdTe solar cells with efficiency of >14% on glass substrate and 12.4% efficiency on polymer films have been achieved. Laser scribing method has been successfully implemented to demonstrate monolithically interconnected flexible solar mini-modules on polymer films. The paper will present a review of research and development contributing to the advancement of CdTe solar cells, and some challenges that need to be addressed for improvement in performance, manufacturing and cost reduction of CdTe solar modules on glass and flexible substrates.

FG-2:IL10 Electrical Characterization of Thin Film CdTe Solar Cells

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The detailed investigation of electrical properties of thin film solar cells by a technique of impedance spectroscopy under varied levels of AM1.5 illumination is reported. A series of CdTe/CdS devices grown by metal organic chemical vapor deposition (MOCVD), with different shallow p-doping by arsenic, as well as variations in structure, were studied. The impedance spectra measured in light and dark have been analyzed by the equivalent circuit approach. First the circuit model has been devised to describe all sets of data for the given series of samples, measured at zero current and under illumination from 1 sun to 1e-4 sun. The same model was found to describe well the dark measurements under varied dc bias, thus the comparison with the light data have been drawn. The detailed information on the properties of the device structure was obtained, including the properties of the main p-n junction under light, minority carrier lifetime, back-contact, as well as the effect of the blocking ZnO layer incorporated between transparent conductor and CdS layers. Also, the comparison of samples with different chemical concentration of As has shown that barrier mobility and series resistance of the device are strongly affected by the doping and are the main factors limiting performance.

FG-2:IL12 Material and Device Properties of High-Efficiency CIGS Solar Cells

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Thin-film copper indium gallium diselenide (CIGS) photovoltaic modules have transitioned from the laboratory to the market place, and production extends from pilot to mature manufacturing. CIGS solar cells and commercial modules have achieved efficiencies of 20% and 11.5% (13.5% champion), respectively. Long-term stability has been demonstrated, but some field failures have been observed, emphasizing the need to understand degradation mechanisms and packaging options. The CIGS module shares common structural elements with other thin-film technologies such as CdTe and a-Si; in principle, such communality should lead to a similar manufacturing cost per unit area. Thus, module efficiency becomes the discriminating factor determining cost per watt. Oft-asked questions about CIGS are: Why is there a significant gap between laboratory cell efficiency and commercial module efficiency? How can the gap be closed? How do we use our laboratory technology base to translate results to manufacturing? In this presentation, I will (1) review the deposition process, material and device properties of >19%-efficient devices, (2) address some challenges to achieving stable, cost-effective high performance modules, and (3) give thoughts on closing the gap between laboratory cells and modules.

FG-2:IL13 New Strategies for Chalcopyrites Based Solar Cells

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High expectations are raised in the future developments of chalcopyrite compounds like Cu(In,Ga)Se2 because they reach the highest efficiency among the thin film solar cells. Production lines for Cu(In,Ga)Se2 solar cells use various deposition processes for absorber thin films. However, module design has not been significantly modified for a long time. The tolerance of chalcopyrite semiconductors regarding grain structure and defects allows to fabricate Cu(In,Ga)Se2 (CIGS) thin films with a variety of deposition technologies and significant differences in the growth parameters and composition. In the long term, modifications of materials and devices are needed in order to overcome limitations of efficiencies and the use of rare materials. Advanced methods for film characterisation facilitate analysis of structural properties of films, also in-situ during film growth. The combination of analytical methods based on X-ray methods and electron beams give new insights in the microstructure and related electronic properties of the absorber films. These investigations lead to a new understanding of growth processes and consequently improve manufacturability of absorber films for low temperature substrates, wide bandgap cells and with In-free materials.

FG-2:L15 Development of Hybrid Sputtering/Evaporation Process for Thin Film Cu(In,Ga)Se2 Solar Cells Grown

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In the last decade, laboratory tests have revealed the interesting potential of the Cu(In1-xGax)Se2 (CIGS) solar cells; the highest reported efficiency among all types of thin film solar cells has been obtained for this absorber material. The main problem for the development of CIGS solar cell technology is the up-scaling of laboratory techniques to the industrial process, both maintaining a high conversion efficiency of the devices, and resulting compatible for the roll-to-roll configuration. Differently from the common co-evaporation process, in this work, an alterative approach for thin film CIGS has been tested: the sputtering deposition of metal elements combined with the selenium evaporation. We have studied the relationships between the growth parameters of our hybrid sputtering/evaporation method and the chemical-physic properties of the CIGS films. Moreover, solar cells were prepared with the deposited absorber layers. The typical solar cell structure is soda lime glass/Mo/CIGS/CdS/ITO. The CdS films has been deposited via Chemical Bath, and the ITO layers were deposited by RF-magnetron at room temperature, respectively. The I-V characteristics of finished solar cells under AM 1.5 solar spectrum irradiation have been measured and the cell parameters analyzed.

Session FG-3
Emerging and New Generation Solar Cells

FG-3:IL01 Applications of Metal Oxides in Organic Photovoltaics

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Improvements in the performance and lifetime of organic photovoltaics (OPV) are critical to its development as a viable technology. Metal oxides can leveraged to improve both of these in OPV devices. The most common use of metal oxides in OPV devices is as a transparent electrode. Alternatives to ITO could help to enhance device performance and lifetime as well as reduce the materials costs. The second application is the use of metal oxides as selective hole or electron transport layers (HTL/ETL) in OPV devices. These allow for ohmic contact to one phase of the active layer while acting as a electron or hole blocking layer to reduce recombination and dependance on unstable electrode materials. Finally, metal oxides have been successfully used as electron acceptors in hybrid-OPV devices through the use of polymer/metal oxide nanoparticle blends or nanostructured metal oxide acceptors. In this talk, I will provide a brief overview of the operational mechanisms of OPV devices and discuss what parameters are currently limiting power conversion efficiencies and lifetimes. Finally, I will discuss our current efforts on new contact materials and device architectures that lead to enhanced device stability and performance as mentioned above.

FG-3:IL02 Novel Photoactive Materials for Polymer Solar Cells

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Polymer solar cells are attractive in view of their potential application for low-cost solar energy conversion. The devices generally consist of a donor-acceptor bulk hetero-junction in which a donor and hole transporting conjugated polymer is mixed with an acceptor and electron-transporting molecule or polymer. The optimization of the device architecture and of the photoactive materials led to significant improvements in the last few years, with power conversion efficiencies reaching values beyond 5%. Further significant improvements in device efficiencies are expected by developing novel photoactive materials. While various conjugated polymers have been tested as donors in bulk heterojunctions, the mostly used acceptor component is PCBM. This fullerene derivative has led so far to the best solar cells performances but it has the drawback of having a weak absorption in the visible region. For this reason there is an interest in studying other acceptor molecules or polymers with better light harvesting respect to PCBM and several groups focused on novel acceptor materials based on perylene bisiimmide dyes. In this contribution we present our work on a series of perylene-based molecule and polymers, designed and tested as acceptor materials in polymer bulk heterojunction solar cells. The relation between their electronic properties, the photoactive film morphologies and device performances is discussed.

FG-3:L03 **Vertical Stratification in P3HT:PCBM Organic Solar Cells**
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It is increasingly recognized that vertical phase segregation and structure within OPV devices is at least as important as the lateral phase segregation, which has received much more attention to date. Despite a number of publications inferring vertical phase segregation in P3HT:PCBM devices, it is only very recently that direct measurements of the vertical composition and structure within the active layer have been reported. The variation of vertical composition must play a critical role in all aspects of the charge generation and extraction process and, as is the case for lateral phase segregation, will heavily influence dissociation and recombination dynamics. Furthermore, vertical composition will have a major influence on charge transport across the active layer/electrode interfaces. Whilst an understanding of relative surface energies of the component materials allows us to infer to what degree vertical phase segregation may occur within these blends a direct study of the actual segregation is crucial to device understanding. The role of thermal treatment in device fabrication has been investigated. In particular, the effect of the post-annealing cooling rate has been studied. The data show that slower cooling rates result in significantly enhanced device efficiencies primarily driven by increased short circuit current and fill factor. Near-edge X-ray absorption spectroscopy (NEXAFS), X-ray diffraction (XRD) and UV-Vis spectroscopy have been used to probe the origin of these differences. The results show evidence for distinct and changing vertical stratification in the device upon annealing with both composition and crystallinity varying through the active layer. The implications of these changes are discussed in terms of device properties.

FG-3:L04 **The Influence of the Electron Acceptor on the Optical Constants of the Photoactive Layer of a Polymer Solar Cell**
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Polymer solar cells have evolved as a promising cost-effective alternative to silicon-based solar cells. One of the problems for the use of such devices in commercial applications is the relatively small device efficiency that have been reached up to now. The short circuit current (Jsc) of these cells is strictly related to the absorption of the blend film. Recently it has been shown that the use of [70]PCBM as electron acceptor can improve the current output of such device because C70 derivatives have a stronger and broader absorption compared to C60 ones. The aim of this work is to study the influence of the fullerene on the optical behaviour of the photoactive blend film of a polymer solar cell. We have determined the optical constants of polymer blend film based on P3HT and [60]PCBM or [70]PCBM. We also studied how different preparative conditions (solvent, annealing temperature, ratio between the components) influence the optical constants of such blend. Afterward, we simulated the optical absorption of the active layer inside the device structure and we calculated the maximum achievable Jsc with the aim to correlate the variation of the optical constants to the output current of the device.

FG-3:L05 **The Suitability of Organic Solar Cells for Different Indoor Conditions**
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Most commercially available photovoltaic solar cells are crystalline silicon cells. However, in indoor environments, the efficiency of Si-cells is poor. Typically, the light intensity under artificial lighting conditions is less than 10 W/m² as compared to 100-1000 W/m² under outdoor conditions. Moreover, the spectrum is different from the outdoor solar spectrum and there is more diffuse than direct light. Taken into account the predicted cheaper costs for the production of organic solar cells, a possible niche market for organic PV can be indoor applications. In this article, we study the properties and suitability of several bulk heterojunction organic solar cells (with distinct different absorption spectra) for different indoor conditions. We simulate different light environments (among others home, office and factory) and use a silicon solar cell as reference. Depending on the required power for the indoor device, we determine minimum requirements for the environment (light intensity and indoor spectrum) and for the organic solar cell (absorption spectrum and surface area). In this way we determine the appropriateness and conditions for a competitive indoor use of organic solar cells.

FG-3:IL06 **Development of Film-type Bifacial Dye-sensitized Solar Cells**
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High efficiency dye-sensitized solar cells (DSSCs) and large-area integrated modules have been constructed on plastic substrates based on the low-temperature TiO2 coating method by using binder-free nanocrystalline TiO2 pastes and ITO-coated plastic film. The glass to plastic conversion contributes to cost reduction by roll-to-roll rapid process. With a miniature test cell sensitized by Ru complex N719, 6-7% power conversion efficiency and IPCE of 70% were obtained under AM1.5 simulated sunlight. Synthetic organic dyes with high extinction coefficients yield 4% and more with much thinner TiO2 film. To make full plastic cells with printing processes, counter electrodes with semi-transparency were prepared by means of coating PEDOT-based mesoscopic films that replace the conventional platinum film used as cathode catalyst. Bifacial type flexible DSSCs were fabricated which show excellent performance even under weak light and indoor illumination. Large-area integrated modules have been constructed for proof-of-concept study. Equipped with current-collecting grids, modules achieved 2-4% depending on the light intensity. A world largest plastic module, integrated with 96 unit cells, of 2 m2 in size, 1 mm in thickness, and lightweight of 1 kg m2 generates more than 110 V under exposure to room illumination. We are testing various façade applications of the modules. The durability of the plastic DSSC showed 1,000 hr under continuous exposure to 1 sun irradiation at a cell temperature of 50 C.

FG-3:IL07 **Mesoscopic Charge Transport in Dye-sensitized Solar Cells**
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Dye-sensitized solar cells (DSC) have reached overall solar-to-electrical energy conversion efficiencies in excess of 11% and present a credible alternative to conventional solar cells. Electrolyte additives, light exposure, as well as thermal aging were reported to have a significant effect on the charge transport and recombination, and consequently the power conversion efficiency and stability of the devices. However, the mechanism of interfacial charge transfer has yet been fully understood and the determination of charge collection efficiency suffers from significant discrepancy among different techniques. Here we will report some of our recent progress on the understanding of the charge collection process through the mesoscopic photoanode system of DSC. The following topics will be discussed in details: (1) Interfacial charge transfer mechanism in the presence of potential determining ions; (2) Reliable measurement of electron diffusion length; (3) Enhanced charge collection by modifying mesoscopic TiO2 electrode; (4) Cross-surface charge percolation for functional mesoscopic counter electrode.

FG-3:IL08 **Tandem and Hybrid Structure for High Efficiency Dye-sensitized Solar Cells**
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Efficiency of dye sensitized solar cells (DSC) has reached 11%. In order to increase the efficiency, we propose 3D DSCs consisting of hybrid and tandem structures to cover wide ranges of wavelengths and collect electrons effectively. Three types of 3D DSCs are reported. One is a DSC consisting of a dye-double layer titania structure. The dye-double layer was prepared by dye staining under a pressurized CO2 process. The top layer absorbs light at shorter wavelength and the bottom layer absorbs that at longer wavelength. They have a parallel connection structure. The second cell is a 3D-DSC consisting of a floating TiO2 porous sheet as the bottom electrode and a porous TiO2 layer on a FTO glass as the top electrode. They are connected in series. The floating electrode was fabricated on a metal mesh electrode which was covered with thin back electron transfer blocking layers. The last one is a fiber type DSC aiming at full spectrum DSCs. This has a TCO-less structure which has an advantage of high transmittance of light in the N-IR and IR regions over conventional flat type DSCs, where FTO glasses absorb light in the N-IR and IR regions. The fabrication process and the fundamental tandem and hybrid performances are reported.

FG-3:L09 **Near-IR Sensitization of Nanocrystalline TiO2 with New Ruthenium Complexes**
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In order to improve the efficiency of dye-sensitized solar cells (DSSCs), the development of sensitizers is an important issue. Ruthenium complexes, so-called red (N3) dye and black dye, are the most popular sensitizers, and they absorbs up to 750 nm and up to 900nm of light, respectively. In order to improve the spectral sensitivities of DSSCs in near IR region, we have tried to tune the energy levels of the Ru complexes both in ground state and in excited state by modifying the ligands. Quinolin rings can be used in the place of pyridine rings in order to tune the energy levels of LUMO of the complexes. Various auxiliary ligands were applied in the place of isothiocyanato ligands to tune the red-ox level of Ru complexes in the ground state (HOMO). Cyclometallated Ru complexes and Ru complexes having pyridinecarboxylato were also examined. Solar cells based on Ru complex having diqunolylpyridine derivative and three isothiocyanato ligands showed a considerable conversion quantum efficiency in near IR region. IPCE of one of the cells sensitized with these dyes was over 35% at 900nm.

FG-3:L10 **DSSC Counterelectrodes Based on Nanocarbons**

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Dye Sensitized Solar Cells (DSSCs) is highly promising technology for low cost high efficiency solar energy conversion. The working principle of DSSCs is a two step process: a photon excites a dye molecule that injects an electron in a porous nanostructured TiO2 layer, a redox reaction in the electrolyte provides to regenerate the dye. The current flows in an external load through the counterelectrode, where the reduction of the redox couple has to be catalyzed in order to maximize the current. Usually Pt nanoparticles are used as catalyst on the counterelectrode, however, by substituting Pt with a stable and cheap material it should be possible to improve the stability of the cell reducing the production costs. Several works have been recently published on carbon and carbon nanotubes substituting Pt at the counterelectrode, nevertheless few about transport properties and catalysis mechanisms are known. We assembled DSSCs with different kinds of nanocarbons counterelectrodes. Electrochemical Impedance Spectroscopy was applied to our cells to relate different carbon nanostructures morphology and electrochemical properties. Carbon nanostructures showed a very low impedance to the charge transfer process,and therefore seem to be ideal candidates as counterelectrode materials in DSSC.

FG-3:IL11 **Italian Road Map for Emerging and Next Generation PV**

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The 21 century brings numerous challenges and opportunities will affect energy production, economic, and environmental security of each nation worldwide. The sun spectrum is the largest energy input into the terrestrial system. Although photovoltaics is not the sole answer to the myriad of renewable energy challenges offered by the clean and economical use of the sun, it can represent an important contribution to the economy of each country. The cost is declined by a factor of nearly 150-160 times since the invention in 1954 of the modern solar cell based on crystalline silicon technology. The fantastic boom of PV technology happend during last years can suggest further development mainly due to the application of innovative concepts to conventional thin film materials and new class of them coming from nanotechnologies, photonics, optical metamaterials, plasmonics and new semiconducting organic-inorganic sciences, all them recognized as 3rd generation approach. The paper will present the main Italian initiatives on research and production to meet the next PV generation of flat and PV concentration options.

FG-3:L12 **Active Materials Based on Implanted Si for Obtaining Intermediate Band Solar Cells**

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First-principles calculations carried out for compounds based on Si implanted with different species, as Ti or chalcogens (S, Se, Te), show that they are solid candidates to be used as intermediate band (IB) photovoltaic materials. This DFT study predicts electronic structures, formation energies, relaxed atomic structures, optoelectronic properties, diffusion paths, for supercells containing up to several hundreds of atoms. The knowledge of Si-based devices is a relevant factor to facilitate the creation of an IB solar cell. Crystalline samples with a concentration of Ti several orders of magnitude above the solubility limit have been already grown. Formation energy calculations agree with the experiment in showing mainly interstitial implantation. Calculated electronic structure presents an IB, which is in agreement with electrical measurements and models, and is expected to cause an increase of the absorption coefficient across the solar spectrum. Chalcogen-implanted Si is an efficient IR absorber when implantation is carried out at ultra-high concentrations. Substitutional implantation produces a filled band inside Si band-gap and our calculations predict that plausible co-doping with IIIA atoms (as Al, B) would allow to obtain an IB fulfilling all the needed requirements.

FG-3:L13 **Single-phase Intermediate Band Materials for PV Cells: Quantum Calculation Assessment and Experimental Realisation**

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An increase in PV efficiency (ideally, from the 40.7% Queisser limit to a 63.2%) has been proposed to be possible using intermediate band (IB) materials, in which an electron can jump from the valence band (VB) to the conduction band (CB) upon absorption of two sub-bandgap energy photons if a partially filled, isolated IB exists between the VB and CB. With DFT simulations we have proposed that partial substitution of Ga by Ti or Cr in GaAs, GaP or CuGaS2 can lead to this property. Our more recent work shows that this can be achieved also substituting by Ti or V the octahedrally coordinated cations in In2S3 (with bandgap Eg=2.0 eV, close to optimum for this purpose) and related materials. This octahedral geometry would allow to insert high metal amounts (in the 10% range), leading to stronger sub-bandgap light response than is possible with other proposed IB schemes. Here we present an overview of different systems where the IB can be achieved in this way according to our DFT calculations, that can predict their band structures and optical absorption spectra, and show the experimental realization of several such materials, mainly of sulphide class, whose optical spectra show for the first time the strong IB-based sub-bandgap photon absorption features predicted for them by DFT.

FG-3:L15 **Electrical Transport Mechanism for Silicon Quantum-dots Based Solar Cells**

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Tandem cells are one of the new third generation PV cells designs proposed to overcome the efficiency limit of classic single junction silicon cells. They are made of a multilayered structure with different band-gap materials which perform a selective absorption of the solar spectrum. The Silicon-Rich Oxide is one of the new materials currently object of research for the realization of such a cell: it consists of non-stoichiometric silicon oxide annealed at high temperature. This makes the excess silicon precipitate forming quantum dots. The quantum confinement effect of carriers induced by this nanostructuration allows the optical band gap of the SRO to be tuned, increasing it from the value it has in bulk silicon. Moreover, there are no concerns about the toxicity of SRO, and its realization process is fully compatible with the microelectronic industry. For this material to be suitable for the realization of solar cells, it is necessary to understand and optimize the charge transport mechanism. In this work we will present the identification of the carrier transport mechanism by the firsts current/voltage (I/V) measurements made in the temperature range from 300K to 10K as well as the optimization of the charge collection by a study of the effects of different types of contacts.

FG-3:L16 **Optimizing Quantum Dot Solar Concentrators with Thin Film Solar Cells**

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Luminescent solar concentrators (LSCs) are a possible low cost alternative for widespread deployment of photovoltaics. These concentrators absorb photons, which can subsequently be re-emitted, with a slight red-shift, and collected on one or more sides of the LSC plate. Currently, organic dyes are used with absorption maxima up to typically 600 nm. Silicon cells, with band gap of 1.1 eV, while readily available, are not the optimum candidate for application in an LSC, as a large part of the solar spectrum (between 600 and 1050 nm) is not absorbed in the LSC. Thus, conversion efficiencies of 3-4% have been reported for LSCs with c-Si solar cells, while 7% is reported for LSCs with higher band gap III-V cells. We propose to use quantum dots (QDs) as luminescent species in the LSC in combination with thin film silicon cells. Tuning of absorption and emission of QDs is easily possible by adapting process conditions during growth. Tuning of the band gap of thin film solar cells is also easy, by adapting process conditions during growth or by alloying. This gives two possibilities for finding the optimum match of QDs and the thin film solar cell, to obtain the highest attainable efficiency. This contribution will present a modeling study that explores the routes for optimization.

FG-3:L17 Cooperative Near-infrared Quantum Cutting in YVO4: Yb3+, Tm3+ Nanophosphors

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The near-infrared quantum cutting phosphors have attracted attention in the last few years for their promising application in silicon solar cells. In this presentation, fine particles Y0.99-xYbxVO4: 0.01Tm3+ (0 = x = 0.3) were prepared by the hydrothermal process. The cooperative energy transfer from Tm3+ to Yb3+ has been investigated by the emission spectra of Yb3+, Tm3+ and the decay lifetime of the 1G4 emission from Tm3+. Upon excitation at 474nm (1G4?3H6 transition of Tm3+), the intensity of emissions from Tm3+ around 647nm (1G4?3F4 transition) were decreased with increase of the concentration of Yb3+, while the emissions from Yb3+ around 980nm and 993nm (2F5/2?2F7/2 transition) were increased. The decay lifetimes of the 1G4 emission from Tm3+ were reduced with increase of the concentration of Yb3+. Therefore, two NIR photons were obtained by Yb3+ (2F5/2?2F7/2 transition) through an efficient cooperative energy transfer from Tm3+ to two Yb3+ ions. According to calculations, the quantum efficiency is proved to be close to the limit of 200% in downconversion process. Accordingly, the NIR QC phosphors YVO4: Yb3+, Tm3+ could be applied potentially in silicon-based solar cells, due to the energy of Yb3+ 2F5/2?2F7/2 transitions does match with the band gap of Si.

FG-3:L18 Thin-Film Si Solar Cells Using Back Reflector with Embedded Metal Nanoparticles

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Light trapping in the absorber layer of thin-film solar cells is of great importance for obtaining a high photocurrent. A novel light-trapping technique is based on light scattering by metal nanoparticles through excitation of localized surface plasmons. In this study, we demonstrate that the plasmon resonance frequency can be tuned by changing the embedding medium and the particle size. Furthermore, amorphous silicon solar cells with Ag nanoparticles embedded in ZnO/Ag back reflector were investigated systematically. By evaporation of Ag layers with different thicknesses followed by thermal annealing, nanoparticles with different sizes were formed. The size distribution of the fabricated nanoparticles inside the solar cell structure was determined by analysis of scanning electron microscope images. The performance of the solar cells was characterized by quantum efficiency and current-voltage measurements. Both the external quantum efficiency in the wavelength region of 600 to 800nm and current density increase as particle size increases, but remain lower than those of the reference device without particles. These results show that nanoparticles can enhance light scattering but also cause significant parasitic absorption. Possible ways to reduce this absorption are discussed.

FG-3:L19 GaAs-based Nanowire Arrays Grown by MOVPE on (111)Si Substrates for PV Applications

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Free-standing nanowires (NWs) of III-V semiconductors were recently demonstrated to show PV properties, with efficiencies exciding a few percent; theoretical considerations suggest that these structures are ideal building blocks for the realization of high efficiency PV cells. Improvements in the NW synthesis and materials properties are needed to meet these potentials. Self-assembly of III-V NWs by the Vapour-Liquid-Solid (VLS) method utilising metalorganic vapour phase epitaxy (MOVPE) appears a most promising approach in terms of process/materials control and industrial scale-up of NW-based cells. The growth of dense and vertically aligned NWs is a pre-requisite for optimal control of the NW size, length and physical-chemical properties. Also, use of Si instead of GaAs as substrate allows to reduce materials costs and increase wafer areas. We report on the growth of free-standing GaAs-based NWs on (111)Si substrates by MOVPE, utilising Au nanoparticles as catalysts for the VLS process. Dense arrays of (111)-oriented (i.e., in the direction normal to the substrate surface plane) GaAs NWs can be obtained upon growth of a thin (few hundreds nm) GaAs epilayer on the substrate. GaAs-AlGaAs core-shell NWs have been grown on GaAs/Si templates and their luminescence properties studied.

FG-3:L21 Metamorphic GaAsP/Si Materials for Spectrum-Optimized Si-based Multijunction Solar Cells

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Recent work (T.J. Grassman *et al*, Appl. Phys. Lett. 94, 232106, 2009) has shown that device-quality GaP layers can be directly grown on Si substrates with the simultaneous elimination of anti-phase domains (APDs), stacking faults (SFs)and microtwins (MTs). This opens the possibility of creating III-V/Si based multijunction solar cells having ideal bandgap profiles with projected one-sun efficiencies >40% while being compatible with silicon manufacturing. Here, optimum GaP/Si substrates are used to achieve high quality GaAsP/Si solar cells in which GaAsP metamorphic buffers can enable optical and electrical connection between high bandgap III-V sub-cells and Si subcells/substrates. This is possible due to the range of lattice constants accessed by the GaAsP alloy system and its wide bandgap compared to the underlying Si. MBE growth produced low dislocation density, relaxed GaAsP buffers on Si without SF, APDs and MTs. Preliminary GaAsP diodes and cells on Si with bandgaps >1.6 eV revealed outstanding I-V characteristics, quantum efficiencies and current output that matches theoretical expectations for these bandgaps. The presentation correlates growth, defects and device performance, and discusses progress toward high performance GaAsP/Si dual junction cells.

FG-3:IL22 Intermediate Band Solar Cells

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Intermediate band (IB)solar cells aim to exploit the energy of below bandgap energy photons in solar cells. They are based in a material that, in addition to the conventional conduction and valence bands, they have an electronic band (named intermediate band) located inside the bandgap and separated from the conduction and valence band by a null density of states. The theoretical limiting efficiency of these cells is equivalent to a triple junction solar cell (63.2% at maximum concentration) but requiring a single material instead. Several approaches are being followed worldwide to take to practice this concept. They can be classified into “bulk” or “quantum dot” approaches. In the “bulk” approach, the IB emerges from the insertion of impurities that can be incorporated inside the semiconductor at high densities (beyond the Mott’s transition) without forming clusters and that typically produce deep centers at low densities. In the “quantum dot” approach, the IB arises from the quantum confinement of the electrons usually in the conduction band. These approaches are reviewed in this work reporting the most recent experimental results.

FG-3:IL23 Quantum Dot-sensitized Solar Cells and Ultrafast Carrier Dynamics Characterization

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Dye-sensitized solar cells have been the focus of attention as a promising alternative to conventional Si solar cells. However, the expensive and using special organic dyes has encouraged the pursuit of alternative light harvesters. Semiconductor quantum dots (QDs)could provide the solutions due to its tunable gaps, large intrinsic dipole moment, and large extinction coefficient. Also, the QD-sensitized solar cells ahve capability of producing multiple exciton generation (MEG). We demonstarte a nobel approach to sensitized solar cells, based on different kinds of TiO2 electrodes and the use of semiconcuctor QDs as sensitizers. The photovolatic performance depends on the morphology of the electrode and significantly improved with surface passivation and use of Cu2S counterelectrode. A photovoltaic conversion efficiency of 3.5% can be attained and this value is relatively high for semiconductor QD-sensitized solar cells. Ultrafast carrier dynamics measured with transieint grating (TG) technique show a fast (hole) and slow (electron) decay processes with lifetimes of a few picosecond and a few tens to hundreds picoseconds, resectively. There is a correlation between the photovoltaic properties and the lifetimes of photoexcited carriers.

FG-3:L24 Efficient Energy Collection for High Efficiency Low-cost Solar Cells

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This paper outlines a novel approach to photovoltaic conversion which divides the process into two natural stages, making use of materials with different optical and electronic properties for each of the two fundamental steps: a molecular / nanostructure collector which efficiently absorbs light and transfers energy (rather than electrons) to a semiconductor converter which separates the photo-generated charges and produces electricity. Each part of the structure can be optimised independently, leading to efficient light absorption and energy conversion within a compact device, with low material requirements and low cost. Since light is absorbed in narrow-band electron states with little energy dissipation to phonons, these structures have much potential for implementing “third generation” technologies to achieve very high overall conversion efficiencies. The key requirement for efficient operation of this structure lies in the energy management and collection, necessitating highly efficient transport of the photogenerated energy to the semiconductor converter. Potential vehicles for this transport, to be discussed in this paper, are photonic fluorescent energy collection, and excitation energy transfer similar to the light harvesting process of photosynthesis.

FG-3:L25 **Thin Film Luminescent Solar Concentrators**

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Luminescent Solar concentrator (LSCs) were developed by Goetzberger and Greubel in the late 1970s and promise to reduce the cost of photovoltaic electricity. LSCs consist of highly transparent plastic and glass plates, in which luminescent species, originally organic dyes and more recently quantum dots, are uniformally dispersed. Total internal reflection ensures a portion of the emitted luminescence travels to the edge of the plastic plate where a solar cell is attached. LSCs have advantage over geometric concentrators in that both direct and diffuse solar radiation can be collected without solar tracking. The development has been limited by the performance of luminescent species parameters, quantum efficiency, re-absorption and photostablity. Thin film LSCs offer the possibility of reducing re-absorption effects by confining all the absorption and emission in the doped thin film while trapping occurs in the transparent substrate. In this paper, the fabrication and characterization of thin film luminescent solar concentrator is described. Thin films of PMMA were embedded with different concentrations of luminescent species deposited on a thicker transparent plate of same refractive index by spin coating and thermally polymerised.

FG-3:L26 **Indium Gallium Nitride on Silicon Solar Cell Grown by Plasma Assisted Molecular Beam Epitaxy**

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With the popularity and the success of Si solar cells, constrains of the Si materials are under careful examination to seek ways of improvements. Due to the intrinsic band structure, Si can cover only a limited range of the entire solar spectrum and more than 50% solar energy is wasted. A logic solution is to combine the mature technology of Si solar cells and the wider solar spectrum covering capability of III-V nitrides, for example, to create a multi-hetero-junction device for higher energy conversion efficiency. From simulation results, to achieve the best energy conversion for a tandem Si solar cell with two junctions, it needs a material which has an energy gap around 1.79 eV which falls just right in the InGaN ternary system. In our work, we use plasma-assisted molecular beam epitaxy system to grow InGaN right on top of a Si solar cell aiming for a hybrid solar cell structure. The surface of the Si solar cell is chemically etched by KOH to form a pyramidal morphology to reduce total reflection. Scanning electron microscopy shows the surface morphology and the cross sectional profile. X-ray diffraction peak of InGaN signal yields an estimation of the In content which is compared with the compositional analyses from the energy dispersive spectrometry. Optical properties are investigated by photoluminescence, cathodoluminescence, and Raman spectroscopy.

Session FG-4

PV Devices, Modules, Systems and Applications

FG-4:IL01 **Cost-reducing Technologies for Crystalline Silicon Solar Cells and Modules**

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Silicon continues to be the dominant technology in the commercial photovoltaic market with about 85% of the market share. To maintain this leading role, silicon photovoltaics (Si PV) must compete with emerging thin-film solar cell technologies, but also, with other existing energy technologies. Si PV faces many challenges, in both technology advancement and cost reduction. Because cell/module efficiencies play a controlling role in the cost of a PV system, improving these efficiencies is of paramount interest in lowering the PV energy cost. The two major costs of Si PV are related to wafer production and module encapsulation. Thus, costs can be reduced on many fronts, including using new, lower-cost cell processing technologies; reducing Si wafer cost; and automating wafer/cell handling and encapsulation. This paper will address technical challenges in significantly lowering the Si PV energy cost. We will emphasize the following issues: (1) production, handling, and cell processing of thinner wafers, (2) advanced solar cell processing techniques that can overcome current efficiency limitations, and (3) module designs with lower optical losses.

FG-4:IL02 **Recent Results of CIS-based Thin-film PV Technology Fabricated by "Sputtering and Sulfurization/Selenization"**

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Taking the opportunity of supply shortage of crystalline-Si solar cells, First Solar with a matured CdTe PV technology is growing up towards a GW-production company. They became the 2nd world largest in 2008 and are currently a price leader in the solar-PV industry, which would be a victory of their business strategy. Cu(InGa)(SeS)2(CIS)-based thin-film PV technology is widely being expected to compete with the first-generation thin-film PV (i.e. amorphous Si and CdTe) on both the performance and the production cost. However, this technology is still immature comparing to them especially on mass production technology. As the result, this is still in the stage of production research of an annual production range of 20 to 30 MW. Many companies worldwide have announced to move towards the production stage since 2006 with wide variety of deposition technologies and different materials for the device structure, not only CIS-based absorber formation by coevaporation or selenization/sulfurization processes, but also other thin film layers. Among them, only Showa Shell Solar K.K., which has been employing a "sputtering and sulfurization after selenization" process for the absorber formation and a Cd-free device structure, decided to move towards the GW production by 2011.

FG-4:IL03 **Fabrication and Processing of Polymer and Organic Solar Cells**

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Polymer solar cells are a technology that is at the brink of commercialisation. The first attempts to manufacture polymer solar cells on a large scale has been documented and while there is some research and development needed before polymer solar cells can contribute towards covering a significant part of the global energy demand the technology in its present form is ready for small applications. The manufacture of polymer solar cells is discussed and examples of first products and demonstrations will be detailed.

FG-4:IL04 **New Design and Integration of High Efficiency Dye Sensitized Solar Cell (DSC) Module**

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The parallel connection and the series connection as Z- or W- type have been widely used for DSC modules design[1-3]. However, the Z-type requires application of the dye by pumping after sealing. This process utilizes much dye and has a risk of dye adsorption on the counter-electrode. The W-type requires the two electrodes produced on one substrate. There are also potential issues of imbalance under different light conditions. All of these requirements result in the complication of manufacture.[2] We designed a new type of DSC module with both of parallel connection and series connection. A new series connection called side-contact was used in our modules. Due to the side-contact, which is easy to carry out, the whole manufacturing processes are as easy as producing the parallel connection only. Based on this new kind of connection, we developed a method to optimize the module design according to the different performance of the small DSCs.

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[1]Han, L.Y. et al, Appl. Phys. Lett., 2009, 94, 013305; [2]Tulloch, G.E.J. Photochem. Photobiol. A, 2004,164, 209; [3]Kato, N. et al, Sol. Energy Mater. Sol. Cells., 2009, 93, 893

FG-4:IL05 16.4% Open Aperture Module Efficiency Using Large mc-Si Metal-wrap-through Cells

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We obtained an independently confirmed module aperture area efficiency of 16.4% using 36 large and thin mc-Si metal-wrap-through (MWT) cells. Advantages of our MWT cell design are for example the higher cell output due to less shading losses, and easy module integration which will result in an additional gain in module output. This gain is caused by the lower series resistance in the cell interconnects and the higher packing density of the cells in the module. A patterned conductive foil is used as the module substrate for series interconnection of the cells. The cells are placed on the foil using a method analogous with pick-and-place technology used for SMD in the electronics industry. This reduces cell handling to just one pick-and-place step so limiting potential damage to the cells. Contact between the cells and the conductive foil is made using a conductive adhesive. Because the processing temperature of the conductive adhesive matches the lamination temperature of the encapsulant (EVA) a single shot module assembly process can be carried out. A dedicated module manufacturing line was designed using this technology to be able to work with extremely thin cells and to provide a high throughput of one 60 cell module per minute. Our 16.4% module was made using this pilot line.

FG-4:L06 Design Analysis of a-Si/c-Si HIT Solar Cell

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A theoretical design analysis using two dimensional computer aided design tool (TCAD) is presented for a-Si/c-Si based heterojunction (HIT) solar cells. Various physical parameters of the layer structure such as doping and thickness of the c-Si layer, defect density in the amorphous Si layers and bandgap discontinuities have been studied. The device performance is further evaluated by implementing special models (surface recombinations, interface traps etc) at top and bottom side of the heterojunction interfaces (semiconductor-semiconductor interface and semiconductor-metal interfaces). With varying bandgap discontinuities and using standard transport model in numerical device simulation, we noticed that the HIT solar cell performance is undervalued (Jsc of 32 mA/cm2, Voc of 0.72V,fill factor of 0.82 and efficiency of 14%). This is the result of the poor photo-generated carrier collection due to the presence of heterojunction at the respective n and p contacts of the device. Implementing thermionic field emission tunneling model at the heterjunction, we obtained improved perforemane (Jsc of 40 mA/cm2, Voc of 0.733 V, fill factor of 0.82 and efficiency of 18%). We further noticed that the device electrical behavior is fairly smooth over large range of bandgap discontinuities.

Poster Presentations

FG:P02 P and Al Diffusion Process for Thin Si Wafers Studied by SEM and EDX

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In order to reduce the cost per watt of photovoltaic power a main issue is the reduction of cell thickness in crystalline or polycrystalline silicon solar cells to save expensive material. However, due to the fragility of the substrate the manufacturing processes have to be adapted to the new conditions of the wafers. The aim of this study is to optimize processes suitable for production of extremely thin cells focusing in two of the solar cell fabrication steps: P diffusion for pn junction and Al diffusion for BSF formation. SEM analysis has been used to monitor BSF junction uniformity and EDX to determine composition of the diffused Al layer formed by screen-printing and rapid thermal processing (RTP). The influence of the preparation conditions is studied in order to avoid the formation of an eutectic Al-Si alloy, that is the responsible for the bow of thin wafers. Phosphorus deposition has been carried out by spray coating, a technique that allows in-line implementation and reduces manipulation of the cell. Samples were prepared on 250 and 100 um silicon wafers, we compare various mixtures of H3PO4 as precursor, the resulting emitters were characterized measuring their surface resistivity and analyzing surface composition by XPS and FTIR.

FG:P05 Quantum Size Effects in a-Si:H Films Prepared by PECVD with Different Hydrogen-diluted Silane

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Quantum size effect (QSE) comprises novel phenomena where structural, mechanical, thermal, electronic and optical properties of solids are affected by the reduction in particle size. Size-dependent properties in semiconductors and dielectrics come into play especially by making one (thin films) or more (quantum wires and dots) dimensions of a sample very small, particularly going from micro to nano-dimensions. One or more dimensional QSE is accompanied with an increase of the light absorption and the blue-shift of the optical band-gap due to a creation or reduction of the crystallite sizes having different dielectric constants (relative permitivity). Understanding the nature of the size-induced properties is of fundamental importance for advanced technological applications. The size-dependent band-gap makes a material attractive for optical absorption-based applications. In this work, a-Si:H films different in thickness were prepared by PECVD technology using different hydrogen-diluted silane. One-dimensional QSE (when film thickness decreased) and three-dimensional QSE (when due to a high hydrogen-silane dilution the nano-crystalline structure of the films appeared) were observed.

FG:P06 Adhesion and Barrier Properties Analysis of Silica-like Thin Layer on Polyethylene Naphthalate Substrates for Thin Film Solar Cells

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In thin film photovoltaic technology, polymer films are very attractive substrates being light, flexible, non-breaking, feasibility of large area series-connection and particularly appropriate for building integration. Although several low-cost plastic foils have been proposed as substrate for thin film solar cells, polyethylene naphthalate (PEN) is the most attractive material due to its low cost and its better thermal (up to 170°C) and mechanical resistance. A biaxially oriented PEN, 125 µm thick extruded foil, was used in this study. The polymer surface is usually hydrophobic and inactive to chemical reactions, causing adhesion problems, furthermore gas desorption from the polymer sometimes causes serious problems to the quality of the devices. To overcome these problems a thin films of silica-like functional material have been developed on polymer foil. Silica-like is suitable as adhesion and diffusion-barrier layer in solar cells. Silica-like films were produced by sol-gel process starting from an organic silanes compound (APTMS) as precursor and the solution was deposited by spin-coating. Amorphous silica-like films were obtained with a hydrophilic surface. They were smooth, dense, homogeneous, transparent and exhibited an excellent adhesion to the polymer substrate due to the chemical bond between amine groups of the APTMS with carbonyl bonds in PEN. Wettability, adhesion and gas permeation of silica-like layer were performed. Structural analysis was carried out by FTIR spectroscopy, morphological and surface properties were studied by SEM and AFM.

FG:P07 Local Mapping of Electrical Properties and Durface Topography of CuInS2 Thin Films Seposited by Spray Pyrolysis on Conductive Layers

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Undoped CuInS2 thin films have been prepared by spray pyrolysis on Al-doped In2S3 / SnO2 / glass substrates. Structural properties of the different layers composing the heterostructure is studied using X-ray diffraction analysis. Crystalline texture is obtained. Cross section electron beam micrographs show agregates of nano-crystallites following columnar growth direction. The local electrical conductivity of the heterostructure is probed at the micrometer scale, using the SnO2 layer as bottom contact, and a metallic refined tip as top contact. Images of the intensity of the electrical current flowing between tip and bottom contact is obtained. It exhibits contrasted domains where electrical conductivity varies by two orders of magnitude, or more. The electrical current flow through the heterostructure is addressed in terms of the effects of the stacking layers. Electron beam micrographs of the CuInS2 surface is performed and compared to the local electrical conductivity images. Correlation between the morphology of nano-crystallite aggregates and the shape and size of the domains observed on the electrical images is discussed.

FG:P12 **Investigation of Thin Film CdS/CdTe Solar Cells with Different Back Contacts**

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The peculiarities of photoelectric processes in thin film CdS/CdTe solar cells (SC) with different back electrodes (Cu/Au, ITO or Cu/ITO) have been studied. Efficiencies of SC glass/FTO/CdS/CdTe/Cu/Au are 10-11%, and for SC glass/FTO/CdS/CdTe/ITO one are 7-8%. The investigation of spectral photosensitivity for SC with ITO back contact demonstrates low quantum efficiency at 500 - 650 nm wavelengths. The researches of capacity-voltage characteristics have revealed that potential barrier height for CdTe/Cu/Au equals 0.3 eV, but for CdTe/ITO it is 2.2 eV. The majority charge carriers concentration near back contact are 9E+20 m-3 and 2E+21 m-3, correspondingly. High majority charge carriers concentration and big potential barrier for CdTe/ITO stipulates tunnel-recombination mechanism for the charge transport. It has been shown that deposition of Cu nano-layer before ITO deposition allows manufacturing of stable SC with 10% efficiency. It has been established that the observed peculiarities of light IV characteristics (IVC) at back lighting of this SC are photo-effect effect on the back contact diode p-CdTe-Cu/ITO. For the modeling of such light IVC we have proposed modified equivalent circuit, which contains two illuminated diodes: frontal diode n-CdSxTe1-x/p-CdTe and back diode.

FG:P13 **Nanofibrous TiO2: A new material with extraordinary properties**

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Nanofibrous TiO2 prepared by means of electrospinning represents a novel material with specific properties resulting from its unique morphology. Anatase or rutile nanofibres exhibit "shape memory". Their shape withstands both high temperature annealing (800 °C) and even chemical transformation. Hence, the product of the reaction of nanofibrous anatase with ammonia in gas phase is nanofibrous cubic titanium oxynitride, c-TiOxNy. In contrary to the preparation of cubic titanium oxynitride from microcrystalline TiO2, requiring temperatures above 800 °C, the conversion of nanofibrous TiO2 to TiOxNy is completed at about 500 °C due to its enhanced chemical reactivity. This conversion is fully reversible; the product of the back reaction is again nanofibrous TiO2. Fibrous anatase has been recently used as a component improving the performance of dye sensitized solar cells; fibrous TiOxNy is a material of huge application potential due to its high electric conductivity and hardness.

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FG:P14 **Band Structure in Amorphous Carbon Nitride Films and Its Application in Thin-Film Solar Cells**

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Amorphous carbon nitride (a-CNx) films with high nitrogen content have been deposited by reactive RF magnetron sputtering at various temperatures. The reactive sputtering method is well known useful technique for deposition of semiconducting a-CNx thin films. In this study, we present localised states in band structure of a-CNx films and its electrical properties on deposition temperature. The effects of deposition temperature on optical band gap, density of defects, bonding states and electric conductivity were studied through X-ray photoelectron spectroscopy, FT-IR spectroscopy, Raman spectroscopy, electron spin resonance, UV-visible transmittance spectroscopy, photothermal deflection spectroscopy, and temperature-dependent I-V measurements. We particularly focus on these properties of the films deposited at 673 K to 853K. The Tauc gap was found to be approximately 1.2 eV for the films deposited at room temperature to 673 K, however, the Tauc gap decreases with increase in deposition temperatures from 673 to 853 K. As the Tauc gap decreases, a tail state extends and the defects density increases. Defect density is examined as a function of the amount of nitrogen incorporation. The defect density of the a-CNx films depends on the amount of nitrogen incorporation.

FG:P15 **Electrochemical Fabrication of CIS Thin Film Solar Cell**

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Thin film solar cell of methal chalcogenide was fabricated by electrochemical and wet solution process. Copper-indium-selenide film was deposited by potentiostatic electrodeposition. Metal chalcogenide buffer layers were deposited by electrochemical deposition and chemical bath deposition. The photochemical property of the multilayered device was investigated in relation to deposition process.

FG:P16 **Structural and Optical Properties of SiOxNy Containing Silicon Nanocrystals Fabricated by Plasma Enhanced Chemical Vapour Deposition Technique**

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Silicon oxynitride (SiOxNy) layers can be of great interest for applications in microelectronics applications and in photovoltaic as a passivation layer, antireflection and photonic conversion. In this work, we investigated the structural and optical properties of deposited SiOxNy films in an ECR-PECVD reactor. These films have been deposited on silicon and quartz substrates heated from 30 to 500 °C by using N2O and SiH4 as precursor gases. A comparative study of the layers composition and their physical properties are discussed as a function of the reactive gas flow. Spectroscopic ellipsometry, Fourier Transform Infrared Spectroscopy, micro-Raman Spectroscopy, Rutherford Backscaterring Spectroscopy and Transmission Electron Microscopy were employed in order to characterize the layers before and after annealing. According to these results, the SiOxNy layers composition can be varied gradually from SiO2 to SiN thanks to the variation of the N2O and SiH4 gas flow. However, the optical constant determined by ellipsometry measurements is increasing from 1.4 to 3, in agreement with the structural results. Moreover, our results have shown a correlation between the deposition rate and the gases' flow. This is for interest for the formation of graded layers or stacked multilayers.

FG:P17 **Comparing Organic Single-carrier-diodes to Bulk-heterojunctions Using Impedance Spectroscopy**

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Organic semiconductors for photovoltaic applications are gaining intensive attention by research groups worldwide. Though there is still a lack of an overall understanding of processes going on in organic solar cells. Impedance spectroscopy is therefore a powerful tool, as it gives access to various magnitudes, e.g. Capacitance. In this study we use impedance spectroscopy to investigate single-carrier-diodes containing either P3HT or PCBM, which are then compared to the P3HT:PCBM-heterojunction. We figure out the particular influences of each material on the behavior of the bulk heterojunction like the evolution of charge carrier mobility or bulk permittivity over the materials ratio.

FG:P23 **Polymeric Additives and Surfactants Used for the Enhancement of Sprayed 3D Solar Cells Photovoltaic Respons**

I. Popovici*, D. Perniu, L. Isac, A. Duta, Transilvania University of Brasov, Brasov, Romania

Third generation solar cells based on solid state semiconductors present great interest for the research community. Many research groups are involved in this field, in order to overcome the challenges imposed by this approach for photovoltaic conversion. The two main directions of development for solid state solar cells, the layer-by layer structures (ETA solar cells) and the reciprocal infiltration of the n and p-type semiconductors (3D solar cells), generate a set of requirements for the two semiconductors (rigorous control over morphology and crystallinity). The present paper propose the use of polymeric additives (hydrophilic and hydrophobic copolymers of maleic anhydride) and surfactants as morphology controlling agents for 3D solar cells, based on n-type TiO2 and p-type CuInS2 obtained by spray pyrolisys deposition. The influence of the additives is investigated in detail for the two semiconductors and improvement in the cells photovoltaic response is correlated with the control over films properties. The results prove that the main problems for 3D solar cells are linked to the reciprocal infiltration of the two semiconductors and that with good control over morphology the photovoltaic response of the cells can be improved.

FG:P25 **Surface Photovoltage Spectroscopy - A Powerful Tool for Evaluation of Electrodes Used in Dye-Sensitized Solar Cells**
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For dye-sensitized solar cells (DSSCs), light absorption occurs in the photosensitive dye molecules adsorbed at the nanoparticulate electrode with a highly porous structure, rather than in the semiconductor layer. Only in the case that the energy levels of the dye and electrode match with each other can the materials be used for solar cells. Hence, it is important to use a simple method to evaluate these materials. Here we demonstrate a non-destructive technique, (electric field-induced) surface photovoltage spectroscopy (SPS), can be used for this purpose. SPS is a useful tool to study the band structure of semiconductors and interfacial electron transfer. TiO2, ZnO, ZnO/TiO2, and TiO2/ZnO transparent electrodes are prepared by an ion-beam sputtering method using ITO glass. TiO2 and ZnO layer is 60 and 30 nm thick, respectively. Dye molecules [Ru(phen)2(PIBH)] are spin-coated onto the electrode. According to the SPS results, ZnO layer can block the transfer of photoelectrons provided by the dye to ITO. Though the recombination of photogenerated charge carriers is suppressed in the composite of TiO2 and ZnO, therefore, TiO2 is still the best candidate for the DSSCs among the four systems. Thus, SPS can be used as a powerful tool for the selection of materials used in solar cells.

FG:P27 **Silicon Nanowire-based Radial p-n Junction Solar Cells**
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Semiconducting nanowires on glass substrates are potential materials components in future thin film solar cells. Their use could yield enhanced absorption at a given thickness and thus reduce materials costs while sticking to well established silicon that permits good efficiencies and device lifetimes. Several Si nanowire (SiNW) based device configurations have been demonstrated that await the transfer from lab based processing to technologically viable production. In this paper, we describe the realization of p-n junction solar cells in a core-shell configuration by deposition of an amorphous Si (a-Si) layer wrapping the single-crystalline SiNW cores. After annealing, the Si shells were investigated as concerns their crystalline and interfacial quality using transmission electron microscopy and X-ray diffraction. Various SiNW cores are tested as well, starting from gold catalyzed bottom-up grown ones following the vapour-liquid-solid growth mechanism or chemically etched SiNWs (top-down) or SiNWs that were grown through an Al film by solid-phase epitaxy (SPE). To realize SPE wires, arrays of holes in a SiO2 layer on Si were fabricated by electron beam lithography, followed by evaporation of a layer-stack of thin Al and a-Si. Furnace anneal initiates the materials transport and solid-phase epitaxy of the a-Si at temperatures below the eutectic point of the Al/Si alloy, so that finally c-Si appears in the holes epitaxially on the underlying Si while the Al resides on top of the c-Si.

FG:P28 **Influence of the Al-BSF in the Efficiency of a Commercial Cz-Si Solar Cell**
C. Vazquez[1], J. Alonso[1], M.A. Vazquez[1], L.A. Caballero[1], J.R. Ramos-Barrado[2]*, [1]Isofoton S.A. Málaga, Spain; [2]Laboratorio de Materiales y Superficie, Dpta. Fisica Aplicada I, Universidad de Malaga, Malaga, Spain

With the reduction of solar cells thickness, back surface field (BSF) becomes more and more interesting in order to decrease the back surface recombination velocity and to increase collection efficiency. It is very important the doping and thickness of the BSF to obtain good passivation properties as was also shown by other studies. In this work, we have analysed screen-printed aluminium BSF in the performance of a commercial Cz-Si solar cell. Before to the experimental study, we have done a simulation with PC-1D of the influence of the BSF in the contact of the rear metalization. The presence of a n+ layer allows the utilization of wafer with high resistance without having sharp falls in the efficiency, because the Voc do not decrease. A detailed study of the processes of screen-printing, drying, firing, (temperature and time), allowed fix a window of temperature of firing without swings in the efficiency of the cells; however, there is a sharp decrease of Fill Factor when the temperature peak firing is insufficient. This decline is due to the front contact which is performed at the same time; this problem is avoided maintaining a suiteabltemperature of firing and increasing the time of the process. An adequate amount of paste deposited allows to avoid the bow of the wafer. The quantum efficiency of the cells show an increase in the efficiency for the long waves range (850-1050 nm); they present an efficiency of 63% for 1000 nm with a Al-BSF and only 51% without it.

Symposium FH

CONCENTRATING SOLAR TECHNOLOGIES: MATERIALS AND TECHNOLOGY SOLUTIONS FOR CPV AND CSP COMPETITIVENESS

Oral Presentations

Session FH-1

New Developments in Materials, and CPV Optics and Thermal Management

FH-1:IL01 **III-V Multijuncion Solar Cells for Ultra High Concentrations**
Carlos Algora, Instituto de Energía Solar, Universidad Politécnica de Madrid ETSI Telecomunicación, Madrid, Spain

CPV based on III-V MJCs seems a robust strategy to contribute that PV will produce an important portion of the world electricity by 2025. Ultra-high concentration (>1000 suns) exhibits an additional potential over regular CPV: higher efficiency and lower cost. Therefore, we develop, optimize and manufacture III-V cells for operation at concentrations of 1000 suns and higher. Accordingly, we have developed and manufactured a lattice-matched GaInP/GaAs solar cell which exhibits the world record efficiency for a 2J solar cell. It exhibits a peak efficiency of 32.6% for a range of concentrations going from 499 to 1026 X and it is still 31% at 3000 X. The theoretical optimization of the cell indicates that an efficiency over 36% at 1000 suns is practically attainable. Our first lattice-matched GaInP/Ga(In)As/Ge 3J solar cells exhibit a peak efficiency of 34% at 1000 suns. Theoretical optimization of the cell shows a reachable efficiency of more than 42% at 1000 suns. If the above characteristics are met, our cost calculations show that an electricity cost below 3 c€/kWh for a place like Madrid (Spain) and a nominal cost for the whole grid-connected installation below 1€/Wp for the medium-term could be attained. If these cost figures were achieved, CPV would become a real breakthrough.

FH-1:IL02 **Improved Concentration Capabilities of Flat-plate Fresnel Lenses**
M.Z. Shvarts*, Ioffe Physical Technical Institute, St.-Petersburg, Russia; A.A. Soluyanov, Technoexan LTD, St.-Petersburg, Russia

This work presents the results of designing, manufacturing and testing circular flat-plate Fresnel lenses for photovoltaic modules with MJ SCs. To minimize chromatic aberration negative effect and to design a lens with high optical-power parameters, a particular attention is given to the procedure and criteria for selecting of the optimum combination of the lens dimension, its focal distance and refracting profile parameters. For calculating optical-power characteristics (OPCs) of lenses a mathematical model has been developed, which is based on tracing of direct beam path through refracting surfaces. Analysis of OPCs of circular Fresnel lenses with conical (the generatrix of surface is a straight line) and curvilinear (the generatrix of surface is a curved line) refracting surfaces has been carried out. Fresnel lens specimens were fabricated and experimental lens OPCs have been obtained. A degree of the effect of the light flux and Fresnel lens geometrical imperfections on validity of the experimental data interpretation has been determined. Correction of the calculation model was done, and the lens optical efficiency values have been established.

FH-1:L04 Optical Methods for Indoor Characterization of Small Size Solar Concentrators

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The light collection properties of different types of solar concentrators have been investigated by applying conventional and innovative methods of characterization. The tested solar concentrators were small-size prototypes used as single optical units in CPV modules installed on in-field CPV systems. They were of the type imaging, like Fresnel lens, pseudo-imaging, like prismatic lens, and nonimaging, like the "Rondine" ones derived by the class of the compound parabolic concentrators (CPC). Three types of optical methods were applied: i) a "direct" method, using a parallel beam simulating the direct component of solar light; ii) a "laser" method, using a laser beam as light source; iii) an "inverse" method, so called as it applies a Lambertian light source at the receiver side, thereby reversing the light path. In this paper we will discuss the relevant optical properties derived by applying the above three discussed methods, that is: i) the overall optical efficiency resolved on the zenithal and azimuthal angles of incidence (direct and inverse method); ii) the distribution of irradiance on the receiver (direct method); iii) the local optical efficiency, associated to local imperfections of the reflective or refractive surfaces (laser method).

FH-1:L05 Assessment of a Phase Change Material System for Moderating Temperature Rise of Solar Cells Under Concentrated Sunlight

E. Casenove, L. Pujol, A. Vossier, A. Perona, V. Goetz, A. Dollet*, CNRS, PROMES Laboratory, Perpignan and Odeillo, France

Due to their ability to absorb a large amount of energy at constant solid-liquid transition temperature, Phase Change Materials (PCM) are good candidates for passive cooling of electronic or photovoltaic devices. In this work, experiments and numerical simulations are carried out to study a PCM system for cooling a photovoltaic cell under concentrated sunlight. A PCM suitable for the temperature range of interest in concentrating photovoltaic (CPV) applications is first selected among several candidates. The cooling device is made of a graphite-PCM composite material inserted in a small aluminum enclosure. A PCM system without solar cell is first considered. Experimental plots of material temperature versus time are recorded for various incident solar powers and compared to thermal simulation predictions. Suitable conditions are identified and then measurements are performed on a GaAs solar cell coupled to the PCM cooling system under concentrated sunlight. The cell temperatures and conversion efficiencies obtained with and without using the PCM are finally compared and the interest of using PCM cooling systems in CPV applications is discussed.

Session FH-2

CPV Cell Components, Module Assembly and Testing

FH-2:IL01 CPV Modules Based on Lens Panels

V.D. Rumyantsev, Ioffe Physical-Technical Institute, St.-Petersburg, Russia

A work on development of the high concentration photovoltaic (HCPV) modules with Fresnel lens panels and III-V multijunction cells is presented. A composite structure of the small-aperture area 40x40 (or 60x60) mm2 lenses, united in a panel, is realized. A front silicate glass sheet serves as a holder for transparent microprisms formed in silicone. Small thickness of the prisms ensures low IR absorption of sunlight. Temperature dependences of the optical properties in such a type of the solar concentrators and PV properties of the cells in passive heat dissipation conditions of a HCPV module are under consideration. The solar cells are the triple-junction InGaP/(In)GaAs/Ge cells with designated illumination area of 1.7-2.3 mm in diameter. A HCPV module consists of the 144 (or 64) sub-modules in 12x12 (or 8x8) configuration. Solar cells are protected from environment in different ways: by side walls of a module body or by a rear glass sheet at integrated sealing the cells in a back-side module panel. Four module designs are under development: without secondaries; with secondary reflective Al-, or glass-based kaleidoscopes; with refractive smooth-surface secondary lenses. A number of solar trackers have been developed and realized for 1-3-5 kWp of installed HCPV modules.

FH-2:IL02 Characterization of III-V Multi-junction Concentrator Cells and Systems

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III-V triple-junction concentrator solar cells have achieved the highest reported photovoltaic conversion efficiencies of over 40%. This makes these cells attractive to be applied in concentrating photovoltaic (CPV) modules in order to produce electricity in a cost competitive manner. Many companies developing CPV systems are currently entering the market. The performance of multi-junction cells and CPV modules applying such cells show a higher spectral sensitivity compared to common Silicon cells and modules. In addition, the angular transmission of CPV modules is limited. Thus, these new types of solar cells and modules require new characterization procedures. A precise calibration of the concentrator solar cells and modules is mandatory in order to establish procedures for the prediction of the energy yield of CPV systems. This in turn is a prerequisite for the acceptance of the CPV technology in the market. The lecture will give an overview on the status of the CPV technology and will focus on the indoor calibration procedure of multi-junction concentrator cells as well as concentrator modules. Additionally the lecture will give an insight to the ongoing work on the development of routines for a rating and prediction of the power generation of concentrator modules.

FH-2:IL03 Modelling, Characterising and Optimising CPV Modules

Damien Buie*, Richard Hoffman, Emcore Corporation, Albuquerque, NM, USA

The levelised cost of energy (LCOE) of a solar concentrating system is governed by the fundamental design, the materials, the location the system is to be deployed and a plethora of other equally contributing factors. By modelling each of these components and coupling them together with cost you can perform a global optimisation of the design space using the LCOE as the metric. Provided your assumptions are correct, the result of the optimisation is both a solution that represents the most cost efficient method for your technology, and also a method that determines the sensitivity of the global solution to the input parameters, driving the focus for the development of the technology. In this paper we present the computational framework adopted at Emcore to optimise the LCOE of their concentrating photovoltaic system and present some fundamental design space trade-offs that appear from the computation.

FH-2:IL04 Towards Accurate Reliability Tests for CPV Modules

A.R. Lagunas*, I. Petrina, J. Diaz, CENER, Sarriguren (Navarra), Spain

A critical point for the implantation of a new photovoltaic technology in the market is the demonstration of its reliability and capacity to work in good conditions for a long time. In the case of CPV modules, there are a difficulty added, related to the wide variety of concentrators, receivers, optics and materials involved, what makes hard to establish some tests to do that might be of general application. The first approach was the IEEE 1513:2001, developed by representatives of US manufacturers, users and evaluators of CPV technology and engineers from Government laboratories. Later, in 2002 started the process for launching the concentrator standard with international validity IEC-62108 that had its first issue in December 2007. It is based on the initial IEEE 1513 document, and on the well experienced IEC-61215 for Crystalline Silicon flat PV modules. As a novelty it includes concepts as "representative samples" for some tests, different temperature of climatic aging steps, and the need to treat separate the receivers and whole assembly. Nevertheless there are still some points missed related to safety tests. In this paper we will review the main facts on the testing of CPV modules from reliability point of view, after the experience obtained by the laboratory, and also will present some proposals on the difficulties encountered while the tests, feedback already to the committee that prepares the next issue of the standard.

FH-2:IL05 CPV Cell Assemblies and Module Qualification and Reliability Testing at Arima EcoEnergy

Chin-Wei Hsu[1,2], Andrew Y.C. Tzeng[1] Michael C.Y. Huang[1]*, C.C. Lee[2], [1]Arima EcoEnergy Technologies Corp., Taipei County, Taiwan; [2]Dept. of Optics and Photonics, National Central University, Taoyuan County, Taiwan

The first CPV module quality qualification standard was officially published by the International Electrotechnical Commission (IEC) in December 2007. The object of the standard is to show, as far as possible within reasonable constraints of cost and times, that the CPV modules and assemblies are capable of withstanding prolonged exposure in open-air climates. Generally for most module manufacturers, as the test procedures are performed, product modifications are often necessary to comply with the IEC requirements, which in turns improve the long-term reliability for the CPV modules as designed. Recently Arima EcoEnergy has passed all IEC 62108 indoor tests and obtained the official approval from ISFOC. In this paper, we will discuss some of the reliability issues in the CPV cell assemblies and module discovered during our path to IEC qualification, specifically from thermal cycling, damp heat, humidity freeze, and other climatic chamber or mechanical impact tests. In addition, we will discuss about the experience of the outdoor exposure test for the CPV module, which illustrates some of the failure mechanisms that may not have been detected by the indoor tests.

FH-2:L06 Effects of High Concentration of Sunlight on Tunneling in Multi-Junction Solar Cells

E.A. Katz*, A. Braun, B. Hirsch, J.M. Gordon, Dept. of Solar Energy and Environmental Physics, J. Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Sede Boqer, Israel; W. Guter, A.W. Bett, Fraunhofer Institut für Solare Energiesysteme, Freiburg, Germany

This talk summarizes results of our experimental studies of a transition from high-conductance tunneling to low-conductance thermal diffusion behavior[1-2] that tunnel diodes in multi-junction concentrator solar cells undergo at high concentrations of sunlight. In particular, a prominent dependence of the threshold photocurrent density for this transition on the degree of localized irradiation[3] is presented and discussed in terms of the lateral spreading of excess majority carriers. The ramifications of our findings for photovoltaic design, diagnostics and performance are addressed.

[1]J.M. Gordon, E.A. Katz, W. Tassew, D. Feuermann, Appl. Phys. Lett. 86, 073508 (2005); [2]W. Guter, A.W. Bett, IEEE Trans. Electron. Dev. 53, 2216 (2006); [3]A. Braun, B. Hirsch, E. A.Katz, J.M.Gordon, W. Guter, A.W. Bett, Solar Energy Mat. Solar Cells, 93, 1692 (2009).

FH-2:L07 Solar Divergence Collimators for Collector Tests

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The optical characterisation of sunlight collectors represents a crucial aspect of the research on renewable energies. The information it provides is twofold. Firstly, it allows evaluating the optical characteristics of each single component, comparing them to the expected performances according to the optical project. Secondly, it allows comparatively characterising the elements of a serial production, thus giving information about production homogeneity. The use of solar divergence collimators is the key for reliable optical tests that reproduce the on-field collector operating conditions. Aiming to test small (<80 mm diameter/diagonal) and large concentrators (80-240 mm diameter/diagonal range), the collimator geometry should be evaluated because of some optical errors introduced by the need of bending the optical axis. This paper discusses the optical characteristics of the beams obtained with straight and bent collimators with solar divergence. The collimated beams are examined by ray tracing simulations, studying the aberrations as a function of bend angle, and measured in laboratory. Finally characterisation tests for sunlight concentrators of various shapes, dimensions and collection features are presented describing instrumentation, optical set-up and methodology to determine collection efficiency, image plane analysis and spot size.

FH-2:IL08 ENEA's Activities on C-PV Technology: Perspectives in Research, Development and Demonstration

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ENEA, Italian Agency for new technologies, energy and sustainable development, has been involved in the C-PV technology for many years. The activities started in 2002 within the PhoCUS (Photovoltaic Concentrators Utility Scale) project, partially financed by the Research Ministry. The project main purpose was the development of a C-PV technology based on the point focus approach by means of refractive primary optic fully integrated in the module. Some 5kW standard units were designed and installed. In conclusion the PhoCUS technology developed by ENEA showed the technical feasibility of the whole approach. The economic competitiveness was to be demonstrated. To do that, ENEA is involved in European (APOLLON) and National (SCOOP) projects aimed to improve the C-PV technologies, and to promote the birth of industrial operators. At the same time ENEA is performing an advisor role for the Economic Development Ministry to define the rules for admitting the C-PV technologies in the feed in tariff support. The main results reached within the PhoCUS project will be presented and discussed, afterwards the APOLLON and SCOOP projects activities will be described with particular attention to the target in terms of performance and cost expected at the end of activities. Finally the national and international market status will be analyzed to demonstrate the importance of the incentives for the diffusion of the C-PV technology.

FH-2:L10 Improvements in the PhoCUS Technology: Realization of a Photovoltaic Concentrator Module Equipped with Multi-junction Solar Cells

R. Fucci*, C. Cancro, G. Flaminio, G. Leanza, A. Merola, C. Privato, A. Sarno, ENEA Research Center, Loc. Granatello, Portici (Naples), Italy

Sunlight concentration onto PV cells can contribute to reduce the total system cost of photovoltaic plants in comparison with the PV-flat cost. The aim of this paper is to describe and analyze the main technical design elements and the assembling techniques used to realize a Concentrator-module (C-module) equipped with Multi-Junction (MJ) concentrator cells. The C-module realized is based on series of 24 cells organized in array of 6*4. A plastic housing to assure the desired mechanical resistance and a good protection against the environmental agents was introduced, and a PMMA (polymethylmethacrilate) optical parquet, based on hybrid lenses, was used. Finally, a secondary optical element (SOE), made of a plastic pyramid having a metallic surface coated inside, was used. In the end a good MJ C-Module assessment in terms of energy performance and economical aspects has been obtained. It must be underlined that the measured MJ C-module operative efficiency (over 26%) is very close to the maximum achievable (27.4%). Potentially the MJ solar cells, working under a concentration ratio in the range of 350÷500 suns, could allow to reach the optimal condition in terms of cost-benefits analysis considering the solar cell cost reduction increasing its working concentration ratio.

Session FH-3

CSP Concentrators and Heat Collection Elements

FH-3:IL01 Materials and Design Requirements for Advanced Concentrators

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Concentrating solar collectors target to direct the direct sunlight towards a focus point or focus line. Critical parameters are the deviation of the concentrator from its ideal shape, its stiffness vs. wind and gravitational loads, the accuracy of the tracking and the solar weighted specular reflectance of the reflector. Additional aspects refer to the long term durability and ease of cleaning of the reflector surface. DLR has recently developed guidelines to measure these characteristics. These methods are combined in DLR's qualification lab QUARZ, where testing of concentrator components as well as of fully assembled concentrators is offered to industry and developers. This presentation will summarize the methods and show typical results for state of the art and advanced concentrators. It will point out what are the key parameters for an efficient concentrator for solar thermal applications.

FH-3:IL02 Solar Concentrators for Power Generation: Indian Experience

N.D. Kaushika, Bharati Vidyapeeth's College of Engineering, New Delhi, India

India has vast potential of renewable resources. The planners have drawn proposals to speed up the use of renewable resources for power generation. Consequently in recent years several such sources as solar, biomass, geothermal, tides, mini-microhydel, wind and waves have been researched for pollution free electricity generation. Solar is most promising and concentrating technologies have shown greatest potential for cost – effective electricity generation. Indian experience on solar concentrating photo voltaic (PV) is rather scant. This paper reviews solar concentrating technologies for generation of high temperature heat, electricity and combined heat and electricity. Three most developed technologies such as parabolic trough, paraboloidal dish as well as solar tower are considered. The description includes the operational as well as optimization efforts with an experimental 50 kW capacity power plant based on parabolic trough technology set up at Solar Energy Centre of MNRE - Govt. of India. The experience with respect to material and technology problems of header and loop-connection pipelines concentrator array design etc. are outlined. Furthermore, the Centre for Energy studies of I I T Delhi has actively collaborated with Energy Research Centre of ANU, Canberra, Australia for research on the viability aspects of dish concentrators which includes large area dish concentrators and semi cavity focal absorbers. It is pointed out that semi cavity designs can be more efficient and cost effective for not only short focal length and inaccurate dishes but also for longer focal length dishes of large size. The above mentioned dish technology also holds promise of near term application in such schemes as solar hybridization with gas turbine power plants and decentralized power supplies for industrial & rural sectors.

FH-3:IL03 **Advances in Reflector and Solar Selective Materials for Application to Concentrating Solar Power Systems**

C.E. Kennedy, National Renewable Energy Laboratory (NREL), Golden, CO, USA

Concentrating solar power (CSP) technologies use large mirrors to concentrate sunlight and the thermal energy collected is converted to electricity. The CSP industry is growing rapidly and is expected to reach 25 GW globally by 2020. Cost target goals for CSP technologies ato produce electricity competitive with intermediate-load power generation (i.e., natural gas at 9-12¢/kWh) by 2015 with 6 hours of thermal storage and competitive in carbon constrained base load power markets (i.e., coal at ~10-12¢/kWh) by 2020 with 12-17 hours of thermal storage. The solar field contributes more than 40% of the total cost of a parabolic trough plant. Together the mirrors and receivers contribute more than 25% of the installed solar field cost. Solar field costs need to be reduced from the current $350/m2 to $200/m2 to reach the 2015 goal. Concentrating solar power (CSP) technologies use large mirrors to concentrate sunlight and the thermal energy collected is converted to electricity. The CSP industry is growing rapidly and is expected to reach 25 GW globally by 2020. Cost target goals for CSP technologies is to produce electricity competitive with intermediate-load power generation (i.e., natural gas at 9-12¢/kWh) by 2015 with 6 hours of thermal storage and competitive in carbon constrained base load power markets (i.e., coal at ~10-12¢/kWh) by 2020 with 12-17 hours of thermal storage. The solar field contributes more than 40% of the total cost of a parabolic trough plant. Together the mirrors and receivers contribute more than 25% of the installed solar field cost. Solar field costs need to be reduced from the current $350/m2 to $200/m2 to reach the 2015 goal. Reduction of operations and maintenance costs will also be needed. CSP systems cannot hit these targets without aggressive cost reductions and revolutionary performance improvements from technology advances. Performance and efficiency gains will have a greater benefit on reducing costs than cost reduction only strategies. The progress to develop low cost, high performance, durable solar reflector and high-temperature receiver materials to meet these needs and their performance will be discussed.

FH-3:L04 **Test Facility for Absorber Specimen of Solar Tower Power Plants**

B. Hoffschmidt, K. Geimer, J. Göttsche, M. Schmitz, M. Sauerborn*, Solar-Institut Jülich, Jülich, Germany

The Solar-Institut Jülich (SIJ) has initiated the construction of the first and only German solar tower power plant and is now involved in the accompanying research. The power plant for experimental and demonstration purposes in the town of Jülich started supplying electric energy in the beginning of 2008. The central receiver plant features as central innovation an open volumetric receiver, consisting of porous ceramic elements that simultaneously absorb the concentrated sunlight and transfer the heat to ambient air passing through the pores so that an average temperature of 680 °C is reached. The subsequent steam cycle generates up to 1.5 MWe. A main field of research at the SIJ is the optimization of the absorber structures. To analyze the capability of new absorber specimens under realistic conditions a special test facility was developed and set up in the laboratory. A high-performance near-infrared radiator offers for single test samples a variable and repeatable beam with a power of up to $300kW/m^2$. The temperatures achieved on the absorber surface can reach more than 1000 °C. To suck ambient air through the open absorber - like on the tower - it is mounted on a special compressor system. An overview about the test facility and some recent results will be presented.

FH-3:IL05 **New Materials in Solar Concentrators and Receivers**

W.J. Platzer*, A. Heimsath, C. Hildebrandt, Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany

Key components for Concentrated Solar Thermal Power are the concentrator system on the one hand side, usually consisting of mirrors, and the receiver part absorbing the solar radiation and transforming that into useful heat at high temperatures. For linearly concentrating collectors like Parabolic Trough and Linear Fresnel Collectors different solutions have been proposed and have been developed in a commercial environment. The receiver element is usually one or several steel tubes with high solar absorptivity and low thermal emissivity. Absorber tubes have been developed on the basis of so-called Cermet coatings, which have to be stable under vacuum or even atmospheric conditions for temperatures up to 400 °C, preferably higher. Spectral emissivity and absorptivity changes have to be evaluated. Experiments show that coatings can improve due to heat treatment compared to freshly sputtered coatings. Both types of coatings, vacuum and air-stable coatings will be treated in more detail in the paper. Curved and flat mirrors are used for primary concentrators, but some systems also use a secondary concentrator to enhance the optical efficiency. Mirror optics using nearly flat primary glass mirrors and a secondary concentrator for the receiver construction are used to achieve a geometrical concentration in the order of 30-50 with respect to tube circumference. Deformations due to construction, internal stress of glass, wind load and gravity may lead to a distortion of the narrow focus line on the receiver. The acceptance angle of the secondary concentrator may deteriorate due to shape imperfections. Deterioration of specular reflectance due to dust and degradation also reduces performance. Several qualification techniques were used to support quality control for production and technical development. Collector performance and possible improvements are discussed together with a comparison to parabolic trough collectors.

FH-3:IL07 **High Temperature Stable Selective Absorber Coating for Receiver Tube**

K. Silmy*, T. Kuckelkorn, J. Schulte-Fischedick, SCHOTT Solar CSP GmbH, Bavaria, Germany

Concentrated Solar Power (CSP) plants use steam to produce energy, in similar manner to conventional steam power plants. The key difference is that CSP plant use emission-free, clean solar radiation to produce heat instead fossil or nuclear fuels. Solar radiation is concentrated in parabolic trough arrays to achieve the required temperatures. These troughs are made of parabolic shaped mirror segments, track the sun over the course day and focus the solar radiation along the focal point of the mirrors onto specially coated and evacuated receiver tubes that convert solar radiation into heat. A heat transfer fluid, which is circulating through the receiver, is heated up to 400°C and then use to generate steam. Increasing the heat transfer fluid temperature more than 500 °C contributes significantly to lower levelized costs of electricity and maximized output. The receiver, being the key component of a CSP plant, has decisive influence on the overall efficiency of the plant. SCHOTT Solar has developed and patented a new selective absorber coating with remarkable optic values 95/10. The long-term thermal stability of absorber coating is a crucial issue for higher working temperature. SCHOTT solar selected absorber coating has proven high stability up to 590°C and more than 4,500 hours.

Session FH-4

Heat Thermal Fluids and Thermal Energy Storage

FH-4:IL01 **Molten Salt Heat Transfer Fluids and Thermal Storage Technology**

Nathan Siegel, Sandia National Laboratories, Albuquerque, NM, USA

Solar energy systems are based on an intermittent resource and benefit from an energy storage mechanism that decouples the solar resource from the load, enabling operation when the resource is unavailable such as during cloud transients and at night. For utility scale power plants decoupling the resource from the load may be achieved using thermal energy storage (TES) systems based on inorganic salt heat transfer fluids and storage media. Combining TES with hybridization via natural gas enables concentrating solar power facilities to provide reliable, dispatchable power day and night, and actually displace conventional power generation facilities fueled exclusively with coal or natural gas. This presentation begins with an overview of TES technology for concentrating solar power production that includes a discussion of the need for thermal storage, its cost, and potential roadblocks to deployment. Also included will be a discussion of ongoing research and development in the United States focused on addressing known technical issues that must be resolved in order to enable the deployment of TES systems in near-term parabolic trough and central receiver power plants. Finally, a discussion of advanced research projects and opportunities related to TES will be presented.

FH-4:IL02 **PCM-Graphite Latent Heat Storage Systems for Industrial Process Heat Recovery**

R. Schmitt*, O. Oettinger, T. Gruenberger, SGL CARBON GmbH, Meitingen, Germany; W.-D. Steinmann, R. Tamme, Institute of Technical Thermodynamics, Stuttgart, Germany

Increasing energy prices and shortage of fossil fuels lead to a growing interest in alternative energy sources. In combination with energy storage systems the generation of solar process heat can be provided independent from the weather and industrial proces heat can be recovered and used for further production steps. For these purposes latent heat storage units with phase change materials (PCMs) can be designed to store solar or industrial process heat within a narrow temperature interval utilizing the high storage density of the different PCMs. As most pure PCMs exhibit a low thermal conductivity, methods to improve heat transfer in PCMs have been under investigation for decades. The heat transfer in a PCM can be increased by addition of high conductive materials. Due to its superior properties - high thermal conductivity, good processibility, and chemical inertness - graphite has distinct advantages for this purpose. Depending on the requirements of the respective application, various routes to combine PCM and graphite are used. This paper gives an overview of actual and potential applications of PCM/graphite latent heat storage systems.

FH-4:IL03 **New Methods to Characterize Phase Change Materials**

E. Palomo del Barrio, TREFLE - Site ENSAM, Talence, France

Main experimental tools available today for thermodynamic characterization of phase change materials (PCM) are Differential Scanning Calorimeters (DSC). Greatest asset of DSC is its capacity to provide precise measurements of latent and specific heats from very small samples. As for limitations and drawbacks, we can mention: a) too long testing times for screening purposes or for reliable enthalpy-temperature functions determination; b) inappropriate for testing hybrid phase change materials with large-size representative volumes; c) inappropriate for reliable and quantitative undercooling analyses of PCM others than i.e. emulsions; c) inappropriate for hybrid PCM characterization at the micro-scale, as well as unable for density or volume expansions measurement. Some alternative and original experimental techniques, aiming to overcome the DSC limitations/drawbacks, are under development and presented in this paper. They allow reliable undercooling analyses, PCM characterization at the micro-scale, bulk enthalpy-temperature functions determination in some few minutes, testing hybrid phase change materials with large-size representative volumes, volume expansions measurements and latent heat estimations in some few seconds.

FH-4:L04 **Solar-thermal Energy Conversion and Storage: Conductive Heat Transfer Using Bulk Graphite for a Domestic System**

C.C. Sorrell*, T.C. Palmer, L.J. Bowen, A. Nakaruk, School of Materials Science and Engineering, University of New South Wales, Sydney, NSW, Australia

Concentrated solar power (CSP) highlights the fact that there is substantially more energy in the sun's heat than there is in its light. However, solar-thermal energy conversion and storage systems using CSP are handicapped by challenges associated with storage technologies, especially high pressures and corrosion. In assessing the possibilities for new materials and designs, issues of thermal properties and heat transfer must be considered. While current technologies largely utilise convective heat transfer of liquids, a promising approach is the use of conductive heat transfer with a new form of highly dense and aligned self-assembled graphite in air as the storage material at temperatures ≤500 °C. Modelling of a small domestic-scale system (4 m diameter concentrator; <200 kg graphite) indicates that, in only 90 min, sufficient heat can be stored to supply 25% more than is required for a typical 24 h electricity usage cycle, operating at a storage temperature of ≤420 °C in air.

FH-4:L05 **Overview of PCMs for Concentrated Solar Power in the Temperature Range 200 to 350 °C**

Thomas Bauer*, Doerte Laing, Rainer Tamme, Institute of Technical Thermodynamics, German Aerospace Center (DLR), Stuttgart, Germany

For concentrated solar power, the type of carrier fluid has a direct impact on the thermal energy storage design. The present paper focuses on pressurized water/steam as a carrier (e.g. for parabolic through, Fresnel collector). The pressure dependent condensation/evaporation occurs between 200 °C (16 bar) and 350 °C (165 bar). The high enthalpy condensation/evaporation process is almost isothermal and requires a suitable storage concept. Here, latent heat storage using a phase change material (PCM) is in particular advantageous. In this concept both the carrier and the storage material undergo a phase change. The presented work focuses on material aspects and gives a comprehensive overview of single and multi-component inorganic salts as potential PCMs. Besides the melting temperature and enthalpy, the work includes other selection criteria such as thermal stability, corrosion, handling and economic aspects. We present detailed results of own experiments on two salts (NaNO3, KNO3-NaNO3). They include thermo-physical measurements (thermal diffusivity by laser flash, thermal conductivity by hot wire and heat capacity by differential scanning calorimeter method). In addition, measurements of the thermal stability and the compatibility with structural materials are reported.

FH-4:IL06 **Thermochemical Energy Storage Systems**

Andreas Hauer, Bavarian Center for Applied Energy Research, ZAE Bayern, Garching, Germany

Thermochemical energy storage is the most advanced method to store thermal energy: A chemical reaction takes up the heat to be stored and the re-reaction releases the heat at discharging. Advantages are high storage capacity and the possibility to vary the charging and discharging temperatures. From the thermodynamically point of view thermal energy storages (TES) can be categorized into direct and indirect storages. Direct TES include sensible and latent energy storages. In general the storage capacity of these systems is limited by the possible change in entropy. Indirect TES systems are not storing the heat, but the entropy free work from a thermodynamic machine. This “converter” can be for example a chemical reaction, transforming thermal into chemical energy. These TES systems utilizing chemical reactions have now no limitation by the entropy change. The theoretical limit is now linked to the reaction temperature. A number of chemical reactions have been investigated over the last decades. The most developed systems are based on the ad- or absorption of water vapour on porous solids (like Zeolite or Silicagel) or liquid salt solutions. The most applications are so far in the range of 80-300 °C. An overview of R&D activities will be given.

FH-4:IL07 **Thermal Energy Storage for Process Heat and Power Generation - Impact of Materials to Realise Efficient and Economic Storage Solutions**

Rainer Tamme*, Thomas Bauer, Claudia Mühlhausen, Franziska Schaube, Doerte Laing, DLR, German Aerospace Center, Institute of Technical Thermodynamics, Stuttgart, Germany

Thermal energy storage (TES) is a key element for effective thermal management in the sectors of process heat and power generation, and it is indispensable for solar thermal applications. The main advantage of concentrated solar power (CSP) plants against other renewable energy sources like PV or wind power is the capability to provide firm, dispachtable power by integrating large scale TES systems. The currently available CSP technology for process heat and power generation covers the temperature range from few hundred °C to nearly 1000 °C using parabolic trough, Fresnel or solar tower technology in combination with various heat transfer fluids such as oil, steam, molten salt or air. This requires the understanding of a broad portfolio of storage designs, media and methods. The paper presents for relevant sensible, latent heat and thermo-chemical storage systems the important role of materials to achieve efficient, economic and reliable thermal energy storage solutions. The scientific challenge in the field of high temperature TES is to identify materials with superior thermo-physical and thermo-mechanical properties as well as efficient thermal design and system integration concepts.

FH-4:IL09 **Advanced Salts Mixtures as Heat Transfer Fluids**
F. Fabrizi*, P. Tarquini, M. Vignolini, ENEA CR Casaccia, Rome, Italy

The molten salts (Na, K and Ca nitrates/nitrites) mixtures are suitable fluids (liquid at low pressure, high thermal capacity) for application in the CSP technologies. A relatively expensive mixture, 60%Na-40%KNO3, is widely adopted in indirect Thermal Energy Storage systems of the actual CSP plants. ENEA has proven the technical feasibility of using this salts mixture as Heat Transfer Fluid also in a parabolic trough solar field. It allows to operate at higher temperatures (up to 550 °C) than thermal oils and eliminates the need for expensive intermediate heat exchangers. In this case a substantial reduction in the costs is expected. Despite this molten salts mixture solidify at rather high temperatures (240 °C), ENEA has proven that a careful design of piping and auxiliary heating systems avoids the salt freezing in the solar field during any condition of operation and maintenance. The molten salts are environmental friendly; in the case of accidental leakage they do not ignite, quickly solidify on the ground and can be wholly removed by mechanic tools. Experimental studies in progress aim to demonstrate the adaptability also of other various mixture of molten salts in many thermal processes useful for multipurpose hybrid CSP plants and other industrial applications.

Session FH-5
Applicative and Commercial Experience

FH-5:IL02 **Solar Thermochemical Production of Hydrogen and Other Fluids**
A. Meier, Solar Technology Laboratory, Paul Scherrer Institute, Villigen PSI, Switzerland

Thermochemical high-temperature processes can efficiently convert concentrated solar energy into storable and transportable fuels such as hydrogen (H2), synthesis gas (mainly H2 and CO), and other synthetic fuels. In the long run, H2O-splitting thermochemical cycles based on metal oxide redox reactions are developed to produce hydrogen from water and sunlight only. In a transition period, fossil energy carriers and carbonaceous waste materials are transformed into valuable fuels by reforming, gasification and decomposition processes using concentrated solar radiation as the energy source of high-temperature process heat. The most promising solar thermochemical processes will be discussed and the latest technological developments will be summarized.

FH-5:L03 **Optical and Thermal Characterization of Solar Receivers for Parabolic Trough Collectors**
M. Sanchez, E. Mateu*, Solar Thermal Energy Department from National Renewable Energy Centre (CENER), Sarriguren (Navarra), Spain; C. Heras, R. Alonso, Universidad Zaragoza: Departamento de Ingeniería Eléctrica y Comunicaciones, Zaragoza, Spain

Concentrating solar power technology demands a better quality control and the receiver has strong impact on the efficiency of CSP plants. The overall receiver efficiency depends on the available aperture length, transmittance of the glass envelope, optical values of the coating and vacuum quality.Today's receiver manufacturers claim new receiver developments with better emisivity values, high transitivity, higher operating temperatures and lower thermal losses. The solar industry is claiming for standardized characterisation and certification procedures. This process will allow not only a better quality control of the components but also a starting point to ask for guarantees. CENER and the Universidad de Zaragoza have joined efforts to develop characterisation equipment able to measure most of the receiver optical and thermal properties. The equipment developed is able to accurately measure at ambient temperature and at different working temperatures the spectral glass transmisivity and absortivity of the solar receiver.Different tests have been performed to fulfil with the technical specifications of the equipment. The final design has been completed and it is expected to have the equipment ready by the beginning of 2010. The initial results will be presented at the congress.

FH-5:IL04 **A Review of CPV Technology and Commercial Progress**
Alexander Slade, Siroc Pty. Ltd, Sydney, Australia

The adoption of CPV for utility power remains highly desirable by many: people and their governments alike. However, the market acceptance of the technology is an important hurdle to overcome due to the predominately large systems developed by industry. This is especially true given that flat-plate or 1-sun PV has had much more field experience to support their claimed reliability. During 2005 to 2008 the short supply of silicon and booming market in Spain placed CPV as an alternative to 1-sun modules. In the current and near future outlook for PV we expect the silicon shortage to subside (and thus a drop in the price of silicon), a tighter market (lower profits) and rising competition from other "green energies" such as solar thermal, geothermal, wind, etc. In light of this, we ask "What is the future direction for CPV ?". A summary of current technologies such as silicon and multi-junction concentrator cells as well as examples of market acceptance for large CPV systems will be given. Furthering this, the presentation will show a contrast between the low concentration+silicon cell and the high concentration+ multijunction cell paths.

FH-5:IL05 **Building Integration Solutions for CPV**
Daniel Chemisana Villegas, University of Lleida, Lleida, Spain

For building integration, concentrating photovoltaic systems (CPV) can offer a host of advantages over conventional flat panel devices, the most notable being: a higher electrical conversion efficiency in the PV cells, better use of space, ease of recycling of constituent materials, and reduced use of toxic products involved in the PV cells' production process. However, the viability of building-integrated concentrating PV systems (BICPV) is dependent on their ability to offer a comparative economic advantage over flat panel photovoltaic technologies whose market prices are decreasing from day to day (<1.8 € / Wp) and which offer other advantages such as ease of replacement of structural elements. A comparative analysis is presented of the main existing CPV systems' suitability for use in buildings, in which the different challenges specific to integration of each system are discussed. The systems are categorised by type of concentration technology and concentration factor. Two further sets of BICPV systems are proposed, one refractive and one reflective, which we consider well adapted for use in buildings in that they are cost and space efficient, structurally practical and conserve architectural harmony.

FH-5:IL06 **On-sun Performance of Flatcon® CPV Systems**
A. Gombert*, I. Heile, J. Wüllner, T. Gerstmaier, S. van Riesen, E. Gerster, M. Röttger, Concentrix Solar GmbH, Freiburg, Germany

Highly efficient concentrator photovoltaic systems (CPV) use an optical concentrator to concentrate the solar radiation onto multi-junction solar cells (MJC) based on III-V semiconductors. Such cell have a record efficiency of 41% under concentration. In order to exploit the high cell efficiency a careful optimisation of the whole CPV system has to be undertaken. Concentrix is manufacturing and installing FLATCON® concentrating photovoltaic CPV systems. FLATCON® modules are based on III-V triple junction cells, a Fresnel lens array and a glass cover and bottom plate. In 2008, Concentrix installed a demo tracker and two power plants in Spain. Field data of these systems with a maximum AC efficiency of 23% are presented and discussed. Further data are from systems installed in 2009 which reached an AC system efficiency of 25%.

Poster Presentations

FH:P01 **Improvement of Radiation Resistance of Multijunction Solar Cells by Application of Bragg Reflectors**
V.M. Lantratov*, V.V. Emelyanov, N.A. Kalyuzhnyy, S.A. Mintairov, M.Z. Shvarts, Ioffe Physical Technical Institute of RAS, St.-Petersburg, Russia

Solar cells (SC) are the main power sources for spacecrafts operating on the near-earth orbits. Important space SC operation parameter is the resistance to the action of high-energy particles. A way to increase the radiation resistance of the single-junction SC by integrating the Bragg reflector (BR) has been considered previously. A similar approach has been applied for rising the radiation resistance of the multijunction (MJ) GaInP/Ga(In)As/Ge SC, the rate of the radiation degradation in which is determined by the Ga(In)As subcell. Increasing the radiation resistance of MJ SC with BR have been shown. The SC structure optimum parameters and the optical reflector design have been chosen. Spectral characteristics and photocurrent values of MJ SC with and without BR at different Ga(In)As subcell thicknesses have been calculated. A good fit of the calculated dependencies to the experimental ones have been obtained. A design of a MJ SC with a BR has been found, whi ch allows ensuring in the Ga(In)As subcell base an effective collection of free-carriers at the decrease of their diffusion length more than in two times. The Ga(In)As subcell photocurrent degradation rate has been reduced essentially at radiation, and increasing the radiation resistance of MJ SC has been demonstrated.

FH:P02 **AlGaA/GaAs Photovoltaic Cells with InGaAs Quantum Dots**

S.A. Blokhin, N.A. Kalyuzhnyy*, A.V. Sakharov, A.M. Nadtochiy, A.S. Pauysov, M.V. Maximov, N.N. Ledentsov, V.M. Lantratov, S.A. Mintairov, M.Z. Shvarts, Ioffe Physical Technical Institute RAS, St. Petersburg, Russia; A.R. Kovsh, S.S. Mikhrin, Innolume GmbH, Dortmund, Germany

In this work self-assembled In(Ga)As quantum dots (QDs) are proposed for heterostructure AlGaA/GaAs solar cells (SC). Detailed study of physical processes of energy conversion in QD media has been carried out and the critical issues related to optimization of QD structures for effective photovoltaic conversion have been made. It was observed that the vertically coupled InGaAs QDs are the most promising medium for solar cells as compared to other types of QDs. For the first time QD-SCs demonstrated 1% increase in short circuit current due to QD absorption in the long-wavelength optical region of solar spectrum and effective separation of photogenerated carriers through minizones. However, the insertion of QDs results in Uoc reduction, which limits the effciency (Eff) at the level of 18.3%. Dark current analysis shown that the insertion of QDs into i-region of QD-SC results in domination of recombination mechanism with sufficiently higher reverse saturation current density (100-fold) as compared to the SCs without QDs. Thus, the drop of Uoc in QD-SC is associated with the radiative recombination in narrowband gap material of QDs. This problem can be solved by using Bragg reflector instead of BSF that simultaneously will allow increasing contribution of QDs in photocurrent.

Symposium FI

RECENT DEVELOPMENTS IN THE RESEARCH AND APPLICATION OF TRANSPARENT CONDUCTING AND SEMICONDUCTING OXIDES

Oral Presentations

Session FI-1
Fundamentals

FI-1:IL01 **Transparent Conductors: From Basic Principles to Controllable Properties**

J. Medvedeva, Missouri S&T, Rolla, MO, USA

Key electronic features essential for achieving good carrier transport while maintaining sufficient optical transmission in post-transition metal oxides are summarized. In particular, the role of the following factors governing the electrical and optical properties is discussed: (i) oxygen coordination and structural anisotropy; (ii) electronic configuration of the cations and the cation-anion hybridization; and (iii) carrier generation mechanism employed. In-depth understanding of the microscopic properties of conventional TCOs provides significant insights into the underlying physical phenomena in these oxides and also reveals ways to controllably manipulate their properties. Moreover, the electronic band structure investigations are instrumental in broadening the range of efficient transparent conductors to include the abundant light metal oxides as well as non-oxide materials.

FI-1:IL02 **Fundamental Properties and Applications of Nb-doped Anatase TiO2 Transparent Conducting Thin Films**

T. Hasegawa, University of Tokyo, Tokyo, Japan, Kanagawa Academy of Science and Technology (KAST), Kawasaki, Japan

Transparent conducting oxides (TCOs) have been recognized as a key component in opto-electronic devices. Recently, antase TiO2 doped with Nb (TNO) has joined the TCO family composed of ITO, ZnO, SnO2 and so on. In fact, epitaxial films of TNO exhibit low resistivity of 2x10-4 Ohm cm and high transparency of >95% in the visible region. Here, we discuss the mechanism of transparent conductivity in TNO, focusing on the role of Nb and excess oxygen in generating and killing carriers, respectively. First principles band calculations have shown that doped Nb atoms hybridize very well with the Ti 3d-nature conduction band, resulting in high carrier density. However, the carrier density of TNO was found to be substantially decreased by annealing in oxidizing atmospheres. Valence-band photoemission measurements revealed evolution of deep p-type levels along with oxygen-annealing, suggesting that excess oxygen atoms occupy interstitial sites to form impurity states. This implies that careful control of oxygen content is of crucial importance for achieving excellent transparent conducting properties in practical TNO films. Our attempts to fabricate highly conducting TNO polycrystalline films on glass or other inexpensive substrates will also be presented.

FI-1:IL03 **Delafossite Mixed Oxides for p-type TCO Applications: Synthesis and Thermostructural Studies**

A. Barnabé*, L. Presmanes, M. Lalanne, E. Mugnier, Ph. Tailhades, Université Paul Sabatier - CIRIMAT, Toulouse, France

The potential of ABO2 delafossite-type oxides as transparent p-type conducting thin films was discovered in 1997. However, only few attempts of low temperature processing of such TCO have been published yet. This is due to the fact that the phase development during the sintering steps had at least required high temperature and quite narrow preparation conditions to obtain phase pure films. In this work, pure and Mg-doped Cu(Fe1-xCrx)O2 delafossite-type thin films were prepared by rf-sputerring. First, a thermo structural study combined with electrical characterization of the complete solid solution $0<X<1$ This work led to a better understanding of the complex reactions and crystallization process which occur in the delafossite material with the aim to develop a versatile preparation method of this oxide films on conventional glass substrate.

FI-1:IL05 **The Origin and Design of n-typness in ZnO and p-typness of Co,Ir and Rh Spinels Based on ZnO**

Alex Zunger, National Renewable Energy Laboratory, Golden, Colorado, USA, Supported by USA DOE Basic Energy Science and in collaboration with S. Lany, H. Raebiger, T. Paudel

ZnO and its Spinel relatives A2ZnO4 (A=Co,Ir,Rh) are some of the most misunderstood yet popular materials. It is well known that ZnO can be readily made n-type, but it is virtually impossible to convert to stable p-type. The n-typeness was thought for a long time to be due to Oxygen vacancies because it correlated with oxygen-poor growth conditions. Theory has shown, however, that oxygen vacancy in ZnO is a (very) deep donor, incapable of emitting electrons, so it can not be the cause.The real cause is not completly understood, but theory has revealed some of its hallmarks: (i) n-type extrinsic impurities have great solubility in ZnO; (ii) more importantly, the Zn-vacancy (an acceptor that kills electrons) has a very high formation enthalpy in ZnO and thus does not compensate effectively the electrons created by extrinsic dopants; (iii) Oxygen vacancy has an excited state that produces n-tyoe Persistent photo conductivity in ZnO. As to p-type Spinels - we show via recent calculations why Co, Ir or Rh can promote p-type carriers without the hole-killers (e.g Oxygen vacancy) compensating them.

FI-1:IL06 **Infrared Spectroscopic Ellipsometry Characterisation of Free Carriers and Conduction Mechanisms in ZnO Thin Films**

B. Abendroth*, G. Gaertner, Freiberg University of Mining and Technology, Freiberg, Germany; S.H.N. Lim, M.M.M. Bilek, D.R. McKenzie, University of Sydney, Australia

Intrinsic defects have an important impact on the functionality of ZnO transparent conducting thin films. Defects introduce donor-type levels and act as scattering centres. However the nature of these native defects is still under lively discussion. In this work the IR dielectric functions of intrinsic ZnO thin films with various levels of defect induced conductivity are measured by IR spectroscopic ellipsometry (IRSE). Specific electronic properties such as free carrier density and mobility are accessed by optical model analysis including the Drude free electron model and lattice vibrations. No straightforward correlation between the grain size, as determined by XRD, and the carrier density was found. Generally, for non-thermal equilibrium growth conditions, higher defect induced carrier densities were observed. The carrier mobility and film resistivity is consistent with the model of ionized impurity scattering over a wide range of carrier concentrations. Due to frequency dependent scattering of electrons at ionized centres, the ideal free electron model is not able to reproduce the measured data perfectly. Temperature dependent IRSE and the analysis of the non-Drude behaviour of the ZnO dielectric function are used to analyse the nature of the scattering defects.

FI-1:L07 Heat-resistant Sb-doped SnO2 Transparent Conducting Films

Kazushige Ueda*, Yusuke Kishigawa, Department of Materials Science, Kyushu Institute of Technology, Japan

In future application of Sb-doped SnO2 as transparent electrodes for oxide electroluminescence(EL) devices, heat-resistant properties, as well as transparent conducting properties, will be required. However, there are few studies that report transparent conducting properties of TCOs treated in air at high temperatures over 500 °C. In this study, Sb-doped SnO2 films were prepared by RF sputtering method and their electrical and optical properties were examined as a function of temperatures up to 1000 °C. Sb-doped SnO2 films were deposited on silica glass substrates in Ar or Ar-O2 atmosphere by RF sputtering method. As-deposited films were annealed in air at every 200 °C up to 1000 °C. The films deposited in Ar were amorphous and showed brownish color. The films crystallized after annealing above 400 °C accompanying color change from brownish to colorless. The optical transmission of the annealed films was over 80% in the visible region. The films deposited in Ar:O2 = 1:1 were polycrystalline in as-deposited state and the transmission was over 80%. Electrical conductivities of the films prepared in Ar were approximately 1 Scm-1 after annealing at 1000 °C in air. On the other hand, those of the films prepared in Ar:O2=1:1 were approximately 150 Scm-1 after annealing.

FI-1:L08 Intrinsic Defects of Transparent Conducting Oxides: A Comparative Hybrid-Functional Study of In_2O_3, SnO_2 and ZnO

Péter Ágoston*, Andreas Klein, Karsten Albe, Institut für Materialwissenschaft, TU Darmstadt, Darmstadt, Germany; Risto M. Nieminen, Martti J. Puska, Department of Applied Physics, Helsinki University of Technology, TKK, Finland

We present a comparative study of point defects in In_2O_3, SnO_2 and ZnO based on the hybrid-functional method within the density functional theory (DFT). For In2O3 and SnO_2, our results provide strong evidence of shallow donor states at oxygen vacancies. For ZnO the donation mechanism is more complex. The formation energies of oxygen vacancies are low both for the doubly positive and neutral charge states. In comparison with the semilocal exchange-correlation approximations in DFT the hybrid-functional method lowers strongly the formation energy of the positive charge state and keeps that of the neutral state nearly intact. The trend is analyzed in terms of changes in the lattice relaxation energy and the electron energy levels near the band gap. The existence of shallow donor states at oxygen vacancies and the consequent n-type conductivity are in line with experimental findings. The results invalidate some former theoretical interpretations.

FI-1:L09 The Mechanism of Catalyzed Nanowire Growth

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A thin (5 nm) layer of polycrystalline gold deposited on a substrate has been used for the catalyzed growth of a number of nanowires. In the case of Si nanowire growth, the Vapor-Liquid-Solid (VLS) mechanism is widely accepted. In VLS the Si vapor adsorbs on the Au surface where it forms a eutectic and melts permitting liquid diffusion to the growing solid nanowires. The details of this mechanism have never been examined and as gold was later found to catalyze the growth of ionic nanowires, like ZnO, many papers have attributed the mechanism to VLS. We have used in-situ XRD as well as high resolution SEM and TEM analysis to elucidate the mechanisms involved in both metalloid and ionic Au catalyzed nanowire growth. The first observation is that by 300°C Au undergoes a solid state reconstruction forming ~30 nm isolated islands of 111 oriented single crystals. These oriented crystals catalyze nanowire growth. In the case of ZnO the Au does not melt and there is no solubility of the ions in the catalyst. Details of the ZnO and Si mechanisms will be presented.

FI-1:IL10 Amorphous In-Zn-O Films: Archetype for a New Class of TCO Materials?

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The traditional transparent conducting oxides (TCOs) such as In2O3:Sn (Indium Tin Oxide, ITO), ZnO:Al and SnO2:F are essentially substitutionally doped wide band gap (~3eV) semiconductors and good crystallinity is generally considered critical to obtain good opto-electronic properties. However, over the past decade, a new class of TCOs that are amorphous has emerged based on double (or triple) oxides of heavy metal cations with nominal ionic electronic configuration (n-1)d10ns0. This class is typified by In-Zn-O (IZO) and In-Ga-Zn-O (IGZO). These amorphous TCO materials can have electrical conductivity and optical transparency comparable to the traditional crystalline TCOs with the added technological benefits of ambient or low temperature deposition (T<100 °C), smooth surfaces and improved thermal stability. Further, by controlling the oxygen partial pressure during growth, the electrical conductivity can be controlled over many orders of magnitude from conductors at ~1000 S/cm down to semiconductors at ~0.0001 S/cm. This talk will address the basic properties of these materials, the current state of the art and the open questions in the context of both the initial design principles established by Hosono in 1995 and the current understanding.

FI-1:IL11 Why Amorphous Oxide Semiconductors Have Superior Performances than Amorphous Silicon

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Amorphous oxide semiconductors (AOSs) are expected for TFTs in flat-panel displays (FPDs) because their TFTs exhibit superior performances compared to conventional a-Si:H and organic TFTs. For example, TFT mobilities of AOS TFTs are >10 cm2/Vs, which are one order of magnitude larger than those of the conventional ones. In addition, they can be transparent owing to the large bandgap of the AOSs. Recently, more practical issues for mass-production of FPDs such as uniformity and long-term stability have been intensively investigated, which also gives expectation that the AOS TFTs can take over the existing a-Si:H TFT technology. In the first part of this talk, we will present a brief review on AOS TFT development, which include 12.1" OLED and 15" LCD. We have revealed that the above superior properties of AOSs originate from the electronic structures specific to the ionic semiconductors. We will discuss them based on experimental results, such as a capacitance-voltage method, hard X-ray spectroscopy and optical analysis, and theoretical results of first-principles calculations and device simulations.

FI-1:IL13 Raman Spectroscopy: A Tool for Understanding Bulk and Surface Properties of Nanocrystalline Oxides

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Within few years, nanomaterials have become the new eldorado for solid state scientists. New designs, new materials, new properties have been extensively studied. There are however some drawbacks near the nanometer border. One of the most important is the difficulty, and sometimes the inability, of studying structures by X-ray diffraction. Raman spectroscopy is an efficient tool to study structures and surface properties of nanocrystalline materials. When the crystal size approaches that of a phonon, confinement effects appear. The surface energy becomes an important part of the internal energy, thus allowing the existence of new phases, unstable for infinite crystals. Moreover, radical changes in the temperature and pressure of phase transitions can be observed, up to hundreds of degrees. More fundamentally, one may ask if a crystal 1 nm in size can be considered as having long range translation symmetry or is better described as a big molecule of some hundreds of atoms. Finally, the number of atoms located at the surface of the crystal becomes of the order of the atoms of the bulk. Interactions of molecules with the nanocrystal surface can thus be observed with all the power of vibrational spectrosocpy to detect the different conformations of the molecule-surface assembly.

FI-1:IL14 Design of Shallow Acceptors in ZnO Through Early Transition Metals Co-doped with N Acceptors

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We perform first-principles density-functional theory calculations to study the atomic and electronic properties of early transition metals (Y, Sc, Ti, and Zr) co-doped with N in wurtzite ZnO. By incorporating early transition metals Y, Sc, Ti, and Zr with N into ZnO simultaneously, we find that the forming complex (Y+Z), (Sc+N), (Ti+2N) or (Zr+2N) indcues a fully occupied impurity band with the N 2p character above the VBM of host ZnO. With further doping of N in ZnO, the complex (Y+2N) , (Sc+2N) , (Ti+3N) or (Zr+3N) has the acceptor ionization energy of around 0.1 eV, which is significantly lower than the ionization energy of 0.33 eV for the isolated N acceptor in ZnO. Our results show that the compensated donor-acceptor complexes could alter the VBM characteristic of ZnO, thus improve the p-type dopability. Under different growth conditions (i.e using an N2O or NO source for the nitrogen atoms), we calculate the formation energies of the defect complexes and compare the dopability of the above four co-doped systems.

FI-1:IL15 **Doping and Transport in Zinc Oxide: New Developments**

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Doping and transport properties of zinc oxide are overviewed with special emphasis on new results. ZnO can be doped n-type up to degenerate high carrier concentrations (≈1021 cm-3). As donors, especially the group III elements B, Al, Ga, In have been used, which form hydrogen-like shallow donors. Hydrogen itself also acts as a shallow donor in ZnO. P-type doping of ZnO is extremely difficult, most probably due to an intrinsic self-compensation process. Hole-doped ZnO films were reported with nitrogen, arsenic and phosphorous as acceptors. The hole concentrations (≈1017 cm-3) as well as the mobilities (≈10 cm2/Vs) were low and often not persistent. The mobility of n-type, non-degenerate ZnO can be described well by theory, the intrinsic mobility limit of ≈230 cm2/Vs (300 K) being due to optical-phonon scattering. Polycrystalline transparent ZnO films are deposited with dopant (mostly Al) concentrations exceeding some at%. The transport is now limited by ionized impurity scattering (m<50 cm2/Vs) and by electrical barriers at grain boundaries for N<1020 cm-3. New results of electron mobilities in epitaxial ZnO films will be presented, pointing to the influence of crystallographic defects. Reported (too) high electron mobilities in ZnO films could be due to lateral inhomogeneities.

FI-1:IL16 **High Mobility Hydrogen-doped In2O3 Films for Si-based Solar Cell Application**

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Near-infrared (NIR)-transparent conductive oxide films have been attracting attention because of the possibility in increasing spectral sensitivity of Si- and CuIn1-xGaxSe2-based solar cells in the region from the visible to the NIR wavelength. The high transparency in the NIR wavelengths can be achieved by reduction of free carrier absorption; i.e., increase in mobility and decrease in carrier density, provided that the same resistivity is required. So far, various cation-doped In2O3 have been investigated. Among them, Ti-, Zr-, Mo-, and W-doped In2O3 films show higher mobility at carrier density over 1020 cm-3, as compared with conventional Sn doped In2O3 films. Meanwhile, it is possible to produce hydrogen-doped In2O3 (In2O3:H) films with higher mobility (>100 cm2/Vs) at low fabrication temperature (~170 C) by the use of solid-phase crystallization of amorphous In2O3:H films, which are sputtered at room temperature with H2O addition in sputtering gas. Here, we will report on the structural, electrical, and optical properties of the amorphous and crystallized In2O3:H films and discuss the origin of high mobility in the crystallized films. The results of a-Si:H/c-Si heterojunction and thin-film microcrystalline Si solar cells incorporating the In2O3:H will also be presented.

FI-1:L17 **Electrochemically Synthesized Titania Nanostructures: Investigation of Crystal Structure and Electronic Properties**

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Arrays of nanoporous and nanotubular titania exhibit high surface area, as well as electronic and electrochemical properties that make them fitting candidates for use in solar cells, fuel cells, batteries, and chemical sensors. In addition, these oxides are appealing because they can be synthesized quickly and in a cost-effective manner using anodization techniques. To successfully utilize these materials in devices however, we need a clear understanding of their structure and properties. The following work closely examines the crystal structure and electronic properties of electrochemically synthesized TiO2 nanostructures. In particular, the detailed crystal structure of the nanotubes and the barrier oxide layer (which exists between the tubes and the metal substrate on which they're grown) will be revealed via HRTEM. Results from Mott-Schottky analysis, photo-electrochemical measurements, and the determination of bandgap values using monochromated EELS will also be reported. It is important to understand the structure-properties relationship in this material system in order to optimize the tube properties for their implementation into practical devices.

FI-1:L18 **DFT-based First-principle Calculation of Nb-doped anatase TiO2 and its Interactions with Oxygen Vacancies and Interstitial Oxygen**

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The structure and electronic properties of Nb-doped anatase (TNO) were studied from first principles using the DFT-based band structure method. Four independent types of unit cells were studied; i.e., pure anatase, anatase with Nb dopant at Ti sites (NbTi), and cells with either interstitial oxygen (Oi) or oxygen vacancies (VO). In addition, a unit cell with an NbTi and Oi, and a cell with NbTi and VO were investigated to clarify the role of nonstoichiometry in TNO. From the calculated results, the importance of the adjacent NbTi-VO and NbTi-Oi structures was pointed out, and the experimental observation of the relationship between nonstoichiometry and electronic conductivity was rationalized. The shape of the impurity states found in these structures was used to comprehend the experimental observation of carrier concentration and the charge state of Nb dopant. The changes in lattice constants supported the existence of these structures as well. On the contrary, the cell with a simple NbTi did not show significant changes in structure and electronic properties, other than the emission of an electron in the conduction band. A stabilization of the impurity state was observed in the adjacent NbTi-VO structure compared with the VO. The possibility of an essential role of this state in electric conduction was discussed.

Session FI-2

Materials Design and Device Development

FI-2:IL01 **Transparent Conductive Amorphous Oxides - Past, Present and Future**

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Amorphous oxide semiconductors are becoming as one of the most promising semiconductor materials for instance, for passive and for active electronic applications, due to the superior electrical performances and better uniformity over large areas, when compared with the conventional primary polycrystalline materials already mentioned: In2O3, SnO2 and ZnO. In polycrystalline material, grain boundaries play a major role in determining a variety of performance characteristics in active electronic devices. Amorphous materials provide a means to eliminate the effects of these boundaries, especially for devices covering large areas. This is one of the reasons why amorphous silicon is massively used in active matrix flat panel displays. Amorphous oxides are known by more than half a century, starting with the work of Denton *et al* on several transition metal oxides, with particular focus on V2O5. Because of the presence of the transition metals, these films are also quite colored and the conductivity was quite low, as well as the mobility of the order of 10-4 cm2/Vs, preventing their use in transparent electronics. In this paper we present results on amorphous transparent conductors for passive electronic applications, like IZO (In2O3:ZnO) with resistivities in the range of 10-4 Ωcm-1.

FI-2:IL02 **Novel Spintronics Application of ZnO based DMS**

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Spin-polarized transport has recently attracted with their functionality in spintronics devices because of coupling with degrees of freedom of both electron charge and spin. We are interested in the magneto-transport property of ZnMnO/ZnO (DMS/semiconductor) hetero-interface, and reported the magneto-transport property of ZnO/ZnMnO/Al-doped-ZnMnO/ZnMnO/ZnO/sapphire (0001)[1]. In this study, ZnO single crystal substrate was employed in order to discuss the intrinsic magneto-transport observed in ZnMnO/ZnO heterostructure. The mobility increases with decreasing the temperature, and reaches to 1000 cm2/Vs around 10 K. The magneto-resistance (MR) was measured in the magnetic field applied parallel to the film surface to eliminate the weak localization and Lorenz force effects. At 1.85K, a positive MR is dominant at the magnetic field below 5 T. The behavior of the positive MR can be well fitted to Brillouin function (S=5/2). Based on these results, it seems to be concluded that there exists an s-d interaction between s electron conducting in ZnO layer and Mn d spin in ZnMnO barrier.[3] This paper describes that the possible application of ZnO based DMS for novel spintronics devices.

[1]T. Edahiro et al, JAP, 93,7673 (2003); [2, 3]K. Masuko et al, JAP, 103,07D124(2008),PRB (2009)accepted

FI-2:L03 Non-oxide Wide-bandgap p-type Semiconductors BaCuChF (Ch = S, Se, Te)

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BaCuChF (Ch = S, Se, Te) is a family non-oxide wide-bandgap p-type semiconductors. BaCuChF thin films and solid solutions prepared by pulsed laser deposition are transparent to most of the visible spectrum. The charge carrier mobility in epitaxial BaCuChF samples is quite high as for a p-type material (8.0 cm ^ 2/Vs in BaCuTeF). Polycrystalline BaCuChF thin films have significantly smaller mobility (0.3 cm ^ 2/Vs in BaCuTeF) because of the anisotropic crystal and band structure and scattering by the oxidized grain boundaries. X-ray and ultraviolet photoemission spectroscopy experiments on BaCuChF pellets confirm that BaCuChF surfaces exposed to the atmosphere are oxidized. Oxygen-free F-deficient surfaces of polycrystalline BaCuSeF thin films have a work function of 4.6-4.9 eV. Concentration of free holes in undoped epitaxial BaCuChF films is 10 ^ 18 - 10 ^ 20 cm ^ -3. Density functional theory calculations suggest that free charge carriers in this material originate from copper vacancies, but attempts to decrease the carrier concentration by increasing the copper content of the films have had limited success. Traditional extrinsic p-type doping of BaCuChF thin films is also challenging, but we attempted some unconventional doping strategies.

FI-2:L04 Unusual Dielectric and Conductive Behavior of ZnO Bicrystalline (000-1) Interfaces

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We prepared the ZnO bicrystals with (000-1) interfaces by diffusion bonding at 1450 degree C together with platinum plates on each (0001) surface. Platinum plates prepared as such formed ohmic contacts stable for the measurements up to 800 degree C in air, and thus well-defined Arrhenius behavior of the barrier was observed in the intermediate temperature range with the activation energies characteristic for dopant elements such as Co, Mn, Ni, Cu, Pr, and Bi, sputtered on the interface before diffusion-bonding. The low temperature ac response was multi-faceted. The barrier heights determined by C-V analysis could not be directly related with the temperature-independent or clearly PTC barrier resistance. While the ac-response of the bicrystals with dopants such as Cu and Mn, may be explained by the presence of deep trap levels by admittance spectroscopy, pseudo-relaxor ferroelectric behavior was observed in the temperature dependence of dielectric response as well as in the polarization hysteresis.

FI-2:L05 Mechanism of Electrical Properties Degradation of ZnO:Al Films During Growth at Elevated Temperatures

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Significant increase of electrical resistivity of ZnO:Al (AZO) transparent electrode during thermal treatment is a known problem in thin film solar cell technology. To study it, AZO films with different Al concentrations were grown by reactive pulsed magnetron sputtering at substrate temperatures Ts=40-600 °C. The electrical resistivity of the films has a minimum and free electron mobility has a maximum at an optimum substrate temperature. At higher temperatures, Al/Zn ratio in the film increases and triggers formation of homologous phase (ZnO)3(Al2O3) according to X-ray absorption near edge structures (XANES) and X-ray diffraction data. XANES peak intensity ratio analysis rules out formation of aluminum oxides and Zn-Al-O spinels. Thus, formation of (ZnO)3(Al2O3) causes decrease of the free electron density by deactivation of Al donor and decrease of free electron mobility due to induced structural disorder. It leads to electrically insulating films at Ts>300 °C in case of high Zn/O flux ratio during growth. Decreasing the latter, it is possible to shift this phase formation to Ts>450 °C. Annealing of (ZnO)3(Al2O3) sample at 900 °C for 2 hours causes its decomposition into ZnO and ZnAl2O4 confirming assumption about metastable character of this homologous phase.

FI-2:IL06 Aqueous Processing for Oxide Electronics

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High-quality oxide films can readily be deposited from aqueous solutions free of organic stablizers. Because water exhibits a high surface tension and precursor species are small solvated nanocluster units, rapid condensation lead to films exhibiting exceptional uniformity and surface smoothness. At the same time, the aqueous environment provides a natural means for limiting carrier concentrations in oxide semiconductors. In this contribution, we will highlight recent results from the solution-deposition of new oxide dielectrics and semiconductors. Dielectric-semiconductor interface characteristics and thin-film transistor device performance will be considered.

FI-2:IL07 TCO Nanoparticles: Properties and Electronic Devices

Roland Schmechel, Faculty of Engineering, University Duisburg-Essen and CeNIDE, Duisburg, Germany

TCO nanoparticles are considered for printing processes as an alternative to plasma or vacuum based coating technologies. In this talk, the application of ITO nanoparticles for printable transparent electrodes as well as semiconducting oxide nanoparticles for thin film transistors will be presented. The effect of post-heat treatment of indium-tin-oxide nanopowders in reducing atmosphere on defect structure, electrical resistivity and transparency will be considered. Further more, a hybride system of ITO and conducting polymer PEDT/PSS was investigated. A decrease in electrical conductivity of PEDT with increasing ITO content up to a volume fraction of about 16 vol % is observed. Above the volume fraction of 16 vol % the conductivity increases very steeply, most probably due to percolation between the ITO-nanoparticles. The results are discussed with respect to changes in the infrared polaron and bipolaron absorption of PEDT and morphological changes. Finally, the application of TCO nanoparticles in thin film transistors will be considered. Device characteristics and environmental dependency are discussed with respect to morphological characteristics.

FI-2:L08 Change of Electrical Properties of a-IGZO TFT Depending on Processing Parameters

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Recently, colossal researches are conducted about a-IGZO as an alternative of a-Si. We studied on the electrical property changes of a-IGZO TFT depending on the process parameters. We used p+ Si substrate as a gate electrode and thermal SiO2 as a gate insulator. An a-IGZO active layer was fabricated using rf-magnetron sputtering on the thermal SiO2 with various power and O2 ratio. We varied rf-power, O2 ratio from 1.5 W/cm2 to 5 W/cm2 and from 1.2 to 1.8, respectively, and we investigated the relation between rf-power, O2 ratio and TFT characteristic such as Vth, on current, S.S, hysteresis changes. We found out that there were remarkable changes in the TFT characteristics with varying power and O2 ratio. As increasing power, S.S was deteriorated and on current was decreased while hysteresis was increased, and as increasing O2 ratio, Vth shifted positive while on current decreased. In order to demonstrate the mechanism of the property change, we investigated the interface between channel layer and gate insulator layer, and also analyzed the density of states(DOS) of the channel layer.

FI-2:L09 Simultaneous Monitoring of Optical and Conductance Changes during the Redox Transformation of Transparent Conducting Layers

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We have recently introduced[1] a new combination of two in situ electrochemical techniques. It makes possible the simultaneous monitoring the conductance and the spectral changes during the redox transformation of electrodeposited films. As an example, the correlation between the development and sustenance of the name-giving property of conducting polymers and the rate of the absorbance increase/decrease of the different charge carriers in the film will be presented and discussed. Similar combination of the data obtained by these parallel, independent methods can be exploited in the elucidation of the redox mechanism of various transparent electroactive layers. Financial support from the Hungarian National Research Fund (OTKA K72989) is gratefully acknowledged.

[1] E. Peintler-Kriván, P.S. Tóth, and C. Visy, Electrochem. Commun. 11, 1947, 2009

FI-2:L10 Inkjet Printing of Transparent Electronics Based on Low Temperature Process of Ternary Metal Oxides

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A category of materials that was shown to provide high performance electronic components is that of amorphous metal oxide semiconductors. The transition from vacuum-based deposition techniques, such as sputtering or pulsed laser deposition, that are used for these materials to an inkjet printing approach is very important in terms of low-cost and large area electronics production. In this work we are presenting the capabilities of inkjet technology in the fabrication of printed circuits of thin-film transistors based on ternary oxide semiconductors of Ga2O3-In2O3-ZnO (GIZO). We examine the production of inks capable of providing functional GIZO semiconductors starting by a scheme of three basic inks corresponding to each one of the three metal oxide components of the ternary oxide. By mixing these three basic inks under different ratios we obtain different compositions of the GIZO semiconductor resulting in different electrical properties. In order to test the semiconductor's performance as an electronic component, TFT devices were fabricated by printing the desired materials on Si-SiO2 or/and glass substrates. The ability of these devices to control other electronic components like LEDs will also be discussed.

FI-2:IL11 P-type Transparent Semiconductors: Synthesis and Applications

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P-type transparent conductors (TCs) are candidate anodes or hole injectors for light-emitting devices. The carrier concentration and work function of a p-type TC may be simultaneously increased, which is not possible in an n-type TC like ITO. BaCuChF (Ch = S, Se, Te) is a family of p-type TCs that do not contain oxygen. Nominally undoped BaCuChF thin films prepared by pulsed laser deposition have a high concentration ($p = 10^{18} - 10^{20}$ cm^{-3}) of reasonably mobile holes and wide optical band gaps that can be tuned continuously from 2.9 - 3.5 eV. Photoelectron spectroscopy experiments show that the work function of a clean F-deficient BaCuSeF surface is 4.6-4.9 eV and that the Fermi level at the surface is pinned by the defects. In-situ interface experiments with zinc phthalocyanine (ZnPc) suggest that the BaCuSeF/ZnPc interface is not reactive and that the hole-injection barrier is lower than for the ITO/ZnPc interface. An electron-depleted ZnPc layer at the interface causes band bending in ZnPc, so there is no valence band discontinuity at the BaCuSeF/ZnPc interface. We will also discuss synthesis issues pertaining to both oxide and chalcogenide p-type TC films.

FI-2:IL12 Transparent Conductors on Polymer Films

Matthias Fahland*, Tobias Vogt, Alexander Schönberger, Fraunhofer FEP, Dresden, Germany; Uwe Partsch, Fraunhofer IKTS, Dresden, Germany

The paper will present a review of different solutions for transparent conducting electrodes on flexible substrates. The analysis of the present situation reveals a gap for low sheet resistance electrodes. Two new approaches to the problem will be presented. The first one is a novel technology for the deposition of zinc oxide on polyethylene terephtalate film. The intention for this process is the establishment of a low cost coating in a roll-to-roll machine. Silicon was used as the dopant material with a concentration varying in different samples between 1 and 4%. The optimum parameters provided a transparent layer with a sheet resistance of 16 Ωsqu. Metal grids are a second promising approach for achieving low sheet resistance electrodes. The combination of these grids with transparent conducting oxides (TCO) will be presented. The TCO were deposited under vacuum in a roll-to-roll coating machine. The grids were applied by aerosol jet printing and subsequent tempering of the film.

FI-2:L13 Emerging p-type Transparent Conductive Oxides: Theoretical and Experimental Studies

Mircea Modreanu[1], Michael Nolan[1], Ekaterina Chikoidze[2]*, Bernard Servet[3], Guy Garry[3], Guido Huyberechts[4], [1]Tyndall National Institute, Cork, Ireland; [2]University of Versailles CNRS (GEMAC), Meudon, France; [3] Thales Research & Technology France, Palaiseau cedex, France; [4]Umicore Group Research & Development, Olen, Belgium

Most of the currently known TCOs exhibit only n-type electrical conductivity and due to the lack of controlled and reproducible p-type conduction in these oxides there is a limited number of oxide-based p-n junctions. In this presentation, we report on a combined modelling and experimental effort towards developing a new Cu_2O-based p-type TCO. Using periodic density functional theory, we have investigated the formation of Cu vacancies as the origin of p-type character in Cu_2O-based TCOs. Based on this and modelling of the impact of doping on the band gap of Cu_2O and $SrCu_2O_2$, Ba doped $SrCu_2O_2$ (BaSCO) has been proposed as a new p-type TCO and has been synthesised and characterised. The optical properties have been inferred from spectroscopic ellipsometry and reflectance/transmission spectrophotometry measurements, over a large spectral range from ultraviolet to Far Infrared. BaSCO offers extended transparency in both UV and infrared range while retaining good electrical properties. We also report the optical constants and the assignment of infrared, Raman active modes for both undoped, and BaSCO thin films. Temperature-resolved resistivity and Hall effect measurements have been used for the conduction mechanism study.

FI-2:L14 Effects of Ag Doping on the Performance of ZnO-based Thin Film Transistor

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Owing to its unique optical and electrical properties, such as transparency and stability, ZnO is a promising oxide semiconductor utilized is multifunctional applications. In particular, the use of ZnO as an active layer in thin film transistors (TFTs) shows many advantages among them the high electron channel mobility leading to higher drive current and device operating speeds. The characteristics of ZnO thin films and then ZnO TFTs can be widely changed by various doping elements such as Al, Ga, N and Ag. Especially Ag doped ZnO thin films have been studied by many groups and it was demonstrated theoretically and experimentally that Ag could be have as acceptors. Furthermore Ag improves the stability of ZnO when it is located in interstitial sites and blocks the formation and migration of new Zn interstitials. However no report has been presented about Ag doped TFT. In this study, we fabricated Ag-doped ZnO thin film transistor (SZO TFT) using a bottom-gate structure on thermally oxidized heavily doped p-Si (100). The SZO thin films were deposited via pulsed laser deposition (PLD) from a 3 wt% Ag-doped ZnO target using a KrF excimer laser (λ, 248 nm) at 300 °C. The SZO TFT (W/L = 50 µm/150 µm) exhibited a μ_{sat} = 3.48 cm^2/Vs, $I_{off} = 1.99 \times 10^{-11}$A and $I_{on} = 1.85 \times 10^{-6}$A.

FI-2:L15 Simple Control of Threshold Voltage in Ag-doped ZnO Nanowire Field Effect Transistors

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The silver doped zinc oxide (SZO) nanowires(NWs) were grown on the (0001) plane of sapphire substrate by hot-wall pulsed laser deposition (HW-PLD) with an Au catalyst at 800 °C. Both enhancement mode (E-mode) and depletion mode (D-mode) field effect transistors (FETs) were fabricated by using SZO NWs on the highly n-type silicon substrate. The threshold voltage (Vth) of the SZO FET could be shifted from 2.45 to -3.2 V depending on the diameter of NWs without any significant change in the subthreshold swing (SS) and current on/off (Ion/off) ratios. We demonstrate that the transfer characterization of SZO nanowires FETs were associated with changing of NWs diameter. The optimized fabrication of the two operation mode of SZO NWs FET is important for the wide application of NW FET logic inverters.

FI-2:IL16 Amorphous Transparent Conductors for Photovoltaic Application

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Amorphous mixed metal oxide transparent conducting oxides (TCOs) are of increasing interest due to the excellent opto-electronic properties and smoothness. Conductivities of $\sigma \geq 2500$ S/cm are common for amorphous In-Zn-O (a-IZO) films grown from ceramic targets while other amorphous oxides such as Zn-Sn-O (a-ZTO) although lower in conductivity display higher work function and provide opportunities for device optimization via ternary In-Zn-Sn-O (a-IZTO) alloys. Here we present the development of amorphous oxides for transparent contacts in PV applications. Specifically, we discuss the use of these amorphous oxides in Si, thin film and organic photovoltaics (PV). In the case of a-IZO and related compounds, their use in place of traditional TCOs may offer better resistance to humidity, reducing water-induced degradation in the resultant PV systems. We discuss our initial thin film PV application testing of a-IZO finished CIGS solar cells with demonstrated efficiencies equivalent to traditionally finished CIGS cells (η = 16.4%). In addition to the CIGS example we will touch upon our use of a-IZO/a-ZTO/a-IZTO in other PV applications. We will also discuss the details of the amorphous oxide growth, electrical conductivity, optical transparency and damp heat testing.

FI-2:IL17 **Structure Controlled TCOs for Solar Cells Using Fast Growth Rate Atmospheric Pressure Chemical Vapour Deposition**

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High performance transparent conducting oxides, in particular doped SnO2, have significance for optimising photovoltaic cell performance. A key aspect of performance is to control the surface morphology. Furthermore, if cost reduction targets are to be met, high throughput coating processing is essential We have employed APCVD processing to deposited F-doped SnO2 using either monobutyl tin trichloride or tin tetrachloride with aqueous HF or trifluoro-acetic acid as the dopant source. A critical aspect of film performance in a-Si cells, is surface structure control, and we will show how a high degree of surface structure control can be obtained by process control. The enhanced performance this offers will be illustrated by comparison with (commercially available) TCO CVD coated glasses, where these TCO coatings show excellent performance resulting in a high quantum efficiency yield for a-Si:H solar cells.

FI-2:L18 **Phosphorus Doped ZnO, p-type and n-type, a Material for Photovoltaic and Other Applications**

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Transparent p-type and n-type ZnO has attracted great interest in recent years, due to their potential applications in photovoltaic, light emitting and some other functional devices. We have carried out a systematic study on phosphorus (P)doped ZnO. It is shown that P:ZnO can either be p-type or n-type, based on the growth and doping conditions. Multi-techniques have been employed to verify the achievement of p-type ZnO. We have also fabricated P:ZnO p-n homo-junctions, which show rectifying behaviour further proving our achievement of p-type ZnO. Various techniques have been employed in the characterization of the samples. The mechanism in the achivement of p-type and n-type ZnO is studied. We propose that the appearance of p-type or n-type ZnO is a competition between acceptors and donors in ZnO. ZnO is known to be a typical n-type material due to the existance of intrinsic oxygen vacancies in the material. To convert ZnO into p-type, we must generate enough acceptor carriers, by doping such as phosphorous into the material in our case. We need firstly compensate donor carriers and then have surplus acceptors. Our experimental results have verified the validity of this proposal. The application of ZnO in solar cells and other devices is also discussed.

FI-2:L19 **Tuning Color of p-type Wide Band Gap Semiconductor via Their Nanostructuration**

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Compared to n-type, p-type TCOs are relatively rare but have gained momentum in research after the discovery of p-type conductivity in CuAlO2 thin films. Since then, different p-type TCO materials were investigated. Nowadays, it is very important to achieve the synthesis of nano-particles of p-type TCOs, in particular for application in p-type dye sensitized solar cells. In this framework, we have embarked on the synthesis of nano-particles of the p-type transparent SC CuGaO2, LaOCuS, NiO and ZnO via hydro and solvo thermal routes. For CuGaO2, we found that the use of ethylene glycol as reducing agent lowers the temperature of formation of the aimed material, and eases the formation of nano-layered particles. Moreover, we observed that the pH of the precursor solution allows tuning of the size and the color of the particles. For LaOCuS, white powder of nanoparticles is synthesized using an original route. The chemical and crystallographic features of these materials were investigated (EDX ,XRD ,TEM) and their p-type character was ascertained by voltamperometric measurements. For NiO, a direct deposition route on a FTO substract has been found. With this route vertical layers are obtained, which is very usefull for dye sensitized solar cells.

FI-2:L20 **Conductive Self-cleaning Films Deposited by Aerosol Assisted Chemical Vapour Deposition**

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In 2008 photovoltaic energy attracted the second highest level of worldwide investment at $33.5bn. Many research groups are investigating methods to reduce the cost of photovoltaic energy through two distinct approaches, (1) increasing the overall efficiency of the photovoltaic cell in producing electricity, and (2) reducing the cost of the cells per unit of power generated. It has been estimated that an output reduction of as much as 50% is observed when contamination occupies as little as 3% of the total area of a photovoltaic module when it is in-situ, effectively cancelling out much of the gains in efficiency and cost per unit of power produced in the laboratory. A number of groups have developed thin film solutions to the problem, based around the popular semiconductor photocatalyst titanium dioxide. In spite of this the technology often requires an additional layer, or substrate to be added to the module, increasing the cost of the cells per unit. With this in mind, we report a low cost method of depositing a transparent conducting compound, suitable for use as a front contact in photovoltaic cells, which shows dual self-cleaning properties in its ability to oxidise organic contaminants and an innate hydrophilic surface.

FI-2:IL21 **Chromogenics for Sustainable Energy**

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Chromogenic materials are characterized by optical properties that can be changed by an external stimulus and are of much interest for energy efficient and comfort-enhancing windows in buildings. This paper first discusses thermochromic thin films and nanoparticles with emphasis on new vanadium-oxide-based materials capable of metal-insulator transition near room temperature and having luminous absorption lower than for earlier known materials. We then present new data on electrochromic nickel-tungsten-oxide-based films with high coloration efficiency and discuss how they can be incorporated in electrochromic thin-foil-devices. Finally we give some perspectives on the combination of thermochromics and electrochromics in energy efficient fenestration.

FI-2:IL22 **Pathways Towards p-type Oxide Layers for Optoelectronic Applications**

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State of the art optoelectronic applications such as thin film solar cells, flat panel displays and light emitting diodes suffer from the non-availability of p-type oxide materials on the industrial scale. Novel technologies such as transparent electronics, UV light emitting diodes and improved thin film solar cells using wide band gap p-type oxide layers as front contact will be available once p-type oxide layers with proper layer and interface properties can be obtained on an industrial scale. In this paper, we report on our progress towards p-type oxide layers for industrial applications. We address the first principles density functional theory modelling of ZnO based layers where a pathway towards p-conductivity is seen taking the nitrogen doping of grain boundaries into account. The second part of the paper is on the synthesis of p-type Delafossite layers such as $CuCr_{1-x}Al_xO_2$:Mg by Sol-Gel and $CuCrO_2$ by hollow cathodes gas flow sputtering. We report on the deposition processes and film properties obtained. Both methods reveal p-type conductivity by means of Seebeck-coefficient measurements.

FI-2:L23 **Au-based Transparent Conductors for Window Applications: Effect of Substrate Material and Temperature**

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Transparent conductors, TCs, are of great importance in many areas of modern technology and often used for window applications. Au-based TCs, with excellent conductivity, have emerged as an interesting alternative to other metal-based and semiconductor-based TCs. Au-based TCs are also electrochemical stable and therefore suitable in harsh environment such as electrochromic devices (“smart windows”). In order to study effects of different substrates, thin layers of Au have been deposited by DC magnetron sputtering onto glass substrates and glass/ITO substrates. The role of different temperatures has also been studied by deposition of thin Au layers onto non-heated and heated glass/ITO substrates. Measurements of electrical conductivity, optical transmittance and reflectance and surface topology by atomic force micrographs and scanning electron micrographs characterize the samples. The results will be presented and discussed in detail.

FI-2:L24 **Fabrication of (001)-oriented Anatase Ti1-xNbxO2 Films on Glass Substrate with Perfectly Aligned LaAlO3 Seed Layer**

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Nb-doped anatase TiO2 (TNO) is a transparent conducting material with some unique features, such as high chemical stability and large refractive index. Recently, we found that the electron effective mass of TNO along the c-axis is ~6 times larger than that along the a-axis, originating from the anisotropic d-orbital-dominated conduction band. Thus, fabrication of (001)-oriented TNO films is a promising way for further improving conductivity of TNO films. To control crystallographic orientation of a thin film, it is effective to introduce a seed layer with specific surface crystalline structure. In this study, we tried to fabricate (100)-oriented LaAlO3 (LAO) films, of which lattice constant is matched with the a-axis length of TNO, on glass substrates by using the crystalline imprint epitaxy (CIE) method. This new method is a kind of solid phase epitaxy, where an amorphous LAO film deposited on a glass substrate was crystallized heteroepitaxially from the surface of a lattice-matched LaSrAlO4 single crystalline template, which was pressed onto the film during post annealing. The LAO films obtained by the CIE method showed smooth surfaces with perfectly aligned crystallographic orientations. We confirmed that the LAO films worked well as seed layers for (001)-oriented TNO films.

FI-2:L25 **The Relationship of Electrical and Structural Properties of Synthetic Melanin Embedded in Matrix of Thin Films Zinc Oxide, for Their Use as Electrodes in Bio-generators**

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Melanin doped zinc oxide thin films were obtained using a process of soft chemistry with pH in the basic region. The electric and structural properties of these films were compared with films of undoped ZnO obtained using the same process. Undoped films show the characteristic diffraction pattern, wurtzite type, polycrystalline ZnO, while the doped films also present other signals associated to the melanin or some derived present phase of this. It is relevant because melanin is reported as amorphous material. Differences of grain size were detected and attributed to the presence of at least two existent phases in the films. Resistivity data were analyzed from the obtained values of films of undoped ZnO and associated to the structural changes. The films have turned out to be stable in bio-generating systems of useful energy.

FI-2:IL26 **Electronic Structures and Energy Band Lineup of Transparent Conducting Materials Studied by Photoelectron Spectroscopy**

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Transparent oxide semiconductors and related materials have attracted much attention due to e.g. expectation for transparent electronics. One of the most promising applications is a transparent thin film transistor (TFT) for next generation LCD / OLED. When we apply these materials to an actual device, it is important to know energy positions of the valence band maxima and the conduction band minima with respect to the vacuum level and energy structures near the Fermi level. In this talk, the energy positions of transparent conducting oxides and related materials are given as an energy band lineup. Energy structures near the Fermi levels in thin films were discovered by bulk-sensitive hard x-ray photoelectron spectroscopy (HAXPES). Furthermore, interfacial electronic structures between transparent conducting materials and organic semiconductors will also be given as an application of the band lineup because high efficient carrier injection is an important issue to be solved to realize high performance heterojunction devices including OLEDs. We have examined RT-stable electride, C12A7:e-, and Cu+ based p-type conductors, LaCuOSe and CuxSe, as candidates of high performance cathode and anode, respectively.

FI-2:IL27 **Thermophysical Properties of Various TCO Films; ITO, IZO, AZO and TTO Films**

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Thermal diffusivity of various transparent conductive oxide (TCO) films, such as polycrystalline Sn-doped In2O3 (ITO), amorphous indium zinc oxide (IZO), Al-doped ZnO (AZO) and Ta doped SnO2 (TTO) films with a thickness of 200 nm has been measured using nanosecond thermoreflectance system. To derive the thermal diffusivity of the TCO films, the thermoreflectance signals were analyzed based upon an analytical solution of the one dimensional heat flow across the three-layered film/substrate system. The resistivity, carrier density and hall mobility of the IZO films ranged from 4.2×10-4 to 22.7 ? cm, from 2.6×1016 to 4.2×1020 cm-3, from 10 to 51 cm2/Vs, respectively[1]. The thermal diffusivity of the IZO and polycrystalline ITO films deposited at the unheated substrate, under total gas pressure of 0.7 Pa was 1.2×10-6 m2/s and 2.2×10-6 m2/s, respectively. The thermal diffusivity of the IZO film was approximately, equivalent as that of amorphous ITO films and smaller than the polycrystalline ITO films[2, 3]. Thermal properties of all the TCO films will be discussed based on Wiedemann-Franz law and thermal transportation by phonon.

[1]T. Ashida, Y. Shigesato, et al, J. Vac. Sci. Technol. A, Vol. 25, No. 4 (2007) 1178; [2]T. Yagi, Y. Shigesato, et al, J. Vac. Sci. Technol. A, Vol. 23, No.4 (2005) 1186; [3]T. Ashida, N. Oka, Y. Shigesato, et al, J. Appl. Phys. 105, (2009) 073709.

FI-2:L28 **Electrical Transport in Al Doped ZnO Grown by Reactive Pulsed Magnetron Sputtering**

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The synthesis of transparent conductive oxides (TCO) with high transmittance in the near infrared (IR) spectral range is a key requirement for increasing the power conversion efficiency in thin film solar cells. As the absorption at energies close to the Si band gap (1.1 eV) is caused by the free electron plasma it is necessary to maximize their mobility at moderate densities (~5x10^20 cm^-3) in order to simultaneously reach low resistivities of ~2x10^-4 Ohm*cm and improve the IR transmittance. Therefore a reactive magnetron sputtering method using metallic Zn/Al alloy targets was developed to achieve high carrier mobilities (~45 cm^2/Vs) in ZnO:Al thin films. The influence of growth temperature, oxygen partial pressure and target Al concentration on the electrical film properties has been investigated systematically by Hall effect measurements. Additionally XRD, X-TEM, AFM, ERDA, RBS and spectroscopic ellipsometry were employed to reveal film structure, composition and optical properties. The experimentally observed limit of mobility in polycrystalline ZnO:Al is discussed in terms of ionized impurity scattering and clustering as well as grain boundary limited transport.

FI-2:L29 **Morphological Control and Photochemical Properties of Nitrogen-doped Titania Nanoparticles by Microwave-assisted Solvothermal Process**

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The combination of microwave and solvothermal techniques has been used in the last few years for the synthesis of nanocrystalline powders. The advantages of microwave-solvothermal process over conventional hydrothermal / solvothermal method are: extremely rapid kinetics of crystallization, very rapid heating to temperature of treatment and possible formation of new metastable phases. In the present research, nitrogen-doped titania nanoparticles were successfully prepared by a microwave-assisted solvothermal process using desired solvents, such as water, methanol, and ethanol. The phase compositions, specific surface areas, photo chemical properties, and morphology of the obtained samples were characterized. The as-prepared samples showed visible-light absorption in the range of 400-550 nm, indicating its potential applications as visible light induced photocatalyst. The effect of treatment solvents and pH value were investigated in details. The morphology of the samples varies from different solvents and pH value, fine powders, nanorods, sphere with needles on the surface were obtained. The results of the present research indicated that the microwave-assisted solvothermal process was an effective/potential way for the synthesis of some novel functional materials.

FI-2:L30 Development of New Oxide Semiconductors for Thin-film Transistors Using Doping Methods

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Currently, many researchers have been investigating oxide semiconductor based thin-film transistors (TFTs). Specially, as amorphous oxide semiconductors, indium-gallium-zinc oxide (IGZO), and zinc-tin oxide (ZTO) have been studied extensively due to the outstanding electrical properties such as high mobility, low sub-threshold swing (SS), high drain current on-off ratio, and low processing temperature. In this paper, based on the conventional oxide semiconductor systems (IGZO, ZTO, ZITO, ZIO, IGO, and so on), we will try to devise new oxide semiconductors by doping methods. The main purpose on doping is to increase the device stability. As doping materials, boron oxide, boron nitride, aluminum oxide, aluminum nitride, and other metal oxides will be used and explored for the application to TFTs.

FI-2:IL31 Chemical Modification of SnO2 as an Approach to Selectivity Enhancement for Gas Sensor Materials

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The serious disadvantage of semiconductor gas sensors is their poor selectivity due to wide spectrum of active surface centers that restricts the possibility for determine the contribution of specific gas molecules into integral electrical signal. One of the ways for improving selectivity is a surface modification directed to the allocation of catalytic modifiers in nano-structured matrix of semiconductor oxide. The conception of sensing materials in the frame of catalytic approaches of “local” centers looks promising enough. The solid - gas interaction in this case is carried out through formation of surface complex so that chemical nature of modifier, its activity in acid-basic or redox reactions plays a decisive role. The choice of modifier for sensing material could be taken with regard of nature of target gas molecule. It is shown that modification of the surface of SnO2 crystallites, forming thick films of conductive sensor materials, with catalytic clusters allows selective response of sensors to different gases, such as CO, NH3, H2S, NO2 and acetone vapor. These selective sensor responses can be obtained in the ranges of gas concentrations close to or below threshold limit values. These results allow us to propose the use of obtained materials in electronic nose systems.

FI-2:L32 Self-diffusion in TCO Materials: A Theoretical Approach

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We present calculations of migration energies for all relevant intrinsic defects in indium oxide, tin oxide and zinc oxide. Total energy calculations are carried out within the framework of density-functional theory on a semi-local level and in conjunction with the nudged elastic band method. Due to the differences in crystal structure the self-diffusion in these TCO materials is substantially different. The structural peculiarities are especially important for indium oxide where we show that the low energy migration processes do not contribute to the diffusion. In that case additional migration pathes with different barriers need to be active for larger displacements to take place. While for cation interstitials we observe a general trend for all materials, the oxygen interstitials migration is very different. A qualitatively different behavior is also found for the cation vacancies. Tin oxide shows a notably high anisotropy which is not found for the other materials. The importance of our findings is discussed in the context of TCOs as electrode material for organic light emitting diodes.

Session FI-3
Applications

FI-3:IL02 High-performance and High-CRI OLEDs for Lighting and Their Fabrication Processes

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The improvement of the basic performance makes white OLEDs the promising candidate of the next generation, environmental friendly lighting source. However, for the practical application, additional properties of higher color rendering index (CRI), long lifetime at high luminance, large area uniform light emission, and high reliability for long time operation are required. Furthermore, innovative fabrication processes specialized for OLED lighting are required to reduce the cost by improving the material utilization and productivity. We developed various technologies for OLED lighting in the Japanese governmental project “High-efficiency lighting based on the organic light-emitting mechanism” from 2007. In this project, high CRI, highly efficient and long lifetime white OLEDs were realized by optically designed two-unit structure with a fluorescent deep blue emissive unit and a green / red phosphorescent unit. A reliable encapsulation structure with high heat radiation and moisture-proof characteristics realized a stable emission at high luminance as well as long storage stability. High speed wet coating process and vacuum deposition process for very thin layers were developed to improve the accuracy, material utilization and productivity.

FI-3:L03 Controlled Threshold Voltage Shift of ZnO Nanowire Field Effect Transistors Depending on the Diameter of Nanowire

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We studied the effect of diameter on the electrical properties of ZnO nanowire FET (Field Effect Transistors). The ZnO nanowires were fabricated with Au catalysts on sapphire substrates by Hot-walled PLD and configured FET by photo-lithography process. In order to control the diameter of nanowires, ZnO nanowires were grown on the various Au catalyst with different thickness. We have confirmed that the nanowires have different diameters as the variation of Au catalyst thickness by FE-SEM measurement. As increasing diameter of the nanowire, the threshold voltage of ZnO nanowire FET shifted negative direction and I-V characteristic is varied. This phenomenon is ascribed to the difference of conductive layer in the nanowires related with various diameter of nanowires.

FI-3:L04 Bipolar Resistive Switching Behavior in Ti/MnO2/Pt Structure for Nonvolatile Resistive Switching

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We examined the electrical properties of Ti/MnO2/Pt devices with stable and reproducible bipolar resistive switching behavior. The dependency of the memory behavior on the cell area and operating temperature suggest that the conducting mechanism in the low resistance states is due to the locally conducting filaments formed. X-ray photoelectron spectroscopy showed that non-lattice oxygen ions form at the MnO2 surface. The mechanism of resistance switching in the system examined involves the generation and recovery of oxygen vacancies with the non-lattice oxygen ions. The Ti/MnO2/Pt device has potential applications in nonvolatile resistive switching memory devices due to the reasonable switching endurance over the course of 105 cycles, long term retention at 85 °C and a uniform distribution of both resistance states and operation voltage. A high content of non-lattice oxygen ions exists on the MnO2 film surface. The switching behavior can be explained by the generation and recovery of oxygen vacancies with non-lattice oxygen ions.

FI-3:IL05 Plasma Enhanced Deposition of Metal Oxide Films for Photovoltaics

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In this talk I will discuss the growth of metal oxide films, by plasma enhanced methods, in particular zinc oxide and aluminum oxide films and combinations there of. The aluminum doped zinc oxide films find wide spread use as the transparent conductor for thin film photovoltaics where aluminum oxide is a excellent passivation layers for c-Si solar cell. Whereas zinc oxide films are polycrystalline and have as a consequence strong roughness and a morphology development, aluminum oxide films are amorphous and homogeneous along the growth direction. However, for aluminum oxide films the internal field, generated by built-in charge on the Al2O3/c-Si interface is of key importance for the excellent passivation quality and proper growth and annealing conditions to be researched. The morphology development in aluminum doped zinc oxide films are monitored in situ by means of spectroscopic ellipsometry, applying a novel techniques of using Kramer-Kronig consistent B-spline fitting routines, reveal a strong sheet resistance gradient with increasing film thickness. This effect is accompanied by pyramid-like film growth development as determined from AFM and cross-sectional SEM. Better understanding of intrinsic and extrinsic parameters on film properties eventually allow to control the film.

FI-3:IL06 Application of ZnO-based Transparent Electrodes to TFT-LCDs as Substitution for ITO

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In our talk, we will report a successful fabrication, whose process is entirely compatible one with conventional manufacturing process of commercial TFT-LCD panels, of 3-inch panels of ZnO-based common electrodes mounting and will show highlight data concerning properties to be required for a wide range of applications. The panel showed the performance equal to TFT-LCD equipped with ITO-based electrodes. We confirmed 1000 h operation without any change of performance under the condition of 60 °C in 90% humidity atmospheres. Then, we will explore the characteristics of GZO films prepared by different type deposition methods: Ion-plating using DC arc discharge, DC magnetron sputtering, and RF power superimposed DC magnetron sputtering were compared in terms of the thermal stability of GZO films. Finally, relationship between effects of grain boundaries and the influence of thermal annealing on electrical properties of GZO films will be discussed by a comparison of Hall effects measurements with optical characterization based on Drude model. The difference between the Hall mobility and the optical mobility were attributed to carrier scattering at grain boundaries. Annealing at rather high temperature caused a decrease in the Hall mobility and an increase in the optical mobility.

FI-3:L07 Nanostructured Metal Oxides as Cathode Interfacial Layers for Hybrid-polymer Electronic Devices

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We report the use of nanostructured metal oxides as cathode interfacial layers for improved performance polymer electronic devices such as polymer light-emitting diodes (PLEDs) and solar cells. In particular, we employ two reduced metal oxides, namely a tungsten oxide and a molybdenum oxide, both deposited as very thin layers between an aluminum (Al) cathode and the (photo)active polymer layer. In both cases, we achieve improved PLED device performance reflected as an increase in the current density, luminance and a reduction of the operating voltage and enhanced solar cell performance demonstrated as an increase in the short-circuit photocurrent and the power conversion efficiency. The improved PLED device characteristics are attributed to enhanced electron injection that primarily results from the lowering of the effective interfacial barrier, as evidenced by photovoltaic open circuit voltage measurements, and improved electron transfer. On the other hand, the observed improvement in the solar cell performance is attributed to the combined effects of the interfacial layer acting as “an optical spacer layer” that enhances optical absorption as a result of light redistribution in the cell, and reducing the contact resistance thus enhancing electron extraction at the cathode interface. Correlation between the metal oxide surface morphology and the device performance is also investigated and will be discussed.

FI-3:L08 Photocatalytic Active Monoclinic WO3 Thin Films

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We report on UV light induced degradation of stearic acid (SA) and octadecylamine (ODA) on crystalline tungsten oxide thin films prepared by DC magnetron sputtering. Different deposition conditions showed a variation of reducibility as well as adsorption of the molecules on the surface. The films were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman, UV-visible and Fourier-transform infrared spectroscopy (FTIR). The XRD spectra revealed a variation of crystal plane orientation and crystal size depending on working pressure, substrate temperature and post annealing procedures. Furthermore, absorption coefficient and band gap were determined from optical measurements. Results showed a shift in position of the absorption edge to higher energies with working pressure. This is correlated with structural properties of the films. WO3 films were spin coated with SA and ODA in methanol solutions, FTIR spectroscopy showed higher adsorption of ODA than SA. This indicates an excess of Brönsted acid sites on the surface of WO3 films. The degradation rate constant for SA and ODA were determined for a wide rang of tungsten oxide films and the monoclinic WO3 films were found to be highly photocatalytic active.

FI-3:L09 Surface Modification of ITO by Al2O3 for Electrodes in Polymer Based OLEDs

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Polymer based organic light emitting diodes (OLEDs) still lack in sufficient life-time for a wide commercial launch due to electrical fatigue. Frequently, ITO is used as an anode material which is discussed to play a role in the degradation of the emitting organic layer. Using high-pressure XPS and conductivity relaxation it is shown that ITO easily exchanges oxygen. Inserting sub-nanometer layers of Al2O3 the exchange can be blocked efficiently. Al2O3 has been deposited by reactive RF-Magnetron sputtering as well as by atomic layer deposition (ALD). The interface formation between ITO and Al2O3 has been studied in-situ by XPS and UPS showing a strong dependence of interface properties on the preparation method. We have further studied the influence of Al2O3 layers on the performance of OLEDs.

FI-3:IL10 3-Dimensional Nanostructured ZnO for Highly Efficient Thin Film Silicon Solar Cells

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Increased optical absorption and full stability of thin film silicon (TFS) solar cells, together with industrial requirements for short deposition time are the main goals of all thin film silicon solar cell developments. Stable solar panel efficiency should increase from present 7-8% levels well above 12%. A crucial component for this development is the front transparent conductive oxide (TCO) layer of the solar cell. We report on several ways how to nanostructure TFS solar cells (single or multiple junction) to make them optically thick but electrically thin. Both, top down and bottom up nanotechnology approaches have been used to make nanocolumns or create nano/micro holes as the part of front TCO electrode. Light scattering, trapping and absorption model data will be presented, together with the measurements on solar cells made on such nanostructured TCO.

FI-3:IL11 Low Voltage Driving Transparent Electroluminescence Devices Composed of Perovskite Oxides

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We have discovered perovskite thin-film electroluminescence (PEL), opening up a new optical application of perovskite materials. All of the films were prepared by the conventional pulsed laser deposition method. Base insulating layer SrTiO3, phosphor layer ((Ca0.6Sr0.4)0.997Pr0.002)TiO3 and top insulating layer SrTiO3 were successively grown on a 1 mol% Nb-doped SrTiO3 (100) substrate. After post-annealing, the transparent SnO2 top electrodes were grown. With increasing driving voltage, the intensity of electroluminescence dramatically increases. The sharp electroluminescence peak at around 610nm at 12 V becomes much stronger with increasing ac voltage. High-quality red color is produced and the working voltage for whole-surface electroluminescence is as low as 10V. The mechanism behind this electroluminescence is thought to be the transition of Pr3+ ions from the 1D2 state to the 3H4 state. The optical transmittance of ((Ca0.6Sr0.4)0.997Pr0.002)TiO3 thin film with 300 nm thickness are >68% in the wavelength range between 400 nm and 800 nm including the effects of the both-side polished SrTiO3 (100) substrate, which optical transmittance of substrate are around 70%. This results showed that the optical transmittance of thin film could be >90%.

FI-3:IL12 Recent Developments on Inorganic Electrochromic Systems

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Since their discovery by Deb at the end of the sixties, electrochromic systems, which optical properties can be modified by an applied voltage, have received significant attention. In particular, in the last decades, great advancements have been achieved in the development of real-world applications, such as rear-view mirrors, helmet visors, car-roof window. A rapid commercialization of smart windows still suffers from issues such as limited durability, neutral color, flexibility, switching speed, etc. In this presentation, using WO3 as the main layer, the performances of neutral color ECDs will be discussed focusing in particular on the improvement of the counter part NiO. For instance, improved durability of NiO thin films was achieved by adding another element/oxide such as Li or TiO2, or by preparing carbon containing film. In addition of significant evolution for ECDs in the visible, recently there has been a growing interest in emissivity modulators for satellites thermal control or for infrared furtivity. The optical performances (i.e; modulation in absorptance in the 3-5 µm and 8-12 µm regions) of various configurations of reflective ECDs, using WO3 as the main active layer, will be compared as a function of several parameters (i.e. layer thickness or location).

FI-3:IL13 Optimisation of Thermochromic Thin Films on Glass; Design of Intelligent Windows

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The atmospheric pressure chemical vapour deposition reaction of vanadyl acetylacetonate and tungsten hexachloride with oxygen led to the production of thin films of tungsten doped monoclinic vanadium dioxide on glass substrates. Scanning electron microscopy and X-ray diffraction indicated that the films had different morphologies and crystallinities depending on the deposition conditions used. Transmission and reflectance measurements showed a significant change in properties in the near inra-red either side of the metal to semiconductor transition. Variable temperature transmission studies show that the metal to semiconductor transition was lowered by tungsten doping. The effect of film thickness was studied with un-doped and doped films. It was found that film thickness limited the intensity of light passing through the film and the extent of the thermochromic transition but was found not to influence the hysteresis width or temperature of transition. Different film growth conditions led to a range of film morphologies which profoundly affected the resulting optical properties of the films. It was found that film morphology and preferred crystallographic orientation had a marked influence on the width and switching temperature of the thermochromic transition. Optical data was used in energy modelling studies to elucidate the films potential as an energy saving coating in architectural glazing. The energy modelling results suggest that for warmer climates the thermochromic nano-composites investigated here lead to significant energy savings when compared with plain glass and other standard industry products. We show that doping of Vanadium Dioxide films with W atoms and gold nanoarticles offer a facile way to improve the materials properties, enabling both the thermochromic onset temperature and film colour to be altered.

Poster Presentations

FI:P01 Analysis on Resistive Switching of Resistive Random Access Memory using Visualization Technique of Data Storage Area with Secondary Electron Image

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Various successes in raising the performance of Resistive Random Access Memory (ReRAM) such as lowering the switching current and improvement of the switching speed. In spite of those successes, the resistance switching mechanism has not been elucidated yet. This is attributed to the difficulty in applying common analytical methods to the resistance switching region due to the facts that resistance switching occurs in the filamentary region covered with a top electrode (TEL) and, furthermore, the thickness of the filament is very thin. Recently, it was demonstrate that both HRS and LRS can be written on over an arbitrary area by applying bias voltage directly to NiO films using conducting atomic force microscopy (C-AFM)[1]. This technique might be a breakthrough for mechanism elucidation, providing a “thick filament” without TEL. In this paper, we clarified that both HRS and LRS of the NiO film written by using conducting atomic force microscopy (C-AFM) can be distinguished using secondary electron image (SEI) as a contrast variation. This suggests that the C-AFM writing decreases the work function of NiO. The fact that resistance state can be identified provides a new prevailing analytical method.

[1] *C. Yoshida et al., APL93, 042106 (2008).*

FI:P02 Interface Electronic Structure of Sputtering Deposited Undoped and Doped ZnO Thin Films on a Commercial Cz-Si Solar Cell Substrate

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ZnO is a promising material for use in solar cell applications requiring antireflective coatings and transparent conducting materials in front contacts. Its resistivity can be reduced by appropriate doping with different group III elements, which act as donors, without sacrificing optical transmission. These characteristics make it one of the most promising and cheap transparent conducting oxides (TCO).The interface between Si and a TCO like ZnO is a critical part of Si-based solar cells, since the conversion efficiency may be profoundly altered by the presence of recombination centers formed at the interface. Undoped and Ga and Al doped ZnO thin films have been deposited by RF magnetron sputtering on a wafer Si solar cell. We have carried out a thorough analysis using photoelectron spectroscopy (PES), ultraviolet photoelectron spectroscopy (UPS), transmission electron microscopy (TEM) and Raman spectroscopy. Special attention has been paid to study differences beetween the ZnO:Ga/Si and ZnO:Al/Si interfaces, and between the former ones and the undoped ZnO/Si interface.

FI:P08 Study on the Electrical, Optical and Durability Characteristics of IZO/Ag-alloy/IZO Transparent Conductive Multilayer System

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The effects of added metallic elements such as Pd, Cu and Au in Ag-alloy layers were examined in the indium-zinc-oxide(IZO)/Ag-alloy/indium-zinc-oxide(IZO) transparent conductive multilayer system. We designed the multilayer system to have high transmittance in the visible region from the calculation of optical constants of IZO and Ag-alloy layers. The correlation between the thickness of the Ag-alloy layer and the electrical and optical properties of the multilayer system were investigated. We also investigated the effects of added metallic elements in Ag-alloys on the durability of the multilayer system under high temperature and various humid environments. After heat treatment tests and humidity tests, we examined the changes in the sheet resistance and the transmittance as well as the density of white dots in the multilayer system. The added metallic elements in Ag-alloy layers were highly effective for the improvement in durability of IZO/Ag-alloy/IZO multilayer under heat treatment and humid environments. Surface analytical tools were used to explore the mechanism of the improvement in durability by the added metallic elements.

FI:P10 Sol Gel Synthesis of Doped ZnO Transparent Electrodes for PV Cells

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Doped ZnO films have received much interest as transparent electrodes due to excellent transparency, good conductivity, non-toxicity and low-cost. This study is based on the sol-gel method, which is an efficient way for fabrication of large-area thin films, allowing excellent compositional flexibility and high deposition rate. The desired stoichiometry is controlled by the salts and solvents in the starting precursors. Other process parameters, such as sintering temperature and time can be altered in order to influence morphological and electrical properties. We examined the effect of different chelating agents on film’s structural properties, such as preferred orientation, and porous structure. Additionally, we investigated the influence of different solvents on layer’s morphology as well as on the optical and electrical properties. The films showed a granular, porous structure. The film’s structure was influenced by the heat treatment and by sol components. The thickness of the layers ranged from 100 to 600 nm. The transparency and resistivity were approximately 90% and 10-2 Ω·cm, respectively.

FI:P11 Control of n-channel Depletion and Enhancement-mode ZnO Nanowire Field Effect Transistors

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The intrinsic Zinc Oxide (ZnO) nanowires (NWs) were grown on the (0001) plane of sapphire substrate by hot-wall pulsed laser deposition (HW-PLD) with an Au catalyst (2nm) at 800 oC. Various range of diameter for the NWs were found, and the field effect transistors (FETs) were fabricated with these NWs of different diameter on highly n-type Si substrate by using photolithography process. The FETs characteristics were demonstrated and the threshold voltages (Vth) of these FETs were found dissimilar for different NWs of different diameter. This variation of threshold voltages (Vth) can be understood by tailored band gap energy (Eg) due to different diameter of NWs. It was determined that the NW of large diameter exhibited an n-channel depletion mode (D-mode), whereas the NW of narrow diameter exhibited an n-channel enhancement mode (E-mode). Therefore, the n-channel D-mode and n-channel E-mode FETs were easily found due to different diameter. One n-channel D-mode and one n-channel E-mode FET of threshold voltages -18V and +6.85V respectively, have been demonstrated. This controlled fabrication of the two operation modes of NW-FETs is hoped to be beneficial for the wide application of NW-FETs in logic circuits.

FI:P13 **Potentiostatic Deposition of Zinc Oxide on Flexible Substrate**

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Transparent thin zinc oxide (ZnO) films on flexible copper-coated polyethylene terephthalate (PET) sheet have been grown by a potentiostatic cathodic deposition technique using aqueous zinc nitrate as electrolyte. ZnO films fabricated at different deposition parameters such as applied potential, electrolyte concentration and bath temperature are characterized by X-ray diffractometer, scanning electron microscope, diffuse reflectance UV-VIS spectrophotometer and photoluminescence spectrometer. The effects of applied voltage, concentrations and temperature on the structural and optical properties of the fabricated ZnO films have been investigated. On the basis of our results, we demonstrate that high quality ZnO films are successfully grown on flexible polymeric substrates using a low temperature potentiostatic cathodic deposition technique.

FI:P15 **Optical Hydrogen Response of Sputtered Pt/WO3 Nanostructured Films - Comparative Studies on Different Transparent Substrates**

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The gasochromic response of WO3 nanostructured films coated with a catalytic Pt layer on different transparent substrates were investigated upon exposure to H2 gas. The WO3 nanostructured films with 400nm thickness were coated with Pt layer of 25Å. The films were prepared on the following transparent substrates: quartz, bare glass, fluorine-doped tin oxide (FTO) glass, indium-doped tin oxide (ITO) glass and SU8 polymer on quartz. The nanostructured WO3 was sputtered by RF magnetron sputtering and Pt layer was deposited by DC sputtering. The microcharacterisation of the film shows different sizes of WO3 nanograins deposited on the different substrates. WO3 grains on quartz and bare glass are 30-40nm in sizes. WO3 grain sizes on ITO glass are 40-60nm and on SU8 polymer are 80-200nm. The grain sizes are 300-500nm for the WO3 on FTO glass. The WO3 films on quartz and bare glass are very uniform and followed by films on ITO glass and SU8 polymer. The WO3 films on FTO glass are rough. Pt/WO3 films were observed to show gasochromic characteristics, with absorbance changes measured in the vis-NIR (400nm-900nm) range. It was observed that the cumulative absorbance response towards H2 is highest and more stabile for Pt/WO3 films on quartz and bare glass compared to the other substrates.

FI:P17 **Effect of Oxygen in Aerosol Assisted CVD of TiO2 Using Titanium Tetra-iso-propoxide/Acetylacetone Solutions**

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Functional titania thin films has been deposited on various substrates to produce self-cleaning surfaces by aerosol assisted chemical vapor deposition in the temperature range 450-650 °C. Titanium tetra-iso-propoxide (TTIP) was used as titanium source in solution with acetylacetone (acac). The influence of an oxygen partial pressure during the growth process has been investigated. The growth rate is increased by 10-40% in the explored temperature range in presence of O2 using a 1.5 M TTIP/acac solution. The films grown at 500 °C on Si or glass in presence of O2 using pure TTIP are single phased (anatase structure) while those synthesized without O2 exhibit a low proportion of rutile. By contrast, always at 500 °C, the presence of O2 favors the formation of rutile for the film grown on steel. Without addition of O2 the C content of the films is high, and it increases with the deposition temperature. It essentially originates from the acac solvent. The C contamination decreases in presence of O2. The by-products were analyzed by IR and NMR to elucidate the role of O2. The hydrophilicity of the layers increases with the O2 partial pressure. The wettability is not improved by UV irradiation likely because the photocatalytic behavior of these layers is not efficient.

Symposium FJ

MATERIALS AND TECHNOLOGIES FOR SOLID STATE LIGHTING

Oral Presentations

Session FJ-1
Material Growth and Processing

FJ-1:IL01 **GaN Optoelectronics on Silicon**
Armin Dadgar, Otto-von-Guericke-Universität Madeburg, FNW-IEP, Magdeburg, Germany

Optoelectronics has always been the main driving force behind GaN development in the past. Due to a better thermal or lattice matching preferred substrates for GaN growth are sapphire or SiC. Having the cracking problem solved for thicker GaN layers on silicon substrates in 2000, these substrates gained more and more interest for LED applications in recent years. But, in contrast to silicon, sapphire and SiC are much better suited for light emitters in the visible to UV region due to their much lower absorption loss. This substrate absorption does lead to a major loss in output power for GaN LEDs on silicon. It accounts to around 80 % if compared to an LED on sapphire. Therefore, trying to manufacture bright LEDs on silicon substrates is not very promising. Possible ways to improve LED efficiency by partial etching or substrate removal will be discussed in this presentation. Another challenging task is scaling to large substrate diameters. The transformation in LED industry from 2 inch to 100 mm in diameter has been already a challenge and is still ongoing. For the growth on silicon scaling up to 150 mm is presently possible. I will discuss the issues that currently limit a further increase of the substrate diameter and present solutions for them.

FJ-1:IL02 **Synthesis of Electroluminescent Organic and Organometallic Materials: Tuning Emission Colour by Molecular Design**
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Interest in organic electroluminescent devices (OLEDs) as solid state sources for low energy consumption lighting is increasingly growing due to their unique flexible-shape, large-area features and low cost processing. Development of efficient white OLEDs for lighting requires optimized emitters of the three fundamental colours (red, green, blue) or of two complementary colours (e.g. blue, orange) combined in mixtures or bound within the same molecular structure. The lecture will discuss several classes of electroluminescent materials with emission colour tunable over the visible spectrum by molecular design. Electroluminescence of poly(p-phenylenevinylene)s (PPVs) can be modulated by functionalization of the conjugated backbone. Selective fluorination enables fine tuning of PPVs' emission colour in the blue region of the visible spectrum[1]. The role of functionalization of ligands in the control of electroluminescence of phosphorescent Ir complexes will be discussed[2].

[1]M. Losurdo, M.M. Giangregorio, P. Capezzuto, A. Cardone, C. Martinelli, G.M. Farinola, F. Babudri, F. Naso, M. Büchel, G. Bruno Adv. Mater. 2009, 21, 1; [2]R. Ragni, E. Orselli, G. S. Kottas, O. Hassan Omar, F. Babudri, A. Pedone, F. Naso, G.M. Farinola, L. De Cola Chem. Eur. J. 2009, 15, 136

FJ-1:IL03 **Zinc Oxide; Bulk Growth, Hydrogen and Schottky Diodes**
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Zinc oxide (ZnO) is a wide band gap semiconductor with attractive features for light emitting devices, photovoltaics and spintronics. In the past 10 years ZnO has received a tremendous attention by the materials science/physics community, and in this contribution recent progress in (i) bulk growth, (ii) understanding hydrogen, and (iii) formation of Schottky barrier (SB) diodes, are discussed. In (i), the emphasis is put on hydrothermally grown material and how the concentration of impurities, e.g., In, Al and Li, can be controlled and modified by high temperature treatment and defect engineering. In (ii), different configurations of hydrogen as shallow donor are evaluated. Further, hydrogen is demonstrated to be highly reactive and the interaction with zinc vacancies and group I elements are elucidated. Especially, the diffusion of hydrogen is found to be rapid (trap-limited) and isolated (free) hydrogen is not very likely to exist. In (iii), a compilation of literature data illustrates that the SB heights for metals deposited on n-type samples have no correlation with the metal work function, violating the fundamental Schottky-Mott model. Finally, results from characterization of point defects employing SB contacts and junction spectroscopic techniques are critically reviewed.

FJ-1:L04 **Catalyst-assisted MOVPE Self-assembly and Properties of Free-standing III-V Nanowires**
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Free-standing nanowires (NWs) of III-V semiconductors are ideal building blocks for realization of novel and efficient nanophotonic devices. MOVPE self-assembly of III-V NWs through the metal-catalyst assisted (so-called Vapour-Liquid-Solid, VLS) mechanism, is a most promising technology for the synthesis of nanowire-based devices. Improvements in the NW synthesis and strict control over their properties are however, needed to meet the materials requirements for fabrication of future nano-devices. We will review current status of researches on the Au-catalysed MOVPE growth of III-V NWs: current approaches, major limitations and possible alternatives will be presented with emphasis on catalyst technology and substrate issues. Results on the MOVPE growth of GaAs, AlGaAs and GaAs-AlGaAs core-shell NWs will be presented as case studies, focusing on the dependence of the NW morphology, size, growth rate, composition and structural properties on catalyst preparation and MOVPE growth conditions. Fundamental mechanisms driving the VLS growth for these materials will be then discussed. The luminescence of as-grown NWs will be finally presented, along with sources of unintentional impurities in the materials and their role in changing the NW electronic/radiative properties.

FJ-1:L05 **Growth of GaN Nanostructures by Halide Vapor Phase Epitaxy**
Carl Hemmingsson*, Galia Pozina, Bo Monemar, Department of Physics, Chemistry and Biology (IFM), Linköping University, Linköping, Sweden

GaN nanostructures have become interesting subjects because of their potential for novel nanophotonics, electronic and sensing devices. Since such nanostructures are as small as several tens to hundreds of nanometers, crystal strain arising from the growth on a foreign substrate is expected to relax, resulting in the reduction of the dislocation density. Thus, this type of nanostructures have one more important applications as seed crystals for producing a low defect density GaN substrates. We report results of growth and characterization of GaN nanostructures grown by halide vapor phase epitaxy. The nanostructures size, shape, density and the selectivity of growth have been studied depending on process parameters and substrate material. The growth was performed at 480 - 600 C using pure nitrogen or a mixture of nitrogen and hydrogen as a carrier gas. It is observed that the shape and density of the nanostructures are dependent on the partial pressure of GaCl and choice of substrate material, respectively. With increasing partial pressure of GaCl, the shape of the nanostructures is changing from dots to nanocolumn-like shape. The typical diameter of the nanostructures is in the range 50-500 nm; however, smaller structures with diameters down to 15 nm have been observed.

FJ-1:IL06 **InAs and GaN Quantum Dots: Similarities and Differences**
A. Hoffmann*, M. Winkelnkemper, C. Kindel, S. Werner, T. Warming, G. Hönig, A. Schliewa, D. Bimberg, Technical University of Berlin, Institute of Solid State Physics, Berlin, Germany

Single quantum dots (QDs) are promising candidates for the realization of electrically triggered sources of single photons or entangled photon pairs for application in quantum cryptography. Single-photon emitters with extraordinary spectral purity have been realized recently using InAs/GaAs QDs. Here, emission with controlled linear polarization is achieved at low temperatures by exploiting the fine-structure splitting of the exciton ground-state. At elevated temperatures this splitting, of up to 500 µeV for large QDs, is smaller than the homogeneous linewidth. Devices based on III-N QDs are operable at much higher temperatures than their arsenide counterparts, and, futhermore, provide the possibility to tune the emission wavelength over a wide range. In this presentation, we study the fundamental processes of photon emission by excitonic complexes confined in single III-N and InAs QDs. Experimental results from time-integrated and time-resolved single-QD spectroscopy are evaluated as well as theoretical results obtained by Hartree-Fock calculations based on realistic eight-band k.p wave functions. The emission properties of excitonic states in QDs are dominated by an interplay of valence-band mixing effects and electron-hole exchange effects within the excitonic states. Excitonic fine-structure splitting and polarization of the emission lines can be controlled by external uniaxial stress.

FJ-1:IL07 Combining GaN and ZnO in Single Heterostructures: Exploiting Their Relative Advantages

Jesus Zuniga Perez, CRHEA (CNRS), Valbonne, France

GaN and ZnO are the base of two families of semiconductors that share many physical properties: they are both wide bandgap materials with energy gaps in the UV region, they have large exciton binding energies (larger than the thermal energy at room temperature) as well as large oscillator strengths, and alloyed with other elements (Al and In for GaN, and Cd and Mg for ZnO) they can cover a very large wavelength region, going from the infrared to the extreme UV. However, the technological development achieved by both semiconductors in the last twenty years is very different and has led them into a completely different status. Due to its numerous applications in the fields of electronics and optoelectronics, in which it has become the central material for blue laser diodes as well as light emitting diodes, GaN has become the second most important industrial semiconductor, far behind silicon. On the other hand, ZnO is mostly employed as a transparent conducting oxide rather than exploiting its semiconductor properties. Under these circumstances, and since ZnO technology does not suffer from the patent problems present in GaN, number of people have proposed to use ZnO as an alternative to GaN and both materials are usually presented as eventual competitors. In this work we will show that we are able to combine these two materials into single heterostructures that allow to exploiting the best properties of each of them. We will first show that high quality AlN/AlGaN DBRs can be grown on silicon substrates, and that they can be used as templates for the growth of ZnO optical microcavities working in the strong coupling regime. In this regime new mixed quasiparticles half-light/half-matter, called cavity polaritons, govern the physics of the system and provide the opportunity to obtaining very low-threshold polariton lasers. The optical properties of such hybrid optical cavities (dielectric DBR/ZnO/GaN-based DBR/Si) including the strong coupling regime at room temperature will be presented[1, 2]. Furthermore, with the aim of increasing the microcavity quality factor an alternative ZnO cavity design, namely ZnO/GaN microdisks, will be investigated. In this case, the improvement in quality factor is possible by employing the whispering gallery modes appearing in such a cavity due to total internal reflection at the microdisk/air interface. Again, this second alternative is an example of ZnO-GaN combination and relies on the possibility of creating GaN microdisks on Silicon[3] as well as on the growth of ZnO on GaN.

[1] F. Medard et al, Phys. Rev. B 79 (2009) 125302; [2] S. Faure et al, Appl. Phys. Lett. 95 (2009) 121102; [3] S. Sergent et al, Appl. Phys. Express 2 (2009) 051003

FJ-1:L08 High Ordered Thin Film of Oligothiophenes Grown by SuMBD: Optical, Electrical and Morphological Characterization

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A critical question in realizing organic devices with good performance is the presently limited ability in controlling growth, a factor that strongly affects the structure, morphology, physical/chemical properties in the solid state and the interfaces formation. Supersonic Molecular Beam Deposition (SuMBD) has shown to be able to achieve unprecedented control on morphology and structure in organic thin film grown. This technique, based on supersonic beams of organics seeded in lighter carrier gasses, permits to overcome some thermodynamic limitations and opens new perspectives in realizing structures controlled at different length scales. We have shown [Y. Wu, et al. Phys. Rev. Lett., 98 (2007) 076601] the key role played by the kinetic energy of the impinging molecules in controlling and determining the morphology and structure of the island growth right from the early stages. Here we report the results achieved growing different oligothiophenes by SuMBD. The morphological, structural and optical characterizations show the high quality of the films deposited by SuMBD and its ability to control the film formation as a function of the deposition parameters. We report also the electrical characterization of devices, showing good electrical properties with optimal carrier mobility.

FJ-1:L09 InGaN Layers for Efficient Light Emission

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The paper will give new experimental information on how the MOVPE growth conditions influence the morphology and microstructure of InGaN layers used in blue LEDs and laser diodes. The following observations were made: i) at low growth temperatures, when N2 is used as a carrier gas, GaN layers contain pinholes; ii) the pinholes disappear when hydrogen is added to the carrier gas and then the step-flow-like morphology of the surface is observed; iii) when InGaN layers are grown using N2 carrier gas, no pinholes were observed, but the steps become jaggy; iv) when adding hydrogen, the steps become linear, but the incorporation of indium is much smaller; v) the substrate misorientation is accompanied by smaller indium incorporation into InGaN layers caused by a smaller step velocity in the step-flow growth mode; vii) these phenomena give rise to an additional surface roughening as the length of the terraces is not uniform; viii) the rough morphology (different step lengths) leads to indium segregation (in parallel to other reasons of this phenomenon: strain, electric fields).

FJ-1:L10 Characterization of Polycrystalline SiC Layers Grown on n-type Si by LPCVD

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Silicon carbide is a promising material used for harsh environment applications. The metal contact properties are very important and are related to surface properties. In this study the structure, surface and electrical properties of silicon carbide (SiC) thin films were studied by X-Ray diffraction (XRD), scanning electron microscope (SEM), Atomic force microscope (AFM), current-voltage (I-V) and capacitance-voltage (C-V) measurements. The cubic SiC film has been grown on n-Si by low pressure chemical vapor deposition (LPCVD) at 1160 K using trimethylsilane (SiH4(CH3)3) as precursor. The crystal structure and crystallinity of film has been confirmed through X-ray diffraction pattern. The crystal structure of SiC found to be cubic with lattice constant 4.24 A0 and crystallize size was 119 nm. The Full Width at Half Maximum (FWHM) of 3C-SiC (111) peak was 0.280 which shows that film was crystalline. It was evident from SEM results that grown 3C-SiC film has rough surface and large number of voids of different shapes. The thickness of film was 1µm and not uniform throughout the whole surface of substrate. Nanopipes of different diameters have been observed on grown film. The AFM study confirmed the SEM results that film was rough. The average roughness was found to be 27 nm. I-V measurements have been taken in the temperature range 149 to 304 K under bias voltage of -2 to 0.94 V. The calculated values of ideality factor (n), barrier height (ΦB) and reverse saturation current (Is) were 2, 0.42 eV and 2×10-6 A respectively at room temperature. The ideality factor (n) and barrier height (ΦB) were strong function of temperature. The ideality factor (n) decreases while value of barrier height (ΦB) increases as temperature was increases. C-V measurements were taken in the temperature range 151 to 305 K under biased voltage from -2 to 0 V. The calculated values of doping concentration (Nd), barrier height (ΦB) and built-in potential (Vbi) were 1.5×1015 cm-3, 1.7 eV and 1.39 V respectively at room temperature. The doping concentration (Nd) was independent of temperature, but barrier height (ΦB) and built-in potential (Vbi) were found to be decrease with increasing temperature.

FJ-1:IL11 Heteroepitaxial Growth of ***m***-plane InN on $LiAlO_2$ Substrates and Its Strong Anisotropic Optical Behaviors

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Non-polar nitride semiconductors have been demonstrated to be absent of internal electrostatic field, an important factor to enhance the luminescence efficiency. Moreover, non-polar InN is highly demanded owing to its potential of being free of surface election accumulation layer and thus helping p-type doping at surface and junction regions.

Here, heteroepitaxial growth of high-purity m-plane InN film on LiAlO2 substrate by plasma-assisted molecular-beam epitaxy will be presented. Surface treatment of LAO substrate plays an important role in controlling the resultant phase and purity of m-plane InN. Structural anisotropy of the m-plane InN epitaxied on LAO is attributed to the I1 type base-plane stacking faults according to the modified Williamson-Hall and TEM analyses. A rectangular-to-rectangular atomic stacking sequence and a commensurately lattice-matched condition in epitaxial direction of [1210]InN||[001]LAO with a small misfit strain of ~0.2% are proposed. Angle-dependent polarized UV-Raman spectra show that all the InN phonon modes with pure structures follow Raman selection rule well. Strong polarization anisotropy is observed, as evidenced by a high polarization degree of 87% of the m-plane InN determined by polarized photoluminescence spectroscopy.

FJ-1:IL13 **Recent Advances in the MOVPE Epitaxy of Indium Nitride**

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Indium Nitride is the least known of the group III Nitride semiconductor family. It has a bandgap energy of 0.65 eV, making it very interesting for infrared emitters and detectors applications. In particular alloying InN with GaN opens a very wide range of applications, including efficient solar cells. However, the growth of InN is still very challenging. In this talk, we will report the progresses made in the growth of InN, and we will compare the MBE and MOVPE technologies. The problem of substrate will be discussed and it will be shown that, even in state of the art material, InN has a columnar structure with an average domain size of 300nm. We will explain how using surfactants and optimized growth conditions has led MOVPE growth to an equivalent level as compared to MBE in terms of crystal quality. However, MOVPE material still contains a large amount of hydrogen, due to the growth process, which acts as efficient donor source. We have established an in-situ thermal treatment that allow us to outdiffuse this hydrogen, and drastically reduce the free carrier concentration and improve electron mobility. The use of non-polar substrates will be also discussed, and we will show that it is a promising alternative for the growth of InN.

FJ-1:L14 **AlN Technology for UV Light Emitting Devices**

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AlN boule expansion was pursued in an inductively-heated reactor capable of temperatures in excess of 2400 °C. Sintered AlN powder was used as a source material and growth was performed in a nitrogen atmosphere. Detailed finite element analysis was used to design radial and axial gradients to follow the desired boule expansion; realistic expectations and limitations of this technique will be discussed. Stable facets observed in AlN crystals grown close to the thermal equilibrium are c, m and r. Single crystalline AlN boules were grown on c+, c-, a and m oriented high-quality AlN seeds. The growth on the N-polar seeds was controlled by one growth center leading to a mirror-like growth facet, while the growth on the Al-polar seeds resulted in numerous competing growth centers. A surface energy model in conjunction with the BCF theory, developed as a framework for AlN crystal growth on different facets, supported experimental observations. AlN boule growth on non-polar seeds was terminated in m-facets, regardless of the seed orientation. Epitaxial thin films were grown on surface-treated AlN substrates by metal-organic chemical vapor deposition (MOCVD), resulting in superior quality of device structures as compared to current technology using heteroepitaxial growth.

FJ-1:L15 **Growth and Characterization of Deep UV-range ZnMgSrO Thin Films Lattice-matched to ZnO Substrate**

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ZnO has been widely used as an active material for UV-LEDs because of its direct band gap and high exciton binding energy. For the optoelectronics application, one of the key issues is the energy band gap(Eg) engineering to realize hetero-junction. ZnMgO films have been mainly studied to obtain Eg higher than that of ZnO(3.3eV) but performance of the ZnMgO/ZnO devices should be compromised due to the mismatch in the lattice constant, as large as 2% in the case of Eg ~4.0eV. It is therefore necessary to develop a new materials system, with wide Eg and lattice matched to the ZnO. In this work, Zn1-x-yMgxSryO films were grown by the magnetron sputtering, with controlled y/x ratio to maintain the lattice matching condition. Structural and optical properties of samples were characterized by TEM, SEM, X-ray diffraction(XRD) and cathodo-luminescence(CL). The CL measurement showed that the ZnMgSrO films emit UV peaks with energies from 3.7eV~4.0eV. The XRD clearly indicated that the films are lattice matched to the ZnO; the (002) peaks appear at the same position, 34.42°. The TEM and the XRD inspection indicated that the films are of single crystalline. It is believed that the ZnMgSrO materials system would be a strong candidate material to achieve high performance ZnO-based devices.

Session FJ-2

Electro-optical Characterisation

FJ-2:IL01 **Relating Microstructure to Transport in n-type Organic Semiconductors**

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The highest n-type field-effect mobility is found in semicrystalline polymers and in solubilized small molecules with a perylene core: PDI8-CN2 and P(NDI2OD-T2). We study the effect of their microstructure on transport. Thin films of PDI8-CN2 are produced with engineered microstructures. The types of grain-boundaries in the film is essentially reduced to two: one low-angle type and one high-angle type. In high-angle grain-boundaries, the molecular orientation across the grain-boundary is such as to reduce the intermolecular transfer integral compared to low-angle grain-boundaries. It is found that the mobility of devices where the current flows across low-angle grain-boundaries (μ~2x10-2 cm2/V.s) is two orders of magnitude higher than that of devices where the current flows across high-angle grain-boundaries (μ~10-4 cm2/V.s). These findings are important in order to design small molecule materials that are relatively insensitive to grain-boundary orientation. Dip-coating is used to produce films of P(NDI2OD-T2) with a preferential orientation. The microstructure of the polymer is studied using synchrotron-based X-ray diffraction. The polymer is highly ordered in the transport plane. The effect of crystallinity and orientation on transport will be described as well.

FJ-2:IL02 **Zinc Oxide a Material for Optoelectronic Applications: Analysis of Fundamental Properties and Their Modification by Hydrogen**

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Research on zinc oxide (ZnO) is driven by a strong desire for blue and ultraviolet light emitting devices. So far, however, the major shortcoming is the lack of reliable p-type doping. Interestingly, the unique properties of hydrogen have been identified as a significant problem that interferes with effective p-type doping. Despite of the recent developments the properties of hydrogen in ZnO are not fully understood. While in some ZnO single crystals the amount of H detected by gas effusion experiments is similar in concentration to the number of free electrons, a large number of samples exhibit much higher H concentrations. In addition, Raman backscattering experiments reveal that a significant amount of H is accommodated at sites that do not give rise to enhanced conductivity; a significant amount of H is bound to carbon and nitrogen impurities forming CH_X and NH. Depending on the method of the sample preparation H concentrations as high as 3.0x10 ^ 21 cm ^ -3 have been observed. In this presentation we will review the properties and the governing physics of hydrogen in ZnO comprising H-related complexes, hydrogen bonding, and H diffusion.

FJ-2:L03 **New Phosphors for White LEDs, the Case of Phosphate Doped with Divalent Europium and Other Luminescent Ions**

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In the frame of the white LEDs, we are developing new phosphates materials in order to obtain a white emission, following an U.V.-Blue excitation coming from the diode, with only one phosphor, in order to replace the YAG:Ce3+ actually used. The main characteristics of the proposed materials are to contain various crystallographic sites what can be the location of alkaline, earth alkaline and rare earth, and to allow various substitutions between all those cations. With those properties, luminescent ions can be included in the materials, and especially the divalent europium. Based on the strong dependency of the Eu2+ emission band in its crystallographic environment, the emission properties of the phosphors is modulated by: * Adjusting the amount of Eu2+, * Substituting the alkaline, earth alkaline and rare earth cations. The structure can be distorted, having a direct influence of the europium environment. * Adding other luminescent ions, like Mn2+, Tb3+, Eu3+,. Following all those possibilities, we are able to modulate the emission characteristics of the phosphors, by varying the several photoluminescent broad emission bands and peaks, what can be adjusted in order to emit a white light as a function of incoming light due to any kind of chips.

FJ-2:L04 Tunable Color and Luminescent Properties of Dy3+ and Tm3+ Co-activated CaZrO3 Phosphor

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Single-phased CaZrO3: Dy3+, Tm3+ series have been successfully synthesized by solid-state reaction,and their luminescent properties were investigated for the first time. Under near ultraviolet (NUV) excitation, CaZrO3: Dy3+ series showed characteristics emission of Dy3+, which exhibited yellowish white color. The quenching content of Dy3+ was determined at 4% and compared with theoretical results. By introducing Tm3+ to the matrix, the emitted hue of the Dy3+-doped sample could be easily tailored to white and blue. The color coordinates of the optimum white-emitting sample is (0.32, 0.31), which was very close to the data of National Television Standard Committee (NTSC, (0.33, 0.33)). The co-activated phosphors presented good match to ultraviolet (UV) light-emitting diodes (LED), which revealed that they could be a novel promising phosphors utilized in white LED application.

FJ-2:L07 Origin of the Green Light Emission in Polyfluorene Based Diodes by Trap Investigations

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Among the active polymers used in OLEDs, polyfluorene is interesting by its ability to emit a blue light and by its high luminescence efficiency. It is also known that in diodes using PF, a green luminescence band appears and grows in the electroluminescence spectrum during the device operation. The origin of this band is not yet well understood but the influence of defect sites on the optical and electrical properties is supposed to play a key role. In this study we used the Q-DLTS technique to investigate the trap parameters of poly(9,9-dioctylfluorenyl-2,7-diyl) based diodes. The diodes emit a blue light, which turned to green when the applied voltages exceeded a limit value. In blue emitting devices, there are six trapping centers whose densities are between 1016 and 1017 cm-3 and whose capture cross section are distributed in the range 1019 -1020 cm2. The determination of activation energy of those traps indicates the presence of both shallow and deep traps, from 0.1 to 0.4 eV from the band edges. The comparison of the trap parameters obtained in devices before and after changes of the emission provides an explanation of the observed modifications in the active films, which is usually assigned to the oxidation of the polymer forming fluorenone species in the backbone.The density of defects is found to decrease globally suggesting a new organization of the film structure, which partially heals the polymer.

FJ-2:L08 Red-emitting CaSrAl2SiO7:Eu3+ Phosphor for Near - Ultraviolet Light-emitting Diodes

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A novel red-emitting phosphor CaSrAl2SiO7:Eu3+ was firstly synthesized through the high temperature solid state reaction at 1300 °C. The structure, diffuse reflection spectra, photoluminescence spectra, color-coordinate parameters and quantum efficiencies (QE) of phosphors were investigated. The obtained CaSrAl2SiO7:Eu3+ phosphors have the same structure with the Ca2Al2SiO7 and Sr2Al2SiO7 phosphor, which have the melilite structure. Optical properties were studied as a function of Eu3+ concentration x, when x>14%, the intensity of absorption of the f-f transitions of Eu3+ at 393nm is stronger than that of the broad charge transfer transition band (CTB) around 250nm, and which is matches well with the output lights of near-UV LEDs, whereas, the concentration of Eu3+ x≤14%, the absorption of 393nm is weaker than that of CTB. The underlying reason of Eu3+ concentration on their luminescent properties was investigated and discussed in detail. As a result, comparing with the commercial red phosphor Y2O2S:Eu3+, the CaSrAl2SiO7:xEu3+(x>14%) phosphor exhibited excellent color purity and much higher brightness and could be considered as a promising red-phosphors for near-UV LEDs.

FJ-2:IL09 Interfacial Modifications in Organic Optoelectronic Devices

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In the past decade, organic optoelectronic devices have made much advances that they become viable technologies. These organic optoelectronic devices involve integration of organics with highly dissimilar materials, e.g. metals, semiconductors, and oxides, with critical device actions taking places at the organic-inorganic interfaces. For examples, in organic photovoltaics, exciton dissociation and carrier separation occur at the donor-acceptor heterojunctions; careful design of junction area and band alignment is critical for optimizing device performance. In this talk, I will show two examples of modifying organic-inorganic interfaces with alkanethiol self-assembled monolayers (SAMs) to improve device performance. Alkanethiols are large band gap molecules that are expected to act as a transport barrier. When the Au cathode in polyfluorene OLEDs is modified with alkanethiol SAMs, the current is found to be lower while the output luminescent intensity higher, leading to higher external quantum efficiency at a given current density. In ZnO-polythiophene hybrid solar cells, increasing alkanethiol SAM length surprisingly leads to higher photocurrent, despite the SAM reduces electron transfer. I will discuss the mechanisms behind these unexpected improvements.

FJ-2:IL10 Defects and the Efficiency of GaN-based LEDs

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As is well known, the efficiency of GaN-based LEDs is much less sensitive to the dislocation density than that of other semiconductor LEDs, for example GaAs. However, there is still a dependence of the efficiency of GaN-based LEDs on the dislocation density, and if we are to maximise the efficiency of GaN-based LEDs, then we must minimise the dislocation density, particularly for the growth of GaN-based LEDs on silicon. We have performed a detailed study of the dependence of the efficiency on the dislocation density for GaN-based LEDs grown on both sapphire and silicon substrates, for a range of wavelengths, from blue to green. We have also used several different dislocation reduction techniques. We will describe our latest results in this paper.

FJ-2:L11 Size-dependent Recombination Dynamics in ZnO Nanowires

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ZnO nanostructures can be regarded as fundamental blocks for next generation optoelectronic devices. A deep understanding of its recombination dynamics is a natural step for a precise design of on-demand nanostructures. In this work, single-crystal ZnO nanowires with different diameters have been grown by the vapour transport method using Au as catalyst. We show that the recombination dynamics of the neutral bound exciton around 3.365 eV for ZnO nanowires depends on the wire diameter, the lifetime decreases as increasing the surface-to-volume ratio. Furthermore, we have observed two broad transitions around 3.419 and 3.310 eV which are related to surface states. In order to study their origin we have investigated the temperature dependence of their photoluminescence intensity as well as their thermal activation energy. These results are of great interest for a precise design of ZnO-based nanostructures, since they represent a step toward a deep understanding of its size-dependent recombination dynamics.

FJ-2:L12 Hydrogen in InN: Ubiquitous Phenomena in Molecular Beam Epitaxy Grown Material

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InN is a key material in current and future generation of III-Nitride based optoelectronic devices. Important open questions are to understand the origin of the intrinsic n-type doping and the properties of the surface electron accumulation layers in InN and In-rich alloys. We report a comprehensive study on hydrogen impurities in InN and provide new insight on their role for the unintentional n-type conductivity in InN. We studied a large number of state-of-the-art InN films with different surface orientations and different bulk free electron concentrations grown by molecular beam epitaxy at four growth laboratories. High amounts of H scaling with the free electron concentrations are measured in the bulk of the films, suggesting a major role of H for the unintentional doping in the material. Furthermore, enhanced concentrations of H are revealed at the film surfaces, which could match the free electron profiles in the films with surface electron accumulation. We further discuss in detail the hydrogen behavior with respect to surface charge, surface orientation, defect structure and surface morphology of the films. Our new findings may have significant impact on the future research strategies and pathways undertaken to control the doping mechanisms in InN and related alloys.

FJ-2:IL13 **Organic Syntheses and Characteristics of Novel Conjugated Polymers for AMOLEDs**

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Conjugated polymers with a stabilized blue emission are of importance for the realization of large flat panel AMOLED displays using polymer light-emitting diodes. Several novel conjugated polymers using newly developed templates for the stabilized EL emission are reported. Poly(2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[def]phenanthrene)) (PCPP) is a new class of blue-emitting polymers utilizing a new back-bone. This material emits a efficient blue EL without exhibiting any unwanted peak in the long wavelength region (green region) even after prolonged annealing at an elevated temperature of 150oC in air, or operation of the device. In addition to this, poly(5,5,10,10-tetrakis(2-ethylhexyl)-5,10-dihydroindeno[2,1-a]indene-2,7-diyl) (PININE) was synthesized. In PININE, the vinylene group was cyclized using two 5-membered rings to prevent the oxidation of the vinylene group. PININE shows stable spectra of UV-vis, and PL, and EL even after harsh irradiation with white light in air, or after operation of the device.

FJ-2:IL14 **Real Time Optical Monitoring of Growth and Processing of Materials for LEDs**

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III-nitrides is the plethora of material options that they offer with energy bandgap (Eg) spanning from the near infrared (InN) to green (InxGa1-xN), blue (GaN) and violet (AlxGa1-xN). For the design of such integrated III-nitrides - ZnO heterostructures and devices, the detailed knowledge of the thickness, composition of each layer in the structure affecting the optical properties is essential for a controlled band gap engineering. In this field, the development of spectroscopic ellipsometry in recent years now favours its application during the growth of ultra-thin semiconductors and furthermore permits the growth control. Its main advantage compared to electron based techniques such as Reflection RHEED is the independence on ultra-high vacuum (UHV) conditions and its non-invasive character. Therefore they can be applied in Molecular Beam Epitaxy (MBE) as well as Metal-Organic chemical vapour deposition (MOCVD) processes. This talk review the recent progress in controlling and optimizing substrate treatments, MOCVD and MBE growth processes and interfaces of III-nitrides and ZnO based heterostructures to understand the interplay process-material-light emission functionality. Real time phenomena related also to the polarity of those materials will also be discussed.

FJ-2:IL15 **VUV Optical Properties of III-Nitrides in the Thin Film Limit**

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Although III-nitrides are already widely used in many commercially available products, several fundamental properties are still under discussion. Uncertainties concern e.g. the question whether zinc blende AlN has an indirect band gap or the impact of electric fields and strain on the electronic band structure. The latter effects are significant in particular for thin films, quantum wells, and super lattice structures. Here also quantum size effects alter the optical properties. We apply broad band spectroscopic ellipsometry from the visible to the vacuum ultraviolet in order to study those peculiarities. First of all it allows a very precise determination of the dielectric function (DF) of single layers. The device performance critically depends on that around the emission wavelength. However, this spectral region is also strongly influenced by all higher inter band transitions according to the Lyddane-Sachs-Teller relation. Furthermore, ellipsometry is an excellent method in order to study electronic band structure peculiarities by means of dipole transition features in the DF. In a comprehensive discussion of the measurements on hexagonal and cubic crystals, we could identify band gap related excitons and all higher interband transitions.

Session FJ-3
Device Structures and Manufacturing

FJ-3:IL01 **White OLEDs for Lighting**

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In the last years, interest in the use of organic LED technology for lighting applications has been rising steadily; accompanying the increasing penetration of inorganic LEDs of the lighting market. To obtain white light for lighting applications, a number of options exist for color mixing. These include one, two, three or more color devices. The OLED designs include individual color patches, stacked OLEDs, combined single OLED designs and external color conversion. Research areas critical for OLEDs for lighting center around the lifetime-luminance tradeoff. For lighting, luminance values in excess of 1000 cd/m2 are needed, but these come at a reduced lifetime. Here much more fundamental work on materials and device layout is required. Also, enhanced light outcoupling could help in this respect. So far, up to 80% of the light generated is absorbed in the device and not emitted. Generally, it can be said that OLEDs for lighting will start to appear in niche markets, where their unique features give them a competitive advantage. When prices come down thanks to large-scale production, OLEDs will penetrate also the general lighting market. The presentation highlights recent developments in research and applications of white OLEDs for lighting and attempts a look at the future.

FJ-3:IL02 **Opto-electronic Grade Zinc Oxide for Device Applications**

David J. Rogers*, Ferechteh Hosseini Teherani Nanovation, Orsay, France

Wurtzite zinc oxide (ZnO) is a direct wide bandgap semiconductor with many established and emerging electronic applications. This is thanks, in part, to: - a very distinctive property set; - well-established procedures for bulk/thin-film/nanostructure growth; - the propensity for tunability of bandgap/transparency/conductivity; - well-developed techniques for device processing. With regards to Solid-State Lighting (SSL), ZnO has been investigated for a number of roles. This talk will give an overview of the use of ZnO for SSL applications, illustrated with examples from our work on: - homo- and hetero-junction ZnO-based LEDs; - use of ZnO as a buffer layer for growth and chemical lift-off of ultra-thin InGaN-based LEDs; - transparent ZnO for use as contact material; - LEDs based on active ZnO nanostructure arrays; - the use of passive ZnO moth-eye-type nanostructures to enhance light extraction from LEDs; - ZnO based photonic crystals.

FJ-3:IL03 **Light Sources for General Lighting**

Klaus Streubel, Osram GmbH, Munich, Germany

Light emitting diodes (LEDs) and their application in “Solid State Lighting” have created a high level of interest in the public. The remarkable increase in efficiency of LEDs within the last decades as well as some of their unique properties such as long lifetimes, small size or flexibility make them almost ideally suited for general lighting purposes. The traditional light sources for general lighting created obviously much less interest. Only the least efficient source, the incandescent bulb could enjoy some publicity thanks to the recent European legislation. However, fluorescent sources offer similar efficiencies as LEDs at much lower costs and will continue to dominate the general lighting market for a long time. High pressure discharge lamps generate huge amounts of light at efficiency levels that are out of reach for any other light source, including LEDs. In this presentation, the latest developments of some traditional and novel light sources will be discussed.

FJ-3:IL04 Nanostructured (In,Ga)N LEDs for Solid-State Lighting: Opportunities and Obstacles

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Many of the obstacles to improving the performance and reducing the first cost of LED lighting technologies have their roots in the limitations of planar (Al,Ga,In)N heterostructures grown on sapphire substrates. Among these limitations are high threading dislocation densities, strain-driven phase separation and roughening in (In,Ga)N grown on GaN buffer layers, and the large polarization-induced electric field in (In,Ga)N quantum wells grown on c-plane GaN. These limitations must be addressed to significantly increase the internal quantum efficiency of LEDs that emit in the "green gap" (~540-560 nm). Nanostructuring alters the character of all of these challenges, presenting new opportunities for circumventing the limitations of planar heterostructures on sapphire. In this talk, we will describe the benefits that arise from nanostructuring, including enhanced elastic relaxation of lattice and thermal expansion mismatch strain, elimination of threading dislocations through image forces, and control of the magnitude of the polarization field by exposing "semi-polar" crystallographic facets during epitaxial growth. Nanostructuring also introduces additional challenges, such as the proximity of free surfaces that enhance radiative and nonradiative recombination through point defects. We will illustrate these implications of nanostructuring within the context of nanopyramid LEDs that have been designed and fabricated at Purdue University.

FJ-3:IL05 ZnO Devices Fabrication Using Pulse Laser Deposition

Ferechteh H. Teherani*, David J. Rogers, Nanovation, Orsay France

Zinc oxide is a unique material that exhibits semiconducting and piezoelectric dual properties. ZnO is of particular interest within the optoelectronic research areas as a result of its wide band gap 3.3 eV at 300 K, transparency to visible light associated to a particularly high exciton binding energy of 60 meV. The combination of these properties opens up to various devices including blue and green light emitting diodes, optoelectronic devices based on cavity coupled polariton lasers operated at room temperature, or as a transparent contact. Currently, there is enormous interest in ZnO because of a number of recent breakthroughs in materials processing and device fabrication. This talk will give an overview of some of the latest materials and device developments and the potential novel applications using pulse laser ablation.

FJ-3:IL06 Blue and White Phosphorescent Organic Light Emitting Devices

Jiangeng Xue, Department of Materials Science and Engineering, University of Florida, Gainesville, FL, USA

We report studies on charge injection/transport and exciton confinement in blue and white organic light-emitting devices (OLEDs) based on the deep-blue electro-phosphorescent dye iridium(III) bis(4',6'-difluorophenylpyridinato)tetrakis(1-pyrazolyl)borate (FIr6). Using high triplet energy charge transport layers and a dual-emissive-layer structure as well as the p-i-n device structure, we have achieved external quantum efficiencies of 20% and maximum power efficiency of 35 lm/W in these deep-blue OLEDs. White OLEDs with a color rendering index of 79 and a maximum power efficiency of 40 lm/W was also demonstrated by incorporating red and green phosphorescent dopants together with FIr6. Attachment of hemispherical lenses to these devices also leads to ~60% enhancement in the overall efficiencies.

FJ-3:IL07 White Light Generation Using Microcavity Blue Phosphorescent OLEDs with Down-conversion Phosphors

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There are several approaches to generate white light from organic light emitting diodes (OLEDs). One approach is to use blue emitting OLEDs in conjunction with down-conversion phosphors. This approach requires highly efficient saturated blue emitters to provide efficient excitation for the phosphors. For blue phosphorescent emitters such as FIrpic, the emission spectrum contains too much green light and it does not excite the phosphors efficiently. In order to enhance the blue excitation for the down-conversion phosphors, we incorporated the microcavity structure and demonstrated highly efficiency white OLEDs. We previously demonstrated high efficient microcavity blue phosphorescent OLEDs (PHOLEDs) with power efficiency of 41 lm/W. With down-conversion phosphors incorporated in the blue micro-cavity PHOLEDs, a maximum luminous efficiency of 68 lm/W for the resulting white emitting device with a color rendering index (CRI) of 83 was achieved. A macrolens was also used to further extract the substrate guided modes from the phosphor film. It was done by directly attaching the macrolens on top of the phosphor film with the same index matching gel used between the OLED glass and the phosphor glass. With the macrolens attached to the phosphor film, we were able to generate white light with a maximum luminous efficiency 99 lm/W.

FJ-3:IL08 Surface Polarity Effects in the Optical and Electronic Properties of ZnO

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In recent years, ZnO has experienced mixed progress in its development as an optoelectronic material. Its much heralded ultraviolet light emitting potential is being frustrated by difficulties in the production of high quality p-type material, while significant progress has been achieved in the fabrication of high quality Schottky contacts and transparent thin-film transistors. From a fundamental perspective, ZnO possesses a number of unusual features that directly impact device performance, but have yet to be satisfactorily explained: These include surface accumulation layers, persistent photoconductivity, and the significant variation of many optical and electrical properties with crystallographic polarity. In this lecture, we review current progress towards an understanding of these usual features and their impact on the development of ZnO as an "ultraviolet" semiconductor.

FJ-3:IL09 Organic-inorganic Hybrid Field-effect Transistors

Thomas D. Anthopoulos, Department of Physics, Imperial College London, Blackett Laboratory, London, U.K

Research on soluble semiconductors is rapidly making progress towards the goal of providing viable alternatives to silicon technologies for applications where lower-cost manufacturing and new product features are desired. One family of materials that has been attracting significant research interest is organic semiconductors. While research in organic materials has been intensifying a different class of semiconductors, namely metal oxides (MOxS), has emerged as a possible alternative technology. MOxS incorporate important qualities that are currently absent from organic semiconductors. For example, they generally exhibit higher carrier mobilities and high transparency. Unfortunately, the vast majority of MOxS demonstrated to date are electron transporting (n-type). This rather generic characteristic represent a major technology bottleneck for the development of high performance circuits. Here, we discuss an alternative approach towards high-performance electronics based on the use of solution processed p-type organics and n-type oxide semiconductors. By developing optimised hybrid heterostructures, we demonstrate transistors with hole and electron mobilities >2 cm ^ 2/Vs. Importantly, both semiconductors are processed from solution under ambient atmosphere without any special prec

FJ-3:IL10 Organic Light Emitting Devices (OLEDs): Device Physics and Architectures for Application in Solid-State Lighting

Max Shtein, University of Michigan, Ann Arbor, MI, USA

Organic light emitting devices (OLEDs) have demonstrated excellent energy efficiency and color rendering properties, suggesting their application in the next generation of efficient, cost-effective solid state lighting. In this talk, I will give an overview of OLED materials, device architectures, and some of the remaining challenges in scaling this technology for application in lighting. The latter include the need for non-brittle, inexpensive, and transparent electrodes, as well as for device architectures and fabrication methods that facilitate cost-effective scale-up. Pertaining to these challenges, I will describe some of the recent advances we have made in indium tin oxide-free OLED structures, top-emitting OLEDs on opaque substrates, OLEDs on fibers that facilitate white light emission and could be woven into textiles, as well as OLEDs taking advantage of plasmon-exciton resonances to improve light outcoupling efficiency.

FJ:P04 Tailoring Optical Properties of Blue-gap Poly(p-phenylene vinylene)s for LEDs Applications

M.M. Giangregorio, M. Losurdo, P. Capezzuto, G. Bruno, IMIP-CNR, Bari, Italy; A. Cardone*, C. Martinelli, G.M. Farinola, F. Babudri, F. Naso, Università di Bari, Dipartimento di Chimica, Bari and ICCOM-CNR, Bari, Italy

There has been growing interest in developing new semiconducting polymers for applications in optoelectronics (OLEDs) due to their exceptional processability and appealing characteristic of manipulating electronic and optical properties by tuning of molecular structure and self-assembling. This study is an investigation on the interplay among supramolecular organization and optical properties of thin films of the poly[2-(2-ethylhexyloxy)-5-methoxy]-1,4- phenylenedifluorovinylene (MEH-PPDFV) conjugated polymer, which has fluorinated vinylene units. This interplay is elucidated exploiting atomic force microscopy, spectroscopy ellipsometry, photoluminescence and electroluminescence. Thin films of MEH-PPDFV have been deposited by drop casting on indium-tin-oxide (ITO), quartz and glass substrates. The dependence of polymer chains self-organization and morphology on substrate surface is presented. Furthermore, it is demonstrated that the presence of F-atoms in the vinylene units of the MEH-PPDFV yields a blue optical band gap with the maximum of the fundamental HOMOLUMO transition at 331nm and photoluminescence at 458nm. The OLED built with the above polymer show a very stable blue-greenish electroluminescence is also achieved at 504nm.

FJ:P05 Interface and Surface Modification of ZnO Induced by Hydrogen and Nitrogen and Their Impact on Light Emission Properties

M.M. Giangregorio*, G.V. Bianco, A. Sacchetti, P. Capezzuto, M. Losurdo, G. Bruno, IMIP-CNR, Bari, Italy

ZnO, which has an optical band gap of 3.4 eV, is one of the more versatile semiconductor materials investigated and applied especially as epitaxial layers grown by molecular beam epitaxy (MBE) and metalorganic chemical vapour deposition (MOCVD) for the blue-violet optoelectronics. It is interesting since it can be used itself as a blue emitter competing with nitrides, since its higher exciton binding energy of 60 meV) or as a substrate for nitrides growth. ZnO/III-nitrides heterojunctions are of considerable technological interest for phosphor-free white light emitters. In this contribution, we address two critical and interesting aspects from both fundamental and technological point of views, which are the polarity of ZnO and the interface reactivity and stability to hydrogen and nitrogen. This is interesting especially because during growth of nitrides on ZnO both hydrogen and nitrogen are present altering the interface morphological and compositional properties, which finally affect the light emission properties of the device. Basic questions, involving the interplay between ZnO orientation/polarity and kinetics of the interaction with nitrogen and hydrogen are solved and the impact of interface mixing in ZnO/III-Nitrides on light emission properties is presented.

FJ:P06 Advanced Real Time Metrology of AlGaN/GaN and InGaN/GaN Epitaxy

Tong-Ho Kim, A.S. Brown, Department of Electrical and Computer Engineering, Duke University, Durham, NC, USA, M.M. Giangregorio, M. Losurdo, G. Bruno, G.V. Bianco*, IMIP-CNR, Bari, Italy

Nitride materials are critical for a range of applications, including UV-visible light-emitting diodes (LEDs). Advancing the performance, reliability and synthesis of AlGaN/GaN and InGaN/GaN heterojunction devices requires a systematic methodology enabling characterization of key metrics like alloy composition, thickness and quality possibly in real time. This contribution reports on the real time characterization of the plasma assisted molecular beam epitaxy of AlGaN/GaN and InGaN/GaN heterostructures. Spectroscopic ellipsometry real time monitoring of the growth process has revealed a number of key process and material issues, such as the roughening of the GaN templates depending on plasma exposure during the substrate cleaning step, the composition of the alloy and the growth mode. Parameters like the plasma conditions, the surface temperature and the atomic flow ratio are investigated to understand the interplay process-materialcomposition/structure-optical properties. The role of the film thickness on the final alloy properties is also addressed. The real time in situ data are corroborated by Raman spectroscopy analysis.

FJ:P07 Organic Synthesis and Characteristics of Novel Conjugated Polymers with Cyano Group and Carbazole Unit for AMOLEDs

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Organic light-emitting diodes (OLEDs) have been researched considerably with several advantages over conventional devices such as a low driving voltage, wide viewing angle, thin film structure, and a simpler manufacturing process for the generation of large area and flexible display. The present investigation deals with the synthesis, characterization and EL properties of new polyfluorenevinylenes, CzCNPFVs, with cyano-substituted vinylene unit and carbazole pendant. In CzCNPFVs, synthesized by the Knoevenagel condensation, the carbazole pendant was introduced to improve the efficiency of reported CNPFV. The PL emission spectra of the CzCNPFVs in chloroform solution show maximum peaks at 476 ~ 479 nm. In thin films, maximum peaks of the CzCNPFVs appeared at 501 ~ 504 nm, red-shifted around 25 nm as compared to those in solution. The maximum luminescence (Lmax) of CzCNPFV2 of the device with the configuration of ITO/PEDOT/CzCNPFVs/Ca/Al is 1724 cd/m2 at 8 V. The maximum luminescence efficiency of CzCNPFV1 is 0.18 cd/A. As compared to CzCNPFV2, CzCNPFV1 is an alternating copolymer formed by one monomer with two carbazole moieties and another monomer with two alkyl groups.

FJ:P08 Dynamics of Donor Bound Excitons in Freestanding GaN Doped by Silicon and Oxygen

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Homoepitaxial growth allows achieving highly efficient GaN-based light emitting diodes and laser diodes with longer operation time. Using GaN substrates the threading dislocation density (TDD) in the nitride active layer in devices can be reduced to the order of TDD in the substrate. From this point of view development of GaN substrates with low defect density is one of the most important challenges for semiconductor industry. So far the most successful technique to produce GaN substrates is halide vapor phase epitaxy (HVPE). We report time-resolved photoluminescence (TRPL) properties of intentionally oxygen and silicon doped HVPE grown thick (300 µm -1 mm) GaN layers. The incorporation of dopants was confirmed by SIMS analysis. Time-integrated photoluminescence spectra for low doped samples are dominated by donor bound exciton (DBE) recombination at 3.474, which is a typical DBE recombination energy in stress-free HVPE GaN material. TRPL demonstrates a rather different low-temperature transient behavior for donor bound excitons depending on the doping type (i.e. silicon or oxygen) and concentration. These observations suggest that recombination mechanism for DBE even at 2 K involves not only radiative processes but also non-radiative recombination channels of different origin.

FJ:P10 Synthesis, Optical and Electrical Properties of Oligo(phenylene-vinylene)s Substituted with Electron-Accepting Sulfonyl Groups

Stefan Glang, Volker Schmitt, Heiner Detert*, Institute for Organic Chemistry, Johannes Gutenberg-Universität Mainz, Mainz, Germany

Oligo(phenylenevinylene)s (OPV) composed of five rings and electron donating or withdrawing sulfonyl substituents on the central and lateral rings are been investigated. Two strategies were used for the syntheses of the C2-symmetrical OPVs, both include PO-activated olefinations as central steps. Six flexible side chains guarantee good solubility in toluene or dichloromethane. In solution and in films stabilised by polystyrene (60%), the chromophores are strongly fluorescent, with emissions in the violet-blue domain from solutions and in the green to orange region from solid films. The redox potentials, determined by cyclic voltammetry, and the optical properties are strongly depending on the position of the acceptor groups.

Symposium FM

ELECTROMAGNETIC METAMATERIALS

Oral Presentations

Session FM-1
Microwave and THz Metamaterials

FM-1:IL02 **Terahertz Metamaterials Under a Near-field Microscope**

A. Bitzer, A. Ortner, M. Walther*, Molecular and Optical Physics, University of Freiburg, Freiburg, Germany

Experimental investigations of the microscopic electric and in particular the magnetic near-fields in metamaterials are highly challenging and current studies rely mostly on numerical simulations to characterize their complicated resonant response. Here, we apply a novel terahertz imaging technique, which allows us to measure the amplitude, phase and polarization of the microscopic near-fields in the vicinity of resonant microstructures. By our approach we can trace the electric field vectors close to the structures with sub-wavelength spatial resolution. From the measured in-plane electric vector fields we are able to reconstruct the out-of-plane magnetic field vectors and thereby obtain a comprehensive microscopic picture of their electromagnetic response. Using this approach we investigate resonances in individual split-rings as well as coupling between the sub-units in metamaterial arrays. We observe trapped mode resonances in asymmetric split-ring resonators and investigate the polarization-dependent response in chiral metamaterials.

FM-1:IL03 **New Concepts for Spoof Surface Plasmon Metamaterials**

Stefan A. Maier, Physics Department, Imperial College London, London, UK

Spoof surface plasmons allow us to create high-confinement electromagnetic surface waveguides in the low-frequency part of the electromagnetic spectrum, well below the plasma frequency of the conductor used for the confining surface. However, for geometries discussed up to this point such as slit and hole arrays, there exists a detrimental trade-off between confinement and bandwidth, which will hamper practical applications. In this talks, we will show how high-bandwidth guiding can be achieved using spoof surfaces based on complementary split ring resonators, and a variety of other topologies sustaining highly tunable effective plasma frequencies. The fundamentals of the new spoofing concept, and first implementations and applications will be discussed.

FM-1:IL04 **Radar Absorbing Material Based on Metamaterials**

A.N. Lagarkov*, V.N. Kisel, V.N. Semenenko, ITAE RAS, Moscow, Russia

One of the important obstacles for overcoming the diffraction limit is a high level of losses in metamaterial, and all principle limitations arising on the way are well known. At the same time those unavoidable losses may be turned for the designing radar absorbing material (RAM) and structures based on metamaterial. Here we discuss frequency dependencies of both electric and magnetic dipole moments excited by incident electromagnetic wave inside the inclusions of different geometrical shapes, the methods of their measurement. The resonance behavior of both dielectric constant and permeability of metamaterials suggests the use of them as selective absorbents. While creating metamaterial-based RAMs the designer may use both frequency domain with positive e and m and the domain where they are negative. In the first region RAMs have properties that are typical for coating with ferromagnetic inclusions. In reality inclusions are manufactured from non-ferromagnetic material, their resonance behavior is responsible for artificial high-frequency magnetism. In the frequency domain where the refraction coefficient is negative RAMs possess unique angle features and some other peculiarities. Those specific features and experiments confirming the above statements are discussed.

FM-1:L05 **Microwave Metamaterials Containing Magnetically Soft Microwires**

L.V. Panina, School of Comp., Comm. and Electr., Univ. of Plymouth, Plymouth, UK; M. Ipatov, V. Zhukova, A. Zhukov*, Dpto. de Física de Materiales, Fac. Químicas, UPV/EHU San Sebastián, Spain

Adjustability of electromagnetic properties is important for many applications. In this paper we discuss the development of metamaterials containing ferromagnetic microwires allowing to tune the effective electromagnetic parameters in the microwave frequency band. Use of magnetic microwires allows tailoring materials with relatively high values of the effective magnetic permeability originated from natural magnetic properties of the wires with a circumferential magnetic anisotropy. The magnetic field in the incident wave along the wire will generate substantial magnetic activity as it will be in the orthogonal position with respect to a static magnetization. In two-dimensional arrays of wires with different spacing for electric (about 1 cm) and magnetic (about 0.1 cm) subsystems it will be possible to achieve a negative index of refraction. Comparing with other left handed materials, we demonstrate an enhanced performance in terms of tenability and simple internal structure. The results involve theoretical modeling and free space measurements of reflection/transmission spectra with extracting the effective parameters. We also discuss the feasibility of using the magnetic wire composites for such applications as tunable microwave systems and remote sensing.

Session FM-2
Photonic and Infrared Metamaterials

FM-2:IL01 **Metamaterials: Going from Microwaves to Optics**

M. Kafesaki*, R. Penciu, FORTH-IESL, Heraklion, Greece; Th. Koschny, Iowa State University, USA; E.N. Economou, FORTH-IESL and University of Crete, Greece; C.M. Soukoulis, FORTH-IESL, Univ. of Crete, Greece, and Iowa State University, USA

In this talk we present a unifying, circuit-model-based approach for the analysis of the wave propagation in magnetic metamaterials and negative index materials, in both microwaves and optical regime. Using this approach we will discuss the main features of the wave propagation in optical metamaterials, as well as design rules for the optimization of such metamaterials.

FM-2:IL02 **Light Propagation in Optical Metamaterials**

F. Lederer*, T. Paul, C. Rockstuhl, C. Menzel, University of Jena, Institute of Condensed Matter Theory and Optics, Jena, Germany

If optical metamaterials (MMs) are required to exhibit magnetic properties (double negative MMs) the unit cells must support magnetic dipole or/and electric quadrupole resonances leading to a certain minimum unit cell size, only a few times smaller than wavelength. Thus the MM constitutes a mesoscopic system where strong spatial dispersion prevents the introduction of so-called bianisotropic constitutive relations with only frequency-dependent effective tensor elements. Thus both the propagation of light within the MM and its in- and out-coupling from/to adjacent media cannot be simply described. One solution would be to establish an involved retrieval algorithm that takes spatial dispersion and additional boundary conditions into account. The other, more appealing option consists in using effective wave parameters as the wave vector and a generalized impedance. If only the fundamental Bloch mode is relevant their dispersion relation provides the required effective wave vector. The coupling to the outside world may be achieved by using an effective MM impedance. The definition and calculation of this impedance is quite involved but feasible. We show how this technique can be exploited to efficiently describe light propagation in arbitrary layered metamaterials.

FM-2:IL03 **Optics of Active Metamaterials**

A.K. Sarychev, Institute for Theoretical and Applied Electrodynamics, Moscow, Russia

Light is in a sense “one-handed” when interacting with atoms of conventional materials. This is because out of the two field components of light, electric and magnetic, only the electric “hand” efficiently probes the atoms of a material, whereas the magnetic component remains relatively unused because the interaction of atoms with the magnetic field component of light is normally weak. Metamaterials, i.e. artificial materials with rationally designed properties, can enable the coupling of both of the field components of light to meta-atoms, enabling entirely new optical properties and exciting applications with such “two-handed” light. For example, specifically shaped metal nanoantennas can exhibit strong magnetic properties in the optical spectral range due to excitation of the magnetic plasmon resonance. A case in which a metamaterial comprising such meta-atoms can demonstrate both left handiness and negative permeability in the optical range is discussed. We show that high losses predicted for optical left-handed materials can be compensated in the gain medium. Gain allows achieving local generation in active metamaterials. The possibility for the metamaterial to exhibit optical ferromagnetism is discussed. We discuss a plasmonic nanolaser, where the metal nanoantenna operates in a fashion similar to a resonator. The size of the plasmonic laser is much smaller than the light wavelength. Therefore, it can serve as a very compact source of coherent electromagnetic radiation and can be incorporated in future plasmonic devices. We consider various collective phenomena like superradiance in an array of nanolasers when phases of all nanolasers are synchronized and they radiate as one super large atom.

FM-2:IL04 **Photonic Metamaterials: Recent Progress**

Martin Wegener, Institut für Angewandte Physik, Institut für Nanotechnologie, DFG-Center for Functional Nanostructures, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Photonic metamaterials are tailored artificial materials that allow for achieving optical properties that are not accessible with natural substances. These man-made nanostructures are composed of metallic and/or dielectric sub-wavelength functional building blocks (photonic atoms) that are densely packed into an effective material. In this talk, I briefly review recent progress regarding magnetism and negative phase velocities at optical frequencies. The emphasis, however, is on recent experiments on three-dimensional bianisotropic and chiral photonic metamaterial structures as well as on three-dimensional invisibility-cloaking structures.

FM-2:IL05 **Manufacturing Metamaterials Using Synchrotron Lithography**

H.O. Moser*, L.K. Jian, S.P. Heussler, S.M.P. Kalaiselvi, S. Virasawmy, S.M. Maniam, Singapore Synchrotron Light Source/National University of Singapore, Singapore

The function of metamaterials relies on their resonant response to electromagnetic waves in characteristic spectral bands. To consider metamaterials as homogeneous, the size of the basic constituent resonant element should be less than 10% of the wavelength. For the THz range up to the visible, structure details of 50 nm to 30 µm are required as are high aspect ratios, tall heights, and large areas. For such specifications, lithography, in particular, synchrotron radiation deep X-ray lithography, is the method of choice. X-ray masks are made from primary pattern generation by means of electron or laser writing. Several different X-ray masks and accurate mask-substrate alignment may be necessary for architectures requiring multi-level lithography. Lithography is commonly followed by electroplating to deliver metallic metamaterials. The process can also yield inserts for plastic molding of metamaterials, thus enabling most cost-effective manufacture. Metamaterials based on rod-split-rings, split-cylinders, S-string bi-layer chips, and S-string meta-foils were made by SSLS. Left-handed resonance bands range from 1.5 to 216 THz. Latest is the all-metal self-supported flexible meta-foil with pass-bands of 45% and 58% transmission at 3.4 and 4 THz depending on geometrical parameters.

FM-2:L06 **Simple Effective Parameters Retrieval Employing Wave Propagation Phenomena**

A. Andryieuski, R. Malureanu, A.V. Lavrinenko*, Technical University of Denmark, Kgs. Lyngby, Denmark

The concept of metamaterials (MTMs) is acknowledged for the new horizons provided on the way to control the light. MTMs possess complex metal-dielectric topology of the unit cell. Assigning bulk effective parameters is the mean to characterise the properties of MTM in the universal way. Existing retrieving methods are mostly grouping either on S-parameters inversion, field averaging or maximization of optical density of states. Their shorthand lies in branch uncertainty or complexity in realization. We propose a straightforward procedure to monitor directly the wave propagation occurred on some distances from several to few dozens of unit cells. We trace the phase advance and amplitude attenuation as functions of the unit cell number. Then restoration of complex refractive index is a matter of routine calculations. Complex impedance retrieved from the input interface reflection is valid provided the absence of multiple reflections inside the MTM slab. So, material losses otherwise treated as drawback of metamaterials become very helpful. Our approach has been tested on various MTM designs spanning all ranges from microwaves till optical frequencies. High accuracy, robustness and simplicity of implementation are the features that allow anticipating high potential of our approach.

FM-2:L07 **Full Scatter Characterization of Novel Photonic and Infrared Metamaterials**

Thomas M. Fitzgerald*, Michael A. Marciniak, Dept. of Engrg Physics, Air Force Institute of Technology, Wright-Patterson AFB, OH, USA

Artificial structures with sub-optical wavelength features can have engineered non-conventional values for material properties such as optical and infrared permeability and permittivity. Such artificial structures are referred to as optical and infrared metamaterials.[1] The application space of electromagnetic metamaterials includes novel sub-wavelength waveguides and antennas, true time delay devices, optical filters, and plasmonic electronic-optical interfaces.[2] In this paper, we present an optical diagnostic technique adapted for measuring and analyzing bidirectional polarimetric scatter from novel photonic and infrared metamaterials of interest that is broadly applicable to other optical/infrared metamaterial structures that are proposed or developed in the future. The specific project goals are to: a) develop a novel metamaterial characterization full-polarimetric diffuse ellipsometry technique to measure desired material properties with stated uncertainty limits for novel photonic and infrared metamaterials of interest; b) incorporate predictive computational codes to estimate the electro-magnetic property values for metamaterial designs and concepts of interest.

[1]R. M. Walser, Proceedings of SPIE 4467, 1 (2001); [2]E. Ozbay, Science 311, 189-193 (2006).

FM-2:L08 **Semiconductor-metal Nanoparticle Structure as Metamaterial with Negative Permeability at Optical Frequencies**

A.B. Evlyukhin, C. Reinhardt*, A.I. Kuznetsov, B.N. Chichkov, Laser Zentrum Hannover e.V., Hannover, Germany

Optical properties of 2D and 3D regular nanoparticle structures consisting of spherical semiconductor and noble metal nanoparticles are theoretically studied. For receiving the magnetic response at optical frequencies silicon nanoparticles are used. In this case, the first Mie resonance in a spherical silicon particle with a size of 130 nm corresponds to a magnetic dipole response in the visible spectral range. A structure arranged from these particles has strong magnetic response at the resonant wavelength. The calculated transmission and reflection spectra for the finite 2D and 3D lattices of the silicon particles demonstrate the development of a magnetic resonant band with a negative effective permeability as a function of interparticle distance. Even only one layer of the silicon particles can provide the stop-band properties. It is shown that metal particle inclusions can significantly change the transmission and reflection coefficients of the total structure. Possibilities to obtain a negative refractive index using gold or silver particles inside the silicon structures are discussed. Applications of hybrid 2D structures for the manipulation of surface plasmon polaritons are suggested.

Session FM-3

Nonlinear and Active Metamaterials

FM-3:IL01 **Nonlinear and Switchable Photonic Metamaterials**

Nikolay Zheludev, Optoelectronics Research Centre, University of Southampton, Southampton, UK

Composite metamaterials containing nonlinear and switchable media offer a new paradigm for improving key photonic functionalities. We overview advances in the field and report on the recent results on carbon nanotube metamaterial that shows giant tailored ultrafast nonlinear response, and chalcogenide glass metamaterial that exploit structural phase change in the glass for high-contrast light modulation.

FM-3:IL02 **Nonlinear Photonics at the Nanoscale**

C. Sibilia, Dipartimento di Energetica, Università di Roma La Sapienza, Roma, Italy

An overview of different nonlinear optical phenomena occurring in nanopatterned materials is presented. In particular a discussion about second order nonlinear effects is reported, including also some nonclassical properties of the interaction with non homogeneous materials.

FM-3:L03 **Frequency-domain Simulations of a Negative-index Material with Embedded Gain**

Y. Sivan[1, 2]*, S. Xiao[1], U.K. Chettiar[1, 3], A.V. Kildishev[1], V.M. Shalaev[1], [1]School of Electrical and Computer Engineering, Purdue University, West Lafayette, IN, USA; [2]Imperial College London, Blackett Laboratory, London, UK; [3]Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, PA, USA

It is well known that the performance of plasmonic metamaterials is limited by the strong absorption losses from metal inclusions. The most explored way to reduce the losses is to incorporate gain media into the metamaterial design. To date, most studies used a phenomenological gain value, or computationally-expensive time-domain simulations. We present an alternative frequency-domain model and show that for sufficiently strong pumping and a sufficiently short probe pulse, it is an excellent approximation to the actual time-domain dynamics. We solve the equations for light propagation in a negative-index material with gain while taking into account the nonlinear nature of the gain material, both for the pump and probe pulses. Our approach allows us to study the gain non-uniformity due to the large E-field non-uniformity in the structure. We show that available gain materials can lead to complete compensation of the losses only if they are put in the regions where the field enhancement is maximal. We also show analytically that the effective gain is determined by the average near-field enhancement rather than the local enhancement. Finally, we discuss possible extensions of the model, such as the effect of metal inclusions on the emitter fluorescence, spontaneous emission etc.

Session FM-4

Antenna and Waveguide Applications

FM-4:IL01 **Fundamentals and Applications of Transmission-line Metamaterials**

George V. Eleftheriades, Loic Markley*, University of Toronto, Dept. of Electrical and Computer Engineering, Toronto, ON, Canada

In this presentation we will describe the fundamentals of transmission-line metamaterials and outline some of their applications. In the fundaments we will show how transmission-line metamaterials can be described in terms of a positive or a negative permittivity and/or permeability. Two points of view will be considered, the first will be based on the excitation of spatial harmonics and the identification of the dominant one and the second will be based on the direct identification of electric and magnetic dipole moments. We will also discuss the origin of the broad left-handed bandwidths and low transmission losses associated with transmission-line metamaterials. Subsequently we will present a number of applications including super-lensing in free space, multi-band and active microwave components, peculiar couplers that support complex waves and small and multi-band antennas.

FM-4:IL02 **On the Way to Improved Plasmonic Structures**

A. Boltasseva[1, 2]*, R.B. Nielsen[1], G. Naik[2], P. West[2], N. Emani[2], V. Shalaev[2], [1]DTU Fotonik, Technical University of Denmark, Kgs Lyngby, Denmark; [2]Birck Nanotechnolocy Center, Purdue University, West Lafayette, IN, USA

One challenge with employing plasmonic components is overcoming the large losses in the metal. Metals work well for low incident light frequencies but begin to suffer from hig! h interband transition losses as the incident light approaches the near infra-red and visible frequencies. In this talk we will give an overview of alternative plasmonic materials, outlining their optical properties and fabrication approaches, ranging from metals and metallic alloys to doped semiconductors. Another factor that determines optical performance of plasmonic components is structural quality of fabricated devices. We will review different fabrication techniques for realization of plasmonic waveguide components and metamaterials. Main features and challenges of different approaches including photo-, electron-beam and nanoimprint lithography will be outlined. On the path to device applications, methods of improving and perfecting the structural quality and surface roughness of plasmonic structures will also be discussed.

Session FM-5

Cloaking and Transformation Optics with Metamaterials

FM-5:IL01 **New Concepts of Microwave and Optical Cloaking**

Sergei Tretyakov, Helsinki University of Technology, Espoo, Finland

Recently, the topic of making objects “invisible” for electromagnetic radiation has gained much attention, following new ideas of using engineered electromagnetic materials with unusual properties for this purpose. This presentation provides a comparative review of the recent developments in this field. The presentation starts from a review of the notions of invisibility and cloaking and their relations to the classical stealth technologies of reducing radar cross section of targets. Next, we make a historical overview of earlier approaches to techniques allowing reduction of scattering from various objects. Recently proposed solutions for cloaking of objects are reviewed and compared, with the emphasis on the fundamental limitations of their performance. This topic is closely linked to the problem of creating artificial materials with engineered electromagnetic properties. In particular, materials with equal values of relative permittivity and permeability are of interest. We will present our recent developments of such materials based on mixtures of spiral inclusions and their use for cloaking applications. Furthermore, we discuss the use of electrically dense meshes of transmission lines and other simple metal structures as cloaking devices.

FM-5:IL02 **Elastodynamic Metamaterials**

M. Briane, IRMAR and INSA de Rennes, France; F. Guevara Vasquez, G.W. Milton*, D. Onofrei, University of Utah, Salt Lake City, UT, USA; J. Willis, Cambridge University, UK

Unlike the equations of electromagnetism and acoustics the standard equations of elastodynamics are not invariant under coordinate transformations. Instead they transform to a form first postulated by Willis to describe the ensemble averaged behavior of composite materials. These are analogous to the bianisotropic equations of electromagnetism. For cloaking purposes one wants materials where the Willis constitutive law is local in space, and applies to a single realization rather than an ensemble average. We construct an example of such a metamaterial. More generally we have a complete characterization of the possible dynamic responses (for all time, not just at a single frequency) of multiterminal mass-spring networks. This characterization should enable one to precisely say what sort of macroscopic behaviors of metamaterials are realizible (in theory) and which are prohibited.

FM-5:IL03 **Selected Applications of Transformation Electromagnetics**

I. Gallina, G. Castaldi, V. Galdi*, University of Sannio, Benevento, Italy; A. Alù, University of Texas, Austin, TX, USA; N. Engheta, University of Pennsylvania, Philadelphia, PA, USA

During the last few years, transformation electromagnetics has emerged as one of the most promising approaches to the systematic design of application-oriented metamaterials, with the perspective of offering unprecedented control on the electromagnetic response of devices and components. In this approach, the formal invariance of Maxwell equations with respect to coordinate transformations is exploited to tailor the desired response in a fictitious auxiliary space characterized by curved metric and suitable topology (e.g., “holes”), and its subsequent interpretation in a conventional Cartesian space filled up with a suitable anisotropic and inhomogenous metamaterial distribution. As a sparse sample of the available application examples, besides the celebrated invisibility “cloaking,” it is worth recalling those pertaining to super/hyper-lensing, field concentrators and rotators, conformal sources, beam shifters and splitters, retroreflectors, as well as the broad framework of “illusion optics.” In this talk, we shall present an overview of selected results from our ongoing investigations within this subject area, with special emphasis on invisibility cloaking/anti-cloaking effects, as well as image displacing and reconstruction.

FM-5:L04 **Applications of Metamaterial Cloaking**

Filiberto Bilotti, Simone Tricarico, Lucio Vegni*, University “Roma Tre”, Department of Applied Electronics, Rome, Italy

In this talk, we present a few applications of metamaterial cloaking technology in different field of science. We start reviewing the scattering cancellation approach to cloaking, with particular emphasis to the actual implementation at both microwave and optical frequencies and on the design of cloaks for arbitrarily shaped objects. Then, the implementation of a microwave cloaking device working for both TE and TM polarizations is presented, considering its application in the antenna field to avoid the blockage phenomenon. The same principle can be used also at optical frequencies and a few implementation design are presented, as well. Moving towards optical frequency, we show how the scattering cancellation is useful to design new high-performing NSOM aperture and aperture-less tips. Finally, the scattering cancellation is related to the reduction of the radiation pressure and several applications are presented, including the reduction of the Casmir force to prevent stiction in MEMS/NEMS components and the possibility to use an NSOM tip to observe floating molecules in aqueous solutions.

FM-5:IL05 Anisotropic Metamaterials Emulated by Tapered Waveguides

I.I. Smolyaninov, BAE Systems, Columbia, MD, USA

We demonstrate that metamaterial devices requiring anisotropic dielectric permittivity and magnetic permeability may be emulated by specially designed tapered waveguides. This approach leads to low-loss, broadband performance. Based on this technique, we demonstrate broadband electromagnetic cloaking in the visible frequency range on a scale ~100 times larger than the wavelength.

FM-5:IL06 Transforming Light with Metamaterials

Vladimir M. Shalaev*, A.V. Kildishev, S. Xiao, V.P. Drachev, A. Boltasseva, School of Electrical and Computer Engineering and Birck Nanotechnology Center, Purdue University, West Lafayette, IN, USA

One of the most unique properties of light is that it can package information into a signal of zero mass and propagate it at the ultimate speed. It is, however, a daunting challenge to bring photonic devices to the nanometer scale because of the fundamental diffraction limit. Metamaterials can focus light down to the nanoscale and thus enable a family of new nanophotonic devices. Metamaterials, i.e. artificial materials with rationally designed geometry, composition, and arrangement of nanostructured building blocks called meta-“atoms,” are expected to open a gateway to unprecedented electromagnetic properties and functionalities that are unattainable with naturally occurring materials. We review this exciting and emerging field and discuss the recent, significant progress in developing metamaterials for the optical part of the electromagnetic spectrum. Specifically, we report on our recent world’s smallest nanolaser, describe the phenomena of artificial magnetism across the whole visible and negative refractive indices in the optical range and discuss the promising approaches and central challenges in realizing optical cloaking. A new, powerful paradigm of engineering space for light with transformation optics will be also discussed.

FM-5:IL07 Non-Euclidean Transformation Optics

Ulf Leonhardt, University of St Andrews, St Andrews, UK; Aaron Danner*, Singapore National University, Singapore

Optical materials seem to distort the geometry of space. In fact, they create effective spatial geometries for light that depend on the optical properties of the materials or metamaterials used. If such a geometry is curved one can exploit some intriguing features of light propagation in curved space for novel practical applications. In particular, I discuss perfect imaging without negative refraction and broadband invisibility.

Session FM-6

Superlenses and Near-field Imaging

FM-6:IL01 Optical Fano Resonance in Nanostructures with Broken Symmetry

B.S. Luk‘yanchuk*, T.C. Chong, L.P. Shi, Data Storage Institute, Agency for Research, Science and Technology, Singapore

Since the time of Fano’s discovery the Fano resonance was generally regarded as a specific feature of quantum systems. Although interference phenomena are ubiquitous in optics, it is not easy to produce Fano resonances in purely optical systems. However, Fano resonances have been seen in the frustrated total internal reflection spectra of prism-coupled square micropilars and in the interactions of a narrow Bragg resonance with a broad Mie or Fabry-Pérot band in photonic crystals. Recently a few groups demonstrated that optical Fano resonance has become observable with plasmonic and nanophotonic materials and nanostructures[1-3]. The key issue for this resonance is the broken symmetry of corresponding structures. Here we review the basic mechanism of the Fano resonance and provide examples of successful experimental realizations.

[1]Fedotov VA et al, Phys. Rev. Lett. 99, 147401 (2007); [2]Hao F et al, Nano Letters, 8, 3983 (2008); [3]Tribelsky MI et al, Phys. Rev. Lett. 100,043903 (2008).

FM-6:L02 Novel Microscopy Techniques Based on Simulated Metamaterial Anisotropy

V.N. Smolyaninova*, Towson University, Towson, MD, USA; I.I. Smolyaninov, University of Maryland, USA; A.V. Kildishev, V.M. Shalaev, Purdue University, USA

Metamaterial anisotropy may be emulated by shape of a tapered waveguide. This has been demonstrated recently in our experiments on electromagnetic cloaking in the visible frequency range (Phys. Rev. Lett. 102, 213901 (2009)). In this presentation we describe novel super-resolution microscopy techniques based on the same principle. Tapered waveguide geometry necessary to perform hyperlens-like imaging will be described. An approximation of a dielectric fish eye superlens recently suggested by Ulf Leonhardt will be also presented.

FM-6:IL03 Metamaterials, High-frequency Magnetism and the Landau-Lifshitz Permeability Argument

Roberto Merlin, University of Michigan, Dept. of Physics, Ann Arbor, MI, USA

Metamaterials made of non-magnetic particles are known to show magnetic properties that seemingly contradict arguments by Landau and Lifshitz indicating that the magnetization loses its meaning at relatively low frequencies. Here we show that these arguments do not apply to composites made of substances with large values of the permittivity. Our general analysis is supported by studies of split-rings and spherical inclusions. The analytical solution to the problem of scattering by a small and thin split ring reveals a close relationship between the permittivity and the dynamic magnetic properties of metamaterials. For small values of the permittivity, the composites exhibit very weak magnetic activity, consistent with the Landau-Lifshitz argument. In contrast, large values lead to strong diamagnetic or paramagnetic behavior characterized by susceptibilities whose magnitude is significantly larger than that of natural substances. The large permittivity requirement poses severe limitations for attaining large susceptibilities at arbitrarily high frequencies. Because of their large extinction coefficient, metals are favored at optical frequencies. Experimental values indicate that magnetism can coexist with the effective-medium condition for wavelengths larger than 2-3 micrometers.

FM-6:IL04 Manipulation of Near Fields by Means of Metamaterials

Pavel A. Belov[1]*, George Palikaras[1], Mario G. Silveirinha[2], Yan Zhao[1], Rostyslav Dubrovka[1], Constantin R. Simovski[3], Yang Hao[1], Clive Parini[1], [1]Queen Mary University of London, UK; [2]University of Coimbra, Portugal; [3]Helsinki University of Technology, Finland

The resolution of conventional imaging systems is restricted by the diffraction limit: the details smaller than half-wavelength of radiation cannot be resolved. Using novel engineered media with extreme optical anisotropy and their waveguiding properties it is possible to overcome the classical limit and create devices capable of transmitting images with subwavelength resolution over long distances. We report experimental results that demonstrate transmission of a microwave image by means of an array of parallel metallic rods over a distance 3.5 times greater than the wavelength. The resolution of such imaging device is 15 times smaller than the wavelength. The magnifying, demagnifying and repeating properties of lenses formed by arrays of metallic rods provide a unique solution for subwavelength imaging at microwave, terahertz and infrared ranges (up to 70 THz). The latter realization is closely related to the hyperlens concept. At microwaves, the resolution of such lenses is determined by the characteristic period, which is limited only by the fabrication capability rather than by any physical constraints. At higher frequencies, the resolution is mainly limited by the skin-depth of the rods material.

FM-6:IL05 Superresolution Through Superoscillations

E.T.F. Rogers*, T.S. Kao, University of Southampton, Southampton, UK; J. Baumgartl, M. Mazilu, S. Kosmeier, K. Dholakia, University of St Andrews, St Andrews, UK; N.I. Zheludev, University of Southampton, Southampton, UK

The recently discovered phenomenon of super oscillation predicts that a properly designed diffraction grating structure can create sub-wavelength localisations of light that propagate several wavelengths away from the structure, into the far-field. This leads to the possibility of a new class of far-field optical imaging devices with better than diffraction limited resolution and provides an alternative to the well known Pendry-Vesselago negative index super-lens. In this talk we will discuss how superoscillation can be used in imaging systems with sub-wavelength resolution. Among these techniques, we will focus on the creation of controllable, sub-wavelength light structures using spatial light modulation and demonstrate the production of isolated sub-wavelength hotspots from binary amplitude masks and quasi periodic arrays of holes.

Session FM-7

Novel Concepts in Metamaterials

FM-7:IL02 Electromagnetic Metamaterials and Computational Electro-magnetics

Tie Jun Cui, State Key Laboratory of Millimeter Waves, School of Information Science and Engineering, Southeast University, Nanjing, P.R. China

In this presentation, I will discuss the following features on computational electromagnetics (CEM) related to the theory and experiments of metamaterials: 1) Efficient algorithms for the full-wave simulation of 3D rotationally-symmetrical dielectric objects with inhomogeneous and anisotropic permittivity and permeability; 2) Effective-medium simulations of 2D artificial metamaterial structures (e.g. wave-bending lens and wave-focusing lens realized by gradient-index metamaterials) using the effective medium theory and CEM algorithms; 3) Full-wave simulations of the whole 2D artificial metamaterial structures (e.g. wave-bending lens and wave-focusing lens realized by gradient-index metamaterials) using the CEM algorithms, which are very time consuming. We conclude that the effective medium theory is an efficient way to describe the artificial metamaterials, which has a very clear physical significance, and needs very small computational loads. On the other hand, the full-wave simulations of the artificial metamaterials with large-amount unit cells are necessary to explore the real distributions of internal fields inside the metamaterials, which cannot be measured through experiment. The simulated near-field distributions have a good agreement to the experimental results.

FM-7:IL03 Magnetophotonic Crystals

F.P. Vinogradov, Institute for Theoretical and Applied Electromagnetics, RAS, Moscow, Russia

Recently, there has been much attention paid to a new kind of artificial materials - magneto photonic crystals (MPC), which are together with ordinary PC of great theoretical and practical significance. In view of this the role the tunability of MPCs' properties by magnetic field is discussed. First of all, the enhancement of magnetooptical effects (the Faraday end Kerr rotation) is discussed. This enhancement is due to resonant interaction of light with special structures in MPC (defects or boundaries) playing the role of the Fabry-Perot resonators. The benefits of employing MPC instead of metallic mirrors originate from the increase of Q factor due to redistribution of the light energy from materials with losses into low loss materials. The effect may be enhanced by the Borrmann effect. In this connection the inverse Borrmann effect, Tamm states and Yeh band gaps are considered. Another possibility to treat the light propagation is to tune the shape of existing band gaps and to form new ones. In particular, the formation of the Yeh band gaps in MPC with anisotropic ingredients is considered. Ultimately, in connection with interaction of Yeh and Brillouin band gaps the problem of slaw light is discussed.

FM-7:IL04 Trapped Rainbow Storage of Light in Metamaterials

Ortwin Hess, Advanced Technology Institute and Department of Physics, FEPS, University of Surrey, Guildford, Surrey, UK

A far-reaching development in photonics has been the conception and practical implementation of materials exhibiting a negative refractive index (NRI). In parallel to the impressive advances in such NRI metamaterials, the aim of producing “slow” or completely “stopped” light has attracted enormous interest]. In this contribution, we will bring these two fields together and discuss the physics of the ‘trapped rainbow’ principle that was recently introduced. We will show that the trapped-rainbow method allows realizing slow and stored broadband light metamaterials. A wave analysis will be followed by a pertinent ray analysis, which illustrates the trapping of the associated light-ray and the formation of a double light-ray cone (‘optical clepsydra’) at the point where the ray is trapped is complemented by full-wave finite-difference time-domain simulations of passive and active metamaterials. Importantly, we shall demonstrate that the trapped rainbow method for stopping light is resilient to the presence of material losses (even in the presence of high losses there are still guided modes) and offers a unique new avenue for slow light amplification by active metamaterials.

FM-7:L05 Laser-induce Transfer - A Novel Approach for Fabrication of Nanoparticle Structures for Plamonics and Metamaterial Applications

A.I. Kuznetsov*, C. Reinhardt, W. Cheng, A.B. Evlyukhin, B.N. Chichkov, Laser Zentrum Hannover e.V., Hannover, Germany

We present a new fabrication method for implementation of metallic nanoparticles as elementary building blocks in 2D and 3D metamaterials. The spherical nanoparticles are generated by femtosecond laser-induced transfer of nanodroplets from thin metal films. Due to the strong surface tension of the molten metal during the transfer process the particles obtain a perfect spherical shape. This method provides unique possibilities to control the final position of the nanoparticles with high accuracy and to place them in close proximity to each other in predefined 1D and 2D arrays on arbitrary dielectric or metallic substrates. Furthermore, this approach allows precise deposition of the nanoparticles inside 3D polymeric structures fabricated by two-photon-polymerization in order to realize dielectric-metallic composite microstructures. This technology opens new ways for the fabrication of plasmonic components and 3D metamaterials. First results and measurements on the realized structures will be presented and compared with theoretical modelling based on the Green's function method and full-wave simulations demonstrating the functionality of the composite structures.

FM-7:L06 Novel Ways to Observe the Handedness of Chiral Optical Metamaterials

V.K. Valev*, T. Verbiest, Molecular Electronics and Photonics, INPAC, K.U. Leuven, Leuven, Belgium; A.V. Silhanek, W. Gillijns, V.V. Moshchalkov, Superconductivity and Magnetism & Pulsed Fields Group, INPAC, K.U. Leuven, Leuven, Belgium; N. Smisdom, B. De Clercq, M. Ameloot, University Hasselt and Transnational University Limburg, BIOMED, Diepenbeek, Belgium

Here we demonstrate several novel ways to observe chirality in optical G-shaped nanostructures made of gold. We start by showing Circular Dichroism (CD) in the Second Harmonic Generation (SHG) signal from the G-shaped structures. The arrangement of the Gs is crucial since upon reordering them the SHG-CD effect disappears. SHG microscopy reveals the presence of hotspot assemblies, which originate in enantiomerically sensitive plasmon modes having the novel property of exhibiting a chiral geometry themselves in relation with the handedness of the material. Furthermore, we demonstrate that SHG microscopy images, with linear polarization, can reveal directly the handedness in the material. And finally, we show that it is possible to distinguish the handedness in this chiral material by rotating the sample between two linear polarizers. This last property is particularly counter-intuitive since chirality is generally invariant under rotational symmetry. Furthermore, contrary to previous optical effect sensitive to chirality, the last one reported here can occur without an electric dipole contribution. These results open new frontiers in studying chirality.

FK - 6th International Conference

SCIENCE AND ENGINEERING OF NOVEL SUPERCONDUCTORS

Oral Presentations

Session FK-1

Materials, Structure, Physical Chemistry and General Properties

FK-1:IL01 **Insight in High-temperature Superconductivity from Cuprate Heterostructures**

Adrian Gozar*, Ivan Bozovic, Brookhaven National Laboratory, Upton, NY, USA

Using a unique molecular beam epitaxy system, we synthesize atomically smooth HTS thin films, multilayers and superlattices.[1] Such heterostructures enable novel experiments that probe the basic physics of HTS. For example, we have established that HTS and anti-ferromagnetic phases separate on Ångstrom scale, while the pseudo-gap state apparently mixes with HTS over an anomalously large length scale ("Giant Proximity Effect").[2] In this talk, I will review our most recent experiments on such films and superlattices, including XRD, AFM, angle-resolved TOF-ISARS, transport measurements, high-resolution TEM, resonant X-ray scattering, low-energy muon spin resonance, ultrafast photo-induced RHEED, COBRA surface crystallography, and ultra-high magnetic field spectroscopy. The results include an unambiguous demonstration of strong coupling of *in-plane* charge excitations to *out-of-plane* lattice vibrations[3], a discovery of interface HTS[4], and evidence that HTS occurs in a single CuO$_2$ plane[5].

**In collaboration with I. Bozovic, G. Logvenov, V. Butko, A. Bollinger, O. Pelleg, H.J. Shim and P. Chaudhari (BNL), P. Abbamonte and S. Smadici (Urbana), D. Miller and L. Fitting Kourkoutis (Cornell), N. Gedik and A. Zewail (Caltech), Z. Radovic (Belgrade) and N. Bozovic (SJSU).*

[1]I. Bozovic et al., Phys. Rev. Lett. 89, 107001 (2002); P. Abbamonte et al, Science 297, 581 (2002); [2]I. Bozovic et al, Nature 422, 873 (2003); Phys. Rev. Lett. 93, 157002 (2004); [3]N. Gedik et al, Science 316, 425 (2007); Z. Radovic et al, Phys. Rev. B 77, 092508 (2008); H. Shim et al, Phys. Rev. Lett. 101, 247004 (2008); [4]A. Gozar et al, Nature 455, 782 (2008); S. Smadici et al, Phys. Rev. Lett. (2009) 102, 107004 (2009), V. Butko et al, Adv. Mater. 21, 1 (2009); [5]G. Logvenov et al, Science 326, 699 (2009).

FK-1:IL02 **Electric Field Induced Superconductivity**

Yoshihiro Iwasa, Institute for Materials Research, Tohoku University, Sendai, Japan

We report that interface superconductivity can be induced through electrostatic charge accumulation at the electric double layer (EDL) formed at interfaces between liquid and solid. This interface has been of central importance from the view point of battery applications and catalytic activities. However, their ability to accumulate high charge density at the interface can be used as a transistor with high capacity and high maximum carrier density, which might provide a significant impact on solid state physics. When voltage is applied between two electrodes in an electrochemical cell, mobile ions in electrolyte move toward corresponding electrodes driven by the electric field. Finally, ions are stabilized right above the electrode surface to form an EDL, a kind of capacitor, where an electric field in the order of 10 MV/cm, which is difficult to achieve in solid capacitors, is produced without any difficulty. This capacitor device, called an electric double layer capacitor (EDLC), is well known for its capability of high density charge accumulation, and is already on market as a high density and high speed capacitor. When one of the electrodes is replaced by a semiconductor with a source and drain electrodes, this device works as a field effect transistor, which can be called an electric double layer transistor (EDLT). This electrochemical device has been investigated for application to ion sensors. Since 2005, we have been investigating EDLT devices aiming at accumulating high density carriers and hopefully inducing electronic phase transitions using organic semiconductors. Recently, we started to apply this technique to oxide semiconductors, and have successfully demonstrated the electric field induced insulator-metal transition in ZnO, followed by superconductivity in SrTiO$_3$. These results may suggest that EDLT could offer a novel direction in materials research at the electrochemical interface between ionic conductors (generally liquid) and electronic conductors (solid). This is not only because both ionic and electronic conductors are of enormously rich variety, but also because this transistor involves rich chemical processes, ranging from electrostatic charge accumulation to chemical reactions at the surface and in the bulk. For example, we found that ionic liquid displayed superior charging capability, which enabled us to observe new electric field induced superconductivity in a layered compound ZrNCl with increased Tc of about 15 K. The present results indicate that EDLT could be a versatile technique for inducing and manipulating superconductivity at interfaces between solid-liquid interfaces.

This work has been carried out in tight collaboration between Kawasaki group at WPI-AIMR Tohoku University (A. Tsukazaki, A. Ohtomo, K. Ueno, M. Kawasaki), Low Temperature Center (T. Nojima, S. Nakamura), and our own team at IMR Tohoku University (H. Shimotani, H.T. Yuan, J.T. Ye, Y. Kasahara).

FK-1:IL03 **Structure and Electrical Properties of the Interface Between LaAlO3 and SrTiO3**

A. Kalabukhov*, R. Gunnarsson, D. Winkler, T. Claeson, J. Börjesson, N. Ljustina, E. Olsson, Chalmers University of Technology, Göteborg, Sweden; Y. Boikov, I. Serenkov, V. Sakharov, Ioffe Physico-Technical Institute, St Petersburg, Russian Federation; V. Popok, University of Gothenburg, Göteborg, Sweden

Interfaces often exhibit properties which are not observed in the bulk. Recently, much attention has been paid to hetero-interfaces between complex perovskite oxides. High electrical conductivity and mobility has been reported in the interface between two wide-band gap insulators, LaAlO3 (LAO) and SrTiO3 (STO)[1]. The interface is also superconducting at low temperature (0.3 K) and the critical temperature can be tuned by an electric field. The conduction has been attributed to "polar catastrophe", oxygen vacancies in the STO, and cation intermixing. The relation between microstructure and electrical properties is crucial for understanding the origin of electrical conductivity since even very small changes in oxygen concentration or cation stoichiometry can result in large variations of electrical properties. We have investigated the interface composition using medium-energy ion spectroscopy, high resolution electron microscopy and Kelvin probe force microscopy. A correlation between cationic intermixing at the interface and electrical properties was found which suggests a new explanation of the interface conductivity based on a percolation model[2].

[1]A. Ohtomo, and H.Y. Hwang, Nature (London) 427, 423 (2004); [2]A. Kalabukhov et al, Phys. Rev. Lett. 103, 146101 (2009).

FK-1:L04 **Synthesis, Structural and Physical Properties of Substituted Eu2Ru2-xIrxO7**

T.E. Sutto, T. Wong, J. Taft, T. Duncan, M. Osofsky, D. Gubser*, Naval Research Laboratory, Material Science and Engineering Division, Washington, DC, USA

Over the past several years, researchers have discovered novel types of superconductors in the pyrochlore family (A2B2O7), such as Cd2Re2O7 and the defect pyrochlores AOs2O6, where A= K, Rb and Cs. One of the more interesting types of behavior seen in a pyrochlore is found in the A2Ru2O7, where A = Tl or Bi. In this instance, temperature independent conductivity is observed from above 300 k to 50K. Below 50 K, the Tl system becomes semiconducting, while the Bi compound becomes metallic. In light of this behavior, we have focused on looking at metal doping of the Ru sites in the parent pyrochlore compound Eu2Ru2O7. X-ray analysis indicated a gradual expansion of the basic cubic unit cell of the pyrochlore as the amount of Ir is increased with no distortion from this symmetry over the entire solid solution range. Temperature dependent magnetic studies indicate a decrease of the Curie temperature as the amount of Ir is increased. Resistivity measurements show a gradual increase in the semiconducting band gap. These results are interpreted in terms of both the electronic structure of the Ru and Ir systems, as well as the frustrated magnetic interactions between the Ru sites as the amount of Ir is increased.

FK-1:L05 Homogeneity and Connectivity of Doped Mgb2 Bulks and Strands as Probed by Heat Capacity, SEM, and Current Transport

M.D. Sumption*, M.A. Susner, Y. Yang, E.W. Collings, LASM, Department of Materials Science and Engineering, The Ohio State University, Columbus, OH, USA

Homogeneity and current percolation have been investigated for MgB2 bulks and strands. PIT strands were compared to dense bulks produced by infiltration and spark plasma synthesis in terms of their homogeneity as measured by heat capacity and resistivity. These samples were also compared to those my by high temperature/high pressure synthesis, where samples are processed at temperatures up to 2300 °C under 1500 PSI. Uo values were extracted by magnetization decay measurements and are compared for the various materials, and to their transport and magnetically determined Fp values. A model which includes extrinsic limitations is used to correlate these properties. In addition, comparisons of transport and magnetization measurements in strands at higher magnetic fields showed the onset of a regime where the anisotropy between Jc parallel to the strand and Jc perpendicular to the strand grows rapidly. This leads to large differences between transport and magnetically measured values of not only critical current, but also the irreversibility fields, Birr. These effects are described in terms of a model which includes key influences from the geometry of the microstructure (as investigated by SEM).

FK-1:L06 YBCO and YbBCO Thin Films and Multilayeres Grown by MOCVD

A.V. Markelov*, A.A.Zakharov, S.V. Samoylenkov, A.R. Kaul, Lomonosov Moscow State University, Russia

Recently, the development of high-temperature superconducting wire has been making great progress. Coated-conductor tapes based on ReBa2Cu3O7 (ReBCO) have higher current-carrying ability in a magnetic field than other HTS based wires. The most investigations were made for YBCO, however, recently the focus is shifting towards various substituted ReBCO. It is known however that smaller rare earth ions in bulk samples lead to the increase of magnetic irreversibility field, even though the critical temperature of ReBCO is decreasing in the same row. It is supposed that the effect is due to decreasing of electronic anisotropy of ReBCO with the lowering of rare earth ionic radius. In present work we performed comparative study of ReBCO thin films based on Y and rare earth with smaller ionic radius, ytterbium. All films were obtained by MOCVD technique on single crystal substrates: MgO, SrTiO3. Optimizing of growth conditions allowed us to obtain YBCO and YbBCO films with high current density above 10 ^ 6 A/cm2 at 77K and self field. The results of the magnetic field dependence of the critical current density will be presented. Various characteristics of YBCO and YbBCO films and their multilayers, such as film morphology and epitaxial quality, will be discussed and compared to each other.

Session FK-2
Pnictides

FK-2:IL01 Iron-based Superconducting Materials: Current Status

Hideo Hosono, Tokyo Institute of Technology, Yokohama, Japan

Superconductivity in iron pnictides was first reported on LaFePO in July 2006, followed by a report of LaFeAs1-xFx with Tc = 26K in February 2008. These discoveries have rekindled the vital superconductivity research like the fever in high-Tc cuprates in late 1980s, and led to the publication of more than 1,000 papers to date. Although a variety of iron-based superconducting materials have been reported, these materials can be classified into 5-types of crystal structures. Each of them commonly contains the square lattice of Fe ion with a formal charge of +2, and each Fe2+ ion is tetrahedrally coordinated by pnictgens (As or P) or chalcogens which are located above and below the iron square lattice. In the present article, I review the current status of these 5-types of iron-based superconducting materials and correlation between Tc and local structure along with recent advances in thin film fabrication

FK-2:IL02 Point-contact Andreev-reflection Spectroscopy and Electron-boson Coupling in Superconducting Pnictides

R.S. Gonnelli*, D. Daghero, M. Tortello, G.A. Ummarino, Dipartimento di Fisica and CNISM, Politecnico di Torino, Torino, Italy; V.A. Stepanov, P.N. Lebedev Physical Institute, Russian Academy of Sciences, Moscow, Russia; R.K. Kremer, Max-Planck Institute for Solid-State Research, Stuttgart, Germany; J. Karpinski, N.D. Zhigadlo, Laboratory for Solid-State Physics, ETH, Zurich, Switzerland; Jianyi Jiang, Appl. Superc. Center, National High Magnetic Field Lab., Tallahassee, USA

In this talk I review our point-contact Andreev-reflection measurements in La-1111 and Sm-1111 (both optimally doped and underdoped) polycrystals, as well as in Ba(Fe,Co)2As2 single crystals. In all the cases, the low-T conductance curves indicate the presence of two nodeless gaps ruling out the existence of order-parameter nodes, at least in the ab plane. A generalized two-band BTK fit of the normalized conductance curves gives gaps that lie slightly below and well above the BCS value, respectively. In Sm-1111, for example, we find D1(0)=6.15 ± 0.45 meV and D2(0)=18 ± 3 meV (2D/kTc = 2.5-3 and 7-9, respectively) and both gaps show a BCS-like temperature dependence. In La-1111 and in Ba(Fe,Co)2As2 we obtained similar gap ratios, but the results are more complex and less ideal. The presence of high-energy features in the conductance of Ba(Fe,Co)2As2 (possibly related to a strong electron-boson coupling) is also discussed, as well as more recent results in SmFeAsPO polycrystals and Ca(Fe,Co)2As2 single crystals. A three-band interband-only s±-wave Eliashberg model can simultaneously reproduce both Tc, the gaps and their temperature dependency in pnictides of both families, provided that high values of electron-boson coupling constants and small typical boson energies are used.

FK-2:IL03 NMR Studies of the New Iron Pnictide Superconductors

H.-J. Grafe*, G. Lang, F. Hammerath, D. Paar, K. Manthey, G. Behr, J. Werner, B. Büchner, IFW Dresden, Institute for Solid State Research, Dresden, Germany

We have performed 139La, 57Fe, and 75As Nuclear Magnetic and Quadrupole Resonance (NMR and NQR) on aligned powders of the new (Sm,La)O1-xFxFeAs superconductor at temperatures up to 480 K. For all three nuclei in the x=0.1 material, it is found that the Knight shift and the spin lattice relaxation rate decrease monotonically with decreasing temperature, suggesting a lack of any q-space structure in the dynamical spin susceptibility that might be expected in the presence of antiferromagnetic correlations. In contrast, for x=0.05 the spin lattice relaxation rate is enhanced at low temperatures, whereas the Knight shift shows a similar temperature dependence as for x=0.1, indicating a growth of antiferromagnetic correlations for the underdoped samples, which is presumably related to the closeness to the spin density wave order in the non-superconducting samples. At the same time, 75As NQR measurements reveal the presence of a nanoscale charge segregation in the underdoped samples, reflecting intrinsic local differences in doping, with low and high doping regions. This charge segregation may also explain the occurrence of magnetic correlations in our samples, and could be consistent with the coexistence of static magnetism and superconductivity in other iron pnictides.

FK-2:L04 Iron Pnictide Thin Film Hybrid Josephson Junctions

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Since there are no high quality superconducting single crystals of the LaFeAsO1-xFx phase available so far, the importance of the deposition of thin films opens the way for fundamental experiments on superconductivity in the iron pnictides. Thus we start to develop tunneling and Josephson junctions with pnictide film electrodes. Different preparation methods for Josephson Junctions were investigated and the first results are shown. Resistive measurements show a high superconductive transition temperature of about 20 K even for the La-1111 electrode after patterning and preparing the tunneling window. The hybrid junctions were completed with an PbIn counterelectrode and different types of barriers like normal conducting gold layers.

FK-2:IL05 Fe Based Superconductors: Superconducting Properties Relevant for Applications

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Two years after the discovery of high temperature superconductivity in oxypnictide LaFeAs(O,F) the ride towards high Tc seems to be stopped, but the interest still grows thank to the discovery of several families of superconductors based on Fe layers (1111, 122, 11, 111). This allows now to compare the superconducting properties of the different families in order to identify which one is the fittest for the quest for better and more practical superconductors. The 1111 family shows the highest Tc, huge but also the most anisotropic upper critical field and in-field, fan-shaped resistive transitions reminiscent of those of cuprates. On the other hand the 122 family is much less anisotropic with sharper resistive transitions as in low temperature superconductors, but with about half the Tc of the 1111 compounds. The behaviour of 11 family is in between showing a rather unique case of low Tc with significant fluctuations. An overview of the main superconducting properties relevant to applications will be presented. Upper critical field, electronic anisotropy parameter, intragranular and intergranular critical current density will be discussed and compared across the Fe-based superconductor families.

FK-2:IL06 **Iron Pnictide Superconductors with Perovskite-type Blocking Layers**

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Since the discovery of high-Tc superconductivity in LaFeAs(O,F), several groups of iron pnictides or chalcogenides are developed such as AEFe2As2 and AFeAs. Meanwhile, still there are continuous demands for new materials containing iron tetragonal lattice. We have discovered new system of iron pnictides (Fe2Pn2)(AE4M2O6). The structure of the compounds consist of stacking of FePn layers and perovskite-type oxide layers. Interlayer Fe-Fe distances of about 16 Å are the longest ever reported in the iron pnictide superconductors. Compared to REFePnO system, perovskite-based system tends to have lower Pn-Fe-Pn angle and higher pnictogen height due to its local structure. Superconductivity at 17 K in (Fe2P2)(Sr4Sc2O6) strongly suggests that this system is a "new family" of iron-based superconductors. Its arsenic relatives were also discovered by several groups such as (Fe2As2)(Sr4Sc2O6), (Fe2As2)(Sr4V2O6) and (Fe2As2)(Sr4(Mg,Ti)2O6). The latter two compounds show superconductivity with Tc up to 39 K at ambient pressure(Mg,Ti) and up to 46 K at 4 GPa(V). These facts indicate the potential of high Tc superconductivity in this system. The large variety of perovskite-type structures and constituent elements will open new windows for search of iron pnictide superconductors.

FK-2:IL07 **Point Contact Andreev Reflection of the Iron Based Superconductors**

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The discovery of superconductivity at 26K in LaFeAsOF just over a year ago[1] prompted a huge surge of effort in order to elucidate details concerning the order parameter in these novel superconductors and potentially, the number of gaps present. One of the techniques at the forefront of this research was point contact Andreev spectroscopy (PCAR). Here we review point contact measurements of the iron based pnictide and chalcogenide systems and extend our earlier work on the "1111" family of NdFeAsO0.85[2] and TbFeAsO0.9F0.1[2]. Data is taken as a function of temperature, magnetic field and with and without a superconducting tip to reveal details about both the order parameter symmetry and the number of gaps present. Furthermore, measurements of the new "42226" system Sr2ScFePO3 and single crystals of LaFePO with two types of point contact technique ("hard" and "soft") are used to investigate whether the height of the pnictogen has a role in determining the order parameter symmetry in these fascinating new materials[4].

[1] Y Kamihara et al, J Am Ceram Soc, 130, 3296 (2008); [2] KA Yates et al, Supercon. Sci. Tech. 21, 092003 (2008); [3] K.A. Yates et al, New J. Phys, (in press), arxiv: 0812.0977 (2008); [4] K Kuroki et al, Phys Rev B, 79, 224511 (2009).

FK-2:L09 **On the Microscopic Magnetic Properties of Superconducting SmFeAsO0.8F0.2**

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We report on the microscopic magnetic properties of the superconducting oxy-pnictide compound SmFeAsO0.8F0.2 obtained by means of 19F-NMR measurements. The temperature dependence of the 19F nuclear relaxation rate 1/T1 strictly follows a power-law upon the explored temperature range, independently of the applied H0. This behaviour can be reproduced in the assumption that the self-consistent renormalization theory by Moriya[1] holds in this system. This suggests that the 4f electrons of Sm3+ ions belong to a sea of weakly itinerant and antiferromagnetically interacting fermions which drive the relaxation of the nuclear magnetization and whose magnetic correlation length is expected to be proportional to the inverse squared root of temperature. A similar trend in the dependence on both temperature and H0 is characteristic of heavy fermion systems with an antiferromagnetic ground state[2]. Moreover, our experimental findings and, in particular, the fact that 1/T1 is not sensitive to the superconducting transition show that the magnetic fluctuations of Sm3+ moments are not directly involved in the pairing mechanisms leading to the superconducting state.

[1] T. Moriya, Spin fluctuations in itinerant electron magnetism, Spinger; [2] P. Carretta et al., Phys. Rev. B68 220404(R).

FK-2:L10 **Universal Normal State Susceptibility in Iron Pnictides**

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The normal state magnetisation of iron pnictides exhibits a universal increase upon heating. In LaFeAsO1-xFx, both the slope and the abolute value of the susceptibility at elevated temperatures are independent on doping, irrespectively whether long range antiferromagnetic order or the non-magnetic superconducting ground state appears. Our data on LiFeAs, NaFeAs, Ba- and Ca(Fe,Co)2As2 single crystals imply the generic nature of this feature. Remarkably, there is quantitative agreement of the slope well above the ground states. We present a scenario of robust local antiferromagnetic correlations persisting even in the superconducting regime of the phase diagram. In addition, we present the phase diagrams of the single crystal series based on our specific heat, thermal expansion, muSR, magnetisation and resistivity data. In particular, our data allow to assess renormalisation effects in CaFe2As2.

FK-2:L11 **Fabrication of Fe-Te-S Superconducting Epitaxial Thin Films by Pulsed Laser Deposition**

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Almost with a year, four new families of Fe-based superconductors with layered structure similar to the cuprates were discovered. So far there are a lot of reports on sintered iron-based superconductors samples, but in order to enlighten their fundamental physical properties and to disclose them to applications a development of research on epitaxial thin films is greatly desired. We report on the fabrication and characterization of Fe-Te-S epitaxial thin films ablating FeTe0.8S0.2 target. Stoichiometric amounts of Fe, Te and S powders were sealed into quartz tube and reacted at 800C×12 h, then pressed in pellets, resealed and sintered at 600C×12 h. Pellets were ablated in PLD chamber to fabricate thin films on MgO and STO oriented substrates under these conditions: P = 10 ^ -5 Pa, T = 200-600 C, E = 200-350 mJ/pulse. Films formed with deposition temperature 300-400 C showed epitaxial c-axis orientation on both STO and MgO single crystal substrates. Superconducting transition was observed from resistance-temperature measurements, with zero resistance Tc=5.5 K (B=0). Since both irreversibility field (Birr = 36.2 T) and upper critical field (Bc2 = 79.7 T) were large, by optimizing the quality of films high-field applications of this class of materials are expected in the near future.

Session FK-3
Properties of Superconductors

FK-3:IL01 **New Trends in the Physics of Heavy Fermion Superconductors**

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Coexistence or competition of magnetic and superconducting order is a topic debated since the discovery of the first heavy fermion superconductors back in 1979. However, more recently, the question has been renewed with the discovery of the role of quantum critical points in the birth of a superconducting ground state. We will present the actual status of the debate focusing on two paradigmatic compounds on which our group made recent advances. - First, the 115 compounds CeCoIn5 and CeRhIn5, where the question of the interplay between quantum critical point, superconductivity, Fermi surface reconstruction, and re-entrant antiferromagnetic phases in the superconducting mixed state is particularly acute. - Second, the ferromagnetic superconductors, notably URhGe and UCoGe, where a unified view of the re-entrant superconducting phases in high fields has been recently uncovered, together with that of multiband superconductivity. A remarkable phenomena, one of the most challenging nowadays in this field, is the robustness of superconductivity in this reentrant phases to fields above 20T.

FK-3:IL02 **Evolution of Superconductive Properties and Texture with Heat Treatment Time in Carbon-Doped In-situ Processed MgB_2 Strands**

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Pieces of monocore in-situ-processed PIT strands (0.4 mm core diam.), initially filled with mixed 99% B and Mg powders doped with 10 wt% malic acid, were encapsulated and heat treated (HT) at 600 °C and 700°C (bracketing the frequently used 650 °C) for exact times of 0.5, 1, 2, 4, 6, 8, and 71 h and ice-water quenched. Short samples were removed for microstructural and superconductive property characterization consisting of: (i) fracture SEMs (at 100,000x) of grain size, (ii) SE- and BSE-SEMs (at ~750x) of polished transverse and longitudinal sections, (iii) transport measurements of T_c , critical fields, and J_c, magnetic (PPMS, VSM) measurements of critical fields and J_c. During the drawing of the B+Mg mixture the Mg particles elongated into stringers typically 27 mm long and 2.5 mm in diameter. During HT the Mg stringers infiltrated the surrounding B, forming MgB_2 and leaving behind elongated pores. As a result the core of the strand resembled a multiply connected cluster of elongated rods, made up (according to fracture-SEM) of randomly arranged 50 nm-size grains. Critical temperature measurements suggested that at 600 °C the formation reaction was incomplete after 8 h while at 700 °C the reaction proceeded very rapidly and was already complete after only 0.5 h of HT. Likewise at 700 °C J_c reached its maximum value after 0.5, 1 and 2 h although it decreased steadily at longer HT times. Grain growth is a possible contributor to this; the F_p versus reduced field curves indicate that MgB_2 is a grain-boundary pinner. Under both HTs grain size increased with time, reaching an average size of ~54 nm. At 600 °C J_c peaked at 4 h of HT while both the 600 °C and 700 °C J_c maxima were lower than that of another strand HT for 1 h at 650 °C which seems to be the optimal HT temperature for this class of strand. The field dependencies of the transport- and magnetic J_cs (now J_{ct} and J_{cm}, respectively) were compared as a result of which it was found that J_{cm} began to fall well below J_{ct} with increasing applied field strength. Since for samples with isotropic J_cs and SC L/D ratios of more than 15 (for the present samples $10<L/D<15$) J_{cm} would differ from J_{ct} by less than 3% over the entire field range of the experiment, the observed deviation is attributed to an anisotropic strand-averaged J_c i.e. $J_{c,transverse} < J_{c,longitudinal}$. This anisotropy, which begins to manifest itself as the applied field becomes stronger and stronger, is a result of a field dependent reduction in transverse connectivity between the MgB_2 stringers, combined of course with the finite L/D ratios of the strand samples.

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FK-3:IL03 **Terahertz Spectroscopy of Novel Superconductors and in Strongly Correlated Materials**

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In this talk the production of terahertz radiation from third and fourth generation synchrotron machines will be reviewed. Its potentialites and applications for spectroscopy will be discussed with particular emphasis on the low-energy electrodynamics of novel superconductors and strongly correlated materials.

FK-3:IL05 **FFLO State in Heavy Fermion Superconductors**

Y. Matsuda, Department of Physics, Kyoto University, Kyoto, Japan

The Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state is a novel superconducting state in a strong magnetic field characterized by the formation of Cooper pairs with nonzero total momentum (k,-k+q), instead of the ordinary BCS pairs (k,-k). A fascinating aspect of the FFLO state is that it exhibits inhomogeneous superconducting phases with a spatially oscillating order parameter and spin polarization. The FFLO state has been of interest in various research fields, not only in superconductors, but also in ultracold atomic gases and in high energy physics. In spite of extensive studies of various superconductors, there has been no undisputed experimental verification of the FFLO state, mainly because of the very stringent conditions required of the superconducting materials. Among several classes of materials, certain heavy fermion and organic superconductors are believed to provide conditions that are favorable to the formation of the FFLO state. Here we present recent experimental and theoretical developments of the FFLO state mainly in heavy fermion superconductors. In particular we address the recently discovered quasi-two-dimensional superconductor CeCoIn5, which is a strong candidate for the formation of the FFLO state.

FK-3:IL06 **Optical Spectroscopy Study on Fe-pnictides**

Nan Lin Wang, Institute of Physics, Chinese Academy of Sciences, Beijing, China

The discovery of superconductivity above 50 K in iron-pnictides has attracted tremendous attention. The close relation between the superconductivity and magnetic instability suggests that the magnetic fluctuation plays an important role. In this talk, I shall present optical spectroscopy investigations on single crystal samples of several different Fe-based systems. For all FeAs-based parent compounds we observed common spectral features: partial energy-gaps formation along with a removal of a large part of free-carrier spectral weight and a steep reduction of the carrier scattering rate in the magnetic ordered state. However, the 11-type FeTe behaves very differently. No energy gap opens in the magnetic state. We proposed that both the itinerancy and local moment interactions of Fe 3d electrons are present, but contribute differently to the magnetic instabilities in different systems. For the doped superconducting samples, we observed the pairing gaps with an s-wave lineshape in the superconducting state. The Ferrell-Glover-Tinkham sum rule is satisfied at a low energy scale.

FK-3:IL07 **Neutron Scattering of Cuprate Superconductor**

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Neutron scattering spectroscopy has been providing key information on the microscopic properties of cuprate superconductors, which is indispensable for the elucidation of the mechanism of superconductivity. In particular, recent neutron scattering studies have evoked duality or multiplicity in magnetism in cuprate superconductors, which probably controls the role of magnetism (cooperation and competition) for superconductivity. The magnetic duality is typically seen in the spin dynamics where both itinerant and localized spins coexist with distinct energy scales. In this talk, we briefly introduce a present view of cuprate superconductors seen by recent neutron scattering spectroscopy and discuss remaining issues related to the magnetic duality in connection with charge duality seen by other probes such as photoemission spectroscopy and scanning tunneling microscopy.

FK-3:L08 **High-pressure Oxygenation of MT-YBCO**

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The possibility to oxygenate the $YBa_2Cu_3O_{7-\delta}$(Y123) structure to $7-\delta \approx 6.9$ atoms at high temperature (800 °C) and 16 MPa oxygen pressure has been shown. Oxygenation of melt-textured $YBa_2Cu_3O_{7-\delta}$ (MT-YBCO) at enhanced pressures and high temperatures decreases the oxygenation time and the amount of cracks and increases the twin density in the material, which positively affects the critical current density, *jc,* and mechanical characteristics of MT-YBCO. The experiments have shown that twins are substantially responsible for high *jc* and irreversibility fields of MT-YBCO ceramics. In the case of high dislocation density (10^{12} cm^{-2}) and low twin density (0-1 μm^{-1}) in the Y123 structure, the *jc* turned out to be an order of magnitude lower than in the case of high twin density (22 μm^{-1}) and absence of dislocations and stacking faults. The density of twins and microcracks in the structure of the $YBa_2Cu_3O_{7-\delta}$ phase has been found to depend on the size of the Y_2BaCuO_5 inclusions and style of their distribution, which in turn is defined by the initial materials. The process allows one to attain record high *jc* values and double the trapped magnetic field as compared to both the bulk MT-YBCO oxygenated under the same conditions and thin-wall MT-YBCO oxygenated at 1 atm and optimal temperature.

FK-3:IL10 **BCS Superconducting Gap in Electron-doped Cuprates**
I. Diamant, Y. Dagan*, School of Physics and Astronomy, Tel Aviv University, Tel Aviv, Israel

The phase diagram of the less explored electron-doped cuprates is somewhat simpler than that of the hole doped. They may therefore present a unique laboratory for study and maybe understand the cuprate superconductors. The tunneling and point contact conductance characteristics into Pr_{2-x}Ce_xCuO_4 as a function of doping temperature and field are reported. The relatively low Hc2 allows us to measure the superconducting phase together with the normal state characteristics. This enables us to cancel any spurious effects arising from the normal state or from the junction barrier itself. We find that the superconducting gap exhibits a BCS-like temperature dependence even for extremely low carrier concentrations. Moreover, the gap follows the doping dependence of Tc, in strong contrast with tunneling studies on hole-doped cuprates. From our results we conclude that there is a single superconducting energy scale in the electron-doped cuprates. From point contact spectroscopy we are able to identify bosonic resonances and follow their doping variation. These excitations disappear above Tc, and Hc2. We find that the energy of the bosonic excitations decreases when increasing the doping level. We discuss the implications on possible pairing mechanism in the electron-doped cuprates.

FK-3:IL11 **Isotope Effects and Multi-band Superconductivity in Layered High-temperature Superconductors**
Hugo Keller*, Physik-Institut der Universität Zürich, Zürich, Switzerland

High-temperature superconductors (HTSs) such as cuprates, MgB2, and the iron-based superconductors appear to have some common features: 1) they have a layered structure with strongly anisotropic properties, 2) they show pronounced isotope effects (on various physical quantities in the cuprates, including the superconducting transition temperature, the superconducting gap, the in-plane penetration depth, the pseudogap temperature, the antiferromagnetic transition temperature, and the spin-glass freezing temperature, 3) they are multi-band superconductors with mixed order parameters. In the first part some isotope effect results obtained for cuprate HTSs, MgB2, and iron-based HTSs are discussed. These results clearly demonstrate that lattice effects play an essential role in the basic physics of these layered HTSs and are the origin of these isotope effects. In the second part it is shown that the cuprate and iron-based HTSs are multi-band superconductors, similar to MgB2. Magnetic penetration depth measurements in cuprate HTSs reveal that the in-plane superconducting order parameter is a mixture of s + d-wave symmetry, whereas it is mainly s-wave along the c-direction. Various experiments indicate that the iron-based HTSs are also multi-band superconductors.

Session FK-4
Theory and Mechanisms

FK-4:IL01 **Energy Scale Phenomenology of Novel Superconductors**
Yasutomo J. Uemura, Physics Department, Columbia University, New York, USA

We discuss three energy scales which correlate with the transition temperature Tc of high-Tc cuprate, FeAs, A3C60, organic BEDT, and heavy-fermion CeCoIn5 systems. These energy scales are: (1) Superfluid density n_{s}/m ^ {*} and the effective Fermi energy derived from that; (2) Energy of magnetic resonance mode in neutron scattering; and (3) Spin fluctuation energy scale. (1) indicates Bose-Einstein condensation of pre-formed pairs in the underdoped region. (2) suggests that Tc is reduced from the values expected for non-interacting Bose gas, due to proximity to the competing antiferromagnetic states. (3) results from nearly equivalent energy scales of charge (effective Fermi energy) and spin (zone-boundary spin wave energy). These observations implie that these unsonventional superconductors lie in the “intermediate coupling” region in Bose Einstein (strong coupling) to BCS (weak coupling) crossover. Combining these with commonalities in phase diagrams[1], we propose a model for pairing based on “resonance” of the charge and spin energy scales, in which spin frustration can be avoided by a charge motion synchronized with spin fluctuations (Traffic light resonance)[2].

[1] Y.J. Uemura, Nature Maters. 8 (2009) 253; [2] Y.J. Uemura, Physica B 404 (2009) 3195.

FK-4:IL02 **Exchange-interaction Induced Pairing in Strongly Correlated Systems**
Jozef Spalek*, Marian Smoluchowski, Institute of Physics, Jagiellonian University, Krakow, Poland and AGH University of Science and Technology, Krakow, Poland

I overview first our and related recents works on the t-J model of high-temperature superconductors. In particular, we show that there is an upper doping concentration, above which the superconductivity disappears.The appearance of this critical doping is regarded as one od the key indications that the pairing is of real-space type and induced by the kinetic exchange. In the second part I discuss related pairing mechanism based on the Kondo-type interaction, which is relevant to some unconventional heavy fermions superconductors. I introduce specific features of the latter systems such as spin-dependent quasiparticle masses, effective field driven by electron correlations, as well as shall discuss the evidence for the novel Fulde-Ferrell Larkin-Ovchinnikov phases in those systems. In general, I shall try to single out the specific properties which are driven by the strong correlations among the electrons in those narrow-band systems.

FK-4:IL03 **Theory for Inhomogeneous Superconductors: Approach from the t-J Model**
Masao Ogata, Department of Physics, University of Tokyo, Japan

Two-dimensional t-J model is a standard model for studying high-Tc cuprate superconductors. This model predicts various states which are actually observed in cuprates, for example, d_{x ^ 2-y ^ 2}-wave superconductivity, antiferromagnetism and a uniform coexistent state of d-wave superconductivity and antiferromagnetism. As an inhomogeneous state, we studied stripe states to find that the next-nearest-neighbor hopping t’ < 0 stabilizes the stripe states accompanied by a spatially-oscillating superconducting order parameter around 1/8-hole doping rate. Although the energy differences are relatively small, a state with antiphase superconducting order parameter is also stabilized, which explains the weakness of the c-axis Josephson couplings. These calculations indicate that the ground state of the t-t’-J model can have strong spatial inhomogeneity. Actually, randomness in the apical oxygen sites affects the magnitude of t’, leading to the inhomogeneity of the superconducting order parameter, or the pseudo-gap function. We discuss the relation to the STS and ARPES experiments due to this inhomogeneity.

Session FK-5
Vortex Lattice Physics

FK-5:IL01 **Summation of Strong Pinning Forces**
Franz M. Sauerzopf, Atominstitut, Vienna University of Technology, Austria

The summation of strong elementary pinning forces in superconductors to a macroscopic pinning force has been an unsolved problem for a few decades. I will present modelling considerations, which offer a solution to the problem. For the first time, a macroscopic pinning force of the correct order of magnitude can be derived from a reasonable set of superconducting material parameters with a plausible defect density and size. This is possible by describing pinning and depinning under the influence of an additional small driving force. The dynamics of the model are characterized by one free parameter, which balances the vortex displacement in the direction of the driving force and the additional adaptive displacements in the vortex lattice. The free parameter is eliminated by optimizing the resulting macroscopic pinning force. I will dicuss the basics of the model, compare results with experiments, and point out possibilities for further development.

FK-5:IL02 **Type-1.5 Superconductivity**
Victor V. Moshchalkov, INPAC-Institute for Nanoscale Physics and Chemistry, Katholieke Universiteit Leuven, Belgium

The existence of the novel superconducting state has been demonstrated in two-component high quality MgB2 single crystalline superconductors where a unique combination of both type-1 and type-2 conditions is realized in a single material: $\lambda1/\xi1 < 1/\sqrt{2}$ for the first component of the order parameter and $\lambda2/\xi2 > 1/\sqrt{2}$ for the second one. Such materials are, in fact, type-1.5 superconductors (PRL 102, 117001 (2009)), since they combine simultaneously both type-1 and type-2 superconductivity. This leads to a drastic change in the vortex-vortex interaction, which results in the appearance of stable vortex stripes, clusters and gossamer-like vortex patterns. We have directly visualized these novel patterns by using Bitter decoration and scanning SQUID microscopy. The observed patterns are in a good agreement with the molecular dynamics simulations based on the vortex-vortex interaction corresponding to the type-1.5 superconductivity.

In collaboration with: A.V. Silhanek, W. Gillijns, J. Van de Vondel, M. Menghini, J. Fritzsche, R. Kramer, T. Nishio, Q.H. Chen, V.H. Dao, L.F. Chibotaru, N.D. Zhigadlo, J. Karpinski

FK-5:IL03 **Critical Current Densities in Ba(Fe,Co)2As2 and FeTe1-xSex**

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The critical current density, Jc, in Ba(Fe,Co)2As2 is characterized by the presence of pronounced fish-tail effect and its value is larger than 1x10 ^ 5 A/cm2 below 10 K. We report the first demonstration of the heavy-ion irradiation effect in FeAs superconductors. Ba(Fe,Co)2As2 crystal is irradiated by 200 MeV Au ions with a dose-equivalent field of 2 T. Magneto-optical (MO) imaging and bulk magnetization measurements confirm the enhanced Jc by a factor of five or more and suppression of the fish-tail effect. TEM observations clearly indicate the presence of columnar defects in the irradiated region. We have also succeeded in growing high-quality single crystals of FeTe1-xSex (Tc=14 K) by slow-cooling followed by annealing at 400 C. We report resistivity, magnetization, and MO images of this crystal. Magnetization measurements show the presence of fish-tail effect, and Jc exceeds 1x10 ^ 5 A/cm2 at zero field below 5 K comparable to Ba(Fe,Co)2As2. The normalized relaxation rate of irreversible magnetization S (= dln M/ dln t) in both Ba(Fe,Co)2As2 and FeTe1-xSex show common and characteristic temperature and field dependence. The origin of such a behavior of S will be discussed.

FK-5:IL04 **Non-centrosymmetric Superconductors: Extreme Vortex Pinning in CePt3Si and Li2Pt3B**

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Vortex dynamics studies in non-cetrosymmetric superconductors CePt3Si and Li2Pt3B revealed for both compounds extremely slow movement of the flux lines in conjunction with modest critical currents. In addition, for the Li2Pt3B which has the highest critical current among the two superconductors (i.e. higher vortex density), the slow decay of the remanent magnetization is followed, in a certain temperature range, by avalanche-like relaxation. The apparent contradiction of extremely low relaxation rates in spite of low critical currents could be explained by the existence of an unconventional and very effective flux trapping mechanism. A possible understanding of such pinning mechanism could be the existence of fractionalized vortices. Since the superconducting phases for both CePt3Si and Li2Pt3B conserve time reversal symmetry the fractionalized vortices would be localized in the twin boundaries of the crystals which would then introduce strong planer barriers for flux-line motion without affecting the critical current. However, this scenario needs independent verification. This discovery might indicate a characteristic of a certain class of non-centrosymmetric superconductors.

Session FK-6
Synthesis and Processing

FK-6:IL01 **Progress in Chemical Solution Approaches to Nanocomposite Superconducting Films**

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Chemical solution deposition (CSD) has emerged as a very competitive low cost technique to obtain epitaxial films, multilayers, nanocomposite films and interfacial templates of high quality with controlled nanostructures and functionalities. The all CSD approach has been shown to be one of the most promising ways for low-cost production of second generation superconducting wires with high performances. The development of high performance nanostructured superconductors with enhanced vortex pinning properties requires the preparation of nanocomposite epitaxial films. In this presentation we will report first about recent innovations concerning processing of YBCO films based on TFA precursors and, second, about different approaches to the preparation of nanostructured YBCO films based either on the use of oxide interfacial nanotemplates also grown by CSD, or through modified metal-organic solutions leading to nanocomposite films. We have particularly investigated the influence of oxygen and total pressure on the TFA route to YBCO films and we have devised a new route to decrease the growth temperature, keeping high superconducting performances. The role of strain engineering to tune interfacial nanostructures and vortex pinning will be highlighted as a very versatile tool to enhance vortex pinning.

FK-6:IL02 **Stability Conditions for Charge Density Wave and Superconducting States in Intercalated 1T-dichalcogenides**

Andrea Gauzzi*, Amine Sellam, Gwenaelle Rousse, Matteo d'Astuto, Abhay Shukla, Matteo Calandra, Francesco Mauri, IMPMC, Universite Pierre et Marie Curie and CNRS, Paris, France; Edmondo Gilioli, IMEM-CNR, Parma, Italy; Igor Mazin, Naval Research Laboratory, Washington DC, USA

By means of high resolution neutron powder diffraction, magnetization and electrical resistivity measurements as a function of temperature, we studied the structural, magnetic and transport properties of pure and intercalated 1T-TaS2 samples synthesized under high pressure. Our data analysis shows that high-pressure synthesis stabilizes sizable changes in the 1T structure which control the competition between charge density wave (CDW) and superconducting (SC) states. These changes mainly consist of an expansion of the out-of-plane (c-) axis and a shrinking of the in-plane (a)-axis, thus enhancing the two-dimensional character of the electronic structure. These changes are concomitant to a stabilization of the SC state at Tc ~ 4 K, in agreement with previous transport studies under high pressure. Complementary ab initio calculations of the electronic structure and of the phonon dispersion within the density functional theory suggest that the above structural changes removes the commensurability of the wave vector at which a phonon instability is observed in the pristine structure. This accounts for the observed suppression of the CDW state and supports a picture of electron-phonon superconducting mechanism in transition metal dichalcogenides.

FK-6:L03 **Deposition of YBCO FOR 2G Conductors Using Laser Direct Write**

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The use of Second Generation High Temperature Superconducting wires in certain applications requires that the conductor be engineered to minimize ac losses. This can be accomplished by dividing the YBCO film into thin filament arrays and the periodic introduction of filament bridges along the conductor length to simulate geometries present in twisted conductors. The process developed for manufacturing 2G superconducting wires by American Superconductor involves preparing YBCO films from the metal organic decomposition of a trifluoroacetate (TFA)-based precursor on buffered substrates. These TFA precursor solutions were used with a new process, based on a laser direct-write (LDW) technique, to deposit thin film patterns and lines on buffered substrates without the need of etching or patterning afterwards. The LDW technique relies on the non-phase transforming laser forward-transfer of complex suspensions or inks to function as a functional materials printer. Since LDW is a non-contact, data driven materials printing process, it is ideally suited for applications where there is a need to deposit a pattern of a given material onto a surface that cannot easily be patterned using standard lithographic techniques, such as a flexible substrate.

FK-6:L04 **Development of Low-loss (Bi,Pb)-2223 Tapes with Interfilamentary Resistive Barriers**

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In this paper, our recent activities for the development of low-loss (Bi,Pb)-

2223 tapes with interfilamentary resistive barriers are presented. To suppress the side effect on the phase formation in the filaments during sintering process, Ca2CuO3 and SrZrO3 were selected as barrier materials. Moreover, small amount of Bi2212 was mixed with these oxides to improve their ductility for cold working. Although some breakages of interfilamentary barrier layers still existed in the tape, the effective transverse resistivity was 15-20 times higher than pure Ag-sheathed tapes without barriers. Coupling frequency (fc), which is related to the inverse of decay time constant (tc) of coupling current, exceeded 300 Hz even in an AC external magnetic field in perpendicular to the wider face of a tape, by both introducing barriers and twisting the filaments tightly. Although the critical current densities (Jc) for the barrier tapes are still much lower than those for commercial one, this achievement is very promising for significant reduction of AC losses in a perpendicular field with power-grid frequency. Moreover, the longitudinal uniformity of a barrier tape with several meter lengths was characterized magnetically and non-destructively by scanning Hall-probe microscopy (SHM).

FK-6:IL07 Novel Processing Techniques of Bulk HTS and the Role of Artificial Nanoparticles

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LRE-Ba-Cu-O ((LRE)BCO, where LRE is a light rare earth element such as Nd, Gd or Sm) bulk superconductors exhibit significantly better field trapping properties than YBCO, but present greater processing challenges. (LRE)BCO superconductors have a high peritectic decomposition temperature, and are fabricated commonly by a hot seeding processing method. In addition, solid state substitution of the LRE ion on the Ba site in the (LRE)Ba2Cu3O7-δ superconducting compound reduces Tc and hence degrades performance. This effect can be controlled by processing the bulk material in an atmosphere of reduced oxygen in a specialist furnace. Finally, good field trapping properties of bulk superconductors require a high, uniform critical current density by engineering fine second phase inclusions within the bulk microstructure. We report a practical TSMG process for the fabrication of high performance (LRE)BCO single grain superconductors in air and a generic seed of melt-textured Mg-doped Nd-123. We also report recent advances in the generation of nano-scale flux pinning sites based on the engineering of RE2Ba4CuMOx (RE-2411) second phase inclusions. Bulk samples of up to 26 mm in diameter have been fabricated by this process and shown to trap record magnetic flux densities at 77 K.

Session FK-7
Power Applications

FK-7:IL01 Fault Current Limiters - Materials, Applications and Prospects

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R&D on fault current limiters has made significant progress in recent years. Especially superconducting fault current limiters (SCFCLs) are very attractive devices for power systems. SCFCLs offer negligible impedance at normal conditions, fast and effective current limitation within the first current rise and repetitive operation with fast and automatic recovery. This paper presents shortly the state-of-the-art of R&D on fault current limiters, shows the different material options and outlines the most important material requirements. In addition some attractive applications are presented and an outlook is given on future R&D activities. It can be summarized that fault current limiters seem very close to commercialization. Many successful large scale prototypes and demonstrators were developed and first successful field tests underline their potential to penetrate the market in near future. Furthermore, superconducting YBCO coated conductor material is an attractive material for SCFCLs because it fulfills all major requirements.

FK-7:IL02 High Temperature Superconducting Generators in Support of Wind Energy

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The increasing demand of clean energy generates a strong interest in off-shore wind farms which represent a significant energy source all around the planet. Off-shore wind farms require large turbines ideally producing power in excess of 10 MW. Therefore, off-shore wind energy is driving the development of large direct-drive power generators with an emphasis on reliability and weight reduction. Conventional drivetrain technologies do not scale advantageously and as power generated goes up, so does the weight of the drivetrain making the tower design and the installation more costly and challenging. Reducing the weight of the drivetrain could help address the problem and enable higher power systems. Conventional generator technology is based on magnetic cores magnetized by copper windings or permanent magnets. Increasing the specific power of those machines while keeping a high efficiency is very difficult as current designs are operating very close to the limits of the material. Improvements has to come from a different technology and different materials, namely superconductors. Superconductors can carry very high current densities with no losses and therefore allow for the design of compact ironless machines. Removing the iron core obviously greatly reduces the weight, removes the air-gap flux limitation due to magnetic saturation and enables development of generators exhibiting specific torques greater than 50 Nm/kg. In order to achieve a cost and performance effective design, trade-off analyses need to be performed including the conductor that must be chosen between the different commercially available superconductors and will drive the design and cooling requirements. Several large superconducting generators are currently developed in the world based on different superconductors and configurations. The presentation will discuss the impact of large superconducting generators on the wind power generation landscape and present the approach, objectives and the major challenges of the different existing projects.

FK-7:IL03 Numerical Modeling of AC Losses in FCL

F. Grilli, Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, Germany

Fault current limiters (FCLs) are one of the most promising applications of high-temperature superconductors (HTS) on large-scale. In order to design efficient FCLs, two operating conditions need to be considered: 1) the superconducting state, in which the FCL operates for most of the time; 2) the transition to the normal state, which occurs during a fault. Numerical models are a powerful tool that can help to design devices with low inductance and low ac losses when they are operating in the superconducting state and to better understand the dynamics during a fault, in order to avoid irreversible damages. In this presentation different numerical models used to investigate the FCL's behavior in the two situations mentioned above are described and examples of their application are shown.

FK-7:IL04 AC Loss in Coated Conductor Tapes and Coils

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Superconducting coils are the key component in many promising applications, such as transformers, motors, generators and scientific magnets. However, the AC loss is still too large and, needs to be reduced, if these coils are made of coated conductors. In this article we discuss the mechanisms for reducing the AC loss in coils. In particular, we simulate and measure the AC loss reduction by means of magnetic diverters or low-loss structures, like striated tapes or Roebel cables. We found that optimised magnetic diverters reduce the AC loss for the self-field situation (e.g., in a transformer). Their optimal shape has to be predicted by simulations. If the external magnetic field is dominant (as in motors or generators), the diverters decrease or increase the AC loss, depending on the orientation of the external magnetic field. Finally, striated tapes are not effective because of the coupling currents at the current leads. These currents are not important in Roebel cables, leading to a further reduction of the AC losses. In conclusion, magnetic diverters and Roebel cables should be used in coils made of coated conductors, specially if the coils are made of stacks of pancake modules.

FK-7:L05 AC Losses in HTSC Tapes with Ferromagnetic Part

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Low level of energy dissipation at transporting AC current, called the AC loss, is essential for the use of high-temperature superconducting (HTSC) materials in electric power devices. Basic understanding of the factors controlling the AC loss has been achieved for both the 1st and the 2nd generation of HTSC tapes provided there are no ferromagnetic materials present in the tape architecture. However, in several cases of promising HTSC conductors the use of a ferromagnetic layer could reduce the production cost or even improve the tape performance. We present the results of an extensive analysis of AC loss behaviour of HTSC tapes containing ferromagnetic parts. The modification of local field due to the ferromagnetic material influences the DC critical current of the tape as well as the process of magnetic flux penetration in AC regime. Additional loss appears in the ferromagnetic material due to its magnetic hysteresis. Numerical simulations are necessary when the behaviour of such complex system should be predicted.

FK-7:IL06 **High Current Low AC Loss HTS-ROEBEL-Cables for Energy Devices**

Wilfried Goldacker*, Stanimira Terzieva, Antje Drechsler, Andrej Kudymow, Reinhard Heller, Rainer Nast, Francesco Grilli, Karlsruhe Institute of Technology, Institute for Technical Physics, Eggenstein-Leopoldshafen, Germany

ROEBEL bars from HTS coated conductors are the most promising choice for low AC loss, high current cables which can be applied in windings of devices. The ROEBEL cable design can be adapted to the prospected different applications as transformers, motors, Fault Current Limiters (FCL) and the requested current class and operation conditions as temperature and field. We present a review and an overview on the status of the R&D on such cables, the variations of cable design which were realized so far and their specific properties. Transport currents, self field effects, mechanical properties and the influence of the HTS tape quality on the cable performance will be addressed. We also present new efforts applying filament structures to the strands. AC losses investigated by transport and magnetic methods show the potential for reduced losses. An outlook about long length fabrication and the application prospects will be given.

FK-7:IL07 **HTS Materials for Magnets in High-radiation Environments**

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This paper will present the results of a series of radiation damage studies that were conducted on second generation (2G) High Temperature Superconductor (HTS) YBCO. Samples of the two conductors from American Superconductor Corporation and SuperPower were irradiated by protons at 142 MeV, 42 micro A at the BLIP facility at Brookhaven National Lab. Samples of each conductor were irradiated to five fluences covering a range from 10 ^ 16 to 4x10 ^ 17 protons/cm ^ 2. This study is critical for the evaluation of the expected performance of HTS magnets in the proposed Facility for Rare Isotope Beams (FRIB) to be constructed at the Michigan State University. Magnets in the fragment separator region will be subjected to extremely high radiation and thermal loads, higher than for any previous superconducting magnet. In particular, the first quadrupole in the fragment separator region will be subjected to ~15 kW in the magnet and ~5 kW/m ^ 3 in the coil. Superconducting magnets made with second generation HTS allow operation of these magnets at ~50 K where heat removal is more than an order of magnitude more efficient than those made with conventional low temperature superconductors operating at ~4K. These results will help establish the radiation tolerance of HTS at FRIB operating condition.

FK-7:IL08 **Seawater Magnetohydrodynamics Power Generator / Hydrogen Generator**

M. Takeda, Kobe University, Kobe, Hyogo, Japan

Seawater magnetohydrodynamics (MHD) power generation / hydrogen generation is a unique system that not only directly transforms the kinetic energy of an ocean current / tidal current into electric energy, but also generates hydrogen gas as a by-product. In our work, experimental and computational studies of the seawater MHD generator using a superconducting magnet have been performed as part of applying superconductivity to maritime sciences. So far, the linear-type seawater MHD generator with a dipole superconducting magnet was constructed, and the experiments of power generation were successfully accomplished. In MHD generation, applied magnetic field is an important factor for the generator output and efficiency. The linear-type generator has a problem of requiring strengthening and enlargement of the superconducting magnet. In order to solve this problem, the use of a solenoid superconducting magnet is expected to be reasonable. Thus, we designed a new helical-type seawater MHD generator using a solenoid superconducting magnet. Experiments using the helical-type MHD generator (100 mm in outer diameter, 300 mm long) were successfully carried out in a magnetic field of 7 Tesla. Experimental values are discussed by comparing the theoretical values and computed values.

FK-7:IL09 **Failure Mechanisms in YBCO Coated Conductors**

Justin Schwartz, Dept of Materials Science & Engineering, North Carolina State University, Raleigh, NC, USA

The development of YBCO coated conductors has now led to a number of successful demonstrations of very high field insert magnets and magnets for power applications. One of the key remaining technological challenges facing YBCO magnets, however, is the quench protection. While it is well known that quench propagation is very slow, thus making quench detection particularly challenging, the corresponding protection limits to avoid conductor degradation are not yet known. Here degradation and failure of YBCO conductors during quench-emulating transients are explored through dynamic magneto-optical imaging, transport and magnetization measurements, and scanning electron microscopy. The conductor transient limits and the underlying causes of conductor degradation are discussed.

Session FK-8

Low Power Applications and Superconducting Electronics

FK-8:IL01 **Potential Future Superconducting Electronics**

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Superconducting Electronics covers a huge area in research and applications, from extremely sensitive devices for the detection of particles and radiation (TES and STJ), the measurement of magnetic flux and field (SQUIDS) to ultra-fast digital computing and elements of Quantum Computing (qubits). Such devices and systems are intensively studied in research applications, but the step towards a broader industrial application still has to be done. In order to meet the needs of a broad industrial application to the benefit of our society, a number of developments has to be started that mark a clear break with the way, Superconducting Electronics has usually been used in the past: instead of bulky cooling and research oriented design we need devices and systems that are easy to use and are not even identifiable on first view as cryogenic systems: it has to be a design which meets the needs of the user in terms of ease of use and application requirements in typical real-world environments. The way towards such systems starts with using the optimum superconducting materials in each part of the Superconducting Electronics, from Niobium to HTS-superconductors, and continues via new system architectures in digital applications to highly efficient and nearly invisible cooling techniques.

FK-8:IL02 **Macroscopic Quantum Tunneling and Resonant Activation in Bi-2212 Intrinsic Josephson Junctions**

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Recent studies on the quantum property of HTSCs suggest the feasibility for implementing HTSC qubits. The anisotropic characteristic found in HTSC seems to be unfavorable for its application to qubits because nodal quasi particles might be the major obstacle against quantum coherence. However, successful observations of macroscopic quantum tunneling (MQT) on HTSC Josephson junctions have been reported by several researchers recently. One of the advantages of HTSC for qubit application is easy implementation of multi-qubits because stacked each junction, which is formed naturally in a crystal, can operate as a qubit. Therefore, studies on its quantum property in terms of MQT or resonant activation are crucially important. In this report, firstly we review recent studies on MQT with HTSCs, and show our experimental results of MQT with Bi-2212 intrinsic Josephson junctions (IJJs). Then we discuss the difference between HTSCs and LTSCs from the viewpoint of MQT observation. Secondly, we show the resonant property of IJJs under microwave irradiation, in which possible factors decreasing Q-factor is discussed. Finally, perspective of an HTSC qubit is given.

FK-8:IL03 **Recent Research Developments in the DC Application of MgB2 Superconductors**

Giovanni Grasso*, Silvia Brisigotti, Simona Berta, Andrea Tumino, Davide Pietranera, Marco Palombo, Lauri Rostila, Roberto Penco, Columbus Superconductors SpA, Genova, Italy

The need of developing MgB_2 superconducting wires on a commercial base is a consequence of the different limiting factors that still make today neither LTS nor HTS perfectly suitable yet for several practical applications in which relevant and extensive electromagnetic fields, low capital, operating and maintenance costs, reliability and robustness are all required factors at the same time. In spite of the appealing market opportunities that could make MgB_2 wires a winning commercial solution, several different technological aspects related to the wire manufacturing process and current carrying performance have to be significantly improved in order to make them definitely ready for a broad industrial implementation. Improvements in the MgB_2 wire properties that are required by the applications cover different aspects, from the enhancement of the magnetic field dependence of the critical current, to a significant improvement of the grain connectivity, and to the reduction of the AC losses. These goals have to be fulfilled using low cost production process, in order to maintain MgB_2 as economically competitive as possible, particularly in comparison with LTS. In this presentation, an overview about the current status of MgB_2 wire development and the near-term perspectives regarding their properties and availability in large quantities will be discussed.

FK-8:IL04 **Coherent and Continuous THz Waves Generated from high Tc Superconductor Bi2Sr2CaCu2O8+d**

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Recently, we have succeeded in generating coherent and continuous THz electromagnetic waves with a power up to 50 microwatt by using high temperature superconductor single crystal Bi2Sr2CaCu2O8+d composed of densely packed intrinsic Josephson junctions (about 770 junctions/1 micrometer thickness). The device is made into a mesa with either rectangular or circular mesa structure on the larger single crystal substrate of Bi2Sr2CaCu2O8+d. The dimension may be ranging from the width of 50-100 micrometers, the length of 300-400 micrometers and the thickness of 1-2 micrometers. Based on the experimental results the mechanism of this emission of THz radiation has been considered as the coherent synchronization of intrinsic Josephson junctions coupled by the non-linear Josephson interaction at the same ac-Josephson frequency determined by f=2eV/h, where V is the voltage applied to each individual junction, e the elementary charge, h the Planck constant. However, the microscopic mechanism has not been understood yet in detail. In order to better understand, we focus on the theoretical model calculations of non-linear equations using a supercomputer and exploration of experimental facts occurring in variety of conditions of mesa. Along with this we have measured the angular dependence of radiation intensity pattern and polarization, higher harmonics, etc. and made theoretical model fit using conventional patch antenna theory. As a result it turns out that the cavity resonance effect in addition to the uniform ac-Josephson current are necessary to account for the experimental results consistently. This result contradicts with the recent theoretical works, which suggest only the cavity resonance mode, providing a new pi kink state dynamically formed in the mesa. I will give a talk based on the recent experimental results supported by our theoretical two source model. Furthermore, I will show the future perspectives of this device to be used in the quantum information technologies.

FK-8:IL05 **Terahertz Radiation from Intrinsic Josephson Junctions**

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Josephson junctions naturally convert dc-voltages into high-frequency electromagnetic radiation, with 1 mV corresponding to 0.483 THz, and many such junctions emitting in phase at the same frequency can produce useful emission power. Therefore, Josephson junction systems are promising candidates for creating solid-state sources of THz-radiation. Stacks of junctions with unsurpassed packing density occur naturally in the layered high temperature superconductor $Bi_2Sr_2CaCu_2O_8$ (BSCCO), in which the superconducting CuO_2-layers are coupled through the intrinsic Josephson effect. However, achieving synchronization of the high-frequency oscillations of all the junctions in the stack has been a major challenge. By patterning mesoscopic crystals of $Bi_2Sr_2CaCu_2O_8$ (BSCCO) into electromagnetic resonators the oscillations of a large number of intrinsic Josephson junctions can be synchronized into a macroscopic coherent state, which - at resonance - enables the emission of strong continuous wave THz-radiation at a power that increases as the square of the number of synchronized junctions. The emission frequency is determined by the size of the resonator and scales as $1/w$, where w is the resonator width. Currently, we have reached an emission frequency of 0.85 THz for a 40-µm wide resonator, and emission powers up to 5 µW. We observe that emission persists over an extended voltage range around the resonance condition. This property allows for the design of THz-sources with voltage-tunable emission frequencies. Furthermore, we will discuss loss-mechanisms limiting the emission power and the effect of applied magnetic fields.

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FK-8:IL06 **Theory on THz Radiation of Intrinsic Josephson Junctions of Cuprate Superconductor**

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Recently an experimental breakthrough has been achieved in stimulating strong and coherent terahertz electromagnetic wave from a mesa of BSCCO single crystal. Analyzing the coupled sine-Gordon equations for the intrinsic Josephson junctions of this layered superconductor, we found a new dynamic state of superconducting phase difference [S.-Z. Lin and X. Hu, PRL,100 (2008) 247006]. The state is characterized by positive and negative pi kinks in phase difference aligned periodically along the c axis. When the phase difference rotates under voltage bias, the pi kinks pump large current and thus energy into the cavity mode of Josephson plasma determined by the lateral size of mesa. A part of the energy is then emitted as THz EM wave into space. The alternative alignment of the positive and negative pi kinks provides a strong “antiferromagnetic” interlock between phase differences in adjacent junctions, and stabilizes the present dynamic state.

This work was supported by WPI Initiative on Materials Nanoarchitectonics, MEXT of Japan and by CREST-JST, Japan.

Poster Presentations

FK:P01 **Ic of Al_2O_3-doped Bi-2212 Single Crystals**

Hiroya Imao, Satoru Kishida*, Matsue College of Technology, Tottori University, Japan

We grew plate-like $Bi_2Sr_2CaCu_2O_x$ (Bi-2212 phase) superconducting single crystals by a self-flux method. The critical currents (Ic) of Bi-2212 single crystals which was measured by a four-probe method, was independent of the thickness of the crystals. This may be caused by the the current path in the single crystals. The pinning center doping is effective for the increase of Ic. We doped the Al_2O_3 to the Bi-2212 single crystals by the diffusion from the surface. Therefore, Al_2O_3 may form the pinning center and the insulator layer in the single crystals. The doping depth of the Al_2O_3 from the surfaces were changed by the process of the heat treatment. The Ic of the single crystal depends on the formation of the pinning center. The Ic of the single crystal increased twice by optimizing the condition of the heat treatment.

FK:P02 **Measurement the Pinning Energy of Partial Melted Superconductors**

Sakiko Takahashi[1]*, Hiroya Imao[1], Satoru Kishida[2], [1]Matsue National College of Technology, Matsue, Japan; [2]Tottori University, Japan

We synthesized a measuring system of magnetic properties of superconductor. The system measures the force which occurs between a superconductor and a magnet. The force is caused by perfect diamagnetic and pinning energy. Magnetic flux is excluded from superconductor by perfect diamagnetic. Excluded flux pushes the magnet, which produces the force of repulsion. Then flux through the superconductor is trapped by a pinning center. When the distance between elements increases, the force of suction occurs. We measured repulsion and suction by a electronic balance in order to determine pinning energy. Partial melted Y-based superconductor shows strong pinning energy. We measured the pinning energy of the sample prepared in several conditions. We found the critical current density is not exactly dependent on pinning energy.

FK:P03 **A Multi-band Model for LaO$_{\{1-x\}}$F$_{\{x\}}$FeAs**

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Based on electronic structure calculations using WIEN2k code for the iron oxypnictide $LaO_{1-x}F_xFeAs$, a multi-band model is proposed. Within the BCS framework a generalized Fermi surface with overlapping bands is introduced. s-wave pairing symmetry and different doping values are considered. This model is used to describe some properties of iron-based oxypnictide superconductors as function of the coupling parameter as well as other relevant parameters of the model. In order to get numerical results the experimental data of $LaO_{1-x}F_xFeAs$ with several doping concentrations provide the input of this work.

FK:P04 Grain Morphology for Ag-sheathed Bi2Sr2CaCu2O8 Tapes Heat-treated in High Magnetic Fields

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The electric field and transport current density (E-J) properties of Ag-sheathed Bi2Sr2CaCu2O8 (Bi2212) tapes are investigated in high fields at temperatures ranging from 10 to 30 K. We prepared the Bi2212 tapes heat-treated in high fields (in-field heat-treated Bi2212) and heat-treated without magnetic fields (out-of-field heat-treated Bi2212), in order to examine the magnetic field effect for the micro-structure of Bi2212. It was found that the E-J properties for the in-field heat-treated Bi2212 tape are different from those for the out-of-field heat-treated one, and are similar to the E-J dependence for Ag-sheathed Bi2Sr2Ca2Cu3O10 (Bi2223) tapes with the sintered-like grain morphology. The differential thermal analysis (DTA) was measured at 10 T using a Bi2212 powder sample. As a result, the DTA suggests that the in-field heat-treatment changes the grain morphology of Bi2212. We found that the in-field heat-treated Bi2212 tape has a large n-value, which is related to the microstructure change.

FK:P06 Synthesis and Precise Analysis of Bi2Sr2Can-1CunOy Superconducting Whiskers

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We synthesized Ca-rich Bi-based superconducting whiskers by an Al2O3-seeded glassy quenched platelet method. The grown whiskers were precisely characterized by synchrotron radiation X-ray photoemission spectroscopy (SR-XPS) and high-resolution transmission electron microscopy (HR-TEM). The Ca-rich Bi-based superconducting whiskers show a high critical current density of 2×105A/cm2 at 40K in self-field. We found that excess Ca2+ ions substitute for the Sr2+ sites and cause pillar-shape nano crystalline domains with shorter-period modulation embedded in the base crystalline. The embedded nano crystalline domains can result in structural distorted defects which work as strong pinning center.

FK:P07 Synthesis and Structural Characterization of Hg(Re)-Pb-Ca-Ba-Cu-O Superconducting Thin Films Grown by Spray Pyrolysis

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In this work, we present the optimal values of growth parameters to obtain a series of superconductor thin films of the type Hg(Re)-Pb-Ca-Ba-Cu-O on MgO substrates, in a spray pyrolysis system with incorporation of Hg by the sealed quartz tube technique. We found parameter values through an experimental fractional factorial design 3(IV-II). Chemical composition was obtained from atomic absorption measurements. Crystalline phase identification was performed by XRD technique in a D8 focus Bruker AXS diffractometer. Quantification of the superconducting phases was determined by Rietveld method.

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FK:P08 Processing by Pulsed Laser Deposition and Structural, Morphological and Chemical Characterization of Bi-Pb-Sr-Ca-Cu-O and Bi-Pb-Sb-Sr-Ca-Cu-O Thin Films

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Bi-Pb-Sr-Ca-Cu-O (BPSCCO) and Bi-Pb-Sb-Sr-Ca-Cu-O (BPSSCCO) thin films were grown on MgO single crystal substrates by pulsed laser deposition. The deposition was carried out at room temperature during 90 minutes. A Nd:YAG excimer laser (λ = 355 nm) with a 2 J/pulse energy density operated a 30 Hz was used. The distance between the target and substrate was kept constant at 4,5 cm. Nominal composition of the targets was $Bi_{1,6}Pb_{0,4}Sr_2Ca_2Cu_3O_\delta$ and $Bi_{1,6}Pb_{0,4}Sb_{0,1}Sr_2Ca_2Cu_3O_\delta$. Superconducting targets were prepared following a state solid reaction. As-grown films were annealed at different conditions. As-grown and annealed films were characterized by XRD, FTIR, SEM and EDX. The films were prepared applying an experimental design. The relationship among deposition parameters and their effect on the formation of superconducting Bi-system crystalline phases and grain size was studied.

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FK:P09 Investigation of the Switching Mechanism of Resistive Random Access Memory Utilizing High Temperature Superconductivity as a Detector for Oxygen Vacancies

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Resistive random access memory (ReRAM) has the simple structure that transition metal oxide is sandwiched between the top and bottom electrodes and is expected to be suitable for an extreme downsizing required for Flash memory substitution. The switching mechanism of perovskite-type ReRAM such as $Pr_{1-x}Ca_xMnO_3$ which based on the migration of oxygen vacancies has been proposed[1-3]. However, the relation between the resistance memory effect and oxygen vacancies has not been clarified yet mainly due to the difficulty in detecting a slight change in the content of oxygen vacancies in oxide materials. In this paper, we fabricated ReRAM which consists of $Bi_2Sr_2CaCu_2O_{8+\delta}$ and investigated the relation between the resistance memory effect and the critical temperature, T_c, which is very sensitive to the content of oxygen vacancies. The memory effect is enhanced in under-doped samples, suggesting that the switching mechanism is closely related to oxygen vacancies.

[1]A. Baikalov et al, APL 83 957 (2003); [2]S. Tsui et al, APL 85 317 (2004); [3]X. Chen et al, APL 87 233506 (2005)

FL - 6th International Conference

MEDICAL APPLICATIONS OF NOVEL BIOMATERIALS AND NANO-BIOTECHNOLOGY

Oral Presentations

Session FL-1
Advances in Biomaterials

FL-1:IL01 Nanostructural Control of Bioceramics and the Merger of Devices with Biologicals

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The last decade has seen a gradual evolution to include biological functionality in devices. Stent surfaces are modified to release Rapamycin; RGD and other peptides are immobilized on device surfaces to stimulate tissue formation. Herein, we will focus on biological functionality of orthopaedic devices from several perspectives. First, in situ biological functionalization will be invoked to explain the excellent tissue response of existing biomaterials, namely the class of bioactive ceramics. Second, biological functionality achieved by controlled delivery from sol gel nanoporous controlled release materials will be discussed. Controlled release silica sol gels are room temperature processed, porous, resorbable materials with excellent biocompatibility. Many molecules including drugs, proteins and growth factors can be released from sol gels and the quantity and duration of the release can vary widely. Processing parameters render these release properties exquisitely versatile. Based on a thorough understanding and an extensive control of release properties, various treatment modalities for unsolved clinical problems are advancing towards the clinic. They include the treatment of osteomyelitis, the treatment of surgical pain and the delivery of labile growth factors.

FL-1:IL02 Essential Factors to Make Excellent Biocompatibility of Phospholipid Polymer Materials

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Phospholipid polymer materials designed by inspiration of cell membrane surface show excellent biocompatibility. That is, they prevented thrombus formation and immune response even when they contacted with living organism. This is due to significant reduction of protein adsorption compared with other conventional materials. We paid attention to the water structure around the surface of the phospholipid polymer materials. Thermal analysis, Raman spectroscopic analysis and nuclear magnetic resonance spectroscopic analysis revealed that the water molecules around the phospholipid polar group(phosphorylcholine group) took clustering structure as the same as bulk water phase. The water structure related very closely to induce hydrophobic interaction. The bulk water like structure prevents hydrophobic interaction between the surface of the phospholipid polymer materials and proteins in the solution. Thus, the protein attached on the surface could detach easily and no stable adsorption was observed. In the lecture, I will also discuss about the direct evidence of weak interaction between proteins and phospholipid polymer materials based on the atomic force microscopic analysis.

FL-1:IL03 Biomedical Applications of Peptide-polymer Conjugates Self-assemblies

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Polymer vesicles are one of the most promising systems for drug delivery applications and may offer many advantages compared to low molar mass lipid vesicles. A vesicle obtained by self-assembly of block copolymers is expected to overcome some of the stability issues related to liposomes and thus allow the development of robust containers of either hydrophilic or hydrophobic species. More precisely, we report here an overview on the self-assembly in water of a series of polysaccharide and polypeptide-based block copolymer vesicles that we have studied these recent years in our group, combining a large range of experimental analysis. Our aim is to exploit the pH-sensitivity of polypeptides' secondary structure to manipulate the size and shape of the supramolecular structures formed by self-organization of these block copolymers in aqueous media. In addition, magnetic polymersomes, including superparamagnetic iron oxide nanoparticles are presented, together with their potential applications as contrast agent for diagnosis and as therapeutic nanoparticles using hyperthermia. Exciting and very promising results about their therapeutic evaluation for tumor targeting and in vivo tumor regression studies will be presented.

FL-1:IL04 Development of Cardiovascular Implants Using Nanocomposite Polymer and Stem Cell Technology: From Lab to Commercialisation

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Cardiovascular implants including bypass grafts, heart valves and stents are prone to calcification, thrombogenicity and structural failure. To overcome these problems we have developed and patented a family of nanocomposite polymers based on polyhedral oligomeric silsesquioxane (POSS) nanoparticles and poly(carbonate urea)urethane (PCU). In addition, we have been working on bonding bioactive molecules and peptides to attract progenitor stem cells from peripheral circulating blood onto the implants with the aim of differentiating them into endothelial cells; these are the cell types which cover the cardiovascular system. At this meeting I will be presenting out data on biocompatibility, biostability, calcification resistance and anti-thrombogenicity of this polymer tested in vitro and in vivo. Currently this polymer has been used for manufacturing small diameter conduits for coronary artery bypass grafts, heart valves as well as coating stents. Data on manufacturing and evaluation as well as in vitro and preclinical in vivo testing will be presented. In conclusion these results, together with its ease of manufacture and low cost, suggest that POSS-PCU nanocomposite could be an attractive material of choice for the development of cardiovascular implants.

FL-1:IL05 Supramolecular Surfaces Modulating Cellular Response

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It has been believed that modulation of cellular response via their dynamic interfaces with biomaterials is one of the goals in development of advanced medicine and therapy. In the last few decades, we have proposed the importance of molecular mobility in the design of biomaterials, and demonstrated that supramolecular-structured polyrotaxanes are a promising tool in performing a variety of biomedical functions: the mobility of cyclic compounds along the chain can be promising on the enhancement of multivalent interaction. The design of polyrotaxane (PRX) surfaces is fascinating as a platform for dynamic surfaces, and we expect these unique surfaces to enhance specific binding with certain proteins and cells through a multivalent ligand-receptor interaction as well as to prevent non-specific interaction with biological molecules. Regarding to this theme, we prepared PRX surfaces exhibiting the mobility of cyclodextrins along a linear polymeric chain fixed both terminals to a solid substrate, and such dynamic surfaces are believed to play one of our important strategies for modulating cellular response.

FL-1:IL06 Molecular Modelling and Experimental Investigation of Hydrolytically Degradable Polymeric Biomaterials

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Biodegradable polymers are used in temporary implants, wound sutures and drug delivery systems. They are also of relevance in applications like scaffolds for tissue engineering and autologous regeneration. A major limitation of established degradable implant materials is the fact, that their degradation behavior can not be reliably predicted applying existing experimental methodologies. Therefore a knowledge-based approach is clearly needed to overcome this problem and to enable the tailored design of biodegradable polymer materials. In this presentation we describe two methods which can be applied in this approach: molecular modeling combining atomistic bulk interface models with quantum chemical studies and experimental investigations of macromolecule degradation in monolayers on Langmuir Blodgett (LB) troughs. The polymers utilized to illustrate the concepts are mostly polyesters and co-polyesters, like polyglycolide (PGA) and poly(L-lactide (PLLA). Characteristic results concern e.g. the influence of the density of polar groups and of co-polymer composition on the respective degradability.

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FL-1:IL07 Nanocomposites with Bone Inductive Properties

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Bone tissue engineering seeks to develop strategies to heal bone loss due to trauma or disease without the limitations and drawbacks of current clinical autografting and allografting treatments. A key of component of the bone tissue engineering paradigm is the scaffold, which functions as a structural support and as a delivery vehicle, providing cells and bioactive molecules necessary for the formation of new bone tissue. The ideal scaffold should possess mechanical properties adequate to support growing bone tissue, degrade upon bone tissue growth, demonstrate good biocompatibility, and have high porosity, with a great degree of pore interconnectivity, to enable bone tissue ingrowth. The development of novel materials that meet all of these requirements is a key objective in bone tissue engineering. Nanocomposites have shown promise in a variety of materials science applications due to their unique physical and chemical properties. However, few studies have evaluated nanocomposite scaffolds for tissue engineering applications. The present lecture will discuss the bioactivity of nanocomposites as used for bone substitution as well as the biosafety issues as involved in the clinical application of nanocomposites.

FL-1:IL08 Nanocrystalline Carbonate Apatite Due to Chemical Conversion of Calcium Carbonates

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Bone apatite is not hydroxylapatite (HAp) but carbonate apatite (CO3Ap). Although both HAp and CO3Ap shows good osteoconductivity, HAp is not resorbed by osteoclast and thus cannot be replaced to bone. To fabricate CO3Ap block, compositional change due to dissolution-precipitation reaction was proposed using low-crystalline CaCO3. as a precursor. Upon exposure of low crystalline CaCO3 to Na2HPO4 solution, CaCO3 dissolve to supply Ca2+ and CO32-, which result in supersaturation with respect to CO3Ap, and thus CO3Ap crystal precipitated, and the crystals interlock each other to form the CO3Ap block. CO3Ap is replaced to bone based on the so-called bone-remodeling process since CO3Ap can be resorbed by ostelclasts. On the other hand, bone formation ability is activated by bone morphologic protein in the case of bone. Therefore, one of the methods to accelerate bone replacement process may be the introduction of BMP into CaCO3. Fortunately, biphasic calcium phosphate (BCP) which consists of HAp and beta-TCP (beta-Ca3(PO4)2) are known to have higher osteoconductivity than HAp. Fortunately, BCP consisting of CO3Ap-CaCO3 can be prepared just by regulating the reaction time. Cell and tissue response to BCP is also discussed.

FL-1:IL09 Novel, Rapidly Resorbable Bioceramic Bone Grafts Produce a Major Osteogenic Effect - The Pre-clinical Evidence

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In implant dentistry considerable efforts have been undertaken to produce rapidly resorbable bone grafting materials. This has led to the synthesis of bioactive calcium-alkali-phosphate bone substitutes. In order to evaluate the osteogenic potential in vitro, we first examined the effect of various rapidly resorbable calcium-alkali-phosphates on the expression of osteogenic markers in vitro as compared to currently clinically used materials. We then examined the effect of the same selection of bioactive ceramics on osteogenic marker expression and bone formation after implantation in the sheep mandible and sinus floor in vivo. Since the cell adhesion and intracellular signaling events which lead to this stimulatory effect on osteogenesis are not fully understood, we then elucidated the mechanisms by which these bone substitutes stimulate the intracellular signaling pathways, which regulate osteoblast differentiation and cell survival. Furthermore, we also correlated the findings from the in vivo preclinical animal studies with in vivo data from clinical studies. Collectively, the gain of knowledge is being used to develop strategies for optimizing these bone grafting materials for a range of clinical applications so as to achieve an optimum stimulatory effect on osteogenesis.

FL-1:IL10 A New Method to Measure Coagulability of a Patient's Blood. Use of a Moderately Thrombogenic Biomaterial and a Miniaturized Flow Reactor

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Contact activation of blood coagulation implies a significant risk for relatively large patient groups, e.g., (i), patients connected to a heart/lung machine; (ii), dialysis patients; (iii), patients with a permanent blood-contacting implant, such as an artificial heart valve. Currently, two routine techniques are available to asses blood coagulation: aPTT and PT. Here, we present a novel method to assess "coagulability". We measure thrombin generation time in full, flowing blood, during controlled passage through a "thrombogenic" channel. A polymeric coating was designed to cause coagulation between 5-8 minutes. This timeframe ensures the possibility to detect hyper- and hypo-coagulability within a reasonable assay-time. The coagulation assay, which is uniquely based on an engineered polymer biomaterial with significant contact activation potential, may help to overcome drawbacks of aPTT and PT methods. These routine methods are -essentially- post-centrifugation measurements on blood plasma under static consitions. Our initial results with the new method (based on whole blood under flow conditions) show excellent reproducibility and consistency woth the routine aPTT and PT assays. Interestingly, the new method may also provide a faster alternative to standard techniques.

FL-1:L13 Mechanistic Study of Deposited Hydroxyapatite(HAp) on Biocompatible TiO2 Nanotubes

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In this study, a vertically aligned nanotubes array of titanium oxide was fabricated on cpTi(commercial pure titanium) substrate by anodic oxidation at 20V from 1h to 4h in 0.5MNH4H2PO4+0.12M NH4F. The phase of self-organized nanotubes which turn into rutile in anatase is transformed by increasing time at fixed voltage. The internal diameter of nanotubes that was observed to under about 100nm more than about 50nm was controlled by adjusting pH(2~7) of the electrolyte. To promote bioactivity, HAp(sigma Aldrich) nano powders were deposited on the surface of TiO2 nanotubes with various phase(anatase or rutile) by using a electrophoretic deposition method at 100V from 10s to 5min. The coated HAp layer on the surface of TiO2 nanotubes is affected by applied potential and time. The nanotubes that HAP was coated were hydrothermally treated to increase adhesion at 80° for 5hr in the distilled water. XRD measurements reveal that hydrothermal treated nanotubes increase crystalinity. As a result of XPS analysis, adhesion of coated HAp on the surface of TiO2 nanotubes is intensified with increasing of electrophoretic deposition time. The self-organized nanotubes are expected to be a good precursor system for the osseointegration of dental implants.

FL-1:L14 Hydroxyapatite and Chlorapatite Thin Coatings Obtained by a Novel Plasma Mini-torch Process

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Hydroxyapatite (HA) is a bioactive material widely used as coating on orthopedic prostheses. The HA coatings obtained by plasma spray process are relatively thick, usually inhomogeneous and not well crystallized. During this process, the starting HA powders may decompose at high temperature to give a coating consisting of calcium oxide and a mixture of crystalline and amorphous phases. Two ways of improving the coating quality have been tested in combination in this study. The first is based on the use of a new low energy plasma mini-torch which has been designed especially to minimise the loss of powder and obtain thinner, less decomposed and more adherent coatings. The second way is to use chlorapatite (ClA), an apatite that melts without decomposition. The effect of different processing parameters on HA and ClA coatings obtained when using the mini-torch were examined by X-ray diffraction and FTIR and Raman spectroscopies. HA was decomposed partly and a small amount of amorphous phase was measured. ClA coatings exhibited also a partial decomposition attributed to the hydrolysis of the powder during plasma spraying and showed a very low amount of amorphous phase. These results appear particularly encouraging concerning the quality of the coatings obtained with the mini-torch.

FL-1:L15 Molecularly Imprinted Polymer Layers for the Selective Uptake and Release of Glutamate for Application in a Neurochemical Switch

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Here results are presented from the development of a biomolecular switch to regulate the concentration of glutamate under physiological conditions. A glutamate selective electrode coating was electro-chemically fabricated using the conjugated polymer polypyrrole (PPy). The PPy films are shown to be conducting and doped with glutamate. The polymer is then overoxidised to create oPPy, which results in the ejection of the glutamate anion from the layer. The oPPy layers are insulating and porous, and have been demonstrated to have molecularly selective properties[1]. In-situ techniques which probe the molecular morphology at the solid-liquid interface are of interest for biological applications; the uptake and release of glutamate from the oPPy layer was investigated using attenuated total reflection infrared spectroscopy (ATR-IR) and electrochemical quartz crystal microbalance (EQCM). Calibration studies were done to determine the concentration of glutamate regulated by the oPPy. Initial selectivity tests of the oPPy layer for L-glutamate were performed. Some biocompatibility checks of the glutamate switch are presented.

[1] *B. Deore, Z. Chen, T. Nagaoka, ANALYTICAL SCIENCES, 15, 827-828, (1999).*

FL-1:L18 Study of BSA Adsorption on Silicon Plasma Deposit with Silver Nanoparticles by QCM and XPS

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An approach to reduce the microbial adhesion is the application of a range of coatings to the surface of the devices. In this study, silver-containing and silver-free deposits were carried out under cold plasma conditions associating silver target sputtering and plasma polymerization in an RF glow discharge fed with argon and hexamethyldisiloxane (HMDSO). The adsorption of bovine serum albumin (BSA) on the coatings was studied in situ using a quartz crystal microbalance (QCM) with a switch-flow cell and ex situ by X-ray photoelectron spectroscopy (XPS). QCM measurements showed that the steady-state of BSA adsorption was reached within 60 minutes after introducing the protein. Silver nanoparticles of the deposit dissolved from the silver-containing coatings during QCM measurements. The equivalent thicknesses of the adsorbed BSA layer estimated in situ by QCM and ex situ by XPS are in good agreement, which are equal to 2.1 ± 0.3 nm (silver-free coatings) and 4.5 ± 0.7 nm (silver-containing coatings and pure Ag films). The results show that silver-free deposits exhibit less adhesive behaviour for the BSA compared to silver-containing deposits and pure Ag films.

FL-1:L20 Hydrothermal Synthesis of Hydroxyapatite Particles from Different Raw Materials and their Characterization

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Hydroxyapatite (HA) is widely used as a component of bone-repairing materials. The properties of HA particles are affected by the morphology, crystallinity, and so on. Therefore, it is important to control these factors to tailor the HA ceramics. We previously reported that a hydrothermal synthesis can provide hydroxyapatite particles with unique morphologies. In the present study, the control of the properties of HA particles was attempted by changing the raw materials and hydrothermal conditions. Rod-shaped HA particles were obtained by the hydrothermal treatment of alpha-tricalcium phosphate in aqueous solution. The aspect ratios of the particles were controlled by the pH of the solution. The plate- or strip-shaped HA particles were obtained by the hydrothermal treatment of octacalcium phosphate in water. The properties, such as morphology, composition and crystallinity, of these HA particles were characterized.

FL-1:L21 Development of Craniofacial Implants Produced by Metal Injection Molding of Titanium Alloy Using Novel Binder System Based on Palm Oil

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Metal Injection Molding (MIM) is a cost-effective technique for producing small, complex, precision parts in high volumes. MIM consists of four main processing steps: mixing, injection molding, debinding and sintering. In the mixing step, the powder titanium alloy (Ti6Al4V) medical grade is mixed with a binder system based on palm stearin to form a homogeneous feedstock. The rheological studies of the feedstock have been determined properly in order to success during injection into injection molding machine. After molding, the binder holds the particles in place. The binder systems then have to be removed completely through debinding step. Any contamination of the binder systems will affect the final properties of the parts. During debinding step, solvent extraction debinding has been used to remove partly of the binder systems. The debound part is then sintered at high temperature under control atmosphere furnace. The properties of the sintered craniofacial implants then was measured and compared. The sintered craniofacial implants also then were determined in term of in-vitro cytotoxicity study using mouse fibroblast lines L-929. The results show that the sintered craniofacial implants of titanium alloy produced by MIM fullfill the in-vitro cytotoxicity test.

FL-1:L22 Tunable Antibacterial Coatings that Support Mammalian Cell Growth

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Bacterial infections present an enormous problem causing human suffering and cost burdens to healthcare systems worldwide. We present novel tunable antibacterial coatings which completely inhibit bacterial colonization by both gram positive and gram negative bacteria, but allow normal adhesion and spreading of osteoblastic cells. The coatings are based on amine plasma polymer films loaded with silver nanoparticles via silver ion in-diffusion followed by reduction. The process of plasma polymerization makes the coatings directly applicable to many biomedical devices. The procedure for loading silver nanoparticles allows flexible control over the amount of loaded silver nanoparticles. The release of silver ions from the coatings is efficiently controlled by applying an additional plasma polymer film of desired thickness. The present coating strategy may open new horizons for the design of the next generation of antibacterial devices.

FL-1:L23 Development of Bone-integrating Hybrid Materials Useful for Hard Tissue Repair

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Apatite-polymer hybrid has attractive features as novel bone substitutes such as both ability of bone-bonding and mechanical performances analogous to those of natural bone, i.e. high strength and high flexibility. As a method for development of such hybrids, biomimetic process has been proposed, where apatite formation is induced on the surfaces of organic substrates at ambient conditions in simulated body fluid (SBF) with ion concentrations similar to those of human extracellular fluid, or related solutions supersaturated with respect to the apatite. In this process, heterogeneous nucleation of apatite is triggered by specific functional groups. This apatite nucleation is enhanced by release of calcium ions ($Ca2+$) from the materials which increases degree of supersaturation of surrounding fluid with respect to apatite. In the present study, we attempted to prepare apatite-polyamide hybrids by biomimetic process. Synthetic polyamides or narutal polypeptides containing carboxyl group (-COOH) were used as a starting material, and apatite formation ability was compared. Apatite formation rate showed tendency to be enhanced with increase in carboxyl group content. In addition, apatite formation was governed by not only COOH content but also ionic interaction with $Ca2+$.

FL-1:L24 Mineralization of Eroded Dental Enamel Seeded with Fluoride and a Tricalcium Phosphate Ternary Biomaterial

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The inability to sufficiently prevent and/or repair chemically-etched dental enamel serves as one example that underlines the importance and need for the development of innovative biomaterials for therapeutic applications. In this work we explored the seeding capability of 225 ppm and 1100 ppm fluoride with and without a novel β-tricalcium phosphate-silica-urea (TCP-Si-Ur) biomaterial to mineralize into acid-etched dental enamel. The nature of the mineralization was evaluated by measuring the fluoride and phosphate uptake into the eroded enamel, as well as the orthophosphate microstructure using infrared (IR) spectroscopy. These enamel fluoride uptake and IR experiments revealed a fluoride dose response exists for eroded enamel treated with fluoride and TCP-Si-Ur. We also found the combination of either 225 ppm or 1100 ppm fluoride plus TCP-Si-Ur at different loading levels leads to unique and significant mineral integration into the PO4 enamel network, including the formation of P-F bonds. Our observations reported herein demonstrate the combination of fluoride plus a novel TCP-Si-Ur biomaterial produces synergistic mineralization and bears significantly on eroded enamel microstructure.

FL-1:L25 In-situ Investigation of Temperature Influence on Calcium Phosphate Cement Hydration

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Material and Methods: α-TCP was synthesized from calcium carbonate and diammonium hydrogen phosphate. The purity of the α-TCP was controlled and confirmed by X-ray diffraction. Hydration of short and longer milled powders were studied at 23 °C, 30 °C and 37 °C. Isothermal calorimetry investigations were performed with a TAM air heat flow calorimeter in an "AdMix-Ampoule" with a 0.2 molar Na2HPO4 - solution with liquid to powder ratio of 0.65. The water was injected into the crucible and the originating slurry was stirred internally for 30 s. In-situ X-ray diffraction investigations were carried out with a Siemens D5000 diffractometer with SolX detector. Samples were sealed with a Kapton® polyimide film to prevent evaporation of H2O. *Results:* The accelerating effect of longer milling times can clearly be shown by heat flow calorimetry. The increased reactivity is on the one hand caused by higher specific surface areas and on the other hand by the amount of defective or amorphous phase fraction. Combination of XRD- and calorimetric measurements show that the amorphous phase fraction is the first to be dissolved and that the second maximum in the heat flow can be directly correlated to the dissolution of crystalline α-TCP.

FL-1:L26 A Novel Rich-phosphate Coating on Zirconia with High Bonding Strength to Surface

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Zirconia as a inert ceramic is not osteoconductive therefore osteoconductivity is the main driving force for coating zirconia with bioceramics. In this study hydrothermal treatment was used as a method for making rich-phosphate coating layer on zirconia. Commercial zirconia plates were used as specimens. The specimens were kept at 200-250 °C for 6 - 48 hrs for hydrothermal treatment. The resultant specimens were characterized using SEM, XPS, XRD, EDS, coating layer bonding strength test on zirconia, laser scanning microscopy, contact angle test and in-vitro biocompatibility test. Zinc phosphate coating layer was formed on zirconia specimens by hydrothermal treatment with zinc phosphate solution at 250 °C for 48 hrs. From SEM results, coating layer were fully covered the sample surface. EDS spectra showed that the coated layer was composed of phosphate, zirconium and zinc elements. Initial cell attachment was done for 3 hrs and 5 hrs. It is concluded that coating layer with different size and different elements ratio are producible by controlling treatment parameters such as time and temperature. Phosphate-rich coating layer with high bond strength to zirconia surface was fabricated in this study. Zinc phosphate coating layer on zirconia promoted cell attachment.

FL-1:L27 Adhesion Mechanisms at the Interface Between Y-TZP and a Veneering Ceramic for Dental Application

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To investigate the mechanism acting at the interfaces between zirconia and a veneering ceramic, the variation induced by sandblasting zirconia with abrasive particles or coating it with a ceramic liner was studied. Several specimens of zirconia material, Y-TZP (e.max ZirCAD; Ivoclar Vivadent) were sintered and divided into 4 groups. Group A: veneered with a low-fusing nano-fluorapatite glass-ceramic (e.max Ceram, Ivoclar Vivadent) without the application of ceramic liner; group B: zirconia liner coated (ZirLiner, Ivoclar Vivadent) and fired before the final veneering; group C: sandblasted and then veneered without the application of a liner layer; group D: specimens were both sandblasted and liner layered before the veneering. The microstructure and phase composition of the zirconia were evaluated by SEM-EDS and XRD respectively. The sandblasted zirconia surfaces were characterized by material detachments and plastic deformation. Furthermore, EDS analysis allowed to recognize the presence of small fragments of silica. The sandblasting operation seems to be able to give a higher reactivity to the zirconia surfaces, that result to be more prone to react with the veneering ceramic increasing in this way the bonding and the mechanical performance of the component.

FL-1:L28 Fabrication of Bioactive Organic Polymer-apatite Nuclei Composite

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Organic polymers are easily processed in various shapes and combined with various materials. If organic polymers acquire bioactivity, it is expected that hard and soft tissue implants possessing various mechanical properties as well as high bioactivity and bioaffinity will be developed. When the pH of simulated body fluid (SBF) with ion concentrations similar to those of human blood plasma is raised, fine particles of calcium phosphate are precipitated. The fine particles are very active for forming hydroxyapatite (HAp) from SBF and we named them Apatite Nuclei (T. Yao et al, PCT Patent, PCT/JP2006/316054, 2006). In the present study, we soaked porous polyethylene (PE) in SBF and precipitated Apatite Nuclei in the pores of the porous PE by raising pH of SBF for Case 1 or deposited Apatite Nuclei in the pores of porous PE by electrophoretic deposition for Case 2 and obtained PE-Apatite Nuclei composite. By soaking in SBF, HAp was induced from Apatite Nuclei in the pores and grew to the whole surface of either composite. Either composite showed high bioactivity. Adhesive strength between HAp and the composite was 4.2MPa for Case 1 or 6.1MPa for anode side surface and 6.5MPa for cathode one for Case 2. High adhesive strength was obtained due to a mechanical interlocking effect.

FL-1:L29 Laser Rapid Prototyping of Microstructured Medical Devices using Inorganic-organic Hybrid Materials

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We have used two photon polymerization (2PP) in order to fabricate microneedle arrays for transdermal drug delivery as well as other microstructured medical devices using Ormocer® inorganic-organic hybrid materials. Unlike conventional medical device fabrication approaches, two photon polymerization is a rapid prototyping process that involves spatial and temporal overlap of photons to bring photopolymerization within well-defined and highly-localized volumes. In plane microneedles, out of plane microneedles, and other microstructured medical devices with arbitrary geometries were produced by polymerizing the material along the laser trace, which was moved in three dimensions using a micropositioning system. An MTT assay indicated that human epidermal keratinocyte growth on Ormocer® was similar to that on control surfaces. Ormocer® microneedles were shown to enable more rapid distribution of a model drug (fluorescein-biotin) solution to the deep epidermis and dermis layers of porcine skin model than topical delivery. Ormocer® microneedle arrays entered cadaveric porcine adipose tissue without fracturing during compression testing studies. It is anticipated that two photon polymerization of microneedles and other microstructured medical devices will increase over the coming years.

FL-1:L30 Nanocrystalline Apatite Coatings and Osteoinduction

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Commercial calcium phosphate ceramics sintered at high temperature exhibit a very low specific surface area and a poor surface reactivity. Although they are excellent osteoconductive ceramics, their osteoinductive properties appear limited. In this work, we hypothesised that a nanocrystalline carbonated apatite coating could improve the surface and biological properties of these ceramics. The physico-chemical analyses showed that such a coating increased the specific surface area and induced formation of nanopores, which could favor the biological activity. The adsorption study of an osteogenic growth factor, rhBMP-2, confirmed the improvement of surface properties. An increased amount of protein was adsorbed and its release was sustained. The biocompatibility of the coated ceramics was demonstrated in vitro. The in vivo osteoinductive property of the modified ceramic was studied in intramuscular sites of an ovine animal model. The modified ceramic associated with BMP-2 promoted the formation of bone. Furthermore, the nanocrystalline coating itself, without added BMP-2, was found to be osteoinductive. This last result testify for a specific role of the nanocrystalline coating in osteoinduction and could lead to short term clinical applications in the field of bone substitutes.

FL-1:L32 Microstructure and Mechanical Properties of Iron-containing Hydroxyapatite/Titanium Composites

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Hydroxyapatite/titanium (HA/Ti) composites have attracted much attention as a potential orthopedic and dental implant material. However, it is challenging to fabricate cost-effectively HA/Ti composite due to the decomposition of HA and degradation of Ti because of the severe reaction between Ti and HA. So far this material could only be synthesized by some special techniques. In the present investigation a new iron-containing HA/Ti composite, using HA powders and Ti-33wt%Fe particles, was synthesized via pressureless sintering in vacuum at relatively low temperatures of 950 °C, 1000 °C and 1050 °C. The microstructure, relative density and mechanical properties of the composites were evaluated. A unique and favorable core/shell structure that consisted of outer titanium and inner iron was observed to form in the composites. Both the decomposition rate of HA and the reaction between HA and Ti reduced due to the addition of iron. Significant enhancements in flexural strength, fracture toughness and cyclic fatigue resistance were achieved compared with pure HA. With increasing sintering temperature the relative density was enhanced. As a result, the composites sintered at 1050 °C showed the highest microhardness, flexural strength and fatigue life due to the improved densification.

FL-1:L33 Nonequilibrium Mechanics of Liquid Crystal Elastomers

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Liquid crystal elastomers exhibit a number of fascinating material characteristics that are useful for artificial muscle and biomedical diagnostic applications. The constitutive behavior of these materials is strongly dependent on the interactions between liquid crystal domain structure evolution and polymer deformation during electrical or mechanical loading, application of heat, or light exposure. An analysis of the interactions between liquid crystals and elastomer networks is presented using nonlinear continuum mechanics and microscale phase field finite element modeling. Finite deformation of an elastomer is coupled to a liquid crystal director force balance to describe nonequilibrium elastomer deformation as a function of the effective liquid crystal molecular orientation. The theoretical model is implemented numerically using a nonlinear finite element phase field model to assess finite deformation for both monodomain and polydomain configurations. It is shown that finite deformation leads to natural coupling between the liquid crystal microstructure and the elastomer network. Lastly, extensions to field coupled behavior including thermoelasticity and photomechanics will be presented.

FL-1:L34 Transparent Nanostructure for Observing Live Cell Proliferation and Migration

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Observing live tissue cells on biomaterial surfaces and analysis of cell migration and proliferation would be impossible without direct measurement of the live cell behaviors in real time observing system. In this study, fabrication of the transparent nanostructures in pure titanium was achieved using e-beam evaporation and developed materials were successfully employed to analyze various tissue cell functions. For achieving nanostructures with transparent condition, nanoscale bumps were created within 35 nm thickness in ultra high vacuum condition and results have shown that small order of nanoscale bumps (surface roughness is less than 2nm) affected altered wettability of titanium surfaces compared to flat titanium at the identical chemistry. Various tissue cells including stem and bone cells, were seeded on developed samples and we found drastic difference of morphology, migration and proliferation of tested cells. Interestingly, initial difference of cell morphology in nanostructures led to altered long term functions of tissue cells. It is important to note that direct observation of tissue cell response on various orders of nanostructures morphology in transparent condition will simplify all post procedures for cell analysis.

Session FL-2
Enabling Tools

FL-2:IL01 Sensing of Protein Adsorption by Composites Consisting of Silver Nanoparticles and Hydroxyapatite

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Silver nanoparticle has sensing capability derived from localized surface plasmon resonance (LSPR) which is the optical property of noble metal nanoparticle. Hydroxyapatite has specific adsorption characteristics of proteins. Thus silver nanoparticles/hydroxyapatite (nanoAg/HAp) composite is expected to have sensing ability of proteins adsorbed on hydroxyapatite, through hybridization of their functionalities. We report development of nanoAg/HAp composites through a reduction of silver ions by sodium tetrahydroborate in a slurry containing hydroxyapatite, without addition of surfactants. The nanoAg/HAp composite had silver nanoparticles in size of approximately 5-15 nm existed on the surface of hydroxyapatite. The sensing of protein adsorption by nanoAg/HAp composites was investigated using a phosphate buffer solution containing bovine serum albumin (BSA) or lysozyme (LSZ). The adsorption of BSA and LSZ on the nanoAg/HAp composites was similar to plain hydroxyapatite. The protein adsorption resulted in peak shifts in localized surface plasmon resonance (LSPR) spectra. The peak shifts clearly corresponded to the concentration of the surrounding proteins up to the point of saturation of adsorption on the hydroxyapatite.

FL-2:IL02 Simultaneous Deposition of Biomaterials and Cells for Regenerative Medicine

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Regenerative medicine is an emerging revolutionary approach in modern medicine aiming to activate the body's inherent ability to regenerate. However, the replication of the complex nature of is still a major hurdle for the translation of regenerative approaches to the clinic. A biomimetic approach may be offered by rapid-prototyping (RP) techniques, creating constructs which have predetermined architecture as well as incorporated cells. We apply an RP technique, 3D fiber deposition, to build heterogeneous cell-laden hydrogel constructs for musculoskeletal tissue engineering and characterised its use with various hydrogel compositions and different progenitor cells. Our results demonstrate that 3D-fiber deposition allows modulating porosity and mechanical properties of the hydrogel scaffolds. We show that cells survive the printing process and have the ability to differentiate in their musculo-skeletal lineage. In addition, we demonstrate that 3DF can be used to print viable, heterogeneous cell-laden hydrogel grafts in which cell-specific differences in matrix formation can be observed between the different parts. The ability of accurately placing cells in heterogeneous scaffolds will be of value in future approaches in the fields of tissue engineering and regenerative medicine.

FL-2:IL03 Antifouling Behavior of Hydrophilic Surface Designed by Polyelectrolyte Brushes

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Various types of hydrophilic polyelectrolyte brushes were prepared on the Si-substrates by surface-initiated atom transfer radical polymerization of methacrylate monomers with ammonium salt, sulfonate, carbobetaine, sulfobetaine, and phosphorylcholine functional groups. Surface wettabilities of polymer brushes with hydrophilic functional groups were studied based on the static and dynamic contact angles of water, diiodemethane, hexadecane in air, and air bubble and hexadecane in water. Water contact angles of the polyelectrolyte brushes were very low compared with non-ionic type hydrophilic brushes, such as poly(vinyl alcohol) and poly(2-hydroxyehtyl methacrylate) brushes. Most of the air bubbles contacting with polyelectrolyte brush surfaces formed sphere-like shapes. It is notable that polyelectrolyte brush surfaces repelled both of air bubble and hexadecane droplet in water. These results evidently described the formation of super hydrophilic surfaces prepared by polyelectrolyte brushes. Under the air atmosphere, a hexadecane wets and spreads on the surface of polyelectrolyte brushes, however, once the brush substrate was dipped into water, hexadecane detached from the brush surface. These properties can be applied to self-cleaning, antifogging, and antifouling systems.

FL-2:IL04 A Window with a View: Two Photon Imaging as a Non Invasive Tool to Study Cellular Form and Function in Vivo

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Most of what we know about the interactions betwen materials and living cells has been obtained in vitro were it is relatively easy to deliver substances to the cells and measure their physiological and biochemical response. However, any notion gathered in vitro should be evaluated in the living organisms, where the full comlexity of the cellular environment if fully expressed. Until recently we were severely limited in our capacity of exploring entire organs by means of non-invasive optical microscopy, but this has changed with the introduction of non-linear microscopy. Indeed, two photon microscopy is emerging as a powerful tool to image form and function in the brain in vivo, due to the remarkable capacity of ultrafast pulsed lasers of exciting fluorescent probes deep inside opaque tissue. Neurons and glia can be visualised in vivo by bulk loading of membrane permeable indicators or by genetically encoded probes. In this presentation we will show how form and structure of nervous cells can be quantitatively observed in vivo in mouse lines expressing the §Green Fluorescent Protein in selected neurons. Furthermore, we will demonstrate the use of Calcium indicators to study the excitability and behaviour of a population of nerve cells.

FL-2:L05 New Block Copolymer Nanoparticles for DNA/RNA Delivery: in Vitro and in Vivo Applications

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We prepared new polymeric micelles as non-viral vectors for DNA/RNA, which showed low toxicity and highly efficiency in complexing, stabilizing and delivering DNA. Polymer made of poly(ethylene glycol) (PEG), as hydrophilic domain, and poly(propylene sulfide) (PPS), as hydrophobic domain, has been conjugated with a linear poly(ethylene amine) (L-PEI) block, which is able to complex DNA, to form asymmetric ABC triblock copolymer. This ABC triblock copolymer can aggregate in water forming micelles with average size of 165nm. The same ABC tri-block copolymer can be mixed with AB diblock-copolymer made of PEG-b-PPS. The mixture is re-suspended in water to get smaller micelles which average size is 30nm and 40nm after addition of DNA. We demonstrated the ability of both of the systems to complex DNA plasmids, transfect them into different cell lines mediating the expression of the reporter gene with efficiency in the range of 50 to 100%. DNA delivery has been observed in vivo, being different tissues targeted. Interesting results have been obtained in melanoma tissues in which GFP expressing plasmid has been transfected as reporter gene by mean of both ABC and AB/ABC micelles, showing the higher efficiency of the smaller micelles.

FL-2:L06 Analysis of Receptor Conformation and its Functional Relations for Biomimetic Device

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The conformational changes of the receptor proteins play an important role in the signal transduction of the brain. Although many studies were carried for understanding the ligand-dependent conformational changes, most of the researches are based on the pharmacological and X-ray analysis. Cryo-TEM is one of the possible tool for observing the conformational changes. However, it is required for low temperature measurement and image averaging. None of the tool allows us to observe real-time conformational change of the receptor except fast scan AFM. We recently reported P2X4 receptor conformational change depending on ligand (ATP) in real-time using high-speed AFM. We use this method for understanding the functions of AMPA, NMDA and GABA receptors depending on the ligand application. As the AFM measurement gives us information at subunit resolution of few nm, the relationship between conformation and function of receptors could be analysis. We also use lipid bilayer for reconstitution of the receptor and for studying its interaction with receptor. Formation of the biomimimetic nano-bio devices based on the receptors with lipid bilayers will be introduced including preliminary results.

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FL-2:L07 Programmable Shape Shifting Polymeric Nanoparticles

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Nanoparticles capable of reversible and defined changes in morphology in response to stimuli are expected to have broad utility in a range of settings including targeted drug delivery, detection strategies and self-healing materials. Programmable materials with these properties remain elusive despite the many elegant examples of stimuli-responsive soft nanoparticles. Inspired by the utility of DNA as an informational molecule in nanotechnology, we report a soft nanoparticle design that allows reversible changes in morphology in a DNA-encoded fashion. The design was based on polymeric micelles from amphiphilic DNA-brush copolymers. Utilizing the sequence selective recognition properties of DNA, and its performance as a substrate for selective enzymatic cleavage, the volume fraction of DNA in the micelle shell is manipulated causing dramatic changes in morphology and particle size. The volume of DNA is reduced for a sphere to cylinder phase transition by sequence specific cleavage and increased for a cylinder to sphere phase transition by hybridization with a specific DNA sequence. This approach provides unprecedented programmability and reversible control over the morphology of a nanoscale object allowing user-defined selection of a given particle shape.

Session FL-3
Medical Diagnosis Applications

FL-3:IL01 DNA Diagnostics Using New Cationic Polymers

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A couple of complementary nucleic acids hybridizes each other to form double helical structure with a sequence specific manner. Sequence selectivity of nucleotide hybridization allows us to detect and amplify a particular nucleic acid sequence out of a massively heterogeneous nucleic acid mixture. However, hybridization frequently occurs even with sequences having partial complementarity, especially with the homologous sequences having single or a few mismatches, resulting in misjudges in nucleic acid detection and functional analyses. Thus, a method to increase the fidelity of nucleic acid hybridization is desired. Here, we described a simple method to increase fidelity of DNA hybridization by regulating hybridization pathway. Fully complementary hybrid was selectively produced out of a mixture containing fully complementary and single-base mismatched single strand DNAs, permitting us to discriminate single-base mismatch in 60 nt long. The method is the first demonstration of highly sequence specific DNA hybridization produced by an engineered nucleation step with the aide of a cationic copolymer producing nucleic acid chaperoning activity.

FL-3:IL02 Sensor Technologies to Probe Cell-material Interactions

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The adhesion of mammalian cells to technical surfaces is an area of active research and attracting considerable interest from various fields of medical technology and biotechnology. However, experimental access to the interface between the cells and the technical surface is limited as it is protected by the cell bodies on the one side and the bulk material on the other. This article will describe two emerging non-microscopic techniques capable of reporting on cell-material interactions from this interface region label-free, non-invasively and in real-time. Both approaches, electric cell-substrate impedance sensing (ECIS) and the quartz crystal microbalance (QCM), are based on substrate-integrated transducers that transduce cellular interactions with the surface into an electrical signal that can be analyzed in quantitative terms. Besides monitoring cell-material interactions, both experimental techniques can also be used to manipulate cell-substrate adhesion in a well-defined manner which opens the field of possible applications significantly. A short introduction of either technique is followed by example data that illustrates the performance of these sensors, the information accessible from the experimental readings, their individual merits and limitations.

FL-3:IL03 **Novel Biomaterials and Nano-biotechnology Approaches in Tumor Diagnosis**

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Each year 10.9 million people worldwide are diagnosed with cancer and it is the third most common disease in world. Early diagnosis of cancer and cure are major challenges. Recent advances in development of novel biomaterials as well as rapid progress in the area of nano-biotechnology has potentials to change all the current modalities of cancer diagnosis and management. The unique physical and chemical properties of nanomaterials are extremely helpful for detection of biomarkers of the disease, molecular imaging as well as specific targeted therapy sparing the normal organs. Nanoparticle (NP) has large surface area which can be conjugated or coated with different molecular probes for diverse detection system (optical, electrical, magnetic etc.) as well as used as a vehicle to carry different biomolecules and anticancer drugs to tumor cells. Semiconductor quantum dot (QD) with novel optical and electronic properties helped to devise a new class of NP probes for molecular, cellular, and in vivo imaging. A large variety of materials ranging from metal, ceramic, polymer, lipid, protein and nucleic acid are used for developing novel nanoparticles with multiple functions which can detect different aspects of cancer biology and progression. The major issue of concern is biocompatibility and safety of these materials and their fate after in-vivo use. However with collaborative interdisciplinary research it will be possible to develop safer nanomaterials in future.

FL-3:L04 **Biomimetic Systems as Luminescent Nanoprobes for Medical Imaging**

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The search of targeted non-toxic luminescent nanoprobes is a major challenge in cancer diagnosis. In this work, new luminescent and fully biocompatible colloids based on europium-doped biomimetic apatite were investigated. The colloids were synthesized by soft chemistry in the presence of a phospholipid moiety, with varying Eu doping rates, and folic acid was associated as a potential targeting agent. Physicochemical features (composition, structure, morphology and luminescence properties) were fully examined. Experimental evidence showed that suspensions prepared from an initial Eu/(Eu+Ca) ratio up to 2 mol.% consisted of single-phased biomimetic apatite nanocrystals covered with AEP molecules as Ca(AEP)2 complexes. TEM analyses showed very homogeneous crystal aspects (ellipsoid morphology) with dimensions around 28 nm (length) and 9 nm (width). The colloids exhibit luminescence properties typical of Eu-doped systems, with long luminescence lifetime (~0.73 ms). Preliminary immunology assays (contact with monocyte cells for up to 48 h) showed that the nanoparticles were not pro-inflammatory. These systems, stable over time (beyond 6 months) and excitable in close-to-visible (392.8nm) or visible (464.2 nm) light appear thus to be very promising for intracellular medical imaging.

FL-3:L05 **NMR Study of Novel Contrast Agents for MRI Based on Mn-ferrites and Co-ferrites**

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The Nuclear Magnetic Resonance Dispersion (NMR-D) profiles of different classes of possible novel contrast agents for MRI are presented. Mn-ferrites and Co-ferrites nanoparticles (NP) with different magnetic cores (Mn3-xFexO4 and Co3-xFexO4) were obtained by rapid decomposition of metalcarbonyl into a hot solvent and a coordinating surfactant, followed by an oxidation step. By controlling the metal/surfactant molar ratio, we obtained samples with different sizes of the monodisperse capped NP. The first measurements we made were headed to a structural and a morphological investigation by XRD and TEM techniques. ZFC and FC SQUID magnetization measurements revealed for these samples a superparamagnetic (SP) behaviour with blocking temperatures in the range 30-150K. NMR-D study revealed relaxivities (i.e. the efficiency in contrasting MR images), for most of our samples, comparable to commercial compounds, resulting in a high efficiency for high-field clinical and research Imagers. Also, the Co-ferrites at low and intermediate nu revealed relaxivities higher than commercial SP compounds. The comparison of the relaxivities of the two series of samples allowed to highlight the crucial role of the magnetic anisotropy and of the kind of magnetic ion for the nuclear relaxation mechanism.

FL-3:L07 **Creation of Superelastic Functional Properties in a Ti-50.7%Ni Wire for the Stapler Suturing of Blood Vessels**

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The technique of aorta-coronary shunting offered by Dr. M. Soutorine by means of the original stapler developed by "Endogene" allows suturing blood vessels by superelastic Ti-Ni staples on "working heart" (without heart switching-off). The material for staples is a 0.30 and 0.315 mm diam. wire which was studied by DSC, shape recovery and mechanical tests. Thermomechanical treatment (TMT) comprised warm drawing, low- temperature (LTMT) by cold drawing with 25-30% strain in the last pass and following post-deformation annealing (PDA) in the 350-550 °C temperature range. LTMT leads to increasing of yield stress in comparison with warm drawing. Treatment of wire under LTMT+PDA at 350-400 °C regime allows obtaining the highest characteristics of functional properties of the wire. The difference between "dislocation" and "transformation" yield stresses $\Delta\sigma = 900$ MPa. Critical stress of superelastic recovery after TMT on the average is 1.5-2 times higher in comparison with warm drawing. The maximum completely recoverable strain $\varepsilon_{r,1}^{max} = 6.5\%$. The maximum obtained force value of staples is $P_r^{su} = 4.78$ H. The shape recovery rate of staples was 85-97% that provided its functionality. Storage in the stapler in straightened condition within 1 month does not worse the staples.

Session FL-4

Regenerative Medicine and Tissue Engineering

FL-4:IL01 **Is Nanotechnology Really Increasing Tissue Growth? Separating the Hype from Data**

Thomas J. Webster, Division of Engineering and Department of Orthopaedics, Brown University, Providence, RI, USA

Nanotechnology is being used to mimic structural components of tissues in synthetic materials intended for various implant applications. Recent studies have highlighted that when compared to flat or micron rough surfaces, surfaces with nanofeatures promote optimal initial protein interactions necessary to mediate cell adhesion and subsequent tissue regrowth. This has been demonstrated for a wide range of implant chemistries (from ceramics to metals to polymers) and for a wide range of tissues (including bone, vascular, cartilage, bladder, skin, and the central and peripheral nervous system). Importantly, these results have been seen at the in vitro and in vivo level. This talk will cover some of the more significant advancements in creating better vascular, cardiovascular, and orthopedic implants through nanotechnology efforts.

It will also cover recent in vitro and in vivo studies which highlight better tissue regeneration. This talk will also address recent concerns of nanoparticle toxicity and the role industry has played in nanomedicine to date.

FL-4:IL02 **Calcium-deficient Hydroxyapatite for Metabolism of Subsequently Formed Bone Tissue**

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Hydroxyapatite (Ca10(PO)4(OH)2; HA) is paid to much attention for the regenerative medicine. In the present study, the authors describe the preparation method and biological evaluation of calcium-deficient HA. The biological response of the hydrothermally synthesized pure calcium-deficient HA composed of rod-shaped particles was different from that of stoichiometric HA synthesized by the conventional sintering method. The calcium-deficient HA revealed a biodegradable nature by osteoclastic resorption. The method to synthesize biodegradable pure calcium-deficient HA is expected to contribute to developing new biodegradable bone substitutes with adequate biodegradability and bone replaceability.

FL-4:L03 **Self-collapse and Sliding of Nanotubes in a Bundle**

Nicola M. Pugno*, Laboratory of Bio-inspired Nanomechanics "Giuseppe Maria Pugno", Dept. of Structural Engineering and Geotechnics, Politecnico di Torino, Torino, Italy; National Institute of Nuclear Physics (INFN), National Laboratories of Frascati, Frascati, Italy; National Institute of Metrological Research (INRIM), Torino, Italy; Consorzio Nazionale Interuniversitario per le Scienze Fisiche della Materia (CNISM), Roma, Italy

We have discovered that the influence of the surrounding nanotubes in a bundle is nearly identical to that of a liquid having surface tension equal to the surface energy of the nanotubes. This surprising behaviour is confirmed by the calculation of the polygonization and especially of the self-collapse diameters (and dog-bone configurations) of nanotubes in a bundle. Accordingly, we have evaluated the strength and toughness of the nanotube bundle, with or without collapsed nanotubes, assuming a sliding failure. Biological applications will be discussed.

FL-4:L05 **Modeling the Elastic Anisotropy of Woven Hierarchical Tissues: Experimental Comparison on Biological Materials and Design of a New Class of Scaffolds**

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In this paper, the elastic properties of 2-D woven hierarchical tissues are modeled, assuming for the warp and fill yarns (level 0) an orthotropic material. The tissue at level 1 is considered as the fabric composed by the warp and fill yarns of the level 0. Warp and fill yarns at the 1st level are defined as "pieces" of such a tissue and have a different mismatch between the inclination of their longitudinal axes and those of composing sub-fibers. Similarly, basing on warp and fill yarns at level 1 we generate warp and fill yarns and thus tissue with 2 hierarchical levels, and so on. Also, we compare our predictions with experiments on fabric from the literature and with direct experimental observations on biological materials, such as natural leaves, using a MTS microtensile testing machine. In fact, various hierarchical structures can be recognized in biological systems (e.g. bones, leaves, etc) and are expected to deeply influence their global mechanical/elastic response, as predicted. The analysis, based on continuum elasticity, shows the possibility of tailoring the elastic anisotropy of the tissue, allowing the design of a new class of hierarchical 2-D scaffolds able to better match the anisotropy of biological tissues to be regenerated and thus to maximize the performance.

FL-4:IL06 **Biomaterial Scaffolds & Intercellular Signaling in Engineered Bone and Cartilage**

John P. Fisher, Kyobum Kim*, Fischell Department of Bioengineering, University of Maryland, College Park, MD, USA

Soluble signaling molecules determine cell phenotype and thus tissue function. We consider the hypothesis that cell encapsulation within biomaterial scaffolds alters the expression and regulation of endogenous signaling molecules, therefore affecting cell phenotype and tissue function. The engineering of specific tissues, particularly bone and articular cartilage, is discussed, with an emphasis on the role of biomaterials in regulating molecular signaling within these engineered tissues. For example, we consider the effects of macroporous architectures upon the endogenous expression of bone morphogenetic protein-2 molecules by mesenchymal stem cells as well as the expression of insulin like growth factor-1 by alginate embedded chondrocytes. In addition, we discuss coculture systems where endogenously expressed factors are utilized to induce specific cellular responses, including mesenchymal stem cell differentiation. Finally, we consider the development of cyclic acetal based biomaterials which have properties specifically developed for facilitated intercellular signaling. The presentation aims to integrate biomaterials development into cell signaling studies so as to initiate new strategies for the engineering of tissues.

FL-4:IL07 **Nano-biointerface for Medical Application**

Yukio Nagasaki*, Keitaro Yoshimoto, Graduate School of Pure and Applied Sciences, Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), Center for Tsukuba Advanced Research Alliance (TARA) and Master's School of Medical Sciences, University of Tsukuba, Satellite Laboratory of International Center for Materials Nanoarchitechtonics, Tsukuba, Ibaraki, Japan

The obstacles that inhibit the development of biosensors are the inactivation of biomolecules such as antibody and oligoDNA molecules due to uncontrolled immobilization as well as the nonspecific adsorption. To solve these problems, one has to achieve site-specific immobilization of biomolecules on substrates while retaining excellent non-fouling characteristics. It is known that antibody Fab' fragments immobilized on a gold surface in an oriented manner via Au-thiolate linkages show higher antigen binding activity than whole IgG physically adsorbed on a gold surface. Previously, we have observed that deposition of a layer composed of a short sulfanyl-ended semitelechelic poly(ethylene glycol) (2k) (hereafter "MeO-PEG-SH") and a long MeO-PEG-SH (5k) on a gold surface provides superior non-fouling characteristics. In this study, we attempted to introduce this mixed-PEG (2k/5k) tethered chain layer onto Fab' fragment preimmobilized gold surface. The newly developed Fab'/mixed-PEG co-immobilized surface was assessed as a sensor platform by surface plasmon resonance (SPR) spectroscopy and 125I radiometric assay. PEG/oligoDNA co-immobilized surfaces were also prepared and investigated in detail using SPR as well as XPS.

FL-4:L08 **Super-hydrophobic Surfaces by Direct Replication of Natural Leaves**

E. Lepore*, N. Pugno, Laboratory of Bio-Inspired Nanomechanics "Giuseppe Maria Pugno", Department of Structural Engineering and Geotechnics, Politecnico di Torino, Torino, Italy

Starting from natural hydrophobic leaves, we perform a series of surface replications by using a template method in order to clarify not only the role of surface roughness but also that of its skewness (asymmetry between peaks and valleys) on super-hydrophobicity. We used a template method, casting liquid wax or a silicone elastomer and its catalyzer on the fresh leaf (original template). After solidification at room temperature, the wax or silicone elastomer layer was carefully peeled off, resulting in a topologically complementary surface (Copy I), with respect to the natural one. Then, we repeated the same procedure considering Copy I as the new original template, obtaining Copy II, and soon, up to Copy X. All the surfaces were characterized with a three-dimensional optical profilometer, scanning electron microscopy and contact angle (CA) measurements. We noted an increasing of the CA for the first odd copies as well as significant differences with respect to the even copies, suggesting an important role of the skeweness (quantified with the surface characterization) in contrast with the classical Wenzel's prediction. Implications in tissue engineering for the regenerative medicine will be discussed.

FL-4:IL11 **Bone-mimetic Laminated Nano-structures for Regeneration of Skeletal Tissues**

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Bone exhibits hierarchical levels of organization from macroscopic to microscopic to nanoscale. The objective of this work was to develop a bone-mimetic composite matrix to provide structural support to the regenerating region and to support the cascade of osteogenic differentiation of progenitor marrow stromal (BMS) cells. Sheets of poly(L-lactide) (L-PLA) nanofibers, fabricated by electrospinning, were coated with a hydrogel/apatite precursor solution, stacked and pressed together, and allowed to crosslink by photopolymerization to form a peptide-reinforced hydrogel/apatite laminated composite. Addition of an osteonectin-derived glutamic acid peptide (Glu6) and lamination resulted in an order of magnitude increase in modulus of the composite to within the range reported for wet human cancellous bone. Lamination significantly increased the extent of mineralization of BMS cells and the laminates reinforced with apatite nanocrystals and conjugated with integrin-binding focal-point adhesion RGD peptide (Lam-RGD-HA) had 3-fold higher calcium content and higher expression of osteogenic markers osteopontin and osteocalcin (compared to laminates without apatite or RGD) after 21 days of incubation in osteogenic media. Laminated osteon-mimetic structures have the potential to provide mechanical strength to the regenerating region as well as supporting the differentiation of progenitor cells to the osteogenic lineage.

FL-4:IL12 Engineered Biomimetic Nanofibers for Regenerative Medicine

Seeram Ramakrishna*, Jayarama Reddy Venugopal, Susan Liao, National University of Singapore, Singapore

Attempts have been made to fabricate nanofibrous scaffolds to mimic the chemical composition and structural properties of extracellular matrix (ECM) for tissue/organ regeneration. Nanofibers with various patterns have been successfully produced from synthetic and natural polymers through a relatively simple technique of electrospinning. The resulting patterns can mimic some of the diverse tissue-specific orientation and three-dimensional (3D) fibrous structure. Studies on cell-nanofiber interactions have revealed the importance of nanotopography on cells adhesion, proliferation and differentiation. Our recent data showed that hematopoietic stem cells (HSCs) as well as mesenchymal stem cells (MSCs) can rapidly and effectively attached to functionalized nanofibers. Mineralized 3D nanofibrous scaffold with bone marrow derived MSCs has been applied for bone tissue engineering. The use of attractive injectable nanofiber for cardiac tissue engineering applications as they allow for the encapsulation of cardiomyocytes/MSCs as well as bioactive molecules for the repair of myocardial infarction. Duplicate 3D heart helix microstructure by the nanofiber might provide functional support for cardiac patch treatment. Furthermore, clinical applications of electrospun nanofibers for regenerative medicine are highly feasible due to the ease and flexibility of fabrication with the cost-effective method of making nanofiber.

FL-4:IL13 In vivo MRI Tracking of Transplanted Stem Cells in Rat Hind Limb Ischemia

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Stem cell transplantation therapy has been recently attracting great attention, but the therapeutic mechanism and the fate of transplanted cells are still unclear. In the present paper, novel water soluble MRI contrast agent for /in vivo/ living cell tracking was developed. The contrast agent is composed of gadolinium chelates and water soluble carrier, which is known to interact with cell membrane or tissue very weakly. As is different from the conventional /in vivo/ cell tracking system based on superparamagnetic iron oxide (SPIO) beads, when the contrast agent goes out of cells upon the cell death, the water soluble contrast agent is excreted due to its very low accumulation in the tissue. The contrast agent was successfully delivered into mesenchymal stem cells or endothelial progenitor cells by the electroporation method with very low cytotoxicity. The delivered contrast agent was localized only in the cytosolic compartment of growing cells and did not leak out of cells for long period of time. The labeled mesenchymal stem cells or endothelial progenitor cells were transplanted to hindlimb ischemia model rats, and relationship between the recovery in the blood flow and the fate of transplanted stem cells was studied.

FL-4:IL14 Tissue Engineering with Natural Tissue Matrices

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Natural tissue, especially autologous tissue is one of ideal materials for tissue regeneration. Decellularized tissue could be assumed as a second choice because the structure and the mechanical properties are well maintained. Decellularized human tissues, for instance, heart valve, have already been developed and applied clinically. Nowadays, decellularized porcine tissues are also investigated These decellularized tissues were prepared by detergent treatment. The detergent washing is easy but sometime it has problems. We have developed the novel decellularization method, which applied the ultra-high pressure (UHP). As the tissue set in the pressurizing chamber is treated uniformly, the effect of the ultra-high pressurization does not depend on the size of tissue. We have reported the UHP decellularization of heart valve, and cornea. Furthermore, UHP treatments are reported to have the ability of the extinction of bacillus. So, the UHP treatment is also expected as the sterilization method. We are investigating efficient processes of decellularization and recellularization of biological tissues to have bioscaffolds keeping intact structure and biomechanical properties. Our recent studies on tissue engineering using UHP decellularized tissue will be reported.

FL-4:IL15 Biomimesis in Bone and Tendon Tissue Engineering

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Bone and tendon injuries require prolonged durations of rest and immobility. When surgery becomes inevitable four material options are available: autografts, allografts, xenografts, and prosthetic devices. Autografts are the best current option but suffer from limited availability and donor site morbidity, while allografts and xenografts have limited inductive ability and may cause an immune response or infections. Prosthetic devices, on the other hand are a temporary solution. To augment the limitations in the current treatments of bone and tendon defects and injuries, researchers have attempted to engineer bone and tendon-like tissue in-vitro that is biocompatible and possesses comparable mechanical properties to the innate tissue. Our goal was to study the influence of fluid shear forces on the osteogenic differentiation of adult stem cells seeded on biomimetic porous poly(L-lactic acid) scaffolds surface modified with biomolecules. We also characterize the fluid dynamic environment inside the porous network of the scaffolds using Lattice-Boltzmann simulations. On the tendon side of the project, the effect of cyclic mechanical stimulation on adult stem cells seeded within decellularized human umbilical veins (HUV) was investigated using histology, RTPCR and mechanical testing.

FL-4:IL16 Tissue Engineering Technology with Biomaterials to Develop Regeneration Medicine and Stem Cell Biology

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To realize tissue regeneration therapy based on the natural healing potentials of body to assist tissues and organs repairing, it is necessary to regulate and promote the proliferation and differentiation of cells which play a central role in tissue regeneration. For successful cell-induced tissue regeneration, it is necessary to artificially create an environment which allows stem and precursor cells of high proliferation and differentiation potentials to naturally function. The local environment of cells can be designed and prepared by tissue engineering based on biomaterial technology for drug delivery and cell scaffold. In vivo tissue regeneration and repairing can be induced by making use of cell scaffold and biosignaling molecules (growth factor and gene) or their combination. One practical strategy to enhance the in vivo efficacy of biosignaling molecules is to make use of drug delivery system (DDS). This DDS system can be combined with cells or/and the cell scaffold to induce the regeneration repairing of tissues and organs. The cell scaffold and DDS technologies can also apply to the basic research of stem cell biology and medicine which scientifically supports tissue regeneration therapy. This paper introduces our recent experimental data with the cell scaffold and DDS.

FL-4:L18 A Hydroxyapatite-collagen Composite Useful to Make Bioresorbable Scaffolds for Bone Reconstruction

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Composites between hydroxyapatite (HA) and collagen (Col) may be used for the fabrication of bioresorbable scaffolds for bone reconstruction. Micro-particles (average diameter about 30 micrometers) of an HA annealed at 1100°C were mixed with a 0.5 M acetic acid solution of Col in the 80:20 HA to Col weight ratio, similar to that present in the natural bone. The resulting suspension was manufactured in films by casting, and then some films were cross-linked by exposure to glutaraldehyde (GTA) vapours. Alternatively, cross-linked sponges were obtained by treating the suspension with transglutaminase, and by lyophilizing the so obtained gel. Characterization by scanning electron microscopy, water sorption test, Col release in water, thermogravimetric analysis and differential scanning calorimetry shows that the cross-linking makes the composite more stable than the not cross-linked one. Conversely, neither the interactions between HA and Col, detected by spotlight FT-IR, nor the degradation by collagenase, which is a requirement for the bioresorbibility, are affected by the cross-linking. As regarding the biocompatibility, a culture of mesenchymal stem cells from umbilical cord on a GTA cross-linked film shows a good adhesion and proliferation of the cells 10 days after seeding.

FL-4:L19 Growth Factor-immobilized PCL Porous Beads as a Bioactive Urethral Bulking Agent

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Stress urinary incontinence, one type of the urinary incontinence, may be caused by urethral hypermobility and/or intrinsic sphincter deficiency. Various injectable bulking agents have been used in the treatment of stress urinary incontinence. However, injection volume decrement with time caused by particle migration and resorption in the body have been main problems for them. In this study, we prepared growth factor-immobilized porous polycaprolactone (PCL)/Pluronic F127 beads as an injectable and bioactive bulking agent which can provide bulking effect and stimulate the defect tissues around urethra for the effective treatment of urinary incontinence. Their morphology, growth factor release behaviors, model cell culture (using muscle-derived stem cells, MDSCs) in the growth factor-immobilized porous bead (in vitro) and the animal study (using an urinary incontinence rat model) to investigate the effectiveness of the porous beads as a bioactive bulking agent (in vivo) were conducted.

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FL-4:L20 Catastrophic Instabilities in the Fracture of Nanotube Bundles

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In a recent letter, Xiao et al. (Composites Science and Technology 68, 2937, 2008) interpreted experimental results on the failure of nanotube bundles using Weibull Statistics. The prediction of the force versus strain curve was a smooth curve, only partially able to capture the observed discrete behavior of the bundle. In particular, abrupt jumps in the force, at nearly constant strains, were clearly observed experimentally, each of them corresponding to the failure of a sub-bundle. Accordingly, we have developed a simple modification of the Weibull Statistics able to rationalize the observed catastrophic failure of the bundle, considering a linear or nonlinear elastic constitutive law. Implications in tissue engineering for the regenerative medicine will be discussed.

Session FL-5
New Therapeutics and Intelligent Delivery Systems

FL-5:IL01 Multi-functional Templates for Smart Targeting Delivery

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The development of molecular devices endowed with targeting functions should enable the specific delivery of toxic molecules or imaging probes or a combination thereof to malignant tissues, thus increasing their local efficacy. Such vectors can pave the way for the development of new classes of therapeutics and diagnosis, which could in the future be called tailor-made medicine. In line with this concept, we have devised Regioselectively Addressable Functionalized Template (RAFT) molecule as adaptor to engineer novel structures with tailor made functions. For this purpose, we have developed efficient conjugation techniques that allows highly efficient modular combination of peptides and sugars as recognition elements with toxic or/and imaging probes. The lecture will provide an overview of the results so far obtained in vitro and in vivo in the field of tumor targeting and synthetic vaccines.

-JL Coll et al, Mol Ther, 2009, 17, 837-843; -D Boturyn et al, Angew Chem Int Edit, 2009, 48, 2576-2579; -P Dumy et al, Org. Biomol. Chem., 2009, 7, 221-224; -P Dumy et al, J. Pept. Sci., 2008 14, 224-240; -P Dumy et al, Molecular Cancer 2007, 6, 1-9; -JL Coll et al, Mol. Imaging, 2006, 5, 188-197; -P Dumy et al, J. Am. Chem. Soc, 2004, 126, 5730-5739.

FL-5:IL02 Development of Ceramic Beads for Cancer Treatment

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Ceramic beads can play an important role in cancer treatment. We successfully prepared highly spherical Y2O3 microspheres, around 25 µm in diameter and with a smooth surface, by a high-frequency induction thermal plasma melting method. The Y2O3 microspheres showed excellent chemical durability in body environment. In animal experiments, we confirmed that the VX2 tumor grew significantly in the rabbit liver without injection, whereas it showed no growth in the rabbit liver infused with radioactive Y2O3 microspheres. This indicates that the infusion of radioactive Y2O3 microspheres is significantly effective for suppressing growth of VX2 tumors. Recently, we also prepared hollow Y2O3 microspheres by utilizing enzymatic reaction. On the other hand, magnetic microspheres, around 25 µm in diameter, composed of small crystals of Fe3O4 and/or gamma-Fe2O3, can be prepared by precipitation from aqueous solution and subsequent heat treatment. The microspheres showed a saturation magnetization of 68 emu/g and coercive force of 198 Oe. We confirmed that thus obtained microspheres can produce heat in agar phantom under alternating magnetic field of 300 Oe, 100 kHz. We will introduce our attempts to prepare ceramic beads for cancer treatment.

FL-5:IL03 Theragnostics for Molecular Imaging and Drug Delivery

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In recent years, advances in medical imaging technology have been emphasized along with new advances in the field of cellular and molecular biology. Emerging field of medical imaging, i.e. Molecular Imaging, allows not a traditional image of anatomical changes, but a biological characterization of disease state at molecular or cellular lever. Interdisciplinary research at the interface of nanotechnology and molecular imaging had led to elucidate key factors that determine specificity in diagnosis and therapeutics. For example, with combining molecular imaging technology and drug delivery system, a novel design of drug screening or new approaches in drug development can be performed in animal models. Polymer nanoparticles bearing near-infrared fluorescent dyes can be utilized in determining optimized therapeutic dosages or frequencies of drug administration. These nanoparticles also can be utilized as molecular probes for visualization of therapeutic efficacy in small animals. Design of novel polymeric nanoparticles with high specificity in cellular or molecular responses, application of molecular imaging probes toward the era of Personalized Medicine will be presented in current study.

FL-5:L03b The Use of HA Ceramic Delivery System to Stimulate Ostegenic Mediators in a Femoral Defect Rat Model

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This investigation was designed to explore, for the first time, the ability of hydroxyapatite ceramic system (HA) to deliver an osteogenetic mediator, thymoquinone (TQ), in a sustained manner using femoral defect animal model. The hypothesis of this project was the sustained delivery of an alternative therapy (TQ) can provide an ideal means to promote osteogenesis. Microcrystals of HA were prepared by following standard lab protocols. The capsules were fabricated by weighing 1 gm of HA, 0.2 g of TQ, 0.2 g of Vancomycin and 0.1 g of lysine (used as a binder). Calcined HA + drug were was cold pressed using a 2/32-die set at a compression load of 5000 lbs. Capsules were gas sterilized prior to surgical implantation. Adult male rats were randomly divided into 3 groups of 5 each. Group I were untreated and served as intact control. Group II were implanted with the HA capsule loaded with antibiotic alone. Group III animals were implanted with HA capsule containing the antibiotic and TQ. Generally, an incision was made to expose the left hind femur where a 2.5 mm defect was created on the proximal side. Each HA capsule was implanted at a close proximity to the femoral defect. Serum was collected and analyzed weekly for four weeks to determine the concentration of serum protein and alkaline phosphatase activity. After 4 weeks, animals were anesthetized and the vital organs (kidney, heart, liver, spleen, lung and adrenal) and reproductive organs (testes, epididymis, prostate and seminal vesicles) were removed, weighed, and processed for histological evaluation. Bone formation was assessed morphologically using Image Pro Software. Analysis of variance was used to compare the groups ad significance differences reported at $p<0.05$. Results obtained from this study demonstrated the HA delivery system was capable of releasing TQ at sustained levels for

30 days. Data obtained revealed no significant changes in body weights of animals treated with TQ compared to the control group. Comparison between the wet weights and histological analysis of vital and reproductive organs revealed no significant changes or alterations. Serum proteins and alkaline phosphatase measurements fluctuated during the four different sampling periods. However, there were no significant differences between the groups for specific sampling dates. Protein levels and alkaline phosphatase activity were higher at the earlier sampling dates and observed to decline with time. Morphological analysis revealed sustained delivery of TQ enhanced cortical bone formation (osteoblastic hyperactivity). Therefore, TQ can be used safely and effectively in a sustained manner to enhance bone formation; additional research is ongoing to establish the mode of action TQ has on bone formation.

FL-5:L04 Functionalized Amphiphilic Macromolecules for Drug Delivery and Biostabilization

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Nanoscale amphiphilic macromolecules (AMs) were designed with high biocompatibility and stability. The hydrophobic region is a sugar backbone functionalized with alkyl branches and the hydrophilic region is PEG attached to the alkylated sugar backbone. Three applications were evaluated. First, to explore the effect on micellization, AMs with varying sugar stereochemistry and conformation were synthesized. Biological activity was evaluated by hydrophobic drug encapsulation and binding to macrophage scavenger receptors. Second, to explore as non-viral vectors for nucleic acid delivery, the AMs were aminated with ethyleneamine. The aminated AMs formed polyplexes with plasmid DNA as well as siRNA and remain stable in the presence of serum proteins. Polyplexes formed with aminated AMs and GFP-encoding plasmids transfected U87 glioblastoma cells. Similarly, GFP-expressing U87 cells with GFP-silencing siRNA polyplexes showed decreased expression. Third, to biostabilize nanocrystals, functionalized AMs coordinate to semiconductor nanocrystal surfaces, rendering them biocompatible. White light-emitting CdSe nanocrystals were solubilized with phosphonic acid-functionalized AM and retained their ability to emit white light and penetrate macrophage nuclei.

FL-5:L05 XPS Characterization of Iron Oxide and Gold Nanoparticles for Tumor Care

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Superparamagnetic iron oxide nanoparticles (SPIO) have a wide range of applications, including high-density magnetic storage, catalytic and separation processes, magnetic resonance imaging (MRI), in vivo imaging of tumor progression. One advantage is that they are sufficiently inert to be injected to the human body without significant counter effects. For these reasons, SPIO are utilized as carriers to target tumor tissues with the aim to visualize the extension of the malignant affection and to cure it. A mimetic coating is then needed to overcome the immune system and ensure a sufficient long life to allow SPIO to reach the tumor tissue. Also gold nanoparticles were functionalized and coated with the same mimetic film. Differently from iron oxide NPs, those based on gold may be utilized to perform Surface Enhanced Raman Spectroscopy (SERS) to obtain spatial and chemical information. In this work we present preliminary results on iron oxide and gold based NPs synthesized in our laboratories. A full characterization was performed by means of XPS to study both the chemical composition of the SPIO nanoparticles of their mimetic coatings, and to get structural information.

FL-5:L06 Novel Silicon Based Gene Carrier Systems

Anett Sommerwerk, Guido Struckmeyer, Janine Tillmann, Michael Uhr, Jens Schäfer, Heinrich Richter, Udo Bakowsky*, University of Marburg, Pharmazeutical Technology and Biopharmazeutics, Marburg, Germany

Transfer of genetic material into mammalian cells, the purpose of which ranges from applications in cell biology in vitro to the development of gene therapy in vivo, can be accomplished by various techniques. Natural viruses have been adapted to allow the delivery of foreign DNA into diseased target cells with the highest efficiency of all transfection systems, but virus particle associated toxicity, or a limited target cell tropism. In recent years, a number of non-viral transfection agents have been developed to circumvent these problems using purpose-made synthetic alternatives. The majority of these non-viral vectors is based on a (poly)cationic element which functions to form interpolyelectrolyte complexes with the polyanionic DNA. Currently, the most investigated non viral transfection systems are cationic liposomes or SLN's with and without fusogenic helper lipids, polycationic polymers, inorganic and organic nanoparticles. In the presented study synthetic organic silicon derivatives are used as novel gene vehicles. Physicochemicalparameters and morphology were studied by photon correlation spectroscopy, zeta potential measurements (NanoZ Malvern) and Atomic Force Microscopy, while the biological activity was determined using a standard in vitro transfection assay.

FL-5:L07 Nanotechnology for Drug Delivery

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The delivery of active substances is currently one of the most stimulating challenge due to the inability of conventional medicine to apply effective therapeutic strategies for the treatment of brain pathologies, including neurodegenerative diseases, brain tumors and HIV-related dementia as well as the application to other cancer diseases or leukemia. The use of nanodevices (ND), such as liposome (Lp) and nanoparticles (Np) have a long-time application as drug delivery systems. Regarding brain delivery, it is notable that these systems, if not engineered, are totally unable to cross the healthy state BBB; thus, the role of ND surface engineering surely represents the milestone for a promising future application in difficult-to-treat brain pathologies. These ND can be modified with specific ligands or, more generally, substances, able to increase their ability to cross BBB by means of specific mechanisms, such as absorptive-mediated transcytosis or receptor-mediated endocytosis. It is the case of specific peptides which have been conjugated with polymeric or lipidic nanodevices to allow a more selective drug delivery across the BBB, giving pharmacological evidences of the increase activity. Regarding other liposomes application, these lipidic non viral vectors have deserved considerable attention, as they have been shown to efficiently incorporate a large variety of drugs, as well as of different biologically active molecules, such as proteins, plasmids, and siRNA/ODN (see background section). Additionally, the modification of the liposome surface with hydrophilic polymers such as polyethylene-glycol (PEG) does not only improve chemical stability of circulating drug-liposome formulations, but it also provides a natural support to conjugate specific ligands (e.g. monoclonal antibodies) on the nanocarrier surface and selectively direct the so-called immunoliposomes towards target cells. Considering the active role of the chronic infection in the development of cancer, the nanotechnological approach can be usefully applied to oncologic medicine, in particular to set up innovative strategies for the treatment of pathogen-associated diseases.

Session FL-6

Progress in Implant Prostheses

FL-6:IL02 A Critical Assessment of the Clinical Efficacy and Cellular Response to Low Intensity Pulsed Ultrasound for Fracture Repair

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Fracture repair continues to be widely investigated, both within the clinical realm and at the fundamental research level. Clinical application of low intensity pulsed ultrasound (LIPUS) has shown great promise as an effective, minimally invasive treatment for fracture repair and has warranted further investigation into the cellular manifestation of applied ultrasound. Toward this end much has been learned about the response of osteoblasts to LIPUS stimulation. In vitro and in vivo studies have revealed an increase in cell proliferation, protein synthesis, collagen synthesis, membrane permeability, integrin expression, and increased cytosolic calcium, to name a few, in response to LIPUS which makes its utility and overall impact on cellular behavior clear. This clear impact suggests that LIPUS would be a powerful tool in the development of novel approaches to bone repair. Regenerative engineering-based approaches to bone healing that incorporate polymeric scaffolds and stem cells may be combined with LIPUS to move beyond fresh fractures to large scale bone defects.

FL-6:IL03 Surface Modification of Titanium-based Implants

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For biomaterials, the main interaction with the biological system of the patient occurs via their surface. Thus, functionalization of biomaterial surfaces with biological signal molecules is a main focus of current biomaterial research. After a general discussion of immobilized components and immobilization principles, the contribution will focus on how to control the (bio)chemical surface properties of titanium based biomaterials, emphasizing the use of electrochemically based methods. For cathodic polarization, the electrochemically assisted deposition of components showing a pH-dependent solubility is discussed for a number of systems (calcium phosphate phases, mineralized collagen, chitosan, and chlorhexidine containing coatings) including cell and animal experiments. For anodic polarization, a nucleic acid based modular immobilization system for biologically active molecules is introduced, allowing (i) the simultaneous immobilization of more than one component, (ii) defined release behaviour, and (iii) applicability after sterilization. The system allows a biomaterial surface to be "loaded" immediately before surgery with a mixture of biologically active molecules tailored to a patient's specific needs and will be discussed from basic principles to cell biological tests.

FL-6:IL04 Sol-gel Derived Titania Coatings for Enhanced Bone and Soft Tissue Attachment on Titanium Implants

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The sol-gel derived TiO2 coatings have many potential applications in reconstructive medicine. TiO2 coatings are considered bioactive due to their capacity to induce Ca-P-formation. The sol-gel coatings can be modified in terms of: porosity, adsorption rate and composition. Thus the method facilitates the fabrication of coatings with varying bioactivities. When compared with amorphous titanium, which is predominant structure in c.p titanium, anatase and rutile containing TiO2 coatings allow the adsorption of the physiological fluids and proteins and tissues to come very close or attach on it directly much more likely than on the amorphous structure. Also due the high energy surface and stronger van der Walls bonds the attachment of biomolecules and the adsorption of e.g. proteins such as fibronectin will exponentially increase the adhesion and spreading of cells which facilitate good tissue integration. For example the studies on human gingival fibroblasts have shown that cell attachment on sol-gel derived TiO2 coated substrate is indeed stronger than that on c.p titanium substrate. The purpose of this presentation is to highlight the possibilites of sol-gel derived TiO2 coatings for improving tissue integration on medical implants.

FL-6:L05 Nano-scale Evaluation of Surface Morphology Before and After Environmental Exposure in Vitro of an Advanced Alumina/Zirconia Composite for Arthroplastic Applications

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In view of the imminent release on the Japanese market of hip prostheses made of an advanced alumina/zirconia, we performed morphologic and spectroscopic assessments of their surfaces with high spatial resolution. Femoral heads were characterized to a degree of statistical accuracy in the as-received state and after long-term exposures in vapor-moist environment. Surface and sub-surface screening was made by atomic force microscopy (AFM) and by confocal Raman spectroscopy, respectively. AFM scanning was systematically repeated with nanometer resolution on portions of surface as large as several tens of micrometers, randomly selected on the head surface, while in-depth scanning by the Raman probe allowed non-destructive analysis of phase structure in the sub-surface slab of material. Polymorphic transformation in zirconia was confined to the first few micrometers below the surface and involved no significant increase in surface roughness even after long-term environmental exposure. Surface roughness lied in a range <10 nm after environmental exposures up to 100 h, corresponding to an exposure time in vivo of several human lifetimes (i.e., according to experimentally derived thermal activation energy).

FL-6:L06 Carbon Nanotubes In Vitro and In Vivo Biological Effects

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We study the effect of buckypaper (BP) of Multi-Walled Carbon Nanotubes on cancer and primary cell lines in vitro and in vivo on laboratory rats. BP is an innovative material with interesting physical/ chemical properties that has possible pharmacological and prosthetic employment. Given that precautions need to taken where carbon nanotubes are injected into human body for drug delivery or as contrast agent carrying entities for MRI or as the material of a new prosthesis generation, we assessed the toxicity of BP carbon nanotubes. BP has structural resemblance to asbestos whose toxicity has been linked to cancer. BP decreased proliferation of human colorectal, breast and leukemic cancer cell line in vitro. However, BP had no effect on the proliferation and viability of normal human arterial smooth muscle cells and human dermal fibroblasts, in vitro. In vivo, BP induced a moderate inflammatory reaction but had no mutagenic effects. The animals after the BP implantation showed an inflammatory reaction followed in the next two weeks by the cicatrisation reaction with the organization and the fibrosis of the scar. These results show a low toxicity of BP both in vitro and in vivo.

FL-6:L07 Closure of Oroantral Communications Using Biodegradable Polyurethane Foam

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An oroantral communication (OAC) is an open connection between the oral cavity and the maxillary sinus and is usually caused by extraction of maxillary posterior teeth. Currently, surgical closure of an OAC is the preferred treatment. A safe and simple alternative treatment strategy for the closure of OACs involving a highly porous biodegradable polyurethane (PU) foam has now been designed. This PU polymer is composed of hard urethane segments and soft segments made of D/L lactide/ e-caprolacton with polyethylene glycol. Animal studies have proven its biocompatibility and its ability to fully fragment into body-friendly monomers. Recently, two consecutive clinical pilot studies were implemented to assess the feasibility of the PU foam. In each study, 10 patients with fresh OACs (existing less than 24 hrs) were included. Standardized evaluations were performed after respectively 2 weeks and 8 weeks. In the first clinical study, cylindrically shaped PU foam was used. In the second study a conical shaped foam was used to optimize the retention of the foam in the extraction socket. In the first study, closure with PU foam was achieved in 7/10 patients without further surgical intervention, whereas closure was achieved in 8/10 patients in the second study. Based on these first clinical studies it was concluded that closure of OACs with biodegradable polyurethane foam is feasible and has the potential to spare a large number of patients with OACs an unpleasant surgical procedure.

FL-6:L08 Role of Grain Size Fluctuations on the Environmental Resistance of Alumina-Zirconia Composite in Comparison with Commercially Available Monolithic Zirconia Femoral Heads

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Total hip arthroplasty (THA) represents a very spread and effective surgical procedure. Surgeons and technologists make daily efforts in improving the outcomes of THA, with the ultimate goal of creating a prosthesis that reliably lasts at least as long as a human lifetime. Most recent innovative trends in THA have focused on the improvement of the tribological behavior of hip joints, challenging the achievement of service lifetimes spanning several decades. Such trends have naturally led to an increasing use of ceramic materials and, in the latest trends, of alumina-zirconia composites. The high fracture strength of such ceramic components and the low percentage of their reported fracture incidence are encouraging; however, this assertion involves two assumptions: (i) the ceramic component in its unused state is conspicuously flawless; and, (ii) its microstructure is strictly controlled. In this paper, we will examine the effect of slight fluctuations in the composite microstructure on its environmental response in vitro. A comparison will be carried out with several monolithic zirconia materials presently available on the orthopedic market.

FL-6:L09 In Vivo Hemostatic Effect of Polyurethane Foam Compared to Collagen and Gelatin

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Various topical hemostatic agents are used in the different surgical disciplines. Most of these agents are based on animal derived products like gelatin and collagen. They carry the potential risk of pathogen transmission. A newly developed biodegradable, fully synthetic hemostatic agent based on polyurethane (PU) foam with 55% polyethylene glycol (PEG) would prevent these potential risks. The hemostatic efficacy of this new agent was compared to gelatin and collagen in a human split-mouth model. After extraction of a molar in the maxilla and mandible a PU foam and gelatin or collagen was inserted in the extraction socket for two minutes. Hereafter the agents were removed and stored in EDTA to stop coagulation. Then the concentration of thrombin and fibrinogen in the agents was measured. Twenty-three out of sixty patients have been included so far. No significant differences were seen in the amount of thrombin and fibrinogen in the three different hemostatic agents. These results show that PU combined with 55% PEG as a topical hemostatic agent is promising. After inclusion of all 60 patients final conclusions can be drawn for the potential of PU with 55% PEG as a topical hemostatic agent.

FL-6:L10 **Stoichiometry and Surface Stress Analyses in Advanced Alumina/Zirconia Composites for Hip Arthroplasty Applications**

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A spatially resolved cathodoluminescence (CL) analysis is used as a means for chemical and mechanical analyses of the highly fracture resistant alumina/zirconia composite surface as a function of environmental exposure. This composite material is designed from both chemical and microstructural viewpoints in order to prevent environmental degradation and fracture events in vivo. CL emission proves extremely efficient in concurrently monitoring the concentration of point defects (e.g., oxygen vacancies) and the surface lattice strain in alumina and zirconia phases with a spatial resolution on the nanometer scale. As a result, information about stoichiometry and the micro-mechanical state of the material surface are obtained from the lattices of the constituent phases that enable one to pattern relevant connections to the environmental resistance of oxide-based bioceramics. Systematically monitoring the optical activity of oxygen vacancies in both alumina and zirconia phase reveals the distinct role of lattice strain accumulation on the kinetics of polymorphic transformation. From the presented data an explicit role is evinced for oxygen vacancy formation in the alumina matrix in the complex cascade of mechanochemical events determining the environmental resistance of the composite.

Poster Presentations

FL:P01 **Shell Scaffolds for Bone Regeneration and Repair**

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A fundamental issue for bone tissue regeneration is the design of bioceramic scaffolds, i.e. temporary templates for cell adhesion and proliferation in a 3D architecture. An ideal scaffold should be highly porous and exhibit adequate mechanical properties. In addition, a resistant and at the same time permeable surface is required in order to have manageable samples. The replication method, which involves the production of ceramic foams by coating a polymeric sponge, has been widely employed to realize porous ceramics. However, the production of scaffolds by means of this technique can lead to samples with poor mechanical properties and fragile surfaces. In this work a new protocol to product bioceramic scaffolds is developed. The scaffolds, realized with 45S5 Bioglass®, are obtained combining a modified replication technique with the usual polymer burning-out method. These samples, named shell scaffolds, have an original structure, characterized by an highly porous internal network together with an external resistant surface similar to a shell. This shell, which behaves as an esoskeleton for the scaffold, ensures high permeability and manageability. Here the proposed protocol is discussed, together with an overview on the structure of the realized samples.

FL:P02 **New Nanostructured Chitosan Films for Reduced Bacterial Adhesion**

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Medical device Biofilm is a result of microbial adhesion onto the device surface. Its early formation step is the reversible primary bacteria adhesion on both the in- and outside surfaces. The implant-associated infections, occurs through this Biofilm are serious and resistance to the most of the known antibiotics. A number of techniques were used to avoid the early adhesion of the bacteria. They include the use of coatings, based on polymers with antibacterial properties, such as chitosan. Chitosan is well-known for its biocompatibility and natural antibacterial activity. It is well-recognized that surface topography at the nanoscale has strong effect on bacteria behaviour. Nanoscale topographic structures can reduce the initial attachment of bacteria. This project focuses on the development and characterization of ultrathin antibacterial and anti-adhesive nanostructured films of chitosan nanotubes. The physio-chemical and biological properties of the supported films were examined by scanning probe microscopy (SPM) regarding their morphology, blood serum and bacterial adhesion.

FL:P05 **XRD Studies on Transformation of Calcium-deficient Apatite to Beta and Alfa TCP in Dynamic and Technological Conditions**

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In medical applications of tricalcium phosphate (TCP) ceramics it is significantly important whether the form of Ca3(PO4)2 is β or α (low or high temperature polymorph). The studies of the β→α TCP transformation and formation of mono, bi or threephase CaPs materials βTCP-αTCP-HA play an important role in the biomaterials knowledge. The stability of calcium phosphate ceramics depends on the stoichiometry of the initial powder, kind and amount of impurities, temperature of preparation, the rate of temperature change, the partial pressure of water during heating and cooling and the type of the sample. In our technological practice "dry" or "wet" method of samples preparation also influenced the phase composition of final CaPs products. The present work concerned the phase changes of TCP studied in dynamic way by high temperature XRD and in static way (technological conditions). As an initial powder Ca-deficient apatite was obtained by reaction of Ca(OH)2 and H3PO4 followed by calcination at 800°C. Two samples prepared without or with using water were measured by XRD. The dynamic studies showed that monoclinic αTCP was considerably stable phase after its creation completed at 1200 °C. Different phase composition was obtained in technological conditions.

FL:P06 **Effects of Mg Additives on Properties of Mg-doped Hydroxyapatite Ceramics**

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The mineral phase composition of human bone consists of intricate mixture of crystalline and amorphous carbonated-hydroxyapatite (HA) with small amount of different elements, mainly magnesium (about 0.5wt%). The aim of this work was to determine the effect of Mg on HA structure as well as sinterability, microstructure, mechanical strength, chemical stability and biological properties of Mg-doped hydroxyapatite ceramics. In our studies undoped HA and HA modified with 0.3; 0.6; 0.9; 1.8 wt% of Mg were prepared by wet method. The addition of magnesium to HA structure influenced its thermal decomposition and chemical stability of calcium-phosphate ceramics. The presence of magnesium promoted above 800°C the decomposition of HA to ßTCP and stabilized this secondary phase. Presence of Mg ions beyond certain limit (0.9wt%) resulted in formation of MgO in Mg-HA ceramics. Chemical stability under in vitro conditions for Mg modified HA below 0.9 wt% Mg was similar to the undoped hydroxyapatite. Biological studies showed that the number of cells cultured on the surface of HA samples with 1.8wt% Mg additive was lower than on the pure HA ceramics. The obtained materials were used as targets for calcium-phosphate coatings deposited by pulsed laser deposition technique on the metal substrates.

FL:P10 **New Corrosion-resistant Bactericidal Nitrogen-containing Steels with Increased Strength**

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The new high-strength stainless steels alloyed by copper and nitrogen and possessing high resistance to corrosion by active micro-organisms in carbon-oxidizing, heterotrophic and sulfate-regenerating bacteria mediums are developed. The introducing of small addition of nitrogen (about 0.12%) to the corrosion resistant steel Ñ0.5Cr15Ni5Cu2NMoNbTi results in a decrease of adhesive micro-organisms quantity on a sample surface by 8 times, while increasing of the nickel content to 9% results in their decrease only by 2 times. It is supposed that the effect of nitrogen can be related to formation of biocide substances. The steels can be used in cast and deformed states, they can be non-magnetic or ferromagnetic ones with a controlled magnetic induction due to a different austenite to martensite ratio. High copper (Cu = 2.5-5%)

nitrogen-containing cast steels are in austenitic (non-magnetic) condition. Due to a dendritic segregation, the structure of steel corresponds to a natural composite structure and it is remained on heating to high temperatures. After cold deformation with up to 85% reduction, the steel preserves the austenitic structure, and its hardness attains a level, close to the hardness level of the martensitic structure. The developed corrosion-resistant antimicrobial steels with the increased hardness can be used as a material for the surgical instrument.

FL:P11 **Evaluation of the Apatite Coating on Silicon Nitride Based Ceramics Sintered with RE2O3 Additives (RE = Y, La, Yb)**

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Silicon nitride ceramics have been successfully used as structural ceramics due to their suitable thermo-mechanical properties, such as high density, high thermal shock resistance, chemical stability and corrosion resistance. These characteristics allow the application of such materials in biomedical field, with a bioinert character. However, the deposition of a hydroxyapatite layer on the bioinert substrate promotes the bioactivity of these materials, so that the osteoconductivity can be improved. It is known that the sintering additives alters the microstructure of final sintered materials. Thus, this work aimed to study this influence on the superficial characteristics of Si3N4 materials after apatite coating. Si3N4 samples containing 9wt% additives (alumina and yttria, lantania or ytterbia) were prepared and sintered. Samples were evaluated with regard to density, microstructure and mechanical properties. The coating process was performed by sodium silicate and Simulated Body Fluid immersion. The coating was characterized by DRIFT, XRD and SEM/EDS The results indicate that a layer of hydroxyapatite could be deposited by biomimetic method on Si3N4 samples surface. Moreover, the rare earth used as sintering additive had influence on the characteristics of the coating.

FL:P14 **Osseointegration and Biocompatibility Study of Macroporous Biphasic Calcium Phosphate (BCP) Ceramics Oobtained by Consolidation Using Albumin**

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The potential of porous materials for applications in the medical, engineering and pharmaceutical areas has been widely reported. Several processing techniques have contributed to the progress in research involving porous biomaterials. To this purpose, a globular protein based (i.e. ovalbumin) consolidation approach has been proposed. In the present study, a porous hydroxyapatite: B-tricalcium phosphate - biphasic ceramics (BCP), was processed by consolidation using the protein-action technique. The processed porous ceramic exhibited appropriate pore configuration in terms of size, morphology and distribution. BCP cylindrical samples were implanted in female rabbits tibia to evaluation of the initial biocompatibility and osseointegration for 30 days period. The morphological analyses, optical microscopy and scanning electron microscopy evaluated the osseointegration. A rough surface pattern displayed by the ceramics seemed to have improved cell adhesion and proliferation processes. Furthermore, the open porosity of samples was an essential requirement for a suitable bone-implant osseointegration. In conclusion, this study revealed that the porous matrices obtained, promoted suitable development for bone tissue growth and also properties for osseoconduction and osseointegration.

FL:P17 **Disperse Materials with Adjustable Curie Temperature for Antitumor Hyperthermia**

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Modern clinical hyperthermia trials are based on the superparamagnetic ironoxide (SPIO) nanoparticles and encounter the problem of the thermal inhomogeneity at the mean temperature 43 °C in the target volume. Even slightly higher temperature leads to the wide-spread necrosis of normal tissue while heating underdose yields recurrent tumor growth. The goal of this work is to introduce new materials as an alternative to SPIO-based particles and thus to launch a new platform for highly controllable hyperthermia cancer therapy. We have drawn attention to fine powders (200 nm) of silver doped lanthanum manganite La1-xAgyMnO3+δ (LAMO) with highly controllable Curie temperature in the temperature range 43-47 °C. A spray pyrolysis method was tried to obtain LAMO particles of spherical form. The water suspension of LAMO spherical particles reached the constant temperature 43 °C (during <1min) under the alternative magnetic field of 800 kHz. Thereby particles of LAMO demonstrate the clear thermostatic behavior for a long time what is necessary for cancer hyperthermia. According to the biocompatibility in vivo testing, spray pyrolysis LAMO particles were not lead the death of animals with doses up to 480 mg/kg.

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FL:P21 **Fiber Optic Capillary Microfluidic Sensor for Biotechnological Applications**

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Optical capillaries are used in capillary gas and liquid chromatography, capillary electrophoresis, absorbance spectroscopy, Raman spectroscopy etc. These micro-fluidic methods find applications in biotechnologies, medical diagnostic, drug discovery and environmental sciences. The sensing system we present uses as its sensing element a short section of a fiber optic capillary which is filled with the examined liquid, to which a local thermal stimulus is applied. The liquid samples volume is below 10-8cm3. The multiparametric information detected as a time domain transmitted intensity LED light signal is dependent on the index of refraction, the turbidity, the boiling point, the viscosity and the surface tension of the sample, and is extracted by neural network analysis of dynamic data from two local phase transitions induced by the heating pulse. The application of the system for the analysis of raw milk for the presence of bacteria and for quantitative analysis of bio-fuels is presented.

FL:P23 **Differential Cellular Responses to Superparamagnetic Iron Oxide Nanoparticles in Primary Fibroblast vs. Fibroblastic Cell Line**

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Superparamagnetic iron oxide nanoparticles (SPIONs) offer some attractive possibilities in biomedicine. SPIONs have led to various opportunities such as improving site-specific drug delivery, magnetic resonance imaging contrast enhancement, hyperthermia treatments and so on. In the present study, we synthesized differently surface-modified SPIONs and then investigated differential cellular responses to SPIONs with various functional groups in normal fibroblasts vs. L-929 fibroblastic cell line via evaluating in vitro cytotoxicity and genotoxicity of SPIONs. Fe3O4 SPIONs were synthesized by co-precipitating Fe3+ and Fe2+ with ammonium hydroxide. For conjugation with various functional groups, they were either functionalized by 3-aminopropyltrimethoxysilane and trisodium citrate or coated with thin layer of silica by tetraethoxysilane. The cytotoxicity and genotoxicity of prepared SPIONs to both fibroblastic cells were assessed by MTT and Comet assays, respectively. It was found that SPIONs affected differentially the cell survival and DNA damage in normal fibroblasts vs. fibroblastic cell line.

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FL:P25 **Investigation of Affinity Interactions with Frustrated Total Internal Reflection Method**

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The important aim for biomedical investigations is to extend the possibility of affinity interactions study. In this paper it is point at opportunity of using in U-shaped multimode cylindrical waveguide for investigation of affinity interactions between the proteins and antibodies. The proposed study investigates potential application of a short arched cylindrical optically homogenous waveguide of 0.5 - 5 mm in diameter, which greatly exceeds the diameter of the optical fiber, in capacity of the basis for an optical chemical sensor. Dimensions of the waveguide and radius of the bend are chosen to make the main part of luminous flux be in the mode of frustrated total internal reflection. This allows using the waveguide as a refractometric sensor. Thin Palladium or polystyrene film was formed on side surface of waveguide. The U-shaped waveguide with Palladium ore polystyrene film owns highly sensitive to changes of optical characteristics at interface light-conductor-environment. We studied changes of intensity of input light of waveguide at the precipitation of A protein, anti-specific antibodies of donkey blood, antibodies extracted from rabbit blood on the waveguide surface. The absorption of light passing the U-shaped waveguide during the precipitation protein molecules and their affinity interaction with antibodies was measured. The results give a possibility to define the kinetic constants of interaction process. This fact may be used for dividing proteins mixtures and their analyses.

FL:P26 Novel Polyphthalocyanines in Medical Diagnosis: Development of H2O2 Detection

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The problem of oxidative stress is very important for modern medicine. The concentration of hydrogen peroxide corresponds most closely to level of oxidative stress and shows inflammation availability. The application of peroxidase into biosensors, which catalyze hydrogen peroxide reduction don’t permit to get a stable electrodes, besides saturation of active centres limits capacity of using. In the recent years special interest attracts to phthalocyanine films in regards with their application in sensors. The purpose of this investigation is to find out the possibility their application as sensor material for analysis in solutions. Electrode reactions of the first time synthesized polyphthalocyanines (PPc), containing Cu with different concentrations had been investigated. The PPc films peculiarity is high electric conductivity and demonstration of electrode reactions at potentials convenient for analysis. The PPc films were tested by the method of flow-injection analysis to determine their sensitivity in solutions for H2O2 microconcentrations. The investigations were held on a specially developed semi-automatic flow-injection analyzer “BIO”. The device includes the “wall-jet” flow-through cell with working sensor electrode - PPc film based on the glass-carbon electrode. The results proved that electrodes have stable sensitivity to H2O2 micro concentrations at levels 10-6 M. It allows investigations continuing to optimization of PPc films forming technology for best results.

FL:P27 Preparation and Characterization of Poly(Vinyl Alcohol) Hydrogel Beads as an Injectable Bulking Agent

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Poly(vinyl alcohol) (PVA) hydrogels have been widely utilized for wound dressing, drug carrier and bulking agent (or filler), due to their high water content, rubbery elastic nature, and non-toxicity as well as their associated easy of processing. PVA hydrogels have usually produced by chemical (using crosslinkers) or physical (using freeze-thawing technique) crosslinking of PVA chains. However, the residual toxic crosslinking agents in the hydrogel (chemical crosslinking) or long processing time (physical crosslinking) are considered as practical limitations. In this study, we prepared PVA hydrogel beads using a simple spraying/quenching technique, which does not need any toxic crosslinking agents and does not include time-consuming steps for PVA hydrogel bead formation. The crystallinity and mechanical properties of the prepared PVA hydrogels were characterized. And the preliminary animal study to investigate its potential use as an injectable urethral bulking agent was also conducted.

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FL:P28 In Vitro Evaluation of Pore Size Effect on Chondrogenesis of Adipose-derived Stem Cells Using Pore Size Gradient Scaffold

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It is well recognized that the pore size of polymer scaffolds plays an important role for cell adhesion, proliferation and differentiation: different kinds of cells were shown to have optimal pore size ranges in the scaffolds for effective cell adhesion/proliferation/differentiation. Recently, the scaffold with pore size gradient has been considered as a powerful tool for basic studies, including the investigation of the interactions between cells/tissues and scaffolds with different pore size, as well as the determination of optimum pore size range for stem cell differentiation to a specific cell type. In this study, we fabricated cylindrical PCL scaffolds with gradually increasing pore size ranges by a centrifugation method. Their morphology, pore size, porosity, and mechanical properties were investigated. The in vitro chondrogenic differentiation behavior of adipose-derived stem cells in terms of scaffold pore sizes were also investigated using the pore size gradient scaffold.

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FL:P29 Hyaluronic Acid/Alginate Mixture Gel as a Tissue Adhesion Barrier

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Tissue adhesions are well known post-surgical complications, including patient’s pain, functional obstruction, and difficult re-operative surgery. To solve these problems, various polymer films, nonwoven fabrics, or gels as tissue adhesion barriers have been extensively investigated. In this study, we prepared hyaluronic acid (HA)/mildly crosslinked alginate (ALG) mixture gel to estimate its potential use as an abdominal adhesion barrier gel. HA gel was considered as a promising material as an effective tissue adhesion barrier, due to its biocompatibility and anti-tissue adhesion property. However, its rapid clearance from the applied site is still remained as a critical limitation. We expected that the mildly crosslinked ALG with flow property can provide the residence stability of HA gel in the applied site during the healing period, thus to keep preventing tissue adhesion. The residence stability in the PBS (in vitro) and postsurgical peritoneal adhesion (in vivo) of the HA/ALG mixture gel was compared with HA and ALG gels.

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FL:P31 Preparation of Porous Scaffold from PLGA/Hydroxyapatite Composite Coated with a Biodegradable Triblock Copolymer for Bone Tissue Engineering

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PLGA/HA composite scaffolds were fabricated by freeze-extraction method. Compared with the freeze-drying method, the presented method is time and energy-saving, with less residual solvent. On the other hand, triblock polymer coating on the scaffolds could enhance their biocompatibility. In addition to the presentation of the morphologies of the fabricated scaffolds, preliminary data of HMSC culture on them are as well included in the present work. Cell adhesion to the scaffold was observed after three days staining with DAPI and observation was confirmed with SEM results. Also, microstructure observation with SEM that suggests the formation of about 50 micrometer size porous structure and interconnected porosity so that cell adhesion within this structure is well in depth. Also, to study cell proliferation rate of cells on the scaffold, the number of 10000 of human mesenchymal cells were cultured on the scaffolds and MTT test was performed on them and showed that the absorption of 570 nm cells grown on the scaffold (in comparison with control samples) has not decreased significantly. The results showed that biodegradable PLGA/HA composite scaffolds coated with triblock copolymer could enhance bone regeneration.

FL:P33 Study on Bone Cell Adaptability of TCP/HAp Functionally Graded Porous Beads for Biomaterials Application

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Porous beads of bioactive ceramics such as HAp(hydroxy apatite), TCP(tri-calcium phosphate) are considered to be promising as excellent scaffolds for cultivating bone cells. To realize this type of beads which maintains the function of scaffold with sufficient strength up to growth of new bone and it is expected to be absorbed completely after the growth, α-TCP/ HAp functionally graded porous beads were fabricated. HAp is bioactive material which has both high strength and better tissue-adhesive properties, but that is not readily absorbed by the human body. On the contrary, α-TCP is highly bioabsorbable; it is quickly absorbed by the body, and, therefore, disappears before bone is completely replaced. Fabricated new beads are composed of α-TCP at the center and HAp at the surface, to control the solubility in living body. Bone cell adaptability of these beads were confirmed in vitro and the appropriate method for implantation was indicated.

FL:P37 Study of Chitosan Addition in the PVP/PVAL Polymeric Blend - A System of Controlled Release of Drugs

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The main objective of this project is the study of the addition of chitosan in the polymeric blend of PVP/PVAL to get a biocompatible hydrogel that can be used as a system of controlled release of drugs. The polymeric blend usage is a recent development that expanded the applications of the polymers, due to the improvement of the properties of a single polymer even if they appear to be conflicting. PVP and PVAL were chosen because they present the main required characteristics to the formation of a hydrogel, such as water absorption and crosslinked formation. The flexibility of the PVP was added with the mechanical resistance of the PVAL. The chitosan biological active polymer molecules addition is to increment the interaction between the hydrogel and the organism. With the concentrations of PVP and PVAL defined, solutions with different levels of chitosan were made to check which presented better properties through different assays, such as mechanical, viscosity and absorption in infrared.

FL:P38 Evaluation of the Effects of Sustained Delivery Demineralized Bone Matrix (DBM) and Osteogenic Protein-1 (OP-1) on Fracture Healing, Osteoclast Activation in a Rat Femur Model

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Fracture healing involves growth factors and cytokines and attempts at supplementing the natural process are being investigated. The relevance and clinical impact of this research is the potential to develop a sustained drug delivery system for osteoinductive agents which could provide a more efficient and cost-effective modality for management of open fractures with associated bone loss. It was hypothesized in this dissertation that: (1) Sustained release of osteogenic protein-1 (OP-1) or demineralized bone matrix (DBM) will induce healing faster than in sham animals and return to fracture strengths similar to control and greater than bones from sham animals; (2) Sustained release of OP-1 or DBM will induce bone formation as evidenced by histopathological staining, but only DBM will induce bone remodeling equivalent to control bone; (3) With immunohistochemical staining for inflammatory markers, sustained release delivery of DBM will demonstrate increased activity longer than OP-1 due to activation of osteoclasts as a part of bone remodeling; and (4) Sustained release of OP-1 or DBM will not induce untoward side effects in vital or reproductive organs. Ninety-six rats were divided into four equal groups (control, sham, DBM, and OP-1). The treatment groups underwent a surgical drill defect in the femur and were harvested at two, four, six, and eight weeks for testing. Biomechanical, histopathological, immunohistochemical evaluations were conducted by following standard laboratory protocols. Data demonstrated biomechanical results similar to previous studies with superiority of control bones at two, four, and six weeks and no significant differences at eight weeks. Histopathological sections showed progressive new bone formation in the DBM and OP-1 groups with increased cortical thickness with OP-1 and persistence of the defect site in the sham group. Treatment with OP-1 does not appear to provide the activation signal for osteoclasts based on immunohistochemical results. In conclusion, data obtained from this study provided significant information in bone research. The present research offers the possibility of treatment with DBM which may be capable of inducing formation of bone equivalent in strength and function to native bone with the presence of osteoclast activation and remodeling not seen with OP-1 treatment.

FL:P39 In Vitro Study of Electrospun Nanofibrous Epigallocatechin Gallate-eluting Anti-adhesion Barrier Composed of Biodegradable Polymer

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Post-operative adhesions are common and serious complications following surgery, as they can involve severe abdominal and pelvic pain, infertility and bowel obstruction. Several agents, such as fibrinolytic agents, anticoagulants, anti-inflammatory agents and antibiotics, have been employed. However, these agents alone did not prevent adhesion formation effectively because of their short-term residence. (-)-epigallocatechin-3-O-gallate (EGCG), a main polyphenolic component of green tea, is well-known for a wide range of pharmacological activities, including antioxidant, anti-proliferative, anti-inflammatory and anti-thrombotic effects. In this study, nanofibrous poly(lactic-co-glycolic acid, PLGA) meshes eluting EGCG were prepared via electrospinning and then characterized to evaluate their application potential to an anti-adhesion barrier. The amounts of EGCG released from the EGCG-eluting PLGA meshes can be controlled by composition rate on electrospun meshes. Proliferation of L-929 fibroblastic cells was inhibited by eluted EGCG. Electrospun nanofibrous EGCG-eluting PLGA meshes might be effectively used as an anti-adhesion barrier.

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FL:P40 Development of Pseudoboehmites for Nanosystems to Release Acyclovir

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The production of confined or adsorbed drugs in inorganic matrix has been increasing in areas like material science and pharmaceutical due to the possibility of the production of nanoadsorbed or encapsulated molecules with new properties like chemical stability, enhancing solubility and controlled release, what implies in new applications of materials. The present work, nanocomposite of acyclovir and a fine ceramic material, pseudoboehmite, was prepared. Pseudoboehmite is based on a monohydroxide aluminum oxide produced from a synthetic route using ammonium hydroxide and aluminum chloride as precursors in the sol-gel process. These systems had been characterized by the following techniques: MEV, TG/DSC, FTIR and UV-vis. The exposition of the drug to the pseudoboehmite at the dissolution equipment was at 37 °C and 100rpm for 30 minutes. With the purpose to observe the interaction of the drug with the adsorbent, it was obtained the concentration of the drug in the solution, before and after the adsorption, using the UV-vis spectroscopy technique. The acyclovir has increased its solubility in at HCl 0,1M, when the weight ratio of Pseudoboehmite: Acyclovir 1:1 was used.

FL:P42 An Efficient Low-pH Range Sensitive Artificial Muscle for Future Active Implantable Systems

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A chemo-mechanical muscle can be founded on the use of a shape changing external enveloppe inside which is placed a chemical agent reacting with a peculiar control input. In a previous work we have shown the feasability of using a McKibben-type braided structure filled with ion-exchange resins to design an original “pH muscle” whose produced force shows similarities with skeletal muscle behaviour(Sensors&Acuators A-phys. 150(1),124-130,2009). More recently, we have shown the possibility to control our prototype by ionic strength variations; this makes way for controlling the pH-muscle with low pH-range buffer solutions (European Conf. on Polymers, Graz (Austria), July 2009). It is now possible to control, in a pH-range of [4.5-8], a 10 cm long and 1 cm diameter artificial muscle generating a maximum force of about 80 N in some minutes. In this paper we analyse how to transform our actual prototype, whose reversible functioning needs distinct basic and buffer solutions tanks, into a future “muscle implant” for incontinence treatment. The proposed approach is based on a closed-cycle circulation through the muscle - generated by micro-pump - of a solution whose ionic strength change is produced by bio-compatible micro-organisms. The case of yeasts is more particularly studied.

FL:P43 Osseointegration of Macroporous Titanium Alloy Obtained by PM with Addition of Gelatin

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Studies on titanium and its alloys that are commonly used as biomaterials, often address bone-implant interface related problems. Improvements in bone-implant interface features determine the quality, bone repair time and thereby, clinical success of the implant. The goal of this study was to evaluate in rats, osseointegration of macroporous implants produced by the powder metallurgy (PM) method, and with controlled addition of gelatin. As a control group, samples of commercially pure titanium (cpTi) and Ti-13Nb-13Zr alloy obtained by the PM process were used. To obtain porous samples, at the most, 15 wt% of gelatin was added to the metal powders. The samples were heat treated in a vacuum oven and sintered at 1150ºC. Osseointegration evaluation was performed in male Wistar rats, for 28 days. Morphological studies, optical microscopy and scanning electron microscopy (SEM) were carried out to qualitatively evaluate osseointegration. In this study, the PM process modified by addition of gelatin enabled porous metallic implants to be obtained. Pore sizes obtained by this technique allowed sufficient nourishment for cell survival. This could be attributed to the highly interconnected network of pores and channels enhancing the osseointegration and osseoconduction features of the porous alloy.

HOT POSTERS

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FA:HP10 Refractoriness, Microstructures and High Temperature Oxidation of TaC-reinforced Iron-based Alloys Protected by Chromium-rich Coatings

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Alloys based on iron and containing several tens percents of chromium are able to display very high solidus temperatures. Eutectic tantalum carbides which appear at the end of solidification can bring them improvements in mechanical properties at high temperature, without significant decrease of their solidus temperature which can remain higher than 1400°C. Such alloys are possible candidates for several high temperature processes and for example for the hottest parts in energy power plants. Unfortunately these alloys are not sufficiently resistant against oxidation, notably when temperature is higher than 1100°C. The aim of this work is to realize chromium-rich coatings by pack-cementation on several alloys synthesized by high frequency induction foundry and to study the behavior of the coated alloys at high temperature. The interdiffusion phenomena between coating and bulk alloy are observed by exposures to high temperature in inert atmosphere followed by measurements of concentrations profiles using microprobe. Their oxidation behavior at high temperature has been characterized by thermogravimetry tests and post-mortem metallographic characterization. The results show that coating the alloys with chromium clearly enhances their resistance to high temperature oxidation.

FB:HP18 Fabrication of Thin and Thick Films of Photocatalytic Titania

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Several methods for the production of thin and thick films of photocatalytic titania have been trialled. These include: electrophoretic deposition, anodisation, gel oxidation, sol-gel dip coating, spin coating, aerosol spray pyrolysis, ultrasonic spray pyrolysis, and aerosol spraying. Some of these methods, such as the pyrolysis-based procedures, are capable of producing fully dense films at temperatures as low as 300 °-400 °C, thereby allowing manipulation of the anatase → rutile phase transformation.

FB:HP19 Lithium Fast-Ionic Conduction in Lithium Borohydride and its Derivatives

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Lithium ion conductivity of Li(BH4) jumps by three orders of magnitude at approximately 390 K due to its structural transition from the orthorhombic room-temperature (RT) phase to the hexagonal high-temperature (HT) phase. We have recently demonstrated the enhanced conductivities in Li(BH4)-LiX (X = Cl, Br and I) and Li(BH4)-Li(NH2). In Li(BH4)-LiI, for example, the HT phase of Li(BH4) can be stabilized even at RT by forming the solid-solutions in the wide composition range, resulting in the lithium ion conductivity (4 × 10-5 S/cm) more than 3 orders of magnitude higher than that of pure LiBH4 (2 × 10-8 S/cm) at RT. Also in the case of Li(BH4)-Li(NH2), two stoichiometric compounds Li2(BH4)(NH2) and Li4(BH4)(NH2)3, show fast-ion conductivities of 1 × 10-4 S/cm at RT due to being provided new occupation sites for lithium ions.

FB:HP20 Nanonickel Catalyst for Kinetic Destabilization of LiAlH4 (lithium alanate) for Facile Discharge of Hydrogen

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Microstructure and catalytic properties of nanometric Ni (nanoNi) produced by a carbonyl nickel CVD process was investigated in respect to kinetic destabilization of LiAlH4 for hydrogen release in a power-compensation differential scanning calorimeter. The morphology of the nanoNi is filamentary and exhibits nanocrystals with low density of lattice defects. For LiAlH4 milled with 5 wt% nanoNi for 1h, hydrogen was released in three endothermic events at: 100-170 °C (peak @ 160 °C), 200-260 °C (peak @ 227 °C), 420-480 °C (peak@ 443 °C). The first peak corresponds to the discharge of 5.3 wt% H2 @ 1bar in the IGA gravimetric hydrogen analyzer. None of the three thermal events can be attributed to melting. Through lowering the energy of activation for dissociation of LiAlH4 molecules into either Li3AlH6 or LiH and Al, desorption of H2 is facilitated so it precede melting that occurs at 170 °C in non-catalyzed alanate. Finally, an observation should be made in respect to often reported yet poorly understood exotherms at ca. 150 °C and 200 °C that are absent in nanoNi-catalyzed LiAlH4: the former is related to occurrence of a mixed hydride-hydrate phase, and the latter to solidification of the alanate melt.

FB:HP21 The Catalytic Effect of Simple Hydrides on the Production of H2 from CH4 and H2O

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Producing H2 from water and methane is a very challenging task. Recent studies showed that the formation of a X-H(δ-)--(δ+)H-Y bridge facilitates the formation of H2. From that viewpoint we used quantum chemical calculations (MP2 and CCSD(T) to construct the potential energy surfaces describing the reactions of methane and water with second and third row hydrides (XnHm). The reaction of water with dialane is found to be greatly facilitated in which the hydride reduces the energy barrier for hydrogen production, creating an almost spontaneous hydrogen release process. In the reaction of methane with XnH¬¬m, we observe that LiH and BH3 yield the best catalytic effects for the production of H2 from methane. Calculated results suggest that simple hydrides can be used as efficient catalysts for H2 production.

FC:HP17 Microstructural Engineering of Apatite Membranes to Enhance Proton Conductivity

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At elevated temperatures, it has been shown that protons are quite mobile along the c-axis of apatite crystals. However, proton mobility in traditional sintered apatite ceramics is limited by grain boundary resistance. Here we report an approach to significantly enhance proton transport through apatite membranes by eliminating grain boundaries and aligning the c-axes of crystal domains through the membrane thickness. A novel multistage synthesis is used to achieve the desired membrane structure. First, apatite seed crystals are deposited onto a substrate electrochemically. Next, hydrothermal growth onto the seed crystals is carried out under conditions that promote c-axis growth normal to the substrate. Finally, a second hydrothermal growth step is carried out under conditions that promote a-axis growth and the formation of a fully dense film. By engineering the membrane micro-structure and composition, we have been able to demonstrate more than four orders of magnitude enhancement in measured proton conductivity when compared to traditional sintered apatite ceramics. The resulting membranes are promising for application in intermediate temperature fuel cells and other electrochemical devices.

FC:HP18 A Novel Anode Based on Ni-Doped Perovskite for Direct Alcohol Solid Oxide Fuel Cells

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Solid oxide fuel cells (SOFCs) are a remarkable alternative for power generation since chemical energy is directly converted into electric power. This allows to achieve higher efficiencies than conventional power generation systems. The solid oxide fuel cells technology has reached a sufficient level of maturity to address problems connected to the remote and distributed generation of electric power. Currently, SOFCs are the optimal choice for the market of stationary power systems, including stand-alone power generation and integrated combined heat and power (CHP) designs and in general for off-grid applications (0.5 - 50 kWel). Evidence of this demand is that the majority of SOFC units installed over the world are being used for domestic power supply, industrial applications requiring uninterrupted power supply (UPS) and military applications or emergency conditions. Practical Solid Oxide

Fuel Cells are fed with natural gas as fuel (internal or external reforming) because of its present availability. Therefore, the choice of liquid fuels is strategic to achieve high energy density as well as to allow a reduction of the size, complexity, and cost of the system. This work concerns with an investigation of a novel Ni-doped perovskite anode resistant towards coke formation under non humidified conditions. This catalyst can directly oxidize methanol instead of hydrogen and methane in an IT-SOFC. The anode catalysts consists of a 10% wt Ni doped $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ (LSFCO) combined to a ceria-based electrolyte. An evaluation of the amount and properties of Ni surface species was carried out to determine their influence on the reaction rate.

FE:HP10 High-Temperature Transport Properties of Indium Filled Cobalt-antimonide Based Skutterudites Processed via Ball-Milling and Subsequent Current Assisted Short-term Sintering

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Skutterudites such as cobalt-antimonides have been widely studied as a promising thermoelectric (TE) material at intermediate temperatures. High thermoelectric figure of merit (ZT) in this material system can be achieved by filling interstitial voids with guest atoms. One of the best improvements in ZT is reported when indium (In) is used as a filler atom. Another approach to lower the lattice thermal conductivity is given by nanostructuring, which leads to increased phonon scattering. The approach in this study is based on planetary ball milling, which allows for grain sizes on the nanometer scale. In favor to confine grain growth, subsequent compaction is carried out by a current assisted short-term sintering system, which can greatly reduce process time in comparison to conventional hot pressing. Phase homogeneity of bulk material has been probed by X-ray diffraction as well as by energy dispersive X-ray analysis. Electrical conductivity, Seebeck coefficient, thermal conductivity has been analyzed in the temperature range from 300 K to 700 K. The functional homogeneity of the samples was evaluated using a Potential-Seebeck Microprobe (PSM). Based on these results, effects evolving from the combination of In filling and nanostructuring on the TE properties will be discussed.

FE:HP11 Thermoelectric Properties of Bi-Sb 22 at% Alloy after Multiple Roll Bonding

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The Multiple Roll Bonding (MRB) process was applied to a water quenched Bi-Sb 22at% alloy. The starting microstructure was dendritic with primary Sb-rich arms up to 50µm in diameter. The plastic strain produced through the mechanical processing of the material caused dendritic arms to elongate in the rolling direction and to flatten in the transverse one. As a result of different starting size and orientation, the dendritic arms were transformed into Sb-rich inclusions of various shapes and dimensions at the end of the MRB process. In particular, inclusions with transverse size down to 20nm were observed. After 3 MRB cycles, an overall area reduction ratio of 4x103 was achieved. Due to the relatively low process temperature, a relevant fraction of dendrites was preserved. Thermoelectric properties were measured using a Quantum Design PPMS (Thermal Ttransport Option). The results displayed a reduction of a factor 2 in the thermal conductivity of the roll bonded sample with respect to the starting material. Seebeck coefficient was unaffected by the mechanical processing, while electrical resistivity was increased, overcoming the factor 2 below 125K. The figure of merit, ZT, of MRB sample was improved for temperatures above 150K, reaching a maximum value of 0.25 between 175 and 275K.

FE:HP12 Synthesis and Characterization of Thermoelectric Materials for High Temperature Applications

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The possibility to convert waste heat into electricity, such as in combustion devices, is attracting great attention on thermoelectric materials. With this view, high temperature materials are necessary to increase the thermoelectric conversion efficiency, which is proportional to Carnot efficiency. Doped Mg2Si1-xSnx and heavily doped SrTiO3 are very attractive thermoelectric materials for intermediate to high temperature applications, presenting high ZT values, low cost, light weight and low toxicity of constituents. This work reports the thermoelectric pellet production of several Mg2Si-Mg2Sn solid solutions by mechanical alloying of pure metallic powders and hot pressing sintering. Y and Nb doped SrTiO3 pellets were produced via solid state reaction and were sinterized in reducing atmosphere. All samples were characterized by FE-SEM, EDS and XRD analyses. Moreover, the thermopower and the electrical conductivity of the samples are presented. Thermogravimetrical analyses were carried out in order to evaluate the magnesium silicide stability in function of temperature in air. With the aim of avoiding the degradation of Mg2Si1-xSnx pellets, different approaches were evaluated, as the coating with protective thin films obtained by sol-gel or magnetron sputtering deposition.

FE:HP13 Highly Scalable Nanostructured Bulk Chalcogenides with Enhanced ZT and Novel Thermoelectric Metrology using Thermal Microprobe and Transient Harman Techniques

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We present a novel class of highly scalable nanostructured bulk chalcogenides and new characterization techniques for thermoelectric materials. Un-optimized, single-component bulk assemblies of Bi_2Te_3 and Sb_2Te_3 single crystal nanoplates show respectively 25% and 60% enhancement in the room temperature thermoelectric figure of merit (ZT) compared with individual bulk counterparts. Our bulk n-type nanostructured Bi_2Te_3 yields a room temperature ZT>1 and lattice thermal conductivity values as low as 0.3-0.5 W/mK without alloying. A scanning thermal microprobe technique for simultaneous characterization of the Seebeck coefficient S and thermal conductivity k with microscale spatial resolution was applied to both thin films and nanostructured bulk samples, and the measured properties are in excellent agreement with the results measured by independent techniques. A Harman method under non-ideal contact and boundary conditions employs bipolar experiments under a wide range of currents and a comprehensive thermoelectric model that takes into account heat loses and electrode contact resistance effects to simultaneously determine k, S, electrical conductivity of the sample, and the electrical and thermal contact resistances with the electrodes.

FF:HP08 Some Materials Aspects of Development and Manufacturing of the Multi-Layer ITER First Wall

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The design of the multi-layer ITER first wall (FW) includes the beryllium armour tiles joined to water-cooled CuCrZr heat sink which is in turn joined to support plate made from stainless steel (SS). Aiming to meet increased heat loads (up to 5 MW/m2 instead of previous 0.5 MW/m2) expected in some areas of the FW (start up limiter, second X-point zone, etc.) an alternative FW hypervapotron (HP) heat exhaust design was proposed. Two joining technologies of CuCrZr to SS: hot isostatic pressure (HIP) and explosion welding were intensively studied as a possible way to manufacture the top part of FW water-cooled structure. Reducing the manufacturing cost is one of the important tasks during the FW series production. With that aim the modified HIP of forming of FW water cooled channels which uses quartz insertions followed by simplified sealing of assembly (without technological outer container) was experimentally checked. Attempt of improving the strength of CuCrZr/SS joint during explosion bonding (by multi-shape pre-grooving of SS plate) is also presented. Paper presents the main results of wide-ranging investigations of mechanical properties and vacuum tightness of CuCrZr/SS joint produced by modified HIP and improved explosion welding.

FF-10:HP07 Radiation hazard of HLW incorporated in glass

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High level wastes (HLW) with an average specific activity of 140 Ci/kg on 90Sr+137Cs were being incorporated in sodium aluminophosphate glass at PA “Mayak” for ~20 years. “The lowest significant specific activity (LSSA)” value will be reached in about 750 years. In Russian Federation any waste is not considered as radioactive if its radionuclide specific activity is less than the LSSA. But actual HLW except Cs and Sr contains different radionuclides as well. Here we consider only long-lived fission products such as 93Zr, 135Cs etc. It is possible to optimize HLW loading in glass so that the specific activity of the radionuclides would be less than the LSSA. However the LSSA is not good enough to estimate potential radiation hazard of conditioned HLW. A new method based on the dose coefficients of radionuclides is discussed.

FF-10:HP08 Study of New Filter Properties for Cs-137 Vapour Capture at High Temperature

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Vitrification of radioactive wastes as well as high temperature synthesis of glass and ceramics for ionizing radiation sources, containing Cs-137, is accompanied by discharge of its vapours. The off-gas contaminated by Cs-137 must be cleaned up using different trapping systems. Earlier it was shown that porous inorganic materials with high content of silica- alumina amorphous phase heated up to 750-1000 °C could be used for effective capturing of Cs-137 vapours. Due to interaction of cesium volatile forms with that amorphous phase formation of chemically durable pollucite-like compound (CsAlSi2O6) was detected[1]. Effectiveness of such filter depends on their total porosity, porous structure and aerodynamic resistance to off-gas flow. To determine aerodynamic resistance of the filters, a test bench was designed and built. It was shown that the aerodynamic resistance of the filter based on porous chamotte was significantly lower than that of the filter based on fly ash microspheres. Thermal treatment at 1400-1500 °C made it possible to increase mechanical strength of the filter based on porous chamotte by factors of 1.5- 3.4 without any significant changes of other characteristics that exceeded similar parameters for the filter based on fly ash microspheres.

[1] A.S. Aloy and A.V. Strelnikov, (2009) "Porous Alumosilicates as a Filter for High-Temperature Trapping of Cesium-137 Vapour", Mater. Res. Soc. Proc. Vol. 1124, pp.219-224.

FG:HP29 **Photocurrent Generation by Novel KrF-laser-synthesised-SWCNTs/Silicon Hybrid Planar Structures Intended for Photovoltaic Applications**

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We report on the UV-laser ablation synthesis of single wall carbon nanotubes (SWCNTs), their characterizations and subsequent use for photocurrent generation over all the 300-900 nm spectral range. The SWCNTs were synthesized by ablating a Co/Ni catalyst loaded graphite target with a pulsed KrF laser (248 nm, 20 ns) under appropriate growth conditions. A furnace temperature (Tf) of 1100 C was found to yield high quality SWCNTs with a very narrow diameter distribution (around 1.2 nm). We will highlight, in particular, the effect of two main growth parameters, namely catalyst content and furnace temperature, on the structural characteristics of the synthesised carbon nanostructures. Thus, the catalyst content is shown to play a key role in obtaining SWCNTs versus fullerene nanostructures. On the other hand, the increase of Tf (from 900 to 1200 C), permits to control the SWCNTs diameter (from 0.8 to 1.4nm). By integrating the purified SWCNTs into photovoltaic (PV) SWCNTs/n-Si hybrid devices, we were able to demonstrate their ability to generate significant photocurrent all over the 300-900 nm range with a particularly high efficiency near ~450 nm. The results on the quantum efficiency and I-V behaviours of these novel SWCNTs/n-Si hybrid devices will be presented and discussed.

FG:HP30 **Non-radiative Energy Transfer from Nanocrystal Quantum Dots to Adjacent Nanowire Conducting Channels Based Photovoltaic Energy Conversion: A New Solar Cell Paradigm**

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We present the results of photovoltaic solar energy conversion employing our recently proposed[1] new paradigm of nonradiative energy transfer (NRET) from the photon absorbing inorganic quantum dots (QDs) to adjacent high charge (electron and hole) carrier mobility inorganic transport channels for collection at the electrodes. This solar energy conversion paradigm may provide a viable trade-off with the bottlenecks of charge carrier generation and/or transport faced by excitonic solar cells given its following advantageous features: (1) high absorption efficiency enabled by QDs, (2) spontaneous exciton breakup at room tempereature in the inorganic channels where typical exciton binding energy is ~10meV, (3) efficient carrier transport in inorganic channels with high mobility (~100-1000 cm2/Vsec). Time-resolved photocurrent in silicon nanowire transport channels induced by NRET from the photon absorbing layer of QDs in proximal contact will be presented. Current-voltage characteristics of QD absorber NRET induced current in silicon p-n junction will be presented. These first results suggest that this new paradigm holds promise as an alternate approach for exploration. The optimal design of the NRET based solar cell architecture and the achievable range of conversion efficiency will be discussed.

[1] S. Lu., A. Madhukar, "Nonradiative Resonant Excitation Transfer from Nanocrystal Quantum Dots to Adjacent Quantum Channels," Nano Lett. 7, 3443-3451 (2007).

FG:HP31 **Tuning of Energy Levels of Organic Dyes for Dye-sensitized Solar Cells by Fluorine Group Substitution**

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Dye-sensitized solar cells have been subject of intensive research due to their potential for low production costs. Suitable energy levels of the HOMO and LUMO of photosensitizer are required to match the redox couple potential and the conduction band edge level of the semiconductor. In this paper, we report the effect of fluorine substitution to decrease the energy levels of the HOMO and LUMO by its electronegativity with small effects on the distribution of the charge densities of base structure. Fluorine has the largest electronegativity of all the elements and relatively small atomic radius makes it have some interesting bonding characteristics. The HOMO and LUMO energy levels were calculated by density functional theory (DFT) in the ab-initio calculation using Gaussian03, Gaussian Inc. We found that the HOMO and LUMO energy levels shift to lower with increasing the number of substitution of fluorine group. The energy levels of synthesized dyes were also experimentally estimated from cyclic voltammetry analyses. The HOMO and LUMO levels became lower by increasing the number of fluorine group. Also the position of fluorine group was also effective to control the energy levels. These results were good agreement with those of the calculations.

FG:HP32 **Nanowire Photodetectors and Photovoltaics**

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The use of nanowires and nanowire structures as photodetectors and photovoltaics is an emerging research topic. Different mechanisms showing advantages of nanowires over conventional thin film technologies have been identified, including efficient radial charge separation, large longitudinal carrier mobility, short carrier transit times, and enhanced light absorption. Several examples from recent experimental results obtained in our groups will be presented, including single ZnO and Si nanowire phototransistors with high photoconductive gain [Nano Lett. 7, 1003 (2007); Appl. Phys. Lett. 93, 121110 (2008)], vertical Si nanowire array photodetectors [J. Nanosci. Nanotechnol. 10, 1430 (2010)], and vertical InAs nanowires grown on Si substrates for broadband photovoltaics [Nano Lett. 9, 2926 (2009)]. An outlook on promising device architectures to be explored in the near future will also be given.

FH:HP05 **A CPV System Integrated into a Greenhouse Based on NIR Reflecting Lamellae: Optimizing of Optics**

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In this paper the results of the optimization process of the optics for a lamellae greenhouse for Dutch greenhouse horticulture are presented. The optimization process is based on a maximal total annual electricity production and is done with a ray tracing model and actual radiation data. This model is developed by Wageningen UR Greenhouse Horticulture and is especially suitable for simulations of large (infinite) objects like greenhouses. Simulations were made for flat lamellae and individually concentrating trough-shaped lamellae. Using concentrating lamellae the PV-cell area can be limited. Results show that the optimization of the lamellae greenhouse can be seen from a theoretical and a practical point of view. Theoretically, for the concept investigated the number of lamellae must be high (>100) and focus with a generic focal length of 3.5 m and glazing bars must be avoided. Then the maximal annual electricity output can be over 26 kWh/m^2. In practice, mechanical restrictions, plant conditions and costs will determine the implementation. The electricity output in a practical situation is to be expected not more then 50% from the theoretical value, given the commercial available NIR-filters and limited mechanical accuracy.

FI:HP18 **Effects of the Deposition Parameters on the Structural Properties of Tungsten Oxide Thin Films Deposited by HFCVD for Use in Hybrid Organic/Inorganic Optoelectronic Devices**

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The structural properties of tungsten oxide thin films with thicknesses between 5-10 nm, grown by Hot Filament Chemical Vapour Deposition (HFCVD) were investigated. These films are to be used as conducting electrodes in advanced hybrid organic-inorganic optoelectronic devices and the optimization of the structural properties in terms of crystallinity and stability are crucial. The films were grown in a specially designed horizontal geometry CVD chamber, and characterised for their structure by XRD, AFM, SEM and IR spectroscopy. The results of the structural characterization revealed the behaviour of the films crystallinity as a function of the substrate temperature, while post thermal annealing and variations of the concentrations of the O2 and H2 gases introduced inside the growth chamber allowed further investigation on the relation between film structure and growth conditions. The films with the higher crystallinity were obtained for substrate temperatures of 250 °C, with intermediate cases observed for the temperature range of 25-140 °C.

FI:HP19 **Short Channel Characteristics of Gallium-Indium-Zinc-Oxide Thin Film Transistors for Semiconductor Applications**

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Amorphous Gallium-Indium-Zinc-Oxide (a-GIZO) thin film transistors with a short channel of 180 nm were successfully fabricated with dual high-k gate dielectric and the trapezoidal active channel. High-κ gate dielectric affords high capacitance allowing efficient charge injection into channels with acceptably low leakage current. The tri-channel transistor offers improvement in short channel performance because the enlargement of gate width provides an additional benefit to improve transistor electrostatics with gate length scaling. For low parasitic capacitance and good scalability, self-aligned top gate structure was employed. A fabricated 180-nm a-GIZO TFT with 5-nm equivalent oxide thickness (50Å-Al2O3/25Å-SiO2) was achieved with the drive current of 100 uA/um, a mobility of 18 cm2/Vs, a sub-threshold slope as low as 70 mV/dec., a negligible drain induced barrier lowering (DIBL) of 20 mV/V, drain source on-to-off current ratio up to 10e6, and a positive threshold voltage of 0.6 V. These promising results indicate that the a-GIZO thin film transistors could be a candidate for selection transistors in three-dimensional cross point stacking memory and can be applicable to numerous semiconductor devices and products.

FI:HP20 **Effects of Dopants on the Structural and Opto-electrical Properties of Indium Tin Oxide Films Deposited by DC Magnetron Sputtering**

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Transparent conductive oxide (TCO) films have been widely used as transparent electrodes for various applications such as smart windows, flat panel display (FPD), touch panel, light-emitting diodes, optical wave guides, and solar cells. It is well known that the TCO films require the properties of wide band gap (>3.0eV), high conductivity, and high transmittance (>80%) in the visible range. Current applications of the TCO films emphasize minimizing resistivity. In general, the characteristics of indium tin oxide (ITO) depend on its oxidation state and the content of impurities. The carrier concentration may also be modified by the dopant activation state because a donor atom can substitute the lattice site producing more than one free electron to increase conductivity. Ti or Ce also can be a donor because the indium is replaced by Ti or Ce in the In2O3-matrix ITO film, which releases one free electron contributing the electrical conductivity. In this work, ITO, ITO:Ce, and ITO:Ti films were deposited on corning glass substrates by DC magnetron sputtering using ITO, CeO2-doped ITO, and TiO2-doped ITO targets, respectively, at room temperature. Effects of Ce and Ti dopants on the structural and opto-electrical properties of the ITO films were investigated.

FJ:HP12 **Nonpolar GaN Substrates: Optical Properties and Spatial Distribution of Extended and Point Defects**

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GaN substrates with nonpolar surfaces open the way for epitaxial growth of high-quality quantum well structures free of polarization-induced electric field. Such structures are expected to be the ultimate solution for the problem with low quantum efficiency in III-nitride based emitters in the green spectral region. We report on structural, electrical and optical properties of a- and m-plane substrates sliced from thick GaN boules grown along the GaN c-axis by HVPE. Nominally undoped, Si- and O-doped, and Fe-doped substrates are examined. All substrates are epi-ready polished and have thickness 400 um and size 8x10 mm. The lattice parameters of the substrates are studied by high-resolution x-ray diffraction and reciprocal space mapping in order to inspect the impact of doping on the residual strain. The dislocation density is evaluated from cathodoluminescence images, while the intrinsic and extrinsic point defects are assessed by monitoring their characteristic optical signatures in photoluminescence spectra. The main emphasis of our study is the spatial distribution of the defects. A variation along the c-axis found for both the threading dislocation density and impuritiy/dopant incorporation is discussed in terms of the peculiarities of the HVPE growth of thick GaN boules.

FJ:HP13 **Novel Phases in the System Li-M-Si-N and their Photoluminescence Properties when Activated by Dopants**

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Nowadays, alkaline-earth nitridosilicates and oxonitridosilicates are of high interest as host lattices for rare-earth doped luminescent materials in phosphor-converted LEDs[1, 2]. New materials having these useful properties are a great challenge. Here we report on the quest for novel luminescent nitridosilicates containing also Li. Former reported compositions in the Li-Si-N[3] system we have modified by adding additional M cations (Li-M-Si-N), and novel phases were obtained. Structural characterization of these phases has been performed using X-ray powder diffraction and solid-state 7Li, 6Li and 29Si MAS NMR. Our preliminary results indicate that the above mentioned phases doped with various activator ions show interesting luminescence properties.

[1]Y.Q. Li, J.E.J. van Steen, J.W.H. van Krevel, G. Botty, A.C.A. Delsing, F.J. DiSalvo, G. de With, H.T. Hintzen, J. Alloys Comp. 417 (2006) 273; [2]R.J. Xie, N. Hirosaki, Sci. Technol. Adv. Mater. 8 (2007) 588; [3]H. Yamane, S. Kikkawa, M. Koizumi, Solid St. Ionics 25 (1987) 183.

FM:HP03 **AFM-patterned 2-D Thin-film Polymer Photonic Crystal Analyzed by Polarimetric Scatterometry**

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An atomic force microscope (AFM) was used to generate a 2-D square array of sub-wavelength surface features from a single material at a scale large enough to permit optical characterization. A diamond nano-indentation AFM probe was used to produce a 325-µm by 200-µm array of indentations in a 120-nm thick polystyrene film deposited on silicon. Indentation spacing of 400 nm produced well-defined surface features with a maximum height of 140 nm. The full-size array was achieved by tiling together single arrays, limited in size by the AFM scanner range, through the use of the AFM's translation stage. A polarimetric scatterometer was then used to measure in-plane bidirectional reflectance distribution at incident angles ranging from 0-80 degrees. Two wavelengths were investigated, 633 and 544 nm, at both s and p incident polarizations. Negative-first-order diffraction peaks were observed and were consistent with feature spacing. An anomalous scatter peak, believed to be associated with guided-mode resonance of the structure, was also observed. This is the first demonstration of an AFM-patterned surface to behave as a 2-D photonic crystal and has potential US Department of Defense applications in laser eye protection and anti-reflection coatings for high power laser optics.

FM:HP04 **Bandpass Filters in the TeraHertz Range Based on Al-on-Si Metamaterials**

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We present a process for the design, the fabrication and the experimental test of terahertz bandpass filters made of 2-dimensional arrays of conducting elements with sub-wavelength dimensions. We used Silicon as the dielectric substrate and we patterned an Aluminum film by electron-beam lithography, following a design defined by electromagnetic simulations based on metamaterial concepts and the Babinet principle. The transmittance of the filters was then measured by Fourier- Transform spectroscopy and displays a single resonance due to induced dipolar currents from microwaves up to the ultraviolet. We then experimentally verified that the center frequency can be tailored from 1 to 5 THz by exploiting the scalability of the Maxwell equations. We simultaneously obtained a frequency-independent quality factor of 7, an agreement between simulations and experiments better than 5%, a peak transmittance of 60% and an off-peak transmittance below 2%. The filters can be easily implemented for applications involving terahertz bolometers or transceivers, as they are obtained through an inexpensive, repeatable, biocompatible process with full freedom of design.

FK:HP10 Reentrance of Macroscopic Quantum Tunneling in Cuprate Superconductors

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We present a theoretical analysis of the transition from thermal activation (TA) regime to the macroscopic quantum tunneling (MQT) regime of the decay from a metastable persistent current state in grain boundary junctions of cuprate superconductors. This transition is conventionally characterized by a single crossover temperature determined by the potential profile and dissipative mechanisms. It is shown that due to the existence of low energy bound states (mid-gap states) for various relative orientations of the crystal axes, there exists a window of parameters where one finds, with lowering temperature, an inverse crossover from MQT to TA, followed by a subsequent reentrance of MQT. It is shown that these predictions are in reasonable agreement with recent experiments.

FK:HP11 Compresssive Strength of Porous MgB2Superconductors

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The MgB2 superconductors can be easily synthesized by the Reactive Liquid Mg Infiltration (Mg-RLI) technology (G. Giunchi, 2003), in which B and Mg reactants are placed side by side, so that the liquid Mg diffuse into the high density compact of B powders obtaining an highly densified MgB2 bulk. If submillimeter spherical particles of Mg are used, it is possible to obtain a quite uniform porous material which have peculiar superconducting and mechanical characteristics. In this study we have prepared several porous MgB2 samples which differ by the initial Mg/B ratio, a different morphology of the boron powders and further, for the addition, in some case, of doping agents, like Cu powders or SiC nanopowders. We obtained massive porous samples of several cm3 in volume, which were characterised in term of porosity (average value of about 40%) and microstructure. From these specimens we cut small parallelepipeds useful for compression tests: from the compression curves it was possible to distinguish an initial elastic behaviour followed by a densification plateau characterized by recursive microcracking and local collapses. The mechanical behaviour of these porous materials has been compared with the behaviour of bulk full dense MgB2 samples obtained by the same the Mg-RLI technique.

FL:HP44 Incorporation of Acrylate Based Spiropyran Monoliths in Micro-fluidic Devices for Photo-controlled Electroosmotic Flow

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Spiropyran photochromic compounds can be switched using light exposure between a non-polar spiro form (SP) and a zwitterionic merocyanine form (MC) that can be subject to protonation (MC-H+). It has recently been demonstrated by Walsh et al. that a vinyl based spiropyran monoliths in acidic environment in the presence of an applied voltage can generate an electroosmotic flow (EOF) that can be modulated using light irradiation. In order to investigate new spiropyran monoliths to be applied as electroosmotic pump (EOP) within a micro-fluidic chip, we report an acrylate based spiropyran monolith which is particularly sensitive to protonation producing a positively charged surface that can be converted to the unpolar SP form by white light exposure. When the MC-H+ form is generated it produces a charged surface which enables a relatively high flow rate (up to 1.6 μl/min) under electroosmotic conditions. Then, upon white light exposure the concentration of MC-H+ decreases due to the conversion to the SP form with up to 19 % reduction of the EOF. The process is reversible and removal of the light source results in flow increase. The ability to alter such property using light has very significant implications as it could lead to the development of a control over liquid flow using light.

FL:HP45 Biodegradable Polymers Derived from Amino acids for Biological Applications

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Optically active α-hydroxy acids derived from amino acids have been synthesized and polymerized into new biodegradable polyesters. The variety of functional side chains enables the design of positively charged, negatively charged, hydrophobic and hydrophilic chiral building blocks or any combination of these constituents. Hydroxy acids of 15 natural amino acids were prepared with retention of configuration using a straightforward and reliable method of diazotization of α-amino acids. Polyesters were synthesized from these hydroxy acids by a number of methods: direct condensation in bulk, microwave assisted synthesis and ring opening polymerization. The molecular weight of the prepared polymers ranges between 2000 to 5000Da for the direct condensation and the microwave methods, whereas the ring opening polymerization results in high molecular weight polymers (20000 to 30000Da). The polymers were analyzed for their optical activity (Circular Dichroism Spectroscopy), thermal properties (DSC), solubility, molecular weight and polydispersity (GPC), and aqueous degradation. These polymers were tested for their compatibility to neuronal cells growth and differentiation.

This study was supported by ISF grant and the Alex Grass Center for Drug Design and synthesis of Novel Therapeutics at the Hebrew University.

1. Cohen-Arazi, N; Katzhendler, J; Kolitz, M; et al. Preparation of New alpha-Hydroxy Acids Derived from Amino Acids and Their Corresponding Polyesters,Macromolecules 41, 20, 7259-7263, 2008; 2. Kolitz, M; Cohen-Arazi, N; Hagag, I; Katzhendler, J; Domb J. Abraham, Biodegradable Polyesters Derived from Amino Acids, Macromolecules, 42, 13, 4520-4530, 2009.

FL:HP46 Specific Cell Cultivation on Nanofibrous Layer

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Recent advances in the preparation of nanofibre layers, especially using the NanospiderTM technology, allow to prepare a sufficiently large area of nanofibrous layer of reproducible thickness and structure. Subsequently, it is possible to employ these layers as cell carriers and evaluate their efficiency in laboratory bioreactors. The construction of the functional hepatal bioreactor is particularly given by the positive response of hepatocyte cells to the used carrier layer as well as by the cell morphology, their viability and biological activity in certain period of time. We compared cell growth on collagen with nanofibres electrospun from selected copolymers of methacrylic esters (HEMA/EOEMA) and from differently prepared polycaprolacton (PCL) layers. The morphology was evaluated using Phaloidin/DAPI staining. On the nanofibres based on methacrylates, the cells survived and showed a common morphology comparing with cells grown on collagen (controls). On the PCL nanofibres, the cells attached well and showed a better growth than cells grown on collagen (controls). The results obtained in laboratory bioreactor proved the biochemical functionality of the studied system.

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FL:HP47 Chitosan porous membranes as nerve guides

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Peripheral nerve lesions are common and serious injuries, generally leading to lifelong disabilities. At present, nerve autografting is the most used method for nerve repair, but it involves some disadvantages, therefore it is extremely important to develop new strategies alternative to autografting. Our purpose is to develop chitosan (CS) flexible porous membranes as outer layer of nerve guides. Porous membranes both via selective dissolution of a porogenic agent and via freeze-drying with a controlled and variable freezing temperature were produced. An interconnected porosity was obtained only via the freeze-drying procedure. The study of an inner layer for these guides, based on a natural polymeric hydrogel (such as agar) loaded with IGF1 growth factors, is in progress. This layer will be then spread on the outer CS porous membrane, forming an implant that, during surgery, can be rolled up around the trunked nerve stumps and sutured along the longitudinal axis. Once the implant is in situ, the inner layer degrades and gradually releases the growth factors, while the porous outer layer, which has a longer degradation time, supports the nerve growth and allows nutrients diffusion.