

SYMPOSIUM A

The Hydrogen Cycle—Generation, Storage, and Fuel Cells

November 27 - December 2, 2005

Chairs

Anne Dillon

Basic Science Dept.
National Renewable Energy Laboratory
MS 3216
1617 Cole Blvd.
Golden, CO 80401-3393
303-384-6607

Charles Olk

Materials & Processes Laboratory
General Motors R&D Center,
30500 Mound Rd.
Warren, MI 48090-9055
586-986-0611

Jim Ohi

Electric & Hydrogen Technologies & Systems
National Renewable Energy Laboratory
MS 1613
1617 Cole Blvd.
Golden, CO 80401-3993
303-275-3706

Constantina Filiou

Institute for Energy, Clean Energies Unit
European Commission - DG JRC
P.O. Box 2
ZG Petten, NL-1755 The Netherlands
31-224-565171

Symposium Support

General Motors Research & Development Center

Proceedings to be published in both book form and online
(see *ONLINE PUBLICATIONS* at www.mrs.org)
as volume 885
of the Materials Research Society
Symposium Proceedings Series.

* Invited paper

TUTORIAL

**FTA: On-Board Hydrogen Storage –
Breakthroughs and Barriers**
Sunday, November 27, 2005
1:30 PM - 5:00 PM
Room 202 (Hynes)

This tutorial will examine novel hydrogen storage materials currently being developed for “on-board” applications that require several challenging constraints, including high-volumetric and gravimetric storage densities. The instructors from the Department of Energy’s (DOE) recently established Centers of Excellence for vehicular hydrogen storage will focus on the three material classes chosen by the DOE – metal hydrides, chemical hydrides, and carbon-based materials – as the most promising for meeting these stringent requirements. After a brief introduction and overview, each of these material classes will be discussed in detail, evaluating their material properties across common themes and benchmarks.

Materials to be Discussed

Metal Hydrides: Metal Hydrides (including MgH₂, AlH₃, etc.); Intermetallic compounds – hydrides; Complex hydrides (including sodium-aluminum hydride, metal imides)

Chemical Hydrides: Amine-Boranes; Boranes; Borohydrides; Novel boron chemistry; Novel Organics

Carbon-Based Materials: Nanotubes; Nanohorns; Metal-organic frameworks; Nanofibers; Doped carbon; Conducting polymers

Topics for Each Material

Materials: Scope of materials; Synthesis; Purification; Activation; Handling considerations

Hydrogen Storage: Binding mechanism; Thermodynamics; Kinetics; Recharging/Regeneration; Optimization targets; Approaches to optimization

Characterization Techniques Unique to Each Material: Material qualification; Hydrogen capacity

Instructors:

Tom Autrey
Pacific Northwest National Laboratory

Weifeng Luo
Sandia National Laboratory

Philip Parilla
National Renewable Energy Laboratory

SESSION A1: Challenges and Requirements for H₂ Fuel
Cell Vehicles
Chair: Anne Dillon
Monday Morning, November 28, 2005
Room 311 (Hynes)

8:00 AM *A1.1

The Implications of Fossil Fuel Combustion for Climate Change. Kristy Ross and Stuart J. Piketh; Climatology Research Group, University of the Witwatersrand, Johannesburg, South Africa.

Emissions from fossil fuel combustion alter the composition of the atmosphere and have been touted as a major cause of climate change. The evidence for anthropogenic climate change, the causes of climate change, and predictions of future change will be discussed. Global warming is thought to occur due to the increased concentration of greenhouse gases which enhance the absorption and emission of infrared radiation by the atmosphere. The amount of CO₂ in the atmosphere, for example, has increased by more than 30% since pre-industrial times, and is still increasing by around 0.4% per year. Combustion also produces aerosol particles, which increase the scattering of incoming solar radiation back to space. Some aerosols, such as soot, absorb solar radiation directly, leading to local heating of the atmosphere. Due to the short lifetime of aerosol particles, however, their effects are likely to be more localized. The changes in atmospheric composition result in a change in radiative forcing, to which the climate system must respond in order to restore the energy balance. The difficulty in attributing the observed climate change to human activities lies in the fact that the anthropogenically-induced warming is superimposed on natural climatic variability. Ocean core

sediments show a regular oscillation, on a 100 000-year cycle, between glacial and interglacial. Superimposed on these long-term oscillations are shorter scale variations. While long-term climatic changes appear to be related to changes in the amount of solar radiation received by the earth due to changes in the earth’s orbit around the sun, shorter term variations are related to a number of factors including feedbacks within the earth-atmosphere system. A firm link between atmospheric composition and temperature has been established from ice core records spanning the last 400 000 years, which show that changes in time of global temperature and atmospheric concentrations of carbon dioxide and methane are tightly coupled. Furthermore, the range over which temperature and trace gas concentrations vary is bounded at upper and lower limits. However, current CO₂ levels of around 360 ppm far exceed the ‘natural’ peak concentration of 280 ppm. Average global surface temperature has increased by approximately 0.6°C since the late 19th century. Surface temperature records indicate that the 1990s are likely to have been the warmest decade of the millennium and 1998 has been the warmest year recorded globally. The warming is far from uniform, however, and often manifests itself as an increase in climatic extremes. The implications of climate change are predicted to be profound for both natural and human systems. Regrettably, those with the least resources have the least capacity to adapt, and are the most vulnerable to climate change.

8:30 AM *A1.2

Hydrogen Effects in Engineering Materials. Chris San Marchi, Brian Somerday and Dorian Balch; Sandia National Laboratories, Livermore, California.

With the evolving hydrogen economy, infrastructure development is anticipated that will require the containment of hydrogen gas at pressures greater than 70 MPa and the means to transport hydrogen gas at energy density competitive with natural gas. Hydrogen atoms dissolve and diffuse in most engineering materials and are known to alter the mechanical properties of these materials. In order to guide the selection of materials for structural components in hydrogen service, a comprehensive understanding of the effects of hydrogen on materials at the microstructural level is needed, as well as knowledge of the materials/microstructural, environmental and mechanical variables that contribute to the degradation of properties in gaseous hydrogen environments. In this presentation we outline the relevant environmental, material and testing variables necessary to understanding hydrogen-assisted fracture of steels in high-pressure hydrogen gas with data relevant to structural materials proposed for hydrogen service. In addition, we summarize activities in our laboratory to address the needs of the engineering community with regard to properties of materials for hydrogen service and to develop appropriate fracture mechanics protocols for characterizing crack growth in high-pressure hydrogen gas.

9:00 AM A1.3

Educational and Scientific Requirements for Viable Vehicular Hydrogen Fuel Cells. Jeff L. Alleman, Linda D. Lung and David S. Ginley; National Renewable Energy Laboratory, Golden, Colorado.

For longer cycle times, small light-weight fuel cells are necessary for future mobile technologies. Transitioning a science demonstration fuel cell to the market will require significant technological advancements. For example, the Pt catalysts generally employed in both the cathodes and anodes are very expensive. Nafion, which is currently the state-of-the-art material for proton exchange membranes, is prohibitively expensive. Also oxidative corrosion of the bipolar plates and electrical contact limits inhibit the ultimate fuel cell efficiency. Finally, a true transition to a hydrogen-based vehicular society requires significant changes in infrastructure and will also require educational outreach. Here we discuss a joint effort between the Materials Research Society and the National Renewable Energy Laboratory’s Center for Photovoltaics and Office of Education Program. In this initiative we are engaging local high school students in the Boston area to design and race model hydrogen fuel cell cars in a sprint competition. The success of this endeavor should spark student interest for careers in science, mathematics or engineering that could ultimately lead to successful research that will make commercialization of fuel cells possible. Finally, demonstrations such as this will make the American public more receptive to the transition to a hydrogen energy economy.

9:15 AM A1.4

Silicon Micro Machining Technologies and Advanced Materials (Porous Silicon and PEEK-WC) for Realization of Micro-PEM Fuel Cells. Elena Tresso¹, Luisa Borello², Enrico Drioli⁵, Giuseppe Gianolio², Salvatore Guastella¹, Denis Perrone¹, Marzia Quaglio¹, Andrea M. Rossi⁴, Ilaria Rosso², Luciano Scaltrito¹ and Francesco Trotta³; ¹Dept. of Physics, Politecnico, Torino, Italy; ²HYSY_Lab, Environment Park, Torino, Italy; ³Dept. of Chemistry, University of Torino, Torino, Italy; ⁴Quantum Research Lab, IEN Galileo Ferraris, Torino, Italy; ⁵ITM-CNR, Consiglio Nazionale delle

Miniaturized fuel cells are very promising for applications in portable electronic communication and in computing devices as well as in medical tools. Much attention has till now been given to polymer electrolyte membrane fuel cells (PEM-fuel cells) where hydrogen or light alcohols are used as a fuel. Among the light alcohols, methanol is considered the best candidate owing to its very high H:C ratio and its availability. Our efforts are focused to the development of a miniature PEM fuel cell operating at low temperature on hydrogen or direct methanol as anodic feed and air as cathodic feed. We will present results on the performances which can be obtained by employing, in micro-fuel cell fabrication, silicon-based microfabrication techniques for efficient fuel distribution and micro-channel architecture, and advanced materials which can be easily integrated in silicon technologies, such as porous silicon for the electrode fabrication and PEEK-WC for membranes alternative to Nafion. We have utilized the MEMS (micro electro mechanical system) technology for obtaining anode and cathode micro-channels for hydrogen and methanol, both in glass and in silicon. The powder blasting technique which is a fast, cheap and accurate directional etch technique for brittle materials such as glass, silicon and ceramics has been utilized. Channel and rib widths in the range 400-900 micron, channel depths in the range 400-500 micron, and different depth profiles and geometries have been obtained and used for fabrication of different sets of bi-polar plates. The sealing between silicon and PEM has been studied and performed by means of a bonding technique based on localized controlled micro-fusion processes, similar to the eutectic bonding for packaging. The bipolar plates have been assembled with a Membrane Electrolyte Assemblies and tested by means of polarization curves, for evaluation of different parameters such as temperature, pressure and inlet gas flow on the fuel cell performance. Quantitative measurements have been carried out with pure hydrogen and with methanol. Thin layers of porous silicon (whose specific surface can be as high as 1700 m²/cm³) have been grown, by means of electrochemical process, on silicon substrates; we have tested the advantages obtained by substituting traditional carbon electrodes with integrated electrodes made of porous silicon on microfluidic channels. New membranes from polyetheretherketones (PEEK-WC) with various degrees of substitution were obtained, following the traditional phase inversion process; sulfonation was carried out to increase hydrophilicity and proton conductivity. The methanol permeability observed in our membranes is 100 times lower than the one obtained with traditional Nafion membranes. Results will be presented and discussed in view of developing highly efficient, low-cost processes and materials for improving fuel cell specific performance and durability.

10:00 AM *A1.5

Effect of Trace Contaminants of PEM Fuel Cell Performance. Richard Rocheleau¹, Keith Bethune¹, Tony Thampan¹ and Douglas Wheeler²; ¹Hawaii National Energy Institute, University of Hawaii, Honolulu, Hawaii; ²DJW Technology, Honolulu, Hawaii.

In 2003, the Hawaii Fuel Cell Test Facility developed by the Hawaii Natural Energy Institute (HNEI), in partnership with Hawaiian Electric Company and UTC Fuel Cells began long-term testing of full size PEM fuel cells. More recently, HNEI has initiated a systematic study to evaluate the effect of select trace contaminants in hydrogen on the performance of PEM fuel cells. This program sponsored by the Hydrogen, Fuel Cell, and Infrastructure Technologies program of the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy seeks to provide data to the ISO TC 197 Working Group on hydrogen quality. Fuel cell hardware for the tests has been provided by GM, Ballard Power Systems and UTC Fuel Cells Inc. Initial tests to evaluate the effects of carbon monoxide poisons under different fuel cell operating conditions have shown a strong dependence on concentration of the impurity over the range 7 μ mole/mole to 29 μ mole/mole. At the higher concentration loss of performance from 0.75 V to 0.38V in less than two hours is observed for cells operated under the following conditions: 0.5A/cm², 80°C, 1.5 atm, 50% RH anode, 100% RH cathode, H₂/Air stoichiometry 2/2. The carbon monoxide can be reversibly removed by raising the anode potential to burn of the impurity. At lower concentrations, e.g., 7 μ mole/mole, an equivalent loss in performance is not observed in over 20 hours of exposure to the carbon monoxide impurity at the same operating conditions. Surface area measurements of the catalyst prior to exposure to the impurity and after exposure and removal of the carbon monoxide indicated no major loss in catalyst surface area. Crossover measurements characterized the quality of the membrane electrode assembly prior to and after exposure to the impurity. Current test plans being developed in collaboration with DOE and NREL call for evaluation of the effect of aromatic hydrocarbons, formaldehyde, and propylene glycol. Benzene poisoning experiments are planned for the 3rd quarter of 2005. Testing as a function of exposure time (hundreds of hours), operating pressure and temperature, and reactant utilization are planned. The results for CO and the early results on benzene will be reported.

10:30 AM *A1.6

(Membrane) Attack of the Killer Radicals. Ned E. Cipollini, Physical Sciences, United Technologies Research Center, East Hartford, Connecticut.

UTC has intensified efforts on PEM durability over the last six years, first focusing on performance-decay and seals. As strategies for performance-decay mitigation were developed and seal durability improved, longer lifetimes were enabled and focus shifted to membrane durability, the subject of this talk. The function of the membrane is to move ions, separate reactant gases and electrically insulate the anode from the cathode electrocatalyst. Membrane failure results from a complex interplay of mechanical stress and chemical attack each having multiple origins. The generally accepted mechanism of chemical attack is that hydrogen peroxide formed on anode and cathode catalysts is converted into hydroxyl radicals by impurity ions in the membrane which enables these (killer) radicals to attack membrane-ionomer. UTC data is consistent with the ionomer attack site being the ionomer end-group. More recently, UTC and others have investigated evidence that Pt plays an important role, not only in peroxide generation, but also in free-radical formation. This talk will provide a perspective of the chemical attack processes leading to membrane failure and then focus on mechanisms of free radical formation in an operating PEM cell. Supporting evidence will be discussed where available. Progress has been made in this area, but the story is not complete.

11:00 AM A1.7

Molecular Dynamics Simulation of Proton Diffusion in Sulfonated Polymer Membranes. James C. Moller¹ and Rajiv J. Berry²; ¹Department of Mechanical and Manufacturing Engineering, Miami University, Oxford, Ohio; ²Materials Laboratory Polymers Branch, U.S. Air Force Research Laboratory, Dayton, Ohio.

Among the pressing needs for proton exchange membrane fuel cell performance are higher operating temperatures and higher proton mobility. Sulfonated polythioethersulfone (SPTES) polymers have shown promise due to their high proton conductivity and high degradation temperature. In this work, molecular dynamics simulations were conducted to study and compare structures and transport among hydrated Nafion and SPTES. The dependence of the glass transition temperature of the dehydrated polymer on the degree of sulfonation was studied. These results served to verify the force fields used. These fields included descriptions of protonated water and deprotonated sulfonate groups. Proton diffusion was modeled by both transport on hydronium molecules as well as hopping among hydronium and water. Various strategies for calculating hopping probability were applied. Segregation and ordering among sulfonated groups, the backbone, and water were studied as a function of temperature. The morphology of water/polymer interfaces was also compared.

11:15 AM A1.8

Mesoscale Simulation of Morphology in Hydrated Perfluorosulfonic Acid (PFSA) Membranes. James T. Wescott², Yue Qi¹, Lalitha Subramanian³ and T. Weston Capehart¹; ¹Materials and Processes Lab, GM R&D Cetner, Warren, Michigan; ²Accelrys Ltd., Cambridge, United Kingdom; ³Accelrys Ltd., San Diego, California.

Current fuel cell proton exchange membranes (PEM) rely on a random network of conducting hydrophilic domains to transport protons across the membrane. Despite extensive investigation, the details of structure of the hydrophilic domains in these membranes remain unresolved. In this study, we applied a dynamic self-consistent mean field theory, to obtain the morphologies of PFSA (ex. Nafion[®]) at equivalent weight of 1100) as a model system at several water contents. A coarse-grained mesoscale model was first developed by dividing the system into three components: backbone, side chain, and water. The interaction parameters were then generated from molecular dynamics. The simulated morphology shows phase separated micelles filled with water, enclosed by the sulfonic side chains, and embedded in the fluorocarbon matrix. The size distribution and connectivity of the hydrophilic domains were analyzed and the small angle neutron scattering pattern was calculated. The shape of water domains also evolves with water content. At low water content the isolated domains are nearly spherical with a domain size smaller than experimentally observed. At higher water content; the domains deform into elliptical and barbell shapes as they merge. Comparison of the simulated morphology, hydrophilic domain size and shape are generally consistent with experimental observations.

11:30 AM A1.9

The Effect of the Fuel Cell Polarization and Steam Content on the Conductivity and Stability of Novel High Temperature

Polymer Electrolytes. Stylianos G. Neophytides^{1,2}, Jannis K. Kallitsis^{2,1}, Maria K. Daletou^{1,2} and Nora Gourdoupi^{2,1}; ¹Institute of Chemical Engineering and High Temperature Processes, Patras, Greece; ²Department of Chemistry, University of Patras, Patras, Greece.

Polymer electrolyte membrane fuel cells are the most promising renewable power generators for zero-emission vehicles and portable applications. High-temperature (>120°C) PEMFCs have recently drawn attention due to their certain advantages. Increased tolerance of the anode to carbon monoxide (>0.1 CO at 150°C), enhancement of reaction's rate, electrochemical performance relatively independent of humidity are some of them. At the heart of the PEM fuel cell is the membrane electrode assembly (MEA). MEA consists of a proton exchange membrane, catalyst layers and gas diffusion layers (GDL). Starting with the membrane, the requirements that should be met concerning its properties are the following: (1) high doping ability with strong acids, (2) high ionic conductivity, (3) low electronic conductivity, (4) low gas permeability, (5) chemical and oxidative stability, (6) thermal stability, (7) good mechanical properties and (8) low cost. Polybenzimidazole, PBI, has been studied by several research groups and seems to be the most promising electrolyte for high temperature PEMFCs. Our approaches to the development of new polymer membranes include the synthesis of new aromatic polyethers containing polar units in the main chain as well as preparation of PBI free blends. Aromatic polyethers were chosen due to their good mechanical properties and high thermal stability. The insertion of polar pyridine units was done with the view of having sites that could interact with phosphoric acid giving thus good doping ability. Characterization of the prepared materials showed that in most cases they fulfilled the prerequisites of a polymer electrolyte. Further more different MEAs were constructed and tested in a single 2x2 cm² fuel cell. There are many parameters involved in the construction of the MEAs. The Pt loading, the ionomer type, the ratio Pt/ionomer, the doping level and the thickness of the membrane, the temperature and pressure of the hot pressing certainly affect the final fuel cell performance. The conductivity of the polymer membrane as well as the different electrode's and MEA's performance were tested by means of A.C. impedance measurements and Tafel plots at various temperatures. The positive effect of polarization and steam content on the conductivity during operating conditions was also studied. Values in the range of 10-2 s/cm were obtained and conductivity increased with the water vapour content and the applied voltage. The single cell performance is similar to the one reported for PBI membranes, although the system is not yet optimized.

11:45 AM **A1.10**

Sol-Gel SiO₂-Polymer Hybrid Heteropoly Acid-Based Proton-Exchange Membranes. John Pern¹, John A. Turner¹, Fanqin Meng² and Andy M. Herring²; ¹Hydrogen and Electricity, Systems and Infrastructure Group, National Renewable Energy Laboratory, Golden, Colorado; ²Department of Chemical Engineering, Colorado School of Mines, Golden, Colorado.

Heteropoly acids (HPAs)-based hybrid proton-exchange membranes (PEMs) for intermediate-temperature (80°-120°C) fuel cell applications were fabricated by using a SiO₂ sol-gel approach, followed by covalent polymerization and cross-linking upon curing at 145° ± 5°C under pressure. The primary objective of this work is to develop low-cost, high-performance HPA-based PEMs to replace the conventional sulfonic acid (SFA)-based PEMs such as Nafion membranes, which require a relatively high level of moisture for proton conduction at temperatures typically below 80°C. HPAs are known to have a high proton conductivity and high thermal stability at temperatures >250°C. Their abilities to conduct protons in the absence of moisture have been demonstrated by our group. In this work, three silicotungstic acids, saturated Keggin H₄SiW₁₂O₄₀ (W12-STA) and custom-synthesized lacunary H₈SiW₁₁O₃₉ (W11-STA) and K₈SiW₁₀O₃₆ (W10-STA), were used in the syntheses that included mainly the use of a binding silane, TEOS for sol-gel conversion into SiO₂, and a polymer host. The binding silane, either a methacrylate-based or an epoxide-based silane, served to bind or bond the STA with its functional group subsequently bonded covalently to the polymer host via crosslinking reaction by curing at ~145°C. The polymer host used was either a glycidyl methacrylate-type copolymer (PEMAGMA) or a special polypropylene oxide (BSPPPO), both stable up to ~225°C. Membranes of such hybrid composites were obtained in previous work, but with a relatively low loading level of W12-STA (< 45 wt%/polymer) to maintain mechanical integrity without cracking or breaking after curing. The low STA loading, coupled with phase separation in the earlier membranes, resulted in low proton conductivity and current density, although a Voc in the 0.8-0.9 V range was obtained. The STA loading level has been increased substantially to >100 wt%/polymer in recent hybrid membranes, achieved by adjusting the formulations in which the relative weight (concentration) ratios of TEOS and binding silane were reduced and a dimethacrylate monomer was added for polymerization and

cross-linking to improve the mechanical strength. These efforts have resulted in the production of hybrid PEMAGMA-based membranes that are mechanically flexible and nearly 100% cross-linked. FTIR-ATR analysis confirmed the presence of SiO₂ and STA in the cured membranes. Depending on the formulation and fabrication details, different levels of SiO₂ and STA losses from cured membranes by water extraction at 85°C for 24 h were observed. More studies are in progress to determine the ion exchange capacity, proton conductivity, and fuel cell performance of the hybrid composite membranes with high STA loadings. Details will be presented in the meeting. This work was conducted at NREL under the U.S. Department of Energy contract number DE-FC02-00CH11088.

SESSION A2: Fuel Cells

Chairs: Jim Ohi and Richard Rocheleau
Monday Afternoon, November 28, 2005
Room 311 (Hynes)

1:30 PM **A2.1**

A new concept of membrane for PEM fuel cell using sol-gel hybrid chemistry. Franck Pereira¹, Karine Valle¹, Philippe Belleville¹ and Clement Sanchez²; ¹CEA, Monts, France; ²Laboratoire de Chimie de la Matiere Condensee, Paris, France.

Fuel cell technology based on proton exchange membrane fuel cell (PEMFC) has attracted much attention as clean energy source for various applications such as electric vehicles, portable electronics and residential power generation. Today, membranes made of

perfluorosulfonic polymers such as Nafion[®] remain the reference material due to their electrochemical performances and chemical stability. They usually operate at temperature below 80°C and in these conditions water easily ensures the protonic conduction. However, in order to enable high energy consumption applications like transportation, the operating temperature must be increased above 100°C. Recently, sol-gel organic/inorganic hybrid materials have been proposed as potentially promising membranes to fulfil high temperature requirement[1]. In this work, we present another innovative way for preparing highly conductive PEMFC membranes able to operate under severe conditions. For this purpose, we have combined the standard sol-gel method to the self-assembly route which uses templates to design desired mesoporosity, in order to create new mesostructured hybrid materials. The growth of high exchange area silica embedded in an organic polymer is therefore described. Amphiphilic block copolymers used as structure-directing agents for the inorganic framework enable the synthesis of mesoscopically ordered materials. Two approaches have been investigated, one starting from Nafion[®] polymer as organic matrix and another starting from a non-conducting polymer to replace expensive Nafion[®]. In this second route, the in-situ mesoporous silica network can be functionalized by conductive groups such as sulfonic moieties to reach the needed conductivity. The high surface area of the mesoporous silica phase enhances the water retention property and allows maintaining high proton conductivity under high operating temperature (95°C) and low humidity rate conditions (75% RH). In both approaches, the as-designed hybrid microstructure leads to higher conductivity performances compared to pure polymeric membrane. These membranes were extensively characterized to highlight their morphology, intermolecular interactions and physicochemical properties. X-ray diffraction analysis shows a d-spacing which was assigned to the internal mesoporous organization of the inorganic network. Scanning electron microscopy characterization reveals the excellent hybrid material homogeneity. The electrochemical properties are detailed regarding water uptake, conductivity measurements using impedance spectroscopy and evaluation of the membranes in H₂/O₂ fuel cell experiments. Very promising results on these new hybrid materials are presented and discussed regarding properties/microstructure features. For instance, an outstanding improvement of 15% of electric power density was obtained with this hybrid membrane compared to Nafion[®] under same severe conditions. [1] Adjemian et al. J.Electrochem.Soc. 149, A256, 2002

1:45 PM **A2.2**

New Super Proton-conductive, High Acid-containing Fluoropolymer PEMs from Cured Liquid Precursors. Zhilian Zhou¹ and Joseph M. DeSimone^{1,2}; ¹Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina; ²Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina.

There is considerable and growing interest in the development of fuel cells for portable electrical devices, transportation and distributed power. The next generation of polymer electrolyte membranes (PEM) must outperform today's most widely used material, Nafion[®]. In this

study, we present a new fluoropolymer PEM material that is prepared from a fluorinated liquid precursor, a mixture of a poly(tetrafluoroethylene oxide-co-difluoromethylene oxide) (PFPE) based macromonomer and a miscible styrene sulfonate ester, which can be cured into crosslinked membranes with extremely high acid loading. This curing process is completely solvent-free, and the membranes can be directly cured into the desired form and thickness. By employing chemical crosslinked membranes, extremely high ion loading can be achieved without dissolution in water. These high acid-containing fluoropolymer PEMs have very high proton conductivity and good mechanical integrity at the same time. Membranes with equivalent weights (EW) of 500 to 2000 have been prepared by this approach. To characterize the properties of these membranes, water uptake, dimensional change and proton conductivity were measured at different temperatures and relative humidities. A membrane with EW 550 displays a conductivity as high as 0.254 S/cm at room temperature under fully hydrated conditions. The thermal and mechanical properties of the membranes were characterized by thermal gravimetric analysis and dynamic mechanical analysis. Fuel cell performance of the membranes has been evaluated and compared with Nafion 117[®] under the same operation conditions. Our membranes show better performance than Nafion 117[®] even though the membrane-electrode assemblies (MEA) fabrication method is developed for Nafion[®]. This liquid precursor approach provides many unique opportunities for fuel cell development that would be otherwise impossible. Patterned, 3-dimensional membranes with micron-sized features can be easily prepared using soft lithography techniques. The patterned membranes can provide a much larger active surface area and therefore increased power density over standard flat membranes. Furthermore, the liquid precursor approach will allow fabrication of PEMs that have controlled properties across the membrane. Conventionally, MEA are fabricated by compressing preformed membrane between two catalyzed electrodes. The intractability of preformed PEMs restricts possible system designs for fuel cells. Liquid precursor approach provides the possibility of injection molding of PEMs between pre-assembled electrodes, and conformability with systems having micro-channels or unique shapes. These possibilities are being studied and will be reported herein.

2:00 PM A2.3

Conductive & Corrosion Resistance Coatings of PEM Fuel Cells Bi-polar Plates. Yair Ein-Eli and Alexander Kravtsov; Materials Engineering, Technion-Israel Institute of Technology, Haifa, Israel.

Metal bipolar plates are a subject of corrosion in course of PEM FC operation, which impedes their implementation. Anode plate develops dissolution, and resulting metal ions impair PEM proton conductivity. Cathode plate is covered with oxide film; this presents low contact conductivity. A suppression of aforementioned corrosion processes plays an important role for fuel cell implementation. Common non-precious corrosion-resistant materials, which are used per se or for protective plating (Ti, Ta, Ni, Cr, etc.) maintain corrosion resistance because of appearance of protective passive layers on their surfaces, that's why such materials don't prevent the loss of contact conductivity. Also, the most common non-precious corrosion-resistant material undergo pitting corrosion under the specific fuel cell operation conditions. Precious metal plating (gold, platinum) is, apparently, prohibitively expensive. The other issue is that bipolar plate materials should have a low contact angle at the bipolar plate/water border, whereas the contact angles at the precious metal/water interface are not enough small. The discovery of non-precious, corrosion-resistant and highly conductive bipolar plate plating is essential for building a viable fuel cell for vehicles. Recently the problem was addressed by offering titanium nitride as a material for such corrosion-resistant plating. Whereas, titanium nitride is none-expensive, stable under fuel cell operating conditions and highly conductive, it does not provide satisfactory protection for bipolar plate material because its film is porous and thus permeable for corroding agents. Also, this plating develops relatively low water affinity, with contact angle close to 60°. We are addressing the problem by introducing protective films, which comprise of binary and ternary nitrides of elements of IVb and Vb groups, which also may contain some elements of II and III groups. Nitrides of IVb and Vb group elements are stable in fuel cell operating conditions and have a high conductivity.

2:15 PM A2.4

Functionalized ORMOSIL-Based Hybrid Membranes for Polymer Electrolyte Membrane Fuel Cells. Silvia Licocchia¹, Maria Luisa Di Vona¹, Zakarya Ahmed¹, Serafina Bellitto¹, Alessandra D'Epifanio¹, Debora Marani¹, Enrico Traversa¹ and Marcella Trombetta²; ¹Chemical science and Technology, University of Rome Tor Vergata, Rome, Italy; ²Interdisciplinary Research Center, University Campus Bio-Medico, Rome, Italy.

Increasing the performances of proton conducting membranes (PEM) is a key issue for the development of Fuel Cells technology. New generation electrolytes should maintain performances above 100 °C to enhance fuel oxidation kinetics and ease thermal balance. Moreover, for automotive application, operating a FC vehicle at ambient temperature above 20 °C requires either a large radiator, a solution certainly not ideal for most car manufactures, or an increase the operation T above 100 °C. For the optimization of water management and thermal balance reasonable standards have been set at an operating temperature of ca. 120 °C with 25 % RH. It is generally accepted that a single material does not possess all the characteristics needed for fuel cells application and several approaches have been proposed to achieve the correct electrochemical and mechanical properties: among them, the use of inorganic fillers for the development of composite systems, acid or basic doping, and association of polymers. We here report on the preparation and electrochemical characterization of new hybrid systems based on sulfonated polyetheretherketone (SPEEK) and functionalized organically modified silanes (ormosils). Aromatic ormosils were chosen because of their structural affinity with the polymer main chain, and because phenyl rings can be easily functionalized with polar functions with the aim of adding a contribution to the overall conductivity. Both acidic and basic functionalization of diphenylsilanediol (DPDO) were performed, and the resulting products were mixed with SPEEK having DS = 0.9. Sulfonated DPDO was used to decrease the average separation between acidic groups, while aminated DPDO was synthesized to generate strong acid-base interactions which are known to improve mechanical and thermal properties and ease proton transfer. Hybrid membranes were successfully prepared by solution casting. Their structure and electrochemical performances were investigated by means of several techniques including 1-H and 29-Si NMR, ATR/FTIR, FE-SEM and EIS. Highly homogeneous samples which showed reduced water swelling, increased thermal stability and significant conductivity (in the range 0.1 - 0.01 S/cm) at temperatures as high as 120 °C were obtained.

3:30 PM A2.5

Crosslinked Hybrid Proton Exchange Polymeric Membranes. Maria Luisa Di Vona¹, Debora Marani¹, Enrico Traversa¹, Silvia Licocchia¹, Marcella Trombetta², Stefano Caldarelli³ and Philippe Knauth⁴; ¹Chemical Science and Technology, University of Rome Tor Vergata, Rome, Italy; ²Interdisciplinary Center for Biomedical Research, University Campus Biomedico, Rome, Italy; ³TRACES (JE 2421), University of Provence, Centre St Jerome, Marseille, France; ⁴MADIREL (UMR 6121 CNRS), University of Provence, Centre St Jerome, Marseille, France.

Numerous proton conducting polymer electrolyte membranes (PEMs) are based on high performance thermoplastic polymers such as sulfonated polyetheretherketone (SPEEK). The main drawback to use these aromatic polymers in fuel cells is maintaining proton conductivity at temperatures above 100 °C. It is known, in fact, that sulfonation of the aromatic backbone modifies the polymer chemical behavior, reduces crystallinity and, consequently, affects solubility. Thus, to achieve the required characteristics, a more complex architecture of polymers must be designed: hydrophobic rigid thermoplastic main chains for mechanical and chemical stability combined with more flexible and hydrophilic sulfonated graft chains. Among the several approaches that can be used to improve ionomeric membranes two seem to be worth taking into consideration: the preparation of crosslinked polymers and the formation of covalent organic-inorganic hybrid membranes. The transport properties of polymeric membranes are strongly dependent on the type and extent of crosslinking, which represents a mean of reducing the degree of swelling. Furthermore, combining organic and inorganic components in a Class II hybrid material allows modulation of the ratio between hydrophilic and hydrophobic groups. In this study, we combined the two approaches preparing a covalently crosslinked sulfonated polyetheretherketone (SOPEEK) with elevated DS by sulfonation with ClSO₃H, and further functionalized it by silylation reaction. The solubility of the -SO₂Cl precursor in organic solvents allowed to easily carry out functionalization reactions in homogeneous conditions, thus introducing covalently linked silicon moieties. No degradation of PEEK was detected upon sulfonation, but only crosslinking via sulfonic groups with formation of SO₂ moieties was observed. The extent of ramification was evaluated by 1H NMR and was 25 % of the total amount of SO₃H groups present in the polymer. Hybrid membranes were successfully prepared by solution casting. Their structure and electrochemical performance were investigated by means of several techniques including 1H and 13C NMR, ATR/FTIR, TG/DTA, FE-SEM and EIS. Transport properties were further investigated by pulsed field gradient NMR.

3:45 PM A2.6

Rapid screening for PEMFC anode sulfur tolerance using RDE and water-soluble H₂S analogs. Jeremy Pietron¹, Rommel

Alvarado¹, Terence Schull², Maggie Teliska¹, Yannick Garsany¹ and Karen E. Swider-Lyons¹; ¹Surface Chemistry Branch, Code 6170, Naval Research Laboratory, Washington, District of Columbia; ²Center for Biomolecular Science and Engineering, Code 6910, Naval Research Laboratory, Washington, District of Columbia.

To use proton-exchange membrane fuel cells (PEMFC) broadly for military applications, their sensitivity to sulfur-containing contaminants, particularly H₂S and SO₂, must be minimized. Hydrogen from reformed strategic military fuels is likely to contain significant amounts of H₂S and other sulfide compounds. PEMFC membrane electrode assemblies (MEA) are poisoned after a few hours of exposure of the operating PEMFC to 50 ppm gas-phase H₂S.¹ We are developing rapid screening methods to assess anode sensitivity to thiols and sulfides to support our efforts to develop sulfur-tolerant catalysts. Using water-soluble thiols, rotating disk electrochemistry (RDE), and vulcan carbon-supported Pt, we measured parts-per-billion sensitivity of the hydrogen oxidation reaction (HOR) to several water-soluble thiols. Using Tafel analysis of the HOR RDE voltammetry as described by Markovic and coworkers,² impact of sulfur poisoning on exchange current densities and thus kinetics are evaluated. In doing so, we are developing both a rapid *ex-situ* screening method of PEMFC catalysts to sulfur compounds, as well delineating the mechanisms by which such compounds poison PEMFC catalysts. We will also describe the sulfur sensitivity of our low-Pt-content supported anode catalysts, such as tantalum phosphate-supported Pt. References: 1. R. Mohtadi, W.-k. Lee, S. Cowan, J.W. Van Zee, M. Murthy; *Electrochem. Sol. State Lett.*, 6 (2003) A272-A274. 2. N.M. Markovic, B.N. Grgur, P.N. Ross; *J. Phys. Chem. B*, 101 (1997) 5405-5413.

4:00 PM **A2.7**

A Comparison of Graphitic and Porous Carbons as Platinum Catalyst Support for Polymer Electrolyte Membrane Fuel Cell Electrodes. Abhishek Guha¹, Thomas A. Zawodzinski² and David A. Schiraldi¹; ¹Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio; ²Case Advanced Power Institute and Department of Chemical Engineering, Case Western Reserve University, Cleveland, Ohio.

Various forms of carbon, such as activated carbon, carbon black, carbon nanofibers and nanotubes, are considered to be ideal support materials for precious metal catalysts (such as Platinum and Ruthenium) used in fuel cell electrodes. The chemically inert carbon surfaces require modification prior to deposition of the catalyst metals. In this work, we compare the ability of high surface area carbon varieties both graphitic (carbon nanofibers) as well as amorphous (activated carbon) to homogeneously support finely divided platinum. The various carbons have been surface modified by oxidative treatment and nature of the oxidized carbon surface investigated with tools such as X-Ray Photoelectron Spectroscopy (XPS) and surface area measurement. Employing well documented literature techniques, nanometer sized Pt particles have been deposited on the oxidized carbon surfaces. Synthesis conditions for preparing the platinum-carbon electrocatalysts have been optimized by comparing the effects of reaction temperature and the nature of the reducing agents used to produce elemental platinum from chloroplatinic acid, on the platinum particle size and its distribution on the carbon surface. A study of the platinum particle size distribution/ dispersion, on each of the carbon supports has been carried out using X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) and correlated with the carbon surface area and its structural/chemical nature. Subsequently, fuel cell electrodes have been prepared using these electrocatalysts and, in combination with a perfluorosulfonated ionomer membrane, membrane electrode assemblies (MEA) have been fabricated. Electrochemical performance of the various MEAs in an actual fuel cell environment has been investigated and from the polarization curve data, various electrochemical parameters determined and compared.

4:15 PM **A2.8**

In-situ Fabricated Platinum Nanoparticles Embedded Carbon Nanofibers for PEM Fuel Cells. Lei Zhang¹, Bin Cheng² and Edward T. Samulski^{1,2}; ¹Curriculum in Applied & Materials Sciences, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina; ²Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina.

Close-packed polyacrylonitrile nanofibers containing platinum(II) acetylacetonate were fabricated by polymerization of acrylonitrile in a porous anodic aluminum oxide template. Subsequent pyrolysis results in carbon nanofibers wherein the Pt(II) salt is reduced in-situ to elemental Pt. High-resolution transmission electron microscopy showed that the Pt nanoparticles are dispersed throughout the carbon nanofibers, have a size range of 1-4 nm, and are single crystals. Rotating disc electrode voltammetry suggests that the dispersion of Pt nanocrystals in the carbon nanofiber matrix should exhibit

excellent electrocatalytic activity. The as-prepared Pt embedded carbon nanofibers were cast on Nafion 117 film. A fuel cell is made and tested using a TELEDYNE MEDUSA RD Fuel Cell Test Station.

4:30 PM **A2.9**

PEM fuel cell electrodes using Single Wall Carbon Nanotubes. Padraig Moloney¹, Chad Huffman², Olga Gorelik², Pasha Nikolaev², Edward Sosa², Sivaram Arepalli² and Leonard Yowell¹; ¹NASA Johnson Space Center, Houston, Texas; ²ERC Inc./NASA Johnson Space Center, Houston, Texas.

Single wall carbon nanotubes (SWCNT) have been considered suitable as a catalyst support in proton exchange membrane fuel cells (PEMFC) [1,2]. This research is heavily driven by the current space exploration effort at NASA which demands higher power densities and reliability from power and energy systems [2]. The new space exploration effort embarked by NASA and its partners demands higher power densities and dependability. Previous research and development of SWCNT for PEMFC catalyst supports has been advanced in this research by utilizing differing SWCNT purities and carbon blacks in differing ratios. New methods of fabrication and impregnation of catalyst ionomer and polytetrafluoroethylene have been researched. A thorough materials analysis and testing protocol has been used to characterize properties such as porosity, particle size, surface area, electroconductivity, purity and overall PEMFC performance. Using TEM ultramicrotomy and SEM freeze fracture, special attention has been paid to the membrane electrode assembly interfaces. TEM, SEM, EDS, XPS, TGA, BET, ICP, ultramicrotomy and CO Chemisorption were used to develop a relationship between material aspects on the nanoscale, and PEMFC performance. 1. H.J. Ruf, B.J. Landi, R.P. Raffaele SWNT Enhanced PEM Fuel Cells. In Second International Conference on Fuel Cell Science, Engineering and Technology, FuelCell2004-2527 ASME 2. C. Huffman, P. Moloney, O. Gorelik, P. Nikolaev, S. Arepalli, L. Oryshchyn, L. Yowell Evaluation of Carbon Nanotube Electrode Assemblies for Proton Exchange Membrane Fuel Cells. 2004 MRS Fall Meeting - Program/Symposium M

4:45 PM **A2.10**

Novel technique for characterizing porous and microporous material in real environment. Method of Standard Porosimetry. Alexander Sakars and Yury Volkovich; Porotech Ltd., Vaughan, Ontario, Canada.

Improving fuel cell, battery or other electrochemical device performance requires a comprehensive understanding of the porous structure of the electrodes, separators and membranes, catalysts and gas distribution layers the main parts of the devices. All of them have porous structure, which determines mass transfer process inside any electrochemical cell and finally its efficiency. Pore volume and specific surface distribution vs. pore radius, specific surface area, information about a shape (corrugation) of pores, liquid distributions in terms of values of its free binding energy with the surface and capillary pressure, sorption isotherms, differential characteristics of swelling, contact angle and its dependence on pore radius, characteristics of lyophilic and lyophobic properties, etc. - there is a list of data we should know for components to optimize the system on the whole. Method of Standard Porosimetry (MSP) allows obtaining all this data in real environment of porous material application in electrochemical systems. MSP was used during research and development of hydrogen-oxygen fuel cells within the framework of the Russian space program Buran-Energia. The invention of MSP and its use in research has allowed for creation of superior hydrogen-oxygen fuel cells. The widely known Method of Mercury Porosimetry (MMP) has several substantial disadvantages and limitation, for example, the necessity to apply high pressures of mercury (up to thousands of atmospheres), which can lead to a deformation or even destruction of the samples and to a distortion of the porosimetric curves (porograms). Other drawbacks MMP are: distortion of the results owing to amalgamation of most metals, different values of the mercury wetting angle for different materials, complexity of the equipment, and toxicity of mercury. The Method of Standard Porosimetry (MSP) and Automated Standard Porosimeter (ASP) have none of these disadvantages and give the possibility of measurements in a widest range of pore sizes (from 0.3 nm to 3x10⁵ nm) for any materials including soft, frail or amalgamating materials [1]. The description of MSP (ASP) and its theoretical substantiation are given. Results of porosimetric measurements of proton exchange membranes, catalysts, gas distribution layers of fuel cells, separators and electrodes of batteries are presented. A technique of the overall performance analysis of the electrochemical device based on the results of research of components porous structure is offered. References Y.M. Volkovich, V.S. Bagotzky, V.E. Sosenkin, I.A. Blinov. In: *Colloid and Surfaces. A: Physicochemical and Engineering Aspects.* 187-188 (2001) 349-365.

8:00 AM *A3.1

Vacuum Deposited Non-Precious Metal Catalysts for PEM Fuel Cells. David G. O'Neill¹, Alison Schmoedel¹, George Vernstrom¹, Dennis O'Brien¹, Manish Jain¹, Radoslav Atanasoski¹, E. B. Easton², Th. Buhrmester², Jeff Dahn² and David Wieliczka³; ¹CRPL, 3M Company, Maplewood, Minnesota; ²Dept. of Physics, Dalhousie University, Halifax, Nova Scotia, Canada; ³Physics, University of Missouri - Kansas City, Kansas City, Missouri.

Several groups are working to develop non-precious metal catalysts for the oxygen-reduction reaction in PEM fuel cells. A technical starting point for these studies is the fact that pyrolyzed Fe-N and Co-N macrocyclic compounds on carbon act as ORR catalysts. Characterization of these transition-metal (TM) catalysts show that only carbon, nitrogen and the metal remain after thermal treatments above 650°C. It has been proposed that the content of nitrogen in pyridinic form in/on the carbon substrate is a prerequisite for high catalytic activity. We are using vacuum vapor deposition techniques to make and study C-N, Fe-N and C-N-Fe materials as potential ORR catalysts. The materials characterization techniques we are using include various microscopies, EXAFS, XPS (ESCA) and UPS with 3p=>3d resonance techniques, while the catalyst performance is measured by measuring I-V profiles in a PEM fuel cell. Changes in the N1s core level with Fe content provide evidence of Fe-N bonding and use of resonant valence band photoemission techniques allows the local electronic structure around the metal atom to be determined. The catalytic behavior, however, is low, despite the fact that our materials have a higher nitrogen and iron content than thermally treated catalysts. Fuel cell testing shows that these materials do not exhibit an iron redox couple and that they are stable in an acidic environment. Combining fundamental characterization techniques with theoretical modeling provides insight into possible bonding configurations between carbon, nitrogen and a transition metal such as iron. This research was supported in part by the U.S. Department of Energy (DOE), Cooperative Agreement No. DE-FC36-03GO13106. DOE support does not constitute an endorsement by DOE of the views expressed in this presentation.

8:30 AM A3.2

Theoretical Modeling of Non-Precious Metal Catalysts for PEM Fuel Cells. Manish Jain¹, Shih-hung Chou¹, Allen Siedle¹ and David G. O'Neill²; ¹Corporate Research Materials Laboratory, 3M Company, St. Paul, Minnesota; ²Corporate Research Process Laboratory, 3M Company, St. Paul, Minnesota.

We used density functional methods to examine the structural and electronic aspects of such non-precious metal catalysts. One, centered on iron, has been extensively studied experimentally in the literature [M. Lefevre, J. P. Dodelet, and P. Bertrand, J. Phys. Chem. B, 104, 11238 (2000)]. While, an atomic level description of these iron-based catalysts has not been achieved, secondary ion mass spectrometric (SIMS) studies indicated that the ion FeN₂C₄⁺ might be a signature of the most active catalytic site. This result has led to the suggestion that the active site might correspond to a graphene lattice into which Fe and N had been substituted; and in which the nitrogen atoms act as ligands that provide binding sites for iron. We studied the thermodynamic stability of some of these proposed catalytic centers in these materials. It is also considered that this fundamental chemistry might be carried out using continuous, vacuum sputtering deposition process technology. We also examine the possible structures formed during the vacuum vapor deposition of C-N and C-N-Fe materials using ab initio molecular dynamics. Combined with characterization techniques, such as EXAFS and UPS, this work provides insight into possible bonding configurations between carbon, nitrogen and a transition metal such as iron in these materials. This research was supported in part by the U.S. Department of Energy (DOE), Cooperative Agreement No. DE-FC36-03GO13106. DOE support does not constitute an endorsement by DOE of the views expressed in this presentation.

8:45 AM A3.3

Carbon-Supported Bimetallic and Trimetallic Alloy Nanoparticle Electrocatalysts. Jin Luo, Mathew M. Maye, Yan Lin, Nancy N. Kariuki, Lingyan Wang, Peter Njoki, Derrick Mott and Chuan-Jian Zhong; Chemistry, State Univ. of New York at Binghamton, Binghamton, New York.

Hydrogen fuel cells and direct methanol fuel cells are becoming increasingly attractive power sources because of the high conversion efficiencies and low pollution and the use for mobile and stationary applications such as on-board electric power sources for advanced

propulsion systems, non-polluting electric vehicles and portable devices. This presentation reports recent results of an investigation of the electrocatalytic methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR) at carbon-supported alloy nanoparticle catalysts. The exploration of the bimetallic and trimetallic composition on carbon black support is aimed at modifying the catalytic properties at the anode and cathode in methanol oxidation fuel cells. In contrast to many traditional approaches to catalyst preparation, our catalyst preparation involved core-shell synthesis of Au and AuPt_{100-n} nanocrystals of 2~3 nm core sizes with organic monolayer shell encapsulation, assembly on carbon black support materials and calcination at different temperatures. The bimetallic AuPt_{100-n} nanoparticles were shown to exhibit alloy properties, and were shown to significantly modify the electrocatalytic properties for the MOR and ORR reactions. The electrocatalytic activities were characterized using voltammetric and rotating disk electrode techniques, and were also compared with those obtained with commercially-available catalysts. The results revealed new insights into the understanding of how the catalyst calcination treatment influences the surface composition and the synergistic catalytic activity of the bimetallic nanoparticle catalysts, and have important implications to the design of highly active catalysts using the core-shell derived nanoparticles.

9:00 AM A3.4

Doped ceria - LaMeO₃ (Me=Mn, Fe, Co) nanocomposites: synthesis via mechanochemical activation route and properties. Liubov Isupova¹, Elena Obyskalova², Vladimir Rogov¹, Sergei Tsybulya¹, Elena Burgina¹, Nataliya Boldyreva¹, Vladislav Sadykov¹ and Nina Orlovskaya³; ¹Boskov Institute of catalysis, Novosibirsk, Russian Federation; ²Novosibirsk State University, Novosibirsk, Russian Federation; ³Drexel University, Philadelphia, Pennsylvania.

Synthesis of inexpensive cathode materials with a high mixed ionic - electronic conductivity and performance stability under contact with CO₂-containing feeds is a very important task for the IT SOFC and bipolar plates design. Single-phase perovskites doped with alkaline-earth cations do not meet these demands. Nanocomposites comprised of fluorite-like oxides (good ionic conductors) and perovskites (electronic conductors) appear to be promising for these applications. A low cost of these nanocomposites required for the practical application can be ensured by using as raw materials industrially available inexpensive mixed oxides of lanthanides Ln₂O₃ (Ln =Ce, La, Pr, Nd, Sm) provided an efficient preparation technique is developed. This can be achieved by using mechanical activation (MA) of the mixture of solid reagents - Ln₂O₃ and simple transition metal oxides in high power planetary ball mills followed by annealing. This work aims at developing approaches to mechanochemical synthesis of such nanocomposites by MA route and studies of their structural properties as well as the lattice oxygen mobility and reactivity. To avoid admixture of 3d oxides in the nanocomposites, the amount of simple oxides in the initial reagents mixture was equal to La content in the Ln₂O₃. After MA, the mixture was calcined at 900, 1000, 1100 °C for 6 h in the air. The structural features of annealed samples were studied by XRD, TEM, IR and Raman spectroscopy, while H₂ TPR was used to characterize the lattice oxygen reactivity and mobility. At all calcination temperatures, two phases were found by XRD: CeO₂* with the fluorite - like structure and LaMeO₃ (Me = Mn, Co, Fe) perovskite. With increasing the calcination temperature, for both phases, the strongest variation of the lattice parameters and IR spectra of the lattice modes was revealed for Co-containing system suggesting progressive incorporation of all Ln³⁺ cations into the perovskite structure. Specific surface area of samples varies from 6-9 m²/g (annealing at 900 °C) to 2 m²/g (annealing at 1100 °C). Even after calcination at 1100 °C, the X-ray domain sizes of both phases remain in the nano-range (up to 50 nm). According to H₂ TPR, there are two peaks of hydrogen consumption their position and intensity depend on the nature of 3d cation. Nanocomposites are reduced much more intense than individual perovskite or doped fluorite-like phases which demonstrates increased mobility of the lattice oxygen in nanocomposites due to efficient percolation leading to conjugation of the ionic and electronic fluxes in MIEC systems. Position of the first peak increases in the order Co > Mn > Fe which is determined by reactivity of oxygen forms located on transition metal cations. Hence, developed nanocomposites appear to be promising for such applications as cathodes and anodes in IT SOFC. This work is in part supported by NATO SFP 980878 Project.

9:15 AM A3.5

Application of Carbon Nanotube/Polymer Composites as Electrode for Polyelectrolyte Membrane Fuel Cells. Kirsten Prehn¹, Suzana Pereira Nunes² and Karl Schulte¹; ¹Polymer Composites, Technische Universitaet Hamburg-Harburg, Hamburg, Germany; ²Institute of Chemistry / Department of Polymer Technology 1, GKSS-Forschungszentrum, Geesthacht, Germany.

Carbon nanotubes (CNTs) possess remarkable mechanical and physical characteristics due to their unique structure. The high electrical conductivity of CNTs in combination with their structural and chemical properties make this material attractive for improvement of the performance of the electrodes in electrochemical devices, such as polyelectrolyte-membrane fuel cells. The requirements in particular for this application are manifold. Since the electrode is the reaction layer in a fuel cell, the electrolyte, being proton conductive, has to be combined with catalytic activity and electron conductivity, as well as chemical stability against the reactants. Employed as an electrode, CNTs offer feasibilities to enhance the efficiency of fuel cells due to an improved contact between electrolyte-membrane, electrode and catalyst. An other promising capacity is the large specific surface area of CNTs on which catalyst particles can be distributed in small clusters. This provides an increase of the catalyst efficiency on account of a higher reactive surface area which enables a reduction of the amount of catalyst required. In combination with a good electron conductivity, a CNT based electrode is a potential alternative fuel cell electrode. The presented work focuses on a membrane assembly, consisting of CNTs as electrode and sulfonated polyether ether ketone (SPEEK), which is used as polyelectrolyte in direct methanol fuel cells (DMFCs) and provides good proton conductivity. Nanocomposites were produced by a modified drop casting technique, leading to the formation of an asymmetric structure. Due to the process, the compounded membranes provided a single-sided electron conductivity on account of the CNTs. By using different 3D-structured CNT-carpets, varying in thickness, density and setup, the properties of the electrode membrane could be adjusted for its special application. In consideration of the insertion of platinum and ruthenium particles as catalyst in nano-sized clusters on the CNTs, carpets were modified and grown in a CVD-process at the TUHH. The evaluation of the assemblies comprised SEM-pictures in order to analyse the 3D-nano-structure, measurements of the surface conductivity as well as tests in a direct methanol fuel cell.

10:00 AM *A3.6

Solid Oxide Fuel Cells: Status, Challenges and Opportunities. Subhash C. Singhal, Pacific Northwest National Laboratory, Richland, Washington.

Solid oxide fuel cells (SOFCs), based on an oxide ion conducting electrolyte such as stabilized-zirconia, offer a clean, low-pollution technology to electrochemically generate electricity at high efficiencies. These cells operate between about 700 and 1000 °C, and some hydrocarbon fuels such as natural gas can be reformed within the cell stack eliminating the need for an expensive, external reformer. The most progress to date has been achieved with the tubular SOFCs; however, their electrical resistance is high and power density low. Planar SOFCs, particularly anode-supported, in contrast, are capable of achieving very high power densities and can be mass produced using low-cost conventional ceramic and microelectronic fabrication techniques. This overview discusses the designs, materials and fabrication processes, and the performance of SOFCs under different operating conditions. Applications of such cells in stationary, mobile and military market sectors are reviewed and future research areas are highlighted.

10:30 AM A3.7

Sputter deposition of alternative multilayer gadolinia-doped ceria and zirconia for fast oxygen ionic conduction. Yiguang Wang^{2,1}, Anthony Cinson¹, Joshua Gilmore¹, Olga Marina¹, Chongmin Wang¹, Vaithiyalingam Shutthanandan¹, Laxmikant Saraf¹, Linan An² and Suntharampillai Thevuthasan¹; ¹Pacific Northwestern National Lab, Richland, Washington; ²Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, Florida.

Development of electrolyte materials that possess high oxygen ion conductance at relatively low temperatures is essential to improve the performance of solid oxide fuel cells. Ceria, doped with a divalent or trivalent cation, exhibits higher ion conductance compared with yttria-stabilized zirconia, the electrolyte currently used in solid oxide fuel cells. In this study, we have synthesized layer-by-layer structures of highly oriented gadolinia doped ceria and zirconia using sputter deposition in order to determine the nanoscale effects on the ion conductance. These films were characterized by several bulk sensitive capabilities including x-ray diffraction (XRD), high resolution transmission electron microscopy (TEM), and Rutherford backscattering spectrometry (RBS). The oxygen ion conductivity measurements were carried out using surface impedance spectroscopy (IS) as a function of temperature up to 9000°C. Reduction and oxidation of these films were studied in the background of hydrogen and 18O, respectively as a function of temperature. 18O uptake in the film was studied using nuclear reaction analysis (NRA) and these results will be discussed along with the effects of individual layer thickness on the ion conductance.

10:45 AM A3.8

Preparation and Electrical Properties of Nano-Sized Doped Ceria for SOFC Anodes. Jumpei Kobayashi^{1,2}, Hitoshi Takamura^{1,2}, Atsunori Kamegawa^{1,2} and Masuo Okada^{1,2}; ¹Department of Materials Science, Tohoku Univ., Sendai, Japan; ²CREST, Japan Science and Technology Agency, Kawaguchi, Japan.

Cerium oxides have been widely investigated as an electrolyte for solid oxide fuel cells (SOFCs), because of their high oxide-ion conductivity. Recently, some cerium oxides, for example Pr and Mn-doped ceria showing a certain level of electronic conduction at elevated temperatures, have also attracted attention for use in ceramics-based anode materials for SOFCs. To improve the electrode properties, it is important to increase the mixed conductivity, especially, electronic conductivity of the doped ceria. For that purpose, nano-particles of Pr and Mn-doped ceria have been prepared, and their electrical properties and morphological stability have been evaluated as functions of temperature and oxygen potential. The samples of Pr and Mn-doped ceria have been prepared by mixing nitrate solutions and hexamethylenetetramine as an oxidizing agent. The particle size was evaluated by means of BET, XRD, and TEM. The particle size of Pr and Mn-doped ceria was found to be approximately 3 nm as prepared. Even though the particle size of doped ceria increases with increasing annealing temperature, the size of less than 20 nm was kept after annealing at 873 K for 10 h. On the other hand, the lattice constant of nano-sized ceria, for example 0.545 nm for 3 nm-size particles, decreases and reaches to the value of bulk material (0.541 nm) as annealing temperature increases. This suggests that the valence state of cerium and the amount of oxygen vacancies strongly depend on the particle size. The size-dependent electrical properties of doped-ceria will be also presented.

11:00 AM A3.9

Fabrication of Gadolinia and Samaria Doped Ceria and Zirconia Vertical Layered Nanostructures for Solid Oxide Fuel Cell Applications. Satyanarayana V. N. T. Kuchibhatla¹, Olga Marina², Chongmin Wang², Bruce Arey², Shutthanandan Vaithiyalingam², Englehard Mark², Laxmikant Saraf², Seal Sudipta¹, Donald Baer² and Thevuthasan Suntharampillai²; ¹University of Central Florida, Orlando, Florida; ²Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington.

Significant amount of research in the field of Solid Oxide Fuel Cells (SOFCs) is being focused on making more economic and efficient electrolyte materials that can operate at lower temperatures. Ceria doped with divalent and trivalent cations has been proposed as a potential alternative to the existing high temperature electrolytes. Doped ceria not only possess an enhanced ionic conductivity but can operate at lower temperatures; there by a significant increase in life time can be achieved. In addition, it is well known that nano scale materials often display properties very different from the base coarse-grained bulk materials. In the present study, we have synthesized vertical layered nanostructures of gadolinia and samaria doped ceria and zirconia using the combination of Glancing Angle Deposition (GLAD) and sol-gel spin coating. These films were characterized by several bulk and surface sensitive capabilities including x-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) and x-ray photoelectron spectroscopy (XPS). Oxygen ionic conductivity measurements were made as a function of temperature in these materials and these results will be discussed along with the details of the film growth.

11:15 AM A3.10

Preparation and Characterization of Proton Conductive Doped Strontium Cerate Thin Films for Fuel Cell Applications. Zhigang Xu and Gukan Rajaram; Mechanical Engineering, North Carolina A&T State University, Greensboro, North Carolina.

Thin film technologies have commonly accepted as a desired way to develop intermediate-temperature solid oxide fuel cells (SOFCs). Another way to reduce the SOFCs operating temperature is to use electrolyte materials with higher conductivities. To develop materials with higher ionic conductivities than YSZ has received great interest from many scientists and researchers. Proton conductors are even more attractive, because they have higher conductivities than oxygen ion conductors at low temperatures. Proton-conductive ceramics is a relatively new group of materials that may reduce the operating temperature to about 400-600 °C; a temperature that still retains the fuel flexibility. The protons attain their high mobility from the ease with which they jump from one oxygen vacancy to the next in the electrolyte. Because the activity energy for proton to achieve certain mobility is much less than that for oxygen ion, the SOFCs based on

proton conduction could be operated at much lower temperatures. In this study, thin film coatings of $\text{SrCe}_{0.95}\text{M}_{0.05}\text{O}_{3-\delta}$ ($M = \text{Yb}$ and Y , $\delta =$ oxygen deficiency per perovskite-type oxide unit cell) was processed with combustion chemical vapor deposition technique on silicon substrates. The combustion chemical vapor deposition technique provided an efficient approach to prepare doped strontium cerate thin films. Metalorganics of all the elements required to form the conductive thin films were dissolved in an organic solvent-toluene. Toluene also serves as the fuel of combustion to produce enough heat for the chemical reactions to take place. The effects of the deposition parameters on the film growth and film properties were investigated. The deposited films were subjected to microstructural study with scanning and transmission electron microscopes. The phases were characterized with x-ray diffraction. Samples for conductivity tests are under preparation.

11:30 AM [A3.11](#)

Chemical Synthesis and Microwave Sintering of Gd Doped CeO₂ /SiO₂ Nanocomposites. Rajalekshmi Chockalingam Pillai, Vasantha R. W. Amarakoon, Sreekumar Chockalingam, Gary E. Del Regno and Herbert Giesche; Ceramic Engineering and Material Science, NYSCC at Alfred University, Alfred, New York.

Gd doped CeO₂ is a candidate electrolyte material for high temperature solid oxide fuel cells (SOFC) due to its high electrical conductivity at intermediate temperatures (500-600°C). CeO₂ /SiO₂ nanocomposites were prepared using a chemical synthesis technique. Mixed oxide powders of the same composition were also prepared. These powders were then dry pressed and consolidated using conventional and microwave sintering techniques. X-ray diffraction, SEM/EDS microstructure and electrical conductivity measurements were used to determine the effect of composition (Gd doping concentration), powder synthesis technique and the sintering procedure on the microstructure and properties of Gd doped CeO₂ /SiO₂ composites.

11:45 AM [A3.12](#)

Theoretical Modeling of Proton Diffusion in Acceptor Doped BaZrO₃. Marten E. Bjorketun, Per G. Sundell and Goran Wahnstrom; Applied Physics, Chalmers University of Technology, Goteborg, Sweden.

In recent years, proton conducting perovskite oxides with composition ABO₃ have attracted attention for their potential application as solid electrolytes in electrochemical devices such as gas sensors, hydrogen pumps and solid oxide fuel cells. Consequentially, much effort has been invested in pinpointing the dominating microscopic proton transport mechanism and in determining how the elementary steps are interrelated [1,2]. Considerably less work has however been devoted to developing suitable diffusion models to provide links between the microscopic parameters of the local protonic motion and the macroscopic transport properties. In this work the long-range protonic migration in acceptor doped BaZrO₃ is evaluated by combining density-functional calculations with a prototype model for protonic diffusion in perovskites. All the microscopic diffusion parameters - including proton binding energies in different surroundings, relevant proton migration paths and corresponding energy barriers - are obtained directly from first-principles. Based on the attained knowledge of the migration process the dynamic structure factor, the proton self-diffusion coefficient and the ac conductivity are calculated and compared with experiments. Finally, the possibility of proton-dopant association (trapping) and its implications for the long-range protonic transport is discussed. [1] Th. Matzke, U. Stimming, Ch. Karmonik, M. Soertramo, R. Hempelmann, F. Guthoff, Solid State Ionics **86 - 88**, 621 (1996). [2] W. Münch, G. Seifert, K.D. Kreuer, J. Maier, Solid State Ionics **86 - 88**, 647 (1996).

SESSION A4: Solid Oxide Fuel Cells
Chair: Ned Cipollini
Tuesday Afternoon, November 29, 2005
Room 311 (Hynes)

1:30 PM [A4.1](#)

Oxygen diffusion in nanocrystalline Ytria-stabilized Zirconia. Harald Drings, Anthony Madubuonu, Ralf Roewer and Hans-Eckhardt Schaefer; Institute for Theoretical and Applied Physics, Universitaet Stuttgart, Stuttgart, Germany.

The oxygen transport properties of zirconia-based materials gives rise to many technical applications, such as solid electrolytes in fuel cells. This is the case especially for yttria-stabilized zirconia ($\text{ZrO}_2\text{Y}_2\text{O}_3$). It has been recently shown that the oxygen diffusivity in the grain boundaries of nanocrystalline $\text{ZrO}_2\text{Y}_2\text{O}_3$ is strongly enhanced (G. Knoener et al., PNAS 100, 3870 (2003)) compared to the volume diffusivity. With an enhanced oxygen diffusivity solid oxide fuel cells

(SOFC) can be operated at lower temperatures and materials deterioration is reduced. The samples were prepared by gas phase synthesis of nanometer-sized ZrY alloy particles which were oxidized and subsequently compacted and sintered. Care was taken to reduce the porosity to avoid any disturbing effects that cavities might have. The efficiency of the oxygen transport could be further increased by reducing the grain size in fully densely sintered materials making use of Al₂O₃ (6mol%) doping. At present the main goal is to compare the oxygen tracer diffusion data obtained by SIMS with electrical impedance data on the same specimens making use of the Nernst-Einstein relationship.

1:45 PM [A4.2](#)

A First-principles Investigation of Superprotonic Activity in CsHSO₄. Brandon Wood and Nicola Marzari; Materials Science and Engineering, MIT, Cambridge, Massachusetts.

With the recent push to realize the hydrogen economy, there has been a surge of interest in viable solid-state materials for use as fuel cell electrolytes. Among the candidates are various derivatives of the anhydrous superprotonic conductor CsHSO₄, which exhibits reasonably high ionic conductivity at relevant operating temperatures while remaining electronically insulating. However, despite being widely characterized experimentally, a truly atomistic picture of the diffusion pathways and mechanisms in the material remains somewhat elusive. To this end, we present results of first-principles static calculations and 100 ps of dynamics simulations on 112-atom supercells of CsHSO₄. We isolate the dominant mechanisms involved in the superprotonic behavior and discuss the impact of correlated diffusive events in enhancing proton transport. We also offer a detailed description of the dynamics of the hydrogen bond network at the diffusing protons are traced through the lattice. The significance of our findings in understanding superionic behavior is discussed.

2:00 PM [A4.3](#)

Performance of solid oxide fuel cells with ultra-thin electrolytes, modified by heavy ion irradiation. Jeremy Cheng, Rojana Pornprasertsuk, Masafumi Nakamura, Pei-Chen Su, Hong Huang, Yuji Saito and Fritz B Prinz; Stanford University, Stanford, California.

Solid Oxide Fuel Cells (SOFC) convert hydrogen into electrical energy using a ceramic, oxide conducting electrolyte. Compared to the more common polymer-based PEM fuel cells, they operate at high temperatures, avoiding the water management and CO poisoning problems of the PEM. Commercial SOFC's today operate around 800°C, but if the operating temperature can be lowered many key design issues can be solved. A wider array of materials can be used for the cathode and for gas sealing. Low temperature operating SOFCs with ultra thin electrolytes were produced using Si microfabrication techniques. Running on hydrogen and air, they could produce a significant power density at 350°C. I-V curves could be measured down to 250°C. The cell performance was limited by reaction losses at the cathode. The conductivity of the electrolyte was studied after treatment with heavy ion irradiation. Dislocations were introduced into epitaxial YSZ thin films with a 150 keV Ar⁺ beam. Following subsequent heat treatment, the conductivity increased by 55% without a significant change in activation energy compared to the as-deposited material. These electrochemical systems were modeled with Quantum Modeling / Kinetic Monte Carlo simulations over a range of dopant concentrations, temperatures, and dislocation densities. The oxygen transport through the electrolyte as well as the electrolyte reaction was studied, with correlation to experimental results.

2:15 PM [A4.4](#)

A Density-Functional Study of Defect Formation in BaZrO₃. Per G. Sundell, Marten E. Bjorketun and Goran Wahnstrom; Applied Physics, Chalmers University of Technology, Goteborg, Sweden.

Proton conductors based on perovskite oxides [1] have potential application as solid electrolytes in various electrochemical devices such as gas sensors, hydrogen pumps or fuel cells. Since the properties of these materials depend sensitively on environmental variables such as atmosphere and temperature, an understanding of their defect chemistry at the microscopic level is essential in order to optimize performance [2]. We have used first-principles density-functional calculations within the planewave/pseudopotential approach to study structural and electronic properties of dopant atoms, anion- and cation vacancies, and hydrogen interstitials in BaZrO₃. By combining the first-principles results with thermodynamic theory, defect formation energies at finite temperature and pressure are calculated and compared with experiments. It is found that trivalent dopants such as Ga, In, Sc or Y preferably substitute for Zr atoms in the lattice. This modifies the electronic structure of the oxide so that holes are formed at the top of the valence band, corresponding to p-type electrical conductivity. At high temperatures and low oxygen partial pressures, dopants are instead charge compensated by a

formation of oxygen vacancies. Upon hydration, interstitial protons can be introduced by dissociative absorption of water into these vacancies. Our results indicate a significant amount of defect-defect interactions, which is predicted to have implications for dopant clustering, hydration energies and the long-range diffusion of protons in the material. [1] H. Iwahara, T. Esaka, H. Uchida and N. Maeda, *Solid State Ionics* **3** – 4, 359 (1981). [2] K. D. Kreuer, *Solid State Ionics* **97**, 1 (1997).

3:30 PM *A4.5

NiO-YSZ Foams for Anodic Application in SOFCs. Alberto Rainer, Francesco Basoli, Silvia Licocchia and Enrico Traversa; Department of Chemical Science and Technology, University of Rome Tor Vergata, ROME, Italy.

Cellular ceramics represent a very interesting class of materials for several applications, since they combine high porosity, light weight and high gas permeability to good mechanical properties and good thermal shock resistance. In this paper, in situ polymerization of a ceramic loaded polyurethane foam has been applied to the fabrication of NiO-YSZ substrates for SOFC applications. A selected quantity of a commercial NiO-YSZ anodic powder (Nextech) was dispersed separately in the two components of a polyurethane system. The two components were mixed together and polymerization occurred into a mould. After polymerization reaction, a dish about 1 mm thick was obtained. The dish was sintered according to parameters assessed from TG-DTA results. Morphological characterization of the foam, performed by scanning electron microscopy (FE-SEM), evidenced the open cell structure and the good sintering of the trabecular elements. Porosity investigation was performed on sintered bodies by means of mercury porosimetry. Reduction of NiO was performed in hydrogen atmosphere at a temperature of 700 °C for several hours. 4 points DC measurements were performed on bar-shaped samples to determine the conductivity of the foam after reduction.

4:00 PM *A4.6

Performance of Intermediate Temperature Solid Oxide Fuel Cell Based on Sr-and-Mg-Doped Lanthanum Gallate Electrolyte. Uday B. Pal, Srikanth Gopalan and Wenquan Gong; Manufacturing Engineering, Boston University, Brookline, Massachusetts.

The objective of this work was to obtain a stable materials system for intermediate temperature solid oxide fuel cell (SOFC) capable of operating between 600-800 C with a power density greater than 0.2 W/cm². The solid electrolyte chosen for this system was Sr-and-Mg Doped lanthanum gallate (LSGM). To select the right electrode materials from a group of possible candidate materials, AC complex impedance spectroscopy studies were conducted between 600-800 C on symmetrical cells that employed the LSGM electrolyte. Based on the results of this investigation, LSGM electrolyte-supported SOFCs were fabricated with composite cathode consisting of LSGM and Sr-and-Fe doped lanthanum cobaltate and a composite anode consisting of La-doped ceria and nickel. A thin barrier layer of La-doped ceria was deposited between the anode and the electrolyte to prevent interaction of Ni in the anode with La in the LSGM electrolyte. Electrical performance and stability of these cells were determined and the electrode polarization behavior as a function of cell current was modeled between 600-800 C. The electrical performance of the anode-supported SOFC was simulated assuming an electrode polarization behavior identical to the LSGM electrolyte supported SOFC. The simulated performance indicated that the selected materials system would provide a stable cell capable of operating between 600-800 C with a power density between 0.2-1 W/cm².

4:30 PM A4.7

Regenerative, Coal-Based Solid Oxide Fuel Cell-Electrolyzers. Srikanth Gopalan and Uday B. Pal; Boston University, Boston, Massachusetts.

Increased energy demands especially from rapidly industrializing countries are placing increasing stresses on fossil fuel reserves. With increasing oil and natural gas prices, coal-based power generation is gaining importance. In this paper we propose and present a theoretical analysis of a coal-based reversible solid oxide fuel cell and electrolyzer capable of operating as a fuel cell during peak demand and as an electrolyzer generating hydrogen during off-peak demand. The hydrogen generated during off-peak demand can be stored on-site and used to supplement the fuel supply to the fuel cell during peak demand. The regenerative solid oxide fuel cell-electrolyzer comprises of a Ni-yttria stabilized zirconia (YSZ) electrode and a second liquid metal electrode which is stable against oxidation. During operation of the device as an electrolyzer, a hydrogen/water-vapor mixture rich in water-vapor is fed to the Ni-YSZ electrode (cathode) and coal to the liquid-metal electrode (anode). Oxygen ions formed through dissociation of the water-vapor transports through the YSZ electrolyte, leaving behind a hydrogen rich gas on the Ni-YSZ

electrode side. The oxygen that transports across the YSZ forms dissolved oxygen species in the liquid metal. The dissolved oxygen then transports to the liquid/coal interface where it reacts to form carbon monoxide. The carbon monoxide evolved on the anode side of the electrolyzer is burnt in a separate catalytic reactor; the heat of the combustion reaction can be used to generate water-vapor. During fuel cell mode, the operation of the cell is reversed. Air is bubbled through the liquid metal (cathode) and the stored hydrogen to the Ni-YSZ electrode (anode). Oxygen dissolved in the liquid metal, transport through the YSZ and combines with hydrogen on the anode side to generate electricity in the external circuit. Calculations of device efficiencies as a function of various operating parameters will be presented in this paper.

4:45 PM A4.8

Hydrogen Production from Methane by Using Composite-Type Oxygen Permeable Membranes.

Hitoshi Takamura^{1,2}, Masayuki Ogawa^{1,2}, Yusuke Aizumi^{1,2}, Atsunori Kamegawa^{1,2} and Masuo Okada^{1,2}; ¹Department of Materials Science, Tohoku Univ., Sendai, Japan; ²CREST, Japan Science and Technology Agency, Kawaguchi, Japan.

Oxygen permeable membranes based on mixed oxide-ion and electronic conductors are of interest in view of their promising applications such as production of syngas or pure hydrogen from natural gas. For PEFCs and SOFCs, these ceramics-based membranes can be used for fuel processor by means of partial oxidation of methane. Among a number of the ceramics-based membranes, ceria-based composites having spinel-type ferrites as an electronic conductive phase are well known to exhibit a high oxygen flux density, reaching to 13.4 sccm/cm², and high CO and H₂ selectivities under methane conversion environments. Compared to perovskite-type materials such as in La-Sr-Co-Fe systems, the advantages of these ceria-based composites are higher mechanical strength and lower thermal expansion coefficient matching that of component materials developed for SOFCs. In this study, planar-type reforming modules comprising of the composite-type membrane prepared by a tape-casting technique and ferric stainless steel supports have been fabricated, and their reforming properties have been also evaluated. By using Ni-based catalysts supported on cerium oxides, high CO and H₂ selectivity of reaching to 95 % was attained under high CH₄ conversion rate of approximately 90 %. The degradation and failure of membranes will be also discussed in the context of operating temperature and oxygen potential gradient.

SESSION A5: Grand Challenge of Hydrogen Storage
Chair: Charles Oik
Wednesday Morning, November 30, 2005
Room 311 (Hynes)

8:00 AM *A5.1

The National Hydrogen Storage Project: Recent Progress in On-Board Vehicular Hydrogen Storage. Sunita Satyapal¹, Carole Read¹, Grace Ordaz¹ and John Petrovic²; ¹Office of Hydrogen, Fuel Cells and Infrastructure Technologies, U.S. Department of Energy, Washington, District of Columbia; ²Los Alamos National Laboratory, Washington, District of Columbia.

Hydrogen-powered vehicles require a driving range of greater than 300 miles in order to meet customer requirements and compete effectively with other automotive technologies. Achieving such a driving distance requires that approximately 5 to 13 kg (range for the overall fleet) of hydrogen must be stored on-board the vehicle. Storage of these quantities of hydrogen within vehicular weight, volume, and system cost constraints is a major scientific and technological challenge. Vehicular hydrogen storage targets for 2010 and 2015 have been established through the FreedomCAR & Fuel Partnership, a partnership between the DOE, U.S. automobile manufacturers, and major energy companies. The National Hydrogen Storage Project was initiated by the DOE through a "Grand Challenge" to the technical community launched in 2003, to meet these targets. Centers of Excellence in metal hydrides, chemical hydrogen storage, and carbon-based materials have been established, each Center involving a number of university, industry, and federal laboratory partners. In addition, independent university and industry projects are being supported in the areas of new concepts/materials, hydrogen storage testing, and storage system analyses. Recent progress achieved in hydrogen storage through the R&D activities of The National Hydrogen Storage Project will be highlighted and discussed. An update on the Storage Analysis Working Group and on storage projects in support of the International Partnership for the Hydrogen Economy will also be presented.

8:30 AM *A5.2

Nanostructured Materials for Hydrogen Storage.

Bruce Clemens, Department of Materials Science and Engineering, Stanford University, Stanford, California.

Technologically useful chemical storage of hydrogen places demands on material properties that are not well met by current material options. Achieving a high mass ratio dictates using only the top few elements of the periodic table, which places constraints on modifying the chemical formulation to achieve favorable hydrogenation and dehydrogenation behavior. An alternative approach is to use particle size and shape to tune the chemical properties of matter. Nanometer sized particles have dramatically different properties than bulk, including the well-known lowering of melting point. However, reaction kinetics, solubility, phase stability are also a strong function of size. This paper discusses the changes in thermodynamics and kinetics associated with changes in particle size. We use metal nanoparticles, carbon nanotubes, and metal-carbon nanostructured hybrid structures as examples. We also discuss the use of thin films to investigate the reaction mechanisms.

9:00 AM *A5.3

Solid-State Hydrogen Storage: Challenges and Progress.

Rex Harris, Paul Anderson and David Book; University of Birmingham, Birmingham, United Kingdom.

One of the major stepping stones on the path to a hydrogen energy-based economy is the development of an effective (cost and performance) solid-state means of reversible hydrogen storage. To reach this goal a number of vital objectives have to be achieved and these include a high wt% and volume density of stored hydrogen (particularly for mobile applications), attractive absorption (or adsorption) and desorption kinetics at convenient temperatures and pressures, and cheap and readily available material. Another, very critical hurdle is long term resistance to poisoning by trace impurities in the hydrogen stream. The material also needs to be safe and preferably reusable after exposure to air. Clearly this is a formidable list and the challenges are greater for mobile applications. In this contribution, we consider the current state of affairs with particular reference to the criteria outlined above. This is followed by a description of storage activities being carried out jointly at the University of Birmingham between Chemistry and Metallurgy and Materials. Some of these form part of the UK Sustainable Hydrogen Energy Consortium (UK-SHEC). The work includes studies on the effects of additives on the hydrogen absorption/desorption kinetics of MgH₂, the dehydrogenation behaviour of milled carbon, synthesis of borohydrides, activation of metal hydrides and detailed studies of a range of zeolites. The use of hydrogen to modify microstructures and improve kinetics will also be discussed.

9:30 AM *A5.4

Neutron Methods for Fuel Cells and Hydrogen Storage

Materials. Dan A. Neumann, NIST Center for Neutron Research, NIST, Gaithersburg, Maryland.

The unusually large neutron scattering cross section for hydrogen (and deuterium) as well as the great penetrating power of neutrons make them particularly well-suited for studying materials and systems for hydrogen-based technologies. In particular, neutron scattering and analysis techniques are routinely used to probe the amount, location, bonding states, and dynamics of hydrogen in a variety of materials for potential use in fuel cells and hydrogen storage beds. Developments over the past decade at the NIST Center for Neutron Research and elsewhere have greatly increased the sensitivity and dynamic range of neutron methods. In this talk, we will provide a flavor of the capabilities of modern neutron instrumentation for the study of energy systems and materials important for fuel cells and hydrogen storage, from atomic-scale characterization of hydrogen location, bonding, and transport mechanisms to imaging of operating fuel cells and hydrogen-storage beds.

10:30 AM A5.5

High Throughput Screening of Complex Hydrides for

Hydrogen Storage. Gregory J. Lewis¹, Adriaan J. W. A. Sachtler¹,

John J. Low¹, David A. Lesch¹, Syed A. Faheem¹, Paul M. Dosek¹, Lisa M. Knight¹ and Craig M. Jensen²; ¹Exploratory and Fundamentals, UOP LLC, Des Plaines, Illinois; ²Hawaii Hydrogen Carriers, LLC, Honolulu, Hawaii.

The discovery that dopants, such as Ti, cause NaAlH₄ to reversibly desorb H₂ at mild conditions has spurred a great deal of research into complex metal hydrides. However, no complex hydride meets the targets for automotive hydrogen storage. High throughput screening accelerates the rate of discovery of improved hydrides and dopants through a combination of Virtual High Throughput Screening (VHTS) with Combinatorial Synthesis and Screening (CSS). Our CSS methods will allow us to screen thousands of samples in a year. These samples will be prepared by ball milling mixtures of hydrides and dopants similar to the reported method of preparing Ti doped NaAlH₄. VHTS

exploits a molecular mechanics method to screen a thousand phases in a month. The combination of combinatorial methods and VHTS will help us discover the most promising complex hydrides for hydrogen storage. We will show the results of our medium throughput CSS and VHTS as applied to mixed alkali-alkaline earth alanate compositions.

10:45 AM A5.6

Laser Ablation Mass Spectroscopy of Combinatorial

Hydrogen Sorbing Metal Alloys. Daad Bourhan Haddad¹ and C.

H. Olk²; ¹Materials Engineering, Purdue University, West Lafayette, Indiana; ²Materials and Processes Laboratory, General Motors Research and Development Center, Warren, Michigan.

An impediment to the discovery of new functional inorganic materials created by combinatorial growth techniques lies in the development of suitable techniques to simultaneously screen multiple samples for desirable properties. This is particularly true when the property of interest is hydrogen sorption, the characteristics of which vary strongly with temperature and pressure, thereby imposing a rigorous set of experimental conditions as well as a narrow choice of sorption detection techniques. We demonstrate, for the first time, the use of spatially resolved laser ablation mass spectroscopy as a high throughput hydrogen-storage candidate screening technique. We analyze mass spectroscopy data, electron probe elemental findings, and atomic force measurements of ablation craters in the search for quantitative relationships. This information is then used in hydrogen storage candidate selection as well as providing direction for further synthesis strategies.

11:00 AM A5.7

Spectroscopic Studies of Hydrogen Release from Ammonia

Borane. Wendy Shaw, Anna Gutowska, Nancy Hess, John Linehan, Ashley Stowe, Maciej Gutowski, Benjamin Schmidt and Tom Autrey; PNNL, Richland, Washington.

We have been investigating the chemical and physical properties of chemical hydrogen storage materials containing boron and nitrogen as potential solid state hydrogen storage materials for on-board applications. In our approach we have focused on our experimental efforts on the thermochemistry and kinetics of thermally activated release of hydrogen from ammonia borane confined within mesoporous silica and the catalytically activated release of hydrogen from dimethylamine borane. To our surprise we discovered that the AB confined within the mesoporous silica (SBA-15) showed a significant rate enhancement for hydrogen release and a change in the enthalpy of reaction for the release of hydrogen. The change in thermochemistry must be accompanied by a change in product formation and the change in kinetics by some in the chemical or physical properties of the AB when confined within the nano-porous channels. Recent mechanistic studies using deuterium labeling lead us to conclude that the formation of hydrogen from neat AB occurs by a bimolecular pathway contrary to what has been suggested in the literature. This was contrary to our in-situ spectroscopic studies of the catalyzed dehydrogenation of dimethylamine borane where the hydrogen formation appeared to proceed by an intramolecular pathway. Thus, while we have discovered much about hydrogen formation from these solid state hydrogen storage materials one important question remains unanswered: What is the origin of the change in the activation barrier and enthalpy of reaction for hydrogen loss from AB in the mesoporous scaffold compared to the reaction in the bulk material? In this presentation we will highlight our recent spectroscopic studies aimed at elucidating the changes in the chemical and physical properties of AB in mesoporous silica.

11:15 AM A5.8

Hydrogen storage reversibility of LiBH₄ based borohydrides.

Ming Au, Savannah River National Lab, Aiken, South Carolina.

LiBH₄ holds large amounts of hydrogen (18.5wt%) more than alanates (7.5wt%) and other conventional metal hydrides (1.4~1.8 wt%).

Unfortunately, heating above 400°C is required to release the hydrogen. However, there is a promising opportunity that the alkali metal borohydrides can be modified to release hydrogen at lower temperature and then be recharged at moderate condition. In our previous work, the modified LiBH₄ releases 9 wt% hydrogen starting from less than 100°C. The modified materials absorb 9 wt% hydrogen after dehydrogenating at 70 MPa and 600°C. In effort to develop LiBH₄ based materials for reversible hydrogen storage, the new compositions and synthesis process have been developed. This paper will present our updated results in the reducing dehydrogenation temperature, moderating rehydrogenation conditions and improving reversibility.

11:30 AM A5.9

Alternative Solvents for Chemical Hydrogen Storage

Compounds. Mohamed Abdul¹, Boyd Davis^{4,5}, Philip Jessop²,

Brant Peppy³ and Sarah Gilchrist¹; ¹Chemical Engineering, Queen's University, Kingston, Ontario, Canada; ²Chemistry, Queen's

University, Kingston, Ontario, Canada; ³Chemistry and Chemical Engineering, Royal Military College, Kingston, Ontario, Canada; ⁴Mining Engineering, Queen's University, Kingston, Ontario, Canada; ⁵Kingston Process Metallurgy, Kingston, Ontario, Canada.

The hydrolysis of sodium borohydride shows great potential for automotive applications of fuel cells given its high hydrogen storage potential relative to other methods. Unfortunately, current system concepts that rely on sodium borohydride suffer from low storage densities because of the way in which the hydrolysis reaction occurs. Recently, experiments performed at Queen's University using non-aqueous solvents have shown that sodium borohydride is stable within these non-aqueous solvents and the only reaction that takes place is the desired sodium borohydride hydrolysis reaction. This paper reports on recent work that was done to quantifiably determine the kinetics of hydrolysis in this non-aqueous solvent. In addition to using non-aqueous solvents, there is this possibility to conduct the hydrolysis reaction at elevated temperatures, in which the kinetics of this reaction would improve significantly. Also, imbedding homogeneous catalyst into the non-aqueous solvents to further promote the hydrolysis reaction is a possibility since preliminary experiments have shown great catalytic effects. It is hoped that the experimental results gathered so far can be built upon to help establish the viability of using non-aqueous compounds as inert solvents to facilitate the rapid release of hydrogen from sodium borohydride.

11:45 AM A5.10

A Combinatorial Thin Film Approach to the Search for New Hydrogen Storage Materials. Bernard Dam¹, Robin Gremaud¹, Andreas Borgschulte^{1,2}, Philippe Mauron¹, Dana Borsa¹, Ruud Westerwaal¹, Herman Schreuders¹, Jan Rector¹ and Ronald Griessen¹; ¹Condensed Matter Physics, Vrije Universiteit, Faculty of Science, Amsterdam, Netherlands; ²Powder and NanoTechnology, GKSS Research Centre Geesthacht GmbH, Geesthacht, Germany.

Due to their high volumetric density, metal-hydrides are attractive for the storage of hydrogen in fuel-cell driven cars. If complex light-weight ternary could be used, also the problem of the weight of these storage materials would be solved. However, for reversible absorption and desorption the required temperatures are too high for use in practical applications. We use a thin film approach to find new ternary hydride storage materials and to understand the role of catalysis in the ab- and (de-)sorption of hydrogen. Co-deposition of metal alloy gradient films gives a fast access to the sorption properties over a wide range of compositions. As all interesting light-weight storage materials investigated so far appear to have an electronic gap, we use optical screening to monitor the sorption properties. This facilitates the search for (complex) metal-hydrides with specific switchable physical properties. The compositional gradient thin films are synthesised by co-sputtering on a 3 inch wafer from three (up to six) off-centred magnetron sources. The (complex) hydride formation during ex-situ hydrogen exposition at well-defined temperatures and hydrogen gas pressures is monitored by the transparency/reflection of the films. The transparency is a good indicator of the amount of absorbed hydrogen. This method is thus applicable to a large class of potential light-weight hydrogen storage materials and electrochromic materials. We studied several Mg-based systems and find that the phases in the as-deposited metallic state are not simply those expected from the phase diagram. In general, the solid solubility range appears to be extended. Secondly, we find that hydrogen absorption can take place close to equilibrium conditions due to the small nanocrystalline grain size obtained by sputter deposition. Taking the well-known Mg-Ni-H as a model system, we identify the plateau pressure for hydrogen absorption. By modelling the pressure dependence of the absorption kinetics, we are able to determine the plateau pressure of the hydrides as a function of the alloy composition and temperature, thus obtaining the heat of hydride formation. We find that the enthalpy of formation depends subtly on the Mg/Ni ratio. As an example of a light-weight storage material, we studied the Mg-Al-H system. We find that, when loading Mg-Al gradient films, a transparent phase is formed at the MgAl₂ composition when exposed to hydrogen gas. The hydrogen is released when the sample is heated to 200°C. This (unfavorable) desorption temperature is reduced to 100 °C by adding a Ti surface layer. In fact, this also shows how powerful this method is to study the role of catalysts.

SESSION A6: Carbon-based Hydrogen Storage
Chair: Philip Parilla
Wednesday Afternoon, November 30, 2005
Room 311 (Hynes)

1:30 PM *A6.1

Advanced Hydrogen Sorption Measurement Techniques: Application to Tailored Singlewalled Carbon Nanotubes.

Alan Cooper¹, Mary K. Haas¹, John M. Zielinski², Peter McKeon², Gennady Dantsin¹, Charles G. Coe² and Guido P. Pez¹; ¹Corporate Science and Technology Center, Air Products and Chemicals, Inc., Allentown, Pennsylvania; ²Corporate Research Services Department, Air Products and Chemicals, Inc., Allentown, Pennsylvania.

Hydrogen isotherms on a variety of singlewalled carbon nanotube (SWNT) samples were measured using a differential pressure adsorption apparatus which provides highly accurate data. A number of these SWNT samples were modified by a non-destructive cutting process which reduced the aspect ratio of the nanotube bundles by two orders of magnitude. There were no apparent differences in the microporosity of SWNT as a function of aspect ratio. The adsorption of helium on SWNT is shown to be non-negligible and results in artificially low hydrogen capacities using conventional adsorption methodology. With no accounting for helium adsorption, the hydrogen adsorption results show that cut and uncut SWNT have similar hydrogen capacities of <1 wt. % at 298 K and pressures up to 110 bar. However, an analysis of hydrogen capacity vs. N₂ BET surface area suggests that there is an enhanced heat of adsorption of hydrogen for SWNT vs. activated carbon. A comparison of this volumetric adsorption isotherm data with an unusual gravimetric technique, never before used for hydrogen sorption measurements, will be presented.

2:00 PM A6.2

Hydrogen Storage Properties of Boron-doped Carbon Nanotubes. Jeff Blackburn¹, Anne Dillon¹, Thomas Gennett^{2,1}, Phil Parilla¹, Katie Gilbert¹, Yong-Hyun Kim¹, Yufeng Zhao¹, Shangbei Zhang¹, Yanfa Yan¹, Kim Jones¹ and Michael Heben¹; ¹National Renewable Energy Laboratory (NREL), Golden, Colorado; ²chemistry, Rochester Institute of Technology, Rochester, New York.

Doping of carbon nanotubes with a heteroatom such as boron affords control over the electronic properties of the nanotubes. Recent theoretical studies suggest that boron-doped carbon fullerenes may show promise as hydrogen adsorbents. These studies propose a three-center bond between boron dopants and hydrogen molecules with a binding energy of ~38 KJ/mol, ideal for hydrogen storage. Essential to this binding is the localized empty pz orbital of the boron dopant. Inspired by these findings, we explore the hydrogen storage properties of boron-doped carbon nanotubes experimentally. Boron-doped nanotubes are produced by a variety of synthetic methods, utilizing in-situ and ex-situ doping. HipCo nanotubes are doped by boron via a high temperature thermo-chemical reaction with boron oxide. In situ doped nanotubes are produced by novel laser vaporization and hot-wire CVD methods. These methods produce tubes with widely varying morphologies and levels of boron doping. The resulting materials are studied by TEM, Raman spectroscopy, thermogravimetric analysis, temperature-programmed desorption, and volumetric techniques to assess their structural, electronic, and hydrogen storage properties. Preliminary results are compared to theoretical predictions.

2:15 PM A6.3

Nuclear Magnetic Resonance Studies of Hydrogen Adsorbed on Carbon based Materials. Alfred Kleinhammes, Shenghua Mao, Marcelo Behar and Yue Wu; Department of Physics and Astronomy and Curriculum in Applied and Materials Sciences, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina.

A hydrogen based economy requires at its foundation an adequate, cheap and safe means of storing and transporting H₂. Carbon nanotubes were proposed as a promising material as were other carbon based materials. As part of a DOE initiative on H₂ storage in carbon based materials it is our goal to evaluate hydrogen storage capacity using nuclear magnetic resonance (NMR). ¹H NMR provides a sensitive and quantitative means of assessing the amount of H₂ adsorbed as gaseous and adsorbed molecules give rise to distinctly different spectral features. The dynamics of the adsorbed molecules will be studied as a function of temperature. Adsorption sites can be identified through ¹³C and ¹H spectroscopy. Evaluating the hydrogen storage capability and capacity of a material with NMR requires a system where the sample can be subjected in situ to H₂ pressure of up to 100 atmospheres, a limit set by practical considerations. A high pressure cell based on a sapphire tube which is inserted into the NMR saddle coil was designed and fully tested at room temperature. A second system capable of measuring hydrogen loading under pressure while varying the temperature from 77 K to room temperature is under construction. The pressure cell will be described in detail. Results on H₂ loading of various carbon based materials as a function of temperature and pressure will be reported. DOE support through participation in the Carbon based Hydrogen Storage – Center of Excellence program is acknowledged.

3:30 PM *A6.4

Prediction of Novel Organometallic Nanomaterials for High

Weight Percent Reversible Hydrogen Storage. Shengbai Zhang, National Renewable Energy Laboratory, Golden, Colorado.

By using first-principles total energy calculations, we have recently explored the non-dissociative H₂ adsorption on the various organometallic nanomaterials ranging from (yet-to-be synthesized) transition metal-coated buckyballs and carbon nanotubes to (already-existing) metallo-carbohedrenes. Our study reinforces the notion that the relatively light-weight 3d transition metal (TM) atoms are superb absorbers for H storage, as their empty d orbital can bind molecular dihydrogen with exceptionally high capacity at nearly ideal energy range for practical applications. However, upon H release, a collection of isolated TM atoms is completely unstable against cohesion. We show that, by "embedding" the TM atoms into a whole range of carbon-based organometallic nanostructures, one can overcome this difficulty, while maintaining the high H capacity. In particular, the amount of H₂ adsorbed on an Sc-coated C₄₈B₁₂[ScH]₁₂ could approach 9 wt%, with binding energies ideal for vehicular applications, 30-40 kJ/mol [1]. TM-coated carbon nanotubes also show similar binding characteristics although important differences do sometimes occur. Complementary to the TM coating, we also explored the metallo-carbohedrenes and TM carbide nanocrystals [2] where the TM atoms are coordinated into the carbon backbone. Our study reveals a similar non-dissociative binding, thereby demonstrating the resilience of the overall mechanism. Moreover, a novel low-energy self-catalysis and spillover process is identified that not only can contribute to the H storage but also suggests other important applications such as in fuel cells. Work in collaboration with Y. Zhao, Y.-H. Kim, A. Dillon, & M. Heben and supported by the U.S. DOE/EERE under contract No. DE-AC36-99GO10337. 1. Y. Zhao, Y.-H. Kim, A. C. Dillon, M. J. Heben, and S. B. Zhang., Phys. Rev. Lett. 94, 155504 (2005). 2. Y. Zhao, A. C. Dillon, Y.-H. Kim, M. J. Heben, and S. B. Zhang., submitted.

4:00 PM *A6.5

Predicting Engineered Nanomaterials for Reversible Hydrogen Storage. Taner Yildirim¹ and S. Ciraci²; ¹NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland; ²Physics Department, Bilkent University, Ankara, Turkey.

Developing safe, cost-effective, and practical means of storing hydrogen is crucial for the advancement of fuel-cell technologies. The current state-of-the-art is at an impasse in providing any materials that meet a storage capacity of 6wt% or more required for practical applications[1-5]. Much effort has been focused on the engineering of carbon-based materials such as nanotubes and transition metal hydrides without success. It is found that while hydrogen-carbon interaction is too weak [1], the metal-hydrogen interaction is too strong for room temperature reversible storage. Here we show a novel way[1-4] to overcome this difficulty by forming artificial metal-carbide like structures on nanotubes[2] and C₆₀ molecules[3]. From the state-of-the-art first-principles calculations, we show that a single Ti-atom coated on a SWNT/C₆₀ can strongly adsorb up to four hydrogen molecules. The hydrogen-metal bonding is an unusual combination of chemi- and physi-sorption, an essential ingredient needed for reversible hydrogen storage medium near room temperature. Remarkably, this adsorption occurs with no energy barrier. At large Ti coverage, we show that a (8,0) SWNT and C₆₀ can store hydrogen molecules up to 8-wt%, exceeding the minimum requirement of 6-wt% for practical applications. Our findings for Ti-decorated C₆₀ are in good agreement with a recent independent work of Yufeng Zhao et. al. [5]. Finally, we present high temperature quantum molecular dynamics simulations showing that these systems are stable and indeed exhibit associative desorption of H₂ upon heating, another requirement for reversible storage. These results [1-5] are quite remarkable and unanticipated. They advance our fundamental understanding of dissociative adsorption of hydrogen in nanostructures and suggest new routes to better storage and catalyst materials. [1] S.Dag, Y. Ozturk, S. Ciraci, and T. Yildirim, Phys. Rev. B (cond-mat/0504694). [2] T. Yildirim and S. Ciraci, Phys. Rev. Lett. 94, 175501 (2005). [3] T. Yildirim, J. Iniguez, and S. Ciraci, Phys. Rev. B (cond-mat/0505046). [4] For more info see <http://www.ncnr.nist.gov/staff/taner/h2> [5] Yufeng Zhao et. al. Phys. Rev. Lett. 94, 155504 (2005).

4:30 PM A6.6

Theoretical Study of Hydrogen Storage with Metallocarbohedrene. Yufeng Zhao, Anne C. Dillon, Yong-Hyun Kim, Michael J. Heben and Shengbai Zhang; National Renewable Energy Laboratory, Golden, Colorado.

A new direction based on binding dihydrogen ligands to nanoscale materials is now under exploration. The hypothetical organometallic buckyball was proposed to be able to reversibly store ~ 9wt% hydrogen at ambient temperature and pressure [1]. Considering the

great potential of such organometallic systems for hydrogen storage, an immediate question is posed: is there any already-synthesized nanoscale structure of transition-metal carbide that could bind dihydrogen ligands? Here we study the adsorption of H₂ on metallocarbohedrene (MetCar), Ti₈C₁₂, and the nanocrystal, Ti₁₄C₁₃, using first-principle calculations. Our results reveal a three-step process. First, the hydrogenation of two Ti atoms in Ti₈C₁₂ and four Ti atoms in Ti₁₄C₁₃ forming transition metal hydrides with relatively bigger binding energies (85.9-137.0 kJ/mol-H₂). Second, the hydrogenation of twelve C atoms in both Ti₈C₁₂ and Ti₁₄C₁₃ is catalyzed by the neighboring Ti atoms in the clusters themselves. The binding energy of hydrides to carbon atoms in Ti₈C₁₂ 61.4 kJ/mol-H₂ is unusually small compared with that of normal carbon hydrides (> 200 kJ/mol-H₂), due to the unique structure and chemistry of the MetCar molecule. Third, single or multiple dihydrogen ligands could further coordinate with Ti atoms at different sites of the clusters. The total amount of hydrogen taken by a Ti₈C₁₂ and Ti₁₄C₁₃ cluster is 17 H₂ and 34 H₂, corresponding to the storage capacity of 6.1 wt% and 7.7 wt%, respectively. Most of the hydrogen atoms and dihydrogen ligands bind with energies between 15.5 and 85.9 kJ/mol-H₂, making these systems a potential candidate for near ambient H storage. Reference [1] Y. Zhao, Y.-H. Kim, A. C. Dillon, M. J. Heben, and S. B. Zhang, Phys. Rev. Lett. 94, 155504 (2005).

4:45 PM A6.7

Hydrogen Storage in Carbon Nanoscrolls: A Molecular Dynamics Study. Vitor Coluci¹, Scheila F. Braga¹, Ray H. Baughman² and Douglas S. Galvao¹; ¹Applied Physics, State University of Campinas, Campinas, SP, Brazil; ²Nanotech Institute, The University of Texas at Dallas, Dallas, Texas.

The continuous increase in energetic needs of our technological society has stimulated the investigation of new potential sources of producing and storing energy. Hydrogen has been considered as a feasible source but its large use has been limited by safety and efficient storage problems. Recently many theoretical and experimental studies have been carried out in order to address whether carbon nanotubes could be a useful material for hydrogen storage. There are many conflicting data in the literature and this issue remains an open question. As new structures of great potential for the storage of gases we can consider carbon nanoscrolls. Nanoscrolls are new pure carbon nanostructures formed by graphene sheets rolled into spirals. They have a great advantage over conventional nanotubes in part due to their great superficial area and free internal volume. They present open extremities and a distance of approximately 3.4 angstroms between the walls of the spiral, which could become easily accessible to hydrogen physisorption. In this work using classical molecular dynamics techniques we have investigated whether carbon nanoscrolls could be an affective alternative to carbon nanotubes as hydrogen storage materials. We have analyzed many configurations varying thermodynamical conditions and compositional hydrogen percentage. Our results show that nanoscrolls (with wt greater than 6%) can outperform carbon nanotubes and be a new class of materials for hydrogen storage.

SESSION A7: Complex Metal Hydrides for Vehicular Hydrogen Storage
Chair: Charles Olk
Thursday Morning, December 1, 2005
Room 311 (Hynes)

8:00 AM *A7.1

Synthesis, Structural Properties, and Hydrogen Release from the Quaternary Hydride Li₃BN₂H₈. Frederick E. Pinkerton¹, Gregory P. Meisner¹, Martin S. Meyer¹, Michael P. Balogh² and Matthew D. Kundrat³; ¹Materials and Processes Lab, General Motors R&D Center, Warren, Michigan; ²Chemical and Environmental Sciences Lab, General Motors R&D Center, Warren, Michigan; ³Natural Sciences Complex, SUNY at Buffalo, Buffalo, New York.

We have synthesized a new quaternary hydride, Li₃BN₂H₈, containing 11.9 wt% hydrogen. Li₃BN₂H₈ is formed by ball milling mixed LiNH₂ and LiBH₄ powders in a 2:1 molar ratio. X-ray diffraction (XRD) results show that as the milling time increases, the LiNH₂ and LiBH₄ diffraction peaks weaken and a new set of peaks emerges. At 40 min, the sample is substantially converted to the new phase, with only a small remnant of LiNH₂ in the XRD pattern. After 300 min the conversion is complete, and continued milling up to 960 min produces no further change. The final XRD pattern appears to be single phase, except for a small amount of Li₂O impurity, and has a background intensity that is essentially unchanged with milling time, implying that ball milling does not produce an amorphous phase. All observed XRD peaks index to a single BCC quaternary phase with a = 10.76 Å. Our in situ XRD data shows that mixed LiNH₂ and LiBH₄ powders without ball milling also form Li₃BN₂H₈ when heated above 95°C. Li₃BN₂H₈ melts at 190°C, and forms a mixture of solid Li₃BN₂

polymorphs upon dehydrogenation above 250°C. Thermogravimetric and volumetric measurements of hydrogen desorption demonstrate that $\text{Li}_3\text{BN}_2\text{H}_8$ releases >10 wt% H_2 from the liquid above ~250°C. Using simultaneous mass spectrometry residual gas analysis we observe that a small amount of NH_3 (2-3 mole% of the generated gas) is released concurrently. The independent volumetric and gravimetric measurements are in excellent agreement regarding the quantities of H_2 and NH_3 released, and the evolved gases satisfactorily account for all of the available hydrogen content. Preliminary differential scanning calorimetry measurements suggest that hydrogen release is exothermic and, hence, not easily reversible; we have not succeeded so far in re-hydrating this material at hydrogen pressures up to 100 bars.

8:30 AM A7.2

Development and Characterization of Novel Complex Hydrides. Ragay Zidan, Hydrogen Technology Section, Savannah River National Laboratory (SRNL), Aiken, South Carolina.

This research is focused on developing novel hydrides for hydrogen storage. Our ultimate goal is to produce materials that have high hydrogen capacity, are stable with cycling and possess favorable thermodynamic and kinetic characteristics compatible with onboard hydrogen storage for transportation applications. In order to achieve this goal a novel method was developed and used to modify and form new complex hydride compounds with desired characteristics. The new method is based on fusing different known complex hydrides at elevated temperatures and pressures. New complex hydrides produced by the new method will be identified along with the structure measurements and thermodynamic characterization of the new materials in order to achieve a more fundamental understanding of their formation and dissociation mechanisms.

9:00 AM A7.3

Thermal and Volumetric Studies of Light Weight Hydrogen Storage Systems. Sesha S. Srinivasan¹, Matthew T. Smith¹, Elias Lee Stefanakos¹, Yogi Goswami² and Craig M. Jensen³; ¹Clean Energy Research Center, College of Engineering, University of South Florida, Tampa, Florida; ²Solar Energy and Energy Conversion Laboratory, College of Engineering, University of Florida, Gainesville, Florida; ³Department of Chemistry, University of Hawaii, Honolulu, Hawaii.

Light weight hydrogen storage systems are indeed essential for the on-board automotive vehicular applications. Complex chemical hydrides bearing light elements such as Li, Na, Mg etc. and the catalytic doping with transition metal species are presently being investigated. The Li-modified Mg_2FeH_6 structure was thermally characterized using DSC and TGA. It was interesting to notice that the reduction in the decomposition temperature of about 100°C was unambiguously observed for the Li modified Mg_2FeH_6 . Besides, there was an enhancement in sorption kinetics was obtained for the titanium doped Mg_2FeH_6 . We have also demonstrated the role of Ti-species on the complex hydride NaAlH_4 by heat flow measurements using high pressure differential scanning calorimetry. A new class of hydrogen storage system $\text{Zn}(\text{BH}_4)_2$ with theoretical hydrogen capacity of 8.4 wt.% was synthesized and their volumetric characteristics have been determined.

9:15 AM A7.4

Electronic Structure Modifications Upon Alloying Ni with B, S and P. Spyros Diplas, Ole Martin Lovvik and Johan Taftø; Centre for Materials Science and Nanotechnology, University of Oslo, Oslo, Norway.

Research on metal-metalloid amorphous alloys is very attractive because of the high catalytic activity of these materials towards hydrogen evolution and hydrogenation reactions. Both electrolytically and electroless deposited Ni-B, Ni-S and Ni-P films exhibit dramatic increases in hydrogen evolution rates. Reaction rates up to 1000 times higher than the typical rates for pure Ni have been reported. The improved catalytic activity with respect to the hydrogen evolution reaction of Ni-B amorphous or nanocrystalline alloys has been attributed to modifications of the Ni electronic structure. In the present study, we compare x-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS) experimental data, such as shifts in the energy of core and valence band features, changes in the shape of the Auger lines and variations in the energy loss features, with the electronic density of states (DOS) achieved from first principles band-structure calculations. The comparison allowed us to comment on the electron redistribution and the subsequent effects on the interatomic bonding in these alloys. The alloying behaviour of Ni in several binary systems with respect to modifications in the electronic structure and their implications on the catalytic behaviour are also discussed.

9:30 AM A7.5

Neutron Scattering Investigations of a Destabilized LiH:Si

System for Hydrogen Storage Applications. Michael R. Hartman¹, Terry J. Udovic¹, Jack J. Rush¹, Robert C. Bowman^{2,4}, John J. Vajo³ and Channing C. Ahn⁴; ¹National Institute of Standards and Technology, Gaithersburg, Maryland; ²Jet Propulsion Laboratory, Pasadena, California; ³HRL Laboratories, LLC, Malibu, California; ⁴California Institute of Technology, Malibu, California.

Lithium hydride alloyed with silicon destabilizes the otherwise strongly bound hydride which increases the equilibrium hydrogen pressure. The destabilization effect is very pronounced with a 20,000-fold increase in the equilibrium hydrogen pressure to ~1 bar at 763 K for an alloyed LiH:Si mixture as compared to the hydride alone. Several neutron scattering techniques have been employed to investigate the LiH:Si system at various stages throughout the dehydrogenation/hydrogenation process to gain further insight into transformations of the distinct Li-Si-H phases. Powder neutron diffraction data has been utilized to extract quantitative phase information. Inelastic neutron scattering has allowed the observation of spectroscopic features of the various hydrogen containing phases. Prompt gamma activation analysis has been employed to provide a quantitative measure of the hydrogen content of the system at various levels of dehydrogenation. Of particular note in the present study are the unique spectroscopic and structural features of a ternary phase containing lithium, hydrogen, and silicon. Results of the various neutron scattering studies are discussed along with their implications for the use of a LiH:Si system as a hydrogen storage medium.

9:45 AM A7.6

Crystal Structure and Thermodynamic Stability of Mixed Alanates. Hendrik W. Brinks¹, Anita Fossdal¹, Magnus S. Sorby¹, Yumiko Nakamura¹, Bjorn C. Hauback¹ and Craig M. Jensen²; ¹Physics department, Institute for Energy Technology, Kjeller, Norway; ²Department of Chemistry, University of Hawaii, Honolulu, Hawaii.

Al-based complex hydrides is one of the most promising groups of reversible hydrogen storage materials. Theoretical reversible storage capacity of the mother compound NaAlH_4 is 5.6 wt% under moderate conditions. This two-step reaction has the same storage capacity as the one-step of the hexahydride Li_3AlH_6 . Unfortunately, the pressure to hydride Li_3AlH_6 is too high to be of practical importance (>85 bar at 80°C) [1]. We have also studied other hexahydrides. The crystal structure [2] and the thermodynamic stability ($\Delta H = 56.4$ kJ/mol) [3] of $\text{Na}_2\text{LiAlH}_6$ have been determined. Furthermore, a new reversible alanate K_2NaAlH_6 has been synthesized and isotherms measured. The mixed alanates have been found to be more stable than the monoalkalmetal hexahydrides. Our results from synchrotron X-ray diffraction on the state of Ti in hexahydrides will also be presented. [1] H.W. Brinks, A. Fossdal, J.E. Fonnelop, B.C. Hauback, J. Alloys Compd. (In press). [2] H.W. Brinks, B.C. Hauback, C.M. Jensen, R. Zidan, J. Alloys Compd. 392 (2005) 27. [3] A. Fossdal, H.W. Brinks, J.E. Fonnelop, B.C. Hauback, J. Alloys Compd. (In press).

10:30 AM A7.7

Detection and Characterization of Point Defects in Doped Sodium Aluminum Hydride. Craig Jensen¹, Rosario Cantelli², Oriale Palumbo², Annalisa Paolone², Sesha Srinivasan¹, Martin Sulic¹, Reyna Ayabe¹, Kristina Morales¹ and Meredith Kuba¹; ¹Chemistry, University of Hawaii, Honolulu, Hawaii; ²Physics, University of Rome, Rome, Italy.

Among the field of new candidate, hydrogen storage materials to have emerged in recent years, Ti-doped NaAlH_4 has the best combination of critical hydrogen storage properties. In recognition of this distinction, United Technologies and GM have both embraced this material as the basis their current projects for the design of a state-of-the-art tank for PEM power vehicles. Thus it appears that a variation of the doped hydride could possibly be developed as practical hydrogen carrier for automotive applications. In hopes of establishing guiding principles for the design and synthesis of such a material, a growing number of research efforts have sought to elucidate the nature of the Ti species responsible for the enhanced hydrogen cycling kinetics of Ti-doped NaAlH_4 . However, we have found that it may not be possible to attain this goal as the majority of Ti in the material is in a kinetically irrelevant "resting state". Accordingly, we have shifted the focus of our studies. We have detected and characterized highly mobile point defects that are generated in the doped material by the active Ti species. These hydrogen-containing entities are strongly interacting and highly mobile. They are apparently responsible for the enhanced hydrogen cycling kinetics of the material. Our studies have included density functional calculations as well as infrared, nuclear magnetic resonance, and anelastic spectroscopy. The details of these studies and their implications on the design of advanced hydrogen storage materials will be presented in this talk.

11:00 AM A7.8

Effect of Microstructure and Composition on the Hydrogenation Kinetics of Mg₂Ni Thin Films.

Ruud Westerwaal¹, Dana Borsa¹, Wiebke Lohstroh², Andreas Borgschulte¹, Bernard Dam¹ and Ronald Griessen¹; ¹Physics and Astronomy, Vrije Universiteit Amsterdam, Amsterdam, Netherlands; ²Forschungszentrum Karlsruhe GmbH, Karlsruhe, Germany.

Mg₂±δNiH₄ is a well-known example of a switchable complex metal hydride. The reversible transition between metal and hydride, makes these materials suited both for hydrogen storage and smart window-coatings. Having such applications in view, understanding the details of the hydrogen uptake by this material is crucial. Upon hydrogen uptake a Mg₂±δNi thin film changes from shiny metallic to transparent insulating. Between these two states there is a third optical state, which is characterized by a low resistivity, a low reflection as seen from the substrate side (<25%) and no transmission. As a result, the film absorbs >75% of the incident light when viewed from the substrate. This "Black State" is the result of a self-organised double layering of the film under hydrogen absorption. The Mg₂NiH₄ phase starts to nucleate at the substrate/film interface, leaving the top Mg₂NiH_{0.3} layer unchanged. This hydrogen absorption behaviour is surprising, since one expects that the hydrogenation process starts just below the Pd cap layer. Rutherford Backscattering Spectrometry (RBS) and Secondary Ion Mass Spectroscopy (SIMS) show that there is no chemical gradient throughout these films. However, microstructural investigation by Scanning Tunnelling Microscopy (STM), Transmission Electron Microscopy (TEM) and Secondary Electron Microscopy (SEM) do show some peculiarities. Up to a thickness of 50 nm, the films consist of small grains and clusters of small grains. On further growth a columnar structure develops. Based on these findings, we relate the anomalous hydrogenation behaviour and preferential nucleation of Mg₂NiH₄ at the substrate/film interface to the specific microstructure of these films. We propose that the nucleation barrier for the formation of the Mg₂NiH₄ phase is smaller for the small grains at the interface, while the columnar grain boundaries promote the hydrogen diffusion to the substrate. Indeed, after modifying the film microstructure e.g by using an atomic hydrogen source during the in-situ preparation of Mg₂NiH₄ films by molecular beam epitaxy, we find an immediate effect on the hydrogen loading behaviour. While the black state in Mg₂±δNi occurs over a wide compositional range, the ensuing hydrogenation process depends on the Mg/Ni ratio. The hydrogenation process is monitored with optical and resistivity measurements. We find that it is characterized by a competition between the growth of the initial Mg₂NiH₄ layer (fast) and the random nucleation (slow) of the same phase but randomly within the upper metallic layer. The predominance of either process depends critically on the stoichiometry of the parent metal alloy. Our findings show that the common diffusion models used in describing the hydrogenation behaviour of these materials may be incorrect, if the defect microstructure is inhomogeneous. Moreover, our results underline the importance of phase nucleation in the transformation kinetics in complex metal hydrides.

11:15 AM A7.9

Direct synthesis of BaAlH₅ and Ba₂AlH₇ hydride phases by ball milling and the effect of Ba substitution by Sr on the hydrogen content. Vasile Iosub and Etsuo Akiba; Hydrogen Energy Group, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan.

The BaAlH₅ or Ba₂AlH₇ hydride phase is obtained by reactive ball milling of BaAl alloy (a mixture of Ba₄Al₅ and Ba bcc phases) if the milling conditions are changed. In order to explain the synthesis of two different hydride phases, the gas atmosphere composition as well as the gas pressure in the vial was modified while keeping constant the other parameters (the ball to powder weight ratio, the rotational speed). The crystallization state of these phases was improved when the milling time was increased or further hydrogenation was used. In addition, the hydrogenation properties of pure intermetallic compound Ba₄Al₅ which is the main phase in the BaAl alloy were also studied. Moreover, the chemical substitution of barium by strontium has been carried out in order to increase the hydrogen capacity and the results will be presented.

11:30 AM A7.10

Hydrogenation Process of Mg-Ni Alloy Through Nano-Porous Silicon Membrane: A Novel Hydrogen Storage Materials.

Tien-Hsi Lee^{1,2}, S.-L. Lee^{1,2}, C.-H. Huang¹, Y.-Y. Yang¹ and J.-C. Tai²; ¹Mechanical Engineering, National Central University, Chung-Li City, Taiwan; ²Institute of Materials Science and Engineering, National Central University, Chung-Li City, Taiwan.

The effect of hydrogen atoms on mass transport in hydrogen storage materials is critical for the uptake and release kinetics of complex hydride storage materials. Although elemental metal materials such as Mg are the main ingredient of light complex hydride hydrogen storage

materials, they do not quickly react with hydrogen by themselves. Transition metals such as Ni are known to catalyze H-chemistry. At exposed Ni in an Mg matrix, the barrier for hydrogen mono-atomic adsorption and recombinative desorption is extremely low because of the elimination of dissociative adsorption process. The surface of nano-pore porous silicon substrate can effectively adsorb hydrogen molecular and dissociate them into hydrogen mono-atoms. We integrate the surface structure of Mg-Ni alloy with porous silicon membranes to form a sandwich structure and the function of porous silicon surface is to transform hydrogen molecule into hydrogen mono-atoms. How mono-atomic hydrogen facilitates Mg mass transport through the effectual formation of mobile MgH_x species is investigated by various hydrogen pressure experiments.

11:45 AM A7.11

Observation of Lattice Defect Formation during Hydrogenation and Dehydrogenation in La(Ni_{1-x}Sn_x)₅ by In-situ Positron Lifetime Measurement. Kouji Sakaki¹, Yumiko

Nakamura¹, Yasuharu Shirai², Robert C. Bowman³ and Etsuo Akiba¹; ¹Energy Technology Research Institute, Advanced Industrial Science and Technology, Tsukuba, Japan; ²Osaka University, Suita, Japan; ³California Institute of Technology, Jet Propulsion Laboratory, Pasadena, California.

LaNi₅ is a typical hydrogen absorption material and has good hydrogenation properties. However, its hydrogenation - dehydrogenation cycle property is not so good. It is improved by the substitution of Sn atoms into LaNi₅ [1]. This is a good candidate of heat pump material for space use. It suggests that the concentration of the lattice defect introduced by the hydrogenation is related with it. If so, the concentration of the lattice defect in La(Ni_{1-x}Sn_x)₅ should be lower than that in LaNi₅. In fact, XRD profiles in La(Ni_{1-x}Sn_x)₅ after the hydrogenation show little peak broadening. The lattice defects introduced by the hydrogenation in LaNi₅ are dislocation and vacancy. To clarify the defect structure including vacancy, in-situ positron lifetime measurement was performed along PC-isotherms measured at 296 K in La(Ni_{1-x}Sn_x)₅. The mean positron lifetime increased with the hydrogen content as well as LaNi₅. Though the mean positron lifetime in LaNi₅ kept almost constant during the dehydrogenation process, the dramatically decrease of the mean positron lifetime was observed in La(Ni_{1-x}Sn_x)₅. It shows that the concentration of the lattice defect introduced by the hydrogenation reversibly change. In other words, the lattice defects are introduced during the hydrogenation process and they are annealed out during the dehydrogenation process. Furthermore, it is clear that the concentration of the lattice defect in La(Ni_{1-x}Sn_x)₅ is quite lower than that in LaNi₅.

SESSION A8: Hydrogen Storage in Complex Metal Hydrides

Chairs: Craig Jensen, Andrew Weisberg and Shengbai Zhang

Thursday Afternoon, December 1, 2005
Room 311 (Hynes)

1:30 PM *A8.1

Alانات for Hydrogen Storage - Density-Functional Calculations of Structural, Electronic, and Thermodynamical Properties. Ole M. Lovvik¹, Ole Swang², Susanne M. Opalka³ and Peter N. Molin¹; ¹Centre for Materials Science and Nanotechnology, University of Oslo, Oslo, Norway; ²SINTEF Materials and Chemistry, Oslo, Norway; ³United Technologies Research Center, East Hartford, Connecticut.

Complex aluminohydrides (alanates) constitute a promising group of materials for solid-state storage of hydrogen for vehicular purposes, due to their high hydrogen density. Sodium alanate NaAlH₄ is the most mature of these materials, with up to 5 wt.% hydrogen reversibly stored at moderate temperature and hydrogen pressure. In this talk results are presented from calculations on alkali (Li, Na, K) and alkaline-earth (Mg, Ca) alanates. The crystal structures and thermodynamic stability of both the pure and a number of mixed alanates are presented; they compare very well with all known experimental data. The electronic structure of the alanates are then presented. The AlH₄ unit is almost identical in all the different compounds, both structurally and electronically, while the bonding between the aluminohydride complex and the cation varies between ionic and polar covalent. Finally, results are presented from calculations on Ti-enhanced sodium alanate. When all known relevant phases are taken into account, it is clear that Ti substitution of all the sites that were investigated is thermodynamically unstable. The most favorable substitution (that is, least unstable) is for Al, near the surface.

2:00 PM A8.2

The Structure and Thermodynamic Properties of Lithium Imide from First Principles. Tim Mueller and Gerbrand Ceder;

Metal-N-H systems have shown promise for reversible hydrogen storage. Lithium imide (Li_2NH) can reversibly store up to 6.5 wt% hydrogen, producing lithium amide (LiNH_2) and lithium hydride (LiH) [1]. Lithium imide combined with Mg_3N_2 can reversibly store up to 6.9 wt% hydrogen, producing $\text{Mg}(\text{NH}_2)_2$ and LiH [2]. Lithium imide has an anti-fluorite structure, with NH groups occupying the anion sites [3]. However the orientation of and interaction between NH groups are difficult to characterize. We present the results of ab initio calculations on lithium imide in which we identify the ground state structure and describe the interactions between NH groups and lithium cations. These results provide a foundation for a more detailed understanding of the atomistic mechanisms for hydrogen storage in metal-N-H compounds. Through Monte Carlo simulations based on ab initio calculations we determine finite temperature thermodynamic properties of lithium imide and analyze the thermodynamic reversibility of hydrogen storage in systems containing lithium imide. [1] Chen, P., et al., Interaction of hydrogen with metal nitrides and imides. *Nature*, 2002. 420(6913): p. 302-304. [2] Leng, H.Y., et al., New metal-N-H system composed of $\text{Mg}(\text{NH}_2)_2$ and LiH for hydrogen storage. *Journal of Physical Chemistry B*, 2004. 108(26): p. 8763-8765. [3] Ohoyama, K., et al., Revised crystal structure model of Li_2NH by neutron powder diffraction. *Journal of the Physical Society of Japan*, 2005. 74(1): p. 483-487.

2:15 PM **A8.3**

Thermodynamic Modeling of Sodium Alanates and Effect of Ti. Caian Qiu¹, Gregory B. Olson^{2,1}, Susanne M. Opalka³ and Donald L. Anton³; ¹QuesTek Innovations, Evanston, Illinois; ²Northwestern University, Evanston, Illinois; ³United Technology Research Center, East Hartford, Connecticut.

The thermodynamic properties of the Al-Na-H system have been assessed using models for the Gibbs energy of the individual phases, where the model parameters were obtained from best fit optimizations to combined experimental data and first principles predicted data. The first principles finite temperature thermodynamic property predictions were based upon density functional theory ground state minimizations and direct method lattice dynamics. The predictions proved to be important for the modeling when experimental data are lacking. It has been shown that the stability of sodium alanates NaAlH_4 and Na_3AlH_6 under various conditions is well described with the present models. The models have been extended to formulate the effect of Ti addition on decomposition of the alanates and formation of new compounds.

2:30 PM **A8.4**

Crystal Structure Determination and Reaction Pathway of Amide-Hydride Mixtures for Reversible Hydrogen Storage. Job Rijssenbeek¹, Yan Gao¹, John Lemmon¹, J.-C. Zhao¹, Suchismita Sanyal² and Mahesh Chandran²; ¹GE Global Research, Niskayuna, New York; ²GE Global Research Center, Bangalore, India.

Combined synchrotron in-situ X-ray diffraction and neutron diffraction studies were performed on mixtures of lithium amide and magnesium hydride, and magnesium amide and lithium hydride, that release hydrogen when heated. Among the dehydrogenated products are mixed lithium and magnesium imides with a general formula of $\text{Li}_{4-2x}\text{Mg}_x(\text{NH})_2$. The crystal structures of these imides are closely interrelated yet they have not heretofore been accurately determined. Furthermore, at elevated temperatures $\text{Li}_2\text{Mg}(\text{NH})_2$ ($x = 1$) undergoes several structural transitions from an orthorhombic structure at low temperature, to a primitive cubic structure at intermediate temperature, to a face-centered cubic crystal structure at high temperature. It appears that disordering of the Li, Mg and cation vacancies at higher temperatures drives the structural transitions. The crystal structure identification based on X-ray and neutron diffraction and reaction pathway information from in-situ X-ray diffraction work will be presented.

3:15 PM ***A8.5**

First-Principles Studies of the Physical Properties of Complex Metal Hydrides. Amra Peles, Yan Wang and Mei-Yin Chou; Georgia Institute of Technology, Atlanta, Georgia.

We present first-principles investigations of the structural properties, electronic structure, and vibrational properties of various complex metal hydrides. The calculations are performed within the density-functional framework, employing norm-conserving and ultrasoft pseudopotentials. Of particular interest are the thermodynamics and the atomistic processes associated with the catalytic reactions in sodium aluminum hydrides, a promising hydrogen-storage material. It is found that the substitutional geometry of the Ti catalyst in NaAlH_4 is not particularly favorable. Examinations of the crystal structures and various diffusion energies

suggest that AlH_3 may be the mobile species in the dehydrogenation reaction. The effect of Ti is likely to facilitate the extraction of AlH_3 from the hydrides and its subsequent decomposition on the surface. In addition, we will also report interesting physical properties and the quantum nature of hydrogen in other hydrogen containing compounds.

3:45 PM ***A8.6**

Density Functional Theory for Hydrogen Storage Materials: What, Whither, When? Jan F. Herbst, Materials and Processes Laboratory, GM R&D Center, Warren, Michigan.

Energetics, bonding characteristics, and other properties of several hydrogen storage materials are discussed on the basis of calculations performed within density functional theory (DFT). For LaNi_5H_n ($\text{P6}_3\text{mc}$ crystal structure) and LaCo_5H_n (Cmmm structure) DFT correctly identifies the preferred hydrogen site configurations, yields the enthalpy of hydride formation accurately, and predicts hydrogen-rich hydrides. These calculations have been extended to assess the existence of LaFe_5H_n compounds, a task both interesting and challenging since La and Fe do not form stable intermetallics. Results for the novel hydrogen storage reaction $\text{LiNH}_2 + \text{LiH} \rightleftharpoons \text{Li}_2\text{NH} + \text{H}_2$ are also described. The continuously expanding body of work in this area demonstrates unequivocally that DFT is a potent tool for understanding the physics and chemistry of hydrogen storage systems.

4:15 PM **A8.7**

Dynamics of Hydrogen in $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ and $\text{Pr}_2\text{Fe}_{17}\text{H}_5$. Eugene Mamontov^{1,2}, Terrence J. Udovic¹, Olivier Isnard^{3,4} and John J. Rush¹; ¹NIST Center for Neutron Research, Gaithersburg, Maryland; ²University of Maryland, College Park, Maryland; ³Laboratoire de Cristallographie, CNRS, associe a l'Universite J. Fourier, Grenoble, France; ⁴Institut Universitaire de France, Maison des Universites, Paris, France.

Hydrogen can insert into $\text{Pr}_2\text{Fe}_{17}$ in large quantities to form the hydrides $\text{Pr}_2\text{Fe}_{17}\text{H}_x$ ($0 < x < 5$). Neutron diffraction results indicate that the first three hydrogen atoms fully occupy the interstitial 9e octahedral sites, whereas the last two hydrogen atoms occupy one-third of the available interstitial 18g tetrahedral sites. It can be expected that in $\text{Pr}_2\text{Fe}_{17}\text{H}_4$, where a hexagon composed of six 18g sites is occupied by a single hydrogen atom, hydrogen hopping through the vertices of the hexagon will take place. On the other hand, in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$, with two hydrogen atoms presumably residing on the diametrically opposed sites at the corners of a hexagon, the hydrogen hopping is expected to be hindered. We used quasielastic neutron scattering measurements to probe the dynamics of hydrogen hopping in $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ and $\text{Pr}_2\text{Fe}_{17}\text{H}_5$. Surprisingly, both compounds demonstrate very similar dynamics of hydrogen hopping. The time between jumps is on the order of 100 ps at 200 K and decreases as the temperature is increased. An Arrhenius temperature dependence of the time between jumps is observed. In order to reconcile the dynamics of hydrogen hopping with the Switendick criterion of minimal hydrogen separation distance in metals one needs to assume an unusual, correlated dynamics of hydrogen pairs in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$.

4:30 PM **A8.8**

Coherent Dual Phase Nanocomposite Hydrogen Storage Materials. Aaron Feaver and Guozhong Cao; Materials Science & Engineering, University of Washington, Seattle, Washington.

A novel dual phase hydrogen storage composite material has been developed, in which magnesium hydride (MgH_2) or ammonia borane (NH_3BH_3) has been integrated into nanostructured carbon cryogels. Such coherent dual phase nanocomposites consist of a percolated carbon network for both electrical and thermal conducting pathways with hydrides coated onto the internal surface of the carbon cryogel network, and thus promise efficient hydrogenation and dehydrogenation. The MgH_2 incorporated inside the mesopores of carbon cryogels resulted in a significantly reduced hydrogen release temperature with a peak rate at 242 °C as compared to > 400 °C for bulk MgH_2 . Such a reduction in decomposition temperature is ascribed to the efficient heat dissipation and possible catalytic effects of coherent carbon nanostructures. Carbon cryogels have pore size distribution, pore volume, and surface area that can be tuned using sol-gel parameters, pyrolysis and activation thus enabling the optimization of these variables to maximize both space for hydrogen storage materials and interfacial surface area for improved reaction kinetics. Carbon cryogels have been fabricated with surface areas greater than 2000 m^2/g , pore size distributions peaks from < 2 nm to > 150 nm, and pore volumes as high as 1.6 cc/g . The relationships between the porous structure of carbon cryogels, filling of hydrides, hydrogen storage capacity, and hydrogenation and dehydrogenation temperature and kinetics will be discussed.

A9.1

Transferred to A2.2

A9.2

Synthesis and Characterization of Photocrosslinkable Aromatic Polymer for PEMFC and DMFC. Myong-Hoon Lee, Hui Liu and Xiangdan Li; School of Advanced Materials, Chonbuk National University, Chonju, Chonbuk, South Korea.

Aromatic high temperature polymers such as polyimides, polysulfones, and poly(arylene ethers) have many advantages against vinyl polymers since they have high mechanical, chemical, thermal, and oxidative stabilities. Many attempts have been made to utilize these polymers as a polymer electrolyte in the fuel cell substituting Nafion[®] which is most widely used in polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs). In spite of many advantages, however, there are some drawbacks associated with these polymers such as poor hydrolytic stability, relatively high methanol permeability, low proton conductivity, and so on. Controlling the micro-structure of polymer morphology is essential to optimize such properties. Crosslinking of soluble sulfonated aromatic polymer, for example, could be one of the possible methods to improve those properties. However, the chemical crosslinking, which mostly involves thermal activation steps, is not attractive because the control of micro-structure is not possible under swollen state due to the possibility of solvent evaporation at the elevated temperature. In this paper, we present the synthesis of novel photoreactive aromatic polymer electrolyte and its attempted photocrosslinking in the presence of electrolytic solvents. The polymer membranes were prepared from a new sulfonated aromatic polymer containing photoreactive groups in the main chain by solution casting. The crosslinking with UV irradiation was attempted in the presence of or without solvent. The characterizations of resulting membrane including the ion-exchange capacity, water sorption, and proton conductivity measurement will be presented with respect to the photocrosslinking degree and the copolymer compositions.

A9.3

Interfacial Reactions of Inorganic Glass Sealants in Planar SOFCs. Kevin B. Stallone and Scott T. Misture; New York State College of Ceramics, Alfred University, Alfred, New York.

Alkaline earth aluminosilicate and boron-containing sealants of current interest were studied to establish the phase evolution sequence and equilibrium phases formed in planar SOFCs with metallic interconnects. Experiments were conducted that model the fuel cell environment by using both air and hydrogen atmospheres. The alloys studied included a chromia former, an alumina former, and a NiO former. In-situ high temperature X-ray diffraction was used as the primary tool to track the crystallization of the glass-ceramic sealant and formation of phases when the sealant is in contact with the anode and interconnect. To simulate the equilibrium condition, bulk accelerated testing was performed by using mixtures of the sealing glass with the oxides and metals in powder form. The results include the first bulk phase formation kinetics and a description of the reaction mechanisms.

A9.4

Proton Conduction and Fuel Cell Performance of SiO₂ solid Electrolyte Formed on Single Crystal Silicon Wafer. Akihiko Yamaji, Tadaharu Adachi, Jyunsuke Takahashi and Wakako Araki; Tokyo Inst. of Tech., Tokyo, Japan.

In this research, the conductivity of SiO₂ (polycrystalline Cristobalite) formed on silicon wafer has been studied by dc measurement and ac-impedance measurement at high temperatures in various controlled atmosphere, and the performance of fuel cell was also tested. The silicon wafer ((111) surface and approximate 0.5 mm thick) was oxidized around at 1300°C for 50 to 150 hours in an atmosphere of dry or water bubbled wet oxygen. The formed oxide layer was confirmed to be a polycrystalline Cristobalite by X-ray diffraction. This Cristobalite layer were found to be a proton conductor at high temperatures, and the conductivity of the Cristobalite layer was 2.5×10 S/m at 1000°C. The conductivity was the same value as that of sintered polycrystalline Cristobalite. Fuel cell was fabricated using 4μm thick polycrystalline Cristobalite layers formed as electrolyte on both surfaces of 0.5 mm thick silicon wafer with porous platinum electrodes to measure capability of the cell. The open circuit voltage was 0.9V at 1000°C and the maximum power density was 4.5μW/cm² at 900°C.

A9.5

Synthesis and characterization of new apatite electrolytes for IT-SOFC. Adrien Vincent^{1,2}, Denis Autissier^{1,2}, Sophie Beaudet Savignat¹ and Francois Gervais²; ¹Materials Dpt, CEA, Monts, France; ²LEMA, Francois Rabelais University, Tours, France.

One way to decrease the working temperature of a SOFC fuel cell is to look for an electrolyte having the same oxide ionic conduction at 700 C than zirconia at 1000 C. The oxy-apatite family looks like promising in this objective. The La₉Si₆O₂₆ apatite structure offers interesting ionic possibilities through the existence of mobile oxygen channels. Different synthesis ways have been explored (multiple classical grinding, attrition grinding, processing in dry atmosphere). The sintering capability has been explored through dilatometric experiments. The good conditions of densification have been determined, and the different phenomena occurring during heating analyzed. The phases formation vs process and temperature was determined by X-Ray diffraction analysis. The different synthesis ways are compared in terms of phase purity. It seems possible to modify the ionic conductivity by changing the lattice parameters via the introduction of doping elements such as barium, strontium and calcium. The ionic conductivities are measured by frequency impedance spectroscopy and the different doping formulation are compared. The best results are obtained for barium substitution (it's the largest ion).

A9.6

Influence of Cu on the photocatalytic activity of ZnS nanoparticles. Shinichiro Senda¹, Takeo Arai², Yoshinori Sato¹, Kozo Shinoda¹, Balachandran Jayadevan¹ and Kazuyuki Tohji¹; ¹Graduate School of Environmental Studies, Tohoku University, Sendai, Japan; ²Energy Technolgy Research Institute, Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Photocatalytic decomposition of hydrogen sulfide is considered as a smart alternative to produce hydrogen compared to splitting of water, which cannot be realized effectively with the present day technology. The hydrogen sulfide has been effectively photo decomposed by using ZnS particles with stratified structure, but only under ultraviolet light irradiation due the large band gap of about 3.7 eV [1]. It was reported that ZnS nanoparticles could be made to respond to visible light by doping the same with copper [2-4]. Thus in this study, we have attempted to dope the stratified ZnS particles with copper using the ion exchange method and evaluated their photocatalytic response. The stratified particles were dispersed in copper solutions with concentrations from 0 to 5%. The structure, composition, morphology and light response of the products were analyzed using XRD (X-ray Diffraction spectroscopy), XRF (X-ray Fluorescence Spectrometer), FE-SEM (Field Emission Scanning Electron Microscope) and UV-VIS (Ultraviolet-Visible spectroscope). From the result of an UV-VIS reflection spectrum, it was confirmed that the light absorption domain of stratified ZnS particles particle was expanded to a visible light. Then the photocatalytic activity of Cu doped ZnS particles were evaluated by measuring the hydrogen evolved from the standard suspension consisting 100 mg of Cu doped ZnS in 150 ml of 0.1 M Na₂S and Na₂SO₃ mixture in a pyrex vessel and exposed to 550 W Xenon lamp (Wacom, KXL-552HPF). The intensity of the light introduced at the bottom of the cell was measured to be 16 W. The Cu doped ZnS particles exhibited higher activity than pure ZnS particle in all cases. However, there existed an optimum value for doping and the maximum activity, which was one order higher than that of pure ZnS, was recorded for the particles doped with 2% Cu. Further details will also be reported and discussed. Reference 1. T. Arai, S. Sakima, H. Yoshimura, K. Shinoda, B. Jayadevan, K. Tohji, A. Kasuya, Y. Nishina, *Proc. Int. Symp. On Cluster Assembled Mater. IPAP Conf.*, Series 3, 75, 2001. 2. A. Kudo and M. Sekizawa, *Catalyst Letters*, 58, 241, 1999. 3. I. Tsuji, H. Kato and A. Kudo, *Angew. Chem. Int. Ed.*, 44, 3565, 2005. 4. I. Tsuji, H. Kato, H. Kobayashi and A. Kudo, *J. Phys. Chem. B*, 109, 7323, 2005.

A9.7

Corrosion Resistance of TiN Coatings Prepared by Filtered Cathodic Vacuum Arc Process. Jin-Bao Wu¹, Yin-Wen Tsai¹, Chin-Te Shih¹, Mei-Yi Li², Ming-Sheng Leu¹ and Chiou-Chu Lai¹; ¹Materials Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan; ²National Nano Device Laboratories, Hsinchu, Taiwan.

For the purpose of developing the corrosion-resistant and low-cost metallic bipolar plates for direct methanol fuel cell (DMFC), Ti mesh, stainless steel and Si(100) were coated with TiN by using the filtered cathodic vacuum arc system (FCVA). These TiN films have received considerable attention because of its high anti-corrosion behavior and low contact-resistance. In order to improve the corrosion protection ability of TiN films and decrease pinholes of coating, growth

modifications such as thickness of the coatings and bias applied to substrates have also been carried out. The microstructures and composition of TiN film were identified by the instrumental analyses such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The corrosion behavior of TiN coatings was studied in 0.5 M H₂SO₄ solutions by using potentiodynamic polarization method. The DC bias of -150 V was applied to the substrates to achieve a dense structure of approximately 500 nm coating of TiN, so that good corrosion protection of the Ti mesh and stainless steel substrates can be achieved. The TiN coating on stainless steel exhibited excellent corrosion behavior especially in lower corrosion current than 2×10^{-7} A/cm².

A9.8

Flame-Made Pt-Carbon Catalysts for Fuel Cell Application. Frank Ernst, Robert Buechel, Reto Strobel and Sotiris E. Pratsinis; Particle Technology Laboratory, ETH Zurich, Zurich, Switzerland.

Most noble-metal-based catalysts consist of nanometer-sized metal particles dispersed on high-surface-area supports. They find application as catalysts in many chemical processes, such as hydrogenation, oxidation, and reforming, but also in electrodes for fuel cells. A gas-phase synthesis method based on flame-technology for the production of metal clusters supported on carbon nanoparticles is presented. This process can be used to synthesize clusters of any metal on carbon nanoparticles or networks thereof. Exemplarily, flame spray pyrolysis (FSP) has been used for the production of carbon black-supported noble metal catalysts (1 to 10 wt% Pt on carbon black). Liquid precursors containing specific amounts of platinum precursor dissolved in xylene were dispersed by nitrogen and combusted in an inclosed flame chamber, resulting in nanostructured powders. The as-prepared powders were collected on a filter and characterized by Raman spectroscopy, scanning transmission electron microscopy, CO chemisorption, nitrogen adsorption, X-ray diffraction. The specific surface areas of the powders ranged from 70 to 300 m²/g depending on the oxygen and precursor flow rates. Noble metals were well dispersed and confined to the carbon surface. This method could also be used for the synthesis of clusters of any metal on carbon supports originating from any source of carbon and a metal precursor.

A9.9

Structure and Stability of Protonated Aurivillius Ceramics for Photocatalysis Applications. Hyun-Joon Kim and Scott Thomas Misture; Department of CEMS, New York State College of Ceramics at Alfred University, Alfred, New York.

Aurivillius ceramics can be converted into the protonated forms through selective leaching of the bismuth oxide layers. Some of these protonated forms have high photocatalytic activity for water splitting. In this study, 3-layer Aurivillius ceramics Bi_{2-x}Pb_xSr₂Nb₂TiO_{12-x/2}, Bi₂Sr₂Nb₂Ti_{1-y}Fe_yO_{12-d}, Bi₂Sr₂Nb₂Ti_{1-z}Mn_zO_{12-d} were synthesized and the transition metal and lead solubility limits were determined. From XRD and high temperature XRD results, it is shown that the protonated forms have tetragonal crystal structures and tend to decompose at temperatures in excess of 900°C. The bandgap energy of each composition has been estimated from UV-Visible diffuse reflectance spectra. The increase of the bandgap energy after the acid treatment and the strong absorption in visible light region of Mn-containing compounds were observed. Preliminary results of the photocatalytic activity for hydrogen evolution will also be presented.

A9.10

Carbon Nanotube-Supported Platinum Electrodes for Proton Exchange Membrane Fuel Cells. Pyoungho Choi¹, Odysseas Paschos¹, Steve J. Buelte², Nazarali Merchant², Richard Pollard² and Pradeep Haldar¹; ¹College of Nanoscale Science and Engineering, Albany, New York; ²PlugPower, Albany, New York.

Carbon nanotubes (CNTs) having very high electrical conductivity and specific surface area were successfully employed as support materials for platinum-based electrodes in proton exchange membrane fuel cells (PEMFCs). Three different kinds of CNTs were utilized for Pt dispersion. The depositions of Pt on CNTs were carried out by vacuum deposition as well as wet preparation methods. The prepared Pt/CNT electrodes were characterized by scanning electron microscopy (SEM), focused ion beam (FIB), X-ray diffraction (XRD), and transmission electron microscopy (TEM). In order to evaluate the Pt/CNT electrodes, the catalytic activity of oxygen reduction reaction (ORR) by half-cell as well as single fuel cell test were carried out. Specifically, the corrosion resistance at open circuit condition, and current density at 0.6 V as well as 0.9 V were measured and compared with commercially available carbon (Vulcan XC-72) supported platinum electrodes. Nafion-based low temperature (~100C) and PBI-based high temperature (~180C) experiments were performed with the Pt/CNT electrodes. The performance of various Pt/CNT electrodes were studied as functions of platinum loading, particle size,

dispersion, surface area, impurities in CNTs, and preparation methods among others. This work has been funded by NIST.

A9.11

On Pt-Ni Catalyst by Hydrazine Reduction for Proton Exchange Membrane Fuel Cell. Ming-Chang Yang and Jui-Don Lu; Department of Chemical Engineering, National Cheng Kung University, Tainan City, Taiwan.

In proton exchange membrane fuel cells (PEMFC), one of the sources of major power loss is slow cathode kinetics. To increase the catalytic activity of the oxygen reduction reaction (ORR) and to lower the cost of the catalysts, various Pt-alloy catalysts has been investigated in the past two decades. In this study, various atomic ratios of platinum to nickel in the catalysts on carbon support were studied by the discharging polarization curves and AC impedance analysis. Carbon powder was impregnated with platinum and nickel salts in ethylene glycol solution. After the catalytic metal was then reduced by hydrazine in 30°C, catalysts with various atomic ratios of platinum to nickel were obtained. The catalysts were characterized by X-ray Diffraction Spectrometer, Transmission Electron Microscope, Energy Dispersive X-ray Spectrometer, and Atomic Absorption Spectroscopy. While the content of nickel in the catalyst increased from 0 to 4, the particle size of metal in the catalyst was reduced from 30~50 nm to 16~30 nm. The structures of catalysts with Ni/Pt ratio 1 remained unchanged in calcination temperature up to 380°C. The catalysts were applied for the cathode in the fuel cell. Discharging test of the fuel cell was carried out in a three-electrode mode. The cell potential was divided into anode and cathode potentials, referred to a normal hydrogen reference electrode. An equivalent circuit model was proposed to explain the results of AC impedance analysis of the anode and cathode. The cathode performance of fuel cell was investigated by comparing the discharging polarization curves and AC impedance analysis. As compared to the Pt/C catalysts, the Pt-Ni/C catalysts with various atomic ratios exhibited higher performance for oxygen reduction reaction. The catalysts with atomic nickel contents higher than 50% showed inferior performance. (Financially supported by the National Science Council of Taiwan, NSC 93-2214-E-006-026)

A9.12

Proton Conducting Electrolyte Membranes based on Tungsten Oxide and Sulfonated PolyEtherEtherKetone Hybrid Composites. Barbara Mecheri^{1,2}, Alessandra D'Epifanio¹, Maria Luisa Di Vona¹, Enrico Traversa¹, Silvia Licocchia¹ and Masaru Miyayama²; ¹Chemical Science and Technology, University of Rome "Tor Vergata", Rome, Italy; ²Research Center for Advanced Science and Technology, The University of Tokyo, Tokyo, Japan.

Proton conducting electrolyte membranes (PEM) are receiving more and more attention due to their possible applications as power sources for vehicles, laptop computers and cellular phones. In the development of PEM, aromatic polymers containing ether links have been widely investigated; among them PolyEtherEtherKetone (PEEK) shows good thermal oxidation resistance, suitable mechanical properties, and high proton conductivity when sulfonated. However, the sulfonation process leads to undesirable swelling of the membrane and, therefore, to the decrease of its mechanical strength. A possible mean to overcome this problem is the introduction of an inorganic filler into the polymeric membrane. In this work, our strategy to improve both proton conductivity and mechanical properties of sulfonated PEEK (SPEEK) membranes consisted in the dispersion of an inorganic proton conducting network in the polymer backbone. Hydrated tungsten oxide (WO₃·2H₂O) was selected because of its relatively high proton conductivity and its layered structure. WO₃·2H₂O was synthesised via acidic hydrolysis of sodium tungstate and characterized by simultaneous Thermogravimetric and Differential Thermal Analysis (TG-DTA), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Electrochemical Impedance Spectroscopy (EIS). Inorganic-organic composite membranes were prepared by mixing proper amounts of SPEEK and WO₃·2H₂O in dimethylacetamide. The composite membranes were characterized by XRD, TG-DTA, SEM, EIS and water uptake measurements as a function of the oxide content in the membrane. The body of results indicated the existence of a coordinative interaction between the water molecules of tungsten oxide and the sulfonic acid (-SO₃H) groups of SPEEK. Such interaction was clearly indicated by XRD measurements that evidenced structural modification of WO₃·2H₂O in the SPEEK-based membrane with respect to pure oxide powder. At the same time, the TG profiles of the composite membranes showed that the temperature of splitting-off of -SO₃H groups increased with increasing oxide content in the membrane. Moreover, EIS data demonstrated that composite membranes have higher proton conductivity than pure SPEEK, suggesting the presence of ion-rich regions where the proton transfer is favoured. The SO₃H - H₂O interaction not only lead to enhancement of the proton conductivity of the membranes but also to improvement of their heat resistance as well as of their mechanical properties.

A9.13 **Ruthenium-iridium Oxide Films Prepared by MOCVD and their Electrocatalytic Activity for Oxygen Evolution.**

Jorge Roberto Vargas-García¹, Elsa Miriam Arce-Estrada¹, Miguel Hesiquio Garduno² and Mayra Zylzila Figueroa Torres¹;
¹Metallurgical Engineering, National Polytechnic Institute, Mexico, Mexico; ²Materials Science, National Polytechnic Institute, Mexico, Mexico.

Ruthenium-iridium oxide films were prepared in an horizontal hot-wall MOCVD apparatus and their electrocatalytic activity was investigated in the oxygen evolution reaction. Metal-acetylacetonates were used as precursors and oxygen as the reactant gas. Appropriate deposition conditions for obtaining bi-metallic oxide films were found as follows: deposition temperature (Tdep), 673 K; and total pressure (Ptot), 133.32 Pa. X-Ray diffracton (XRD), Rietveld refinement and scanning electron microscopy (SEM) results demonstrated that MOCVD method is a viable alternative to growth RuIr1-xO2 films, which consisted of a single-phase of a very homogeneous distribution of elements. The electrocatalytic activity of the RuIr1-xO2 films was investigated by cyclic voltammetry and anodic polarization curves in a 0.5 M H2SO4 solution at room temperature. The single-phase Ru0.37Ir0.63O2 films showed to be very promising for the oxygen evolution reaction because of a sinergetic effect.

A9.14 **Gas Separation Properties of Layer-by-Layer Assembled Membranes for Fuel Cell Applications.** J. Nathan Ashcraft and Paula T. Hammond; Chemical Engineering, MIT, Cambridge, Massachusetts.

A simple and cheap method to produce polyelectrolyte membranes for fuel cell applications is the layer-by-layer (LBL) assembly technique. In particular, proton exchange membranes (PEMs) comprised of thin films of poly(ethylene oxide)/poly(acrylic acid) (PEO/PAA) deposited on inert, porous membrane substrates have shown very promising results in recent work. One aspect of these membranes that has received little attention is their gas separation properties. This study investigates the permeability and selectivity of these membranes and how these properties are impacted by film thickness, deposition conditions, and environmental temperature.

A9.15 **Understanding the Oxygen Reduction Reaction in Oxide Materials: A Microelectrode Study on La_{1-x}Sr_xMnO_{3-d}.** Gerardo Jose La O¹, Yang Shao-Horn¹ and Bilge Yildiz²; ¹MIT, Cambridge, Massachusetts; ²Argonne National Laboratory, Argonne, Illinois.

Solid oxide fuel cells (SOFCs) are high temperature (~800°C) ceramic fuel cells that generate electrical power at high efficiency (>50%) and provide high grade waste heat to increase overall system efficiency under combined cycle operation. Due to high operating temperatures, SOFCs utilize non noble-metal catalysts and typically use Ni at the anode and Sr-doped LaMnO3 (LSM) at the cathode. In principle, SOFCs using advanced anode materials are capable of operating under various fuels, in addition to hydrogen, such as light hydrocarbons making these attractive for distributed generation applications. As operating temperatures of these systems are lowered (~600°C) to decrease overall system cost, SOFC performance is limited by the cathode and its associated oxygen reduction reactions (ORR), which contribute the highest resistive losses. ORR in LSM has been extensively studied in past decades. However, there is still no final agreement on the precise rate-limiting step (rls) and reaction pathways. In this study, experimental and modeling investigation of ORR is performed. Square-shaped and dense microelectrodes of defined size (~20-200µm) and thickness (~100-500nm) are fabricated by sputtering LSM onto 8YSZ, and patterned by photolithography. The microelectrode structure and chemical contents are characterized by AFM, SEM, TEM, and XPS. Electrochemical testing is performed by current-voltage and electrochemical impedance spectroscopy (EIS) techniques. Kinetic modeling of ORR is performed by using reaction models that includes oxygen adsorption, electronation, and diffusion at the surface and bulk of LSM. The model does not assume any rls for ORR and instead evaluates the coupled contributions of all the reaction steps to the resulting EIS. Preliminary experimental results have shown a change in the dominant pathway from tpb to bulk as electrode parameters are varied. The simulated EIS response compares consistently to experiments. The relationships between the microelectrode parameters, modeling and oxygen reduction pathway will be discussed in detail.

A9.16 **Exploiting Micro- and Nano-Structural Features of Dendritic Zinc Oxide Electrodes for the Enhancement of Photoelectrochemical Properties.** Carmen M. Lopez and

Zinc oxide is an n-type semiconductor that can serve as a photoanode in photoelectrochemical cells. Development of zinc oxide-based devices is made attractive and practical by the abundance and nontoxicity of zinc oxide. The efficiency of polycrystalline photoelectrodes can be significantly affected by morphological features at the interfaces (e.g. size, shape, grain boundary, interconnection of the particles). Therefore, controlling macro-, micro-, and nano-structural features at the interfaces and understanding their effects on photoelectrochemical and charge transport properties are the key to producing high performance, low cost photoelectrode materials. In this study we describe the use of non-aqueous media to electrochemically stabilize dendritic growth of zinc metal that can be converted to zinc oxide through thermal oxidation without significant morphological change. Temperature and electrochemical windows allowed for electrodeposition in non-aqueous plating media (i.e. dimethyl sulfoxide, foramide) are significantly wider than those in aqueous medium. These extreme temperature and potential conditions that are newly accessible can be utilized to facilitate inorganic growth far from equilibrium, resulting in various intricate dendritic/branching patterns with significantly increased surface areas. We will describe in detail key synthetic conditions to stabilize various dendritic growth patterns of zinc metal in electrodeposition and discuss how the resulting morphology affects the photoelectrochemical properties of the corresponding ZnO electrodes. This work is one of the first few examples of exploiting micro- and nano-crystallinity, high surface areas, and good electrical continuity of inorganic dendritic growth to enhance desired functional properties of photoelectrodes.

A9.17 **Degradation of Al-Fe Coating Layer for Separator of Molten Carbonate Fuel Cells(MCFC) Fabricated by the Laminating of Al Foil.** Jaewoong Choi, Wanhee Lee, Gilho Hwang, Seokjun Hong and Sunggoon Kang; Hanyang University, Seoul, South Korea.

One of the major material problems in molten carbonate fuel cells(MCFC) is the corrosion of the separator plates in molten carbonate and the wet-seal area of the separator, which contacts directly with molten carbonate experience the most severe corrosion. LiAlO2 may be a suitable material to meet these requirements such as high corrosion resistance, high melting point, no electrical conductivity, and no dissolution in molten carbonate. Consequently, Al containing alloys or Al coatings have been developed. In this study, 50 micron in thickness aluminum foil was applied to form the Al-Fe coating layer on the AISI316L by laminating process to reduce the cost and the length of the process. Al foil was loaded on the AISI316L by using a jig and pre-annealed at 630oC for 5h. And the Al foil laminated AISI316L was diffusion heat treated for 3h at 700~850oC in a vacuum furnace respectively. The laminated Al-Fe coating layers on AISI316L were analyzed by XRD, SEM/EDS, GDMS and the degradation of coating layers was evaluated by immersion test in molten carbonate at 650oC.

A9.18 **Tungsten Fuel Cell Catalysts.** Joel Christian, Osram Sylvania, Towanda, Pennsylvania.

A new tungsten fuel cell catalyst has been discovered for PEM fuel cells. This material is synthesized using high-purity chimie douce (soft chemistry) techniques. The material has shown a high level of activity as a fuel cell catalyst in a variety of test cell configurations and operating conditions, with power output levels demonstrated within an order of magnitude of conventional platinum electrocatalysts. Preliminary tests also show catalytic activity in reformat type fuel streams, up to and including pure CO (carbon monoxide) and high sulfur tolerance.

A9.19 **Abstract Withdrawn**

A9.20 **Modified NiO/YSZ Composite Powder Prepared by Surface-Modification of YSZ Powder.** Kyoung Ran Han, Chang-Sam Kim and Yoonji Jung; Materials Science & Engineering, KIST, Seoul, South Korea.

Solid oxide fuel cell (SOFC) is an all solid device that converts chemical energy into electricity via electrochemical process. It is a promising electricity generating system due to its inherently high efficiency and little pollution over the traditional powder generation technologies. It consists of anode, electrolyte and cathode. To minimize the polarization losses of the fuel oxidation reaction in SOFC, anodes should be highly electroconductive, sufficiently electrocatalytic, porous enough for efficient gas transportation, and compatible with other cell components. Considering cost and

performance, the Ni/YSZ cermet materials are still the most common anodes for SOFC. NiO/YSZ anode materials are usually prepared by conventional mechanical mixing of commercial NiO and YSZ powders. The properties are substantially affected by the microstructure and distribution of Ni and YSZ phases, so uniform microstructures are preferred. Therefore, wet chemical synthesis have been tried to improve the homogeneity of Ni and YSZ phase distribution to improve the electrode performance and stability. Efforts were mostly focused on coating NiO particles with nanosize YSZ particles to suppress sintering of NiO, but the other way would be worth to try because characteristics of the YSZ powder such as uniform, spherical, crystalline, and nanosize, can be advantageously taken to prepare NiO/YSZ composite powder. NiO/YSZ composite powder for SOFC was synthesized by surface-modification of YSZ powder with nickel precursors. Nickel carbonate hydroxide was used with nickel nitrate as nickel precursors. Agglomerate-free NiO/YSZ composite powder was obtained in particle size of 0.3 ~0.8 micrometer by double heat-treatments of the NiO/YSZ powder at 800 C/2 h and then followed by 1200 C/2 h. The Ni/YSZ cermet with homogeneous and rigid YSZ skeleton was obtained by sintering at 1400 C/3 h and then followed by reduction at 1000 C/3 h. Further efforts to increase TBP(triple phase boundary) length, surface modification with MgO and GDC(gadolinium doped ceria) was tried. The results show that the surface modification method is a cost-effective way to prepare NiO/YSZ cermet powder by ball milling.

A9.21
Synthesis and Characterization of Gold-platinum Nanoparticles as Electrocatalysts for Fuel Cell Reactions. Peter N. Njoki, Jin Luo, Mathew M. Maye, Rizwan Munawar, Aisley Jacob and Chuan-Jian Zhong; Chemistry, State Univ. of New York at Binghamton, Binghamton, New York.

Nanostructured catalysts are showing great promise for energy storage and fuel cell catalysis. The challenge is the development of the ability to precisely control the size and composition of the nanostructures. This presentation discusses recent results of an investigation of new and refined synthetic and processing protocols for the control of size and shape of Pt, Au and AuPt nanoparticles. The work is aimed at understanding the fundamental basis for the delineation of the control parameters. One important finding is that AuPt alloy nanoparticles (1-30 nm) with different bimetallic compositions can be prepared by controlling the synthetic feed ratios. Results from characterizations of the size, structural, morphological, loading and electrocatalytic properties of the catalysts using transmission electron microscopy, infrared reflection spectroscopy, thermogravimetric analysis and electrochemical methods will be discussed. Implications of the results to the design of bifunctional nanoparticle catalysts will also be discussed.

A9.22
Retaining of Unidirectionally Aligned Carbon Nanotube Geometry on Wet Electrochemical Processing for Potential Fuel Cell Applications. Xiang-Rong Ye¹, Li-Han Chen¹, Joseph F. Aubuchon¹, Jan B. Talbot² and Sungho Jin¹; ¹Materials Science and Engineering, University of California, San Diego, La Jolla, California; ²Chemical Engineering, University of California, San Diego, La Jolla, California.

Well-aligned carbon nanotubes (CNTs) on conductive and porous substrates such as on a three-dimensional, microfiber network of carbon exhibit very large accessible surface area for a number of catalytic and electrochemical applications including fuel cells and sensors. However, the critical flaw of the wet electrochemical or chemical processing of aligned nanotubes is an undesirable agglomeration/bundling of CNTs and a collapse of aligned and laterally separated geometry, which significantly decreases the useful surface area. In this study, we use applied electric field to align or bend CNT growth¹, and then introduce wet electrochemical oxidation to achieve ultrafast (just a few seconds) and complete Ni catalyst removal in order to eliminate electrochemically undesirable metals associated with nanotube growth. As ultrafine Pt catalyst nanoparticles are desirable for fuel cell electrodes², we then use electrochemical reduction to precipitate and attach high-density Pt catalytic nanoparticles on the side walls of such open-tipped, highly dense, aligned multiwall nanotubes. Using supercritical fluid drying technique, we demonstrate that the originally aligned and laterally spaced geometry of carbon nanotubes can be fully retained after the wet electrochemical processing. It is also discovered that the open-tipped CNTs can be electrochemically harvested off the supporting substrates if needed. Preliminary experiments indicate that such open tipped, well-aligned CNTs are potentially useful as efficient fuel cell electrodes and biosensor platform. 1. J. F. AuBuchon, L.H. Chen, C. Daraio, and S. Jin, Multiple Sharp Bending of Carbon Nanotubes during Growth to Produce Zig-Zag Morphology, *Nano Lett.* 4, 1781 (2004). 2. X. R. Ye, S. Jin, J. Talbot, Y. Lin and C. M. Wai, Supercritical Fluid Attachment of Palladium

Nanoparticles on Aligned Carbon Nanotubes, *J. Nanosci. & Nanotech.* 5, 964-969 (2005).

A9.23
Preparation of Porous Ceramic Membrane for Hydrogen Separation at High Temperature. Younghee Kim, Woo-Teck Kwon, Soo-Ryong Kim and Bang-Geun Song; Eco-Materials Team, Korea Institute of Ceramic Engineering and Technology, Seoul, South Korea.

Ceramic membranes having nano sized pores have great potential for gas separation at high temperature since they have a good stability at high temperatures. Moreover, nanoporous silicon carbide membrane can be expected to use under hydrothermal condition at high temperature as membrane reactors for conversion enhancement in steam reforming reaction of natural gas. The use of membrane allowed separating simultaneously hydrogen gas during the steam reforming reaction. In this research, nanoporous SiC membrane has been developed on the porous alumina plate for the hydrogen separation using preceramic polymers such as hydridopolycarbosilane, polycarbosilane. The prepared SiC membrane was characterized with SEM, TEM, FT-IR and thin film XRD and so on. The nanoporous hydrogen selective SiC membranes show promise for application in membrane reactor for steam reforming reaction of natural gas and water gas shift reactions.

A9.24
Development of a Ceramic Molecular Membrane for Hydrogen Separation at High Temperature. Laurent Lelait¹, Anatoly Soudarev², V. Konakov², Andrei Souryaninov², A. Molchanov² and Philippe Stevens¹; ¹European Institute for Energy Research, Karlsruhe, Germany; ²Boyko Research Engineering Center, Saint Petersburg, Russian Federation.

Pollution of the platinum group of metals applied as catalysts to the PEMFC membrane device electrodes is a detrimental factor entailing the degradation of the PEMFC. That is why, the challenge to supply of hydrogen into the fuel cell with a CO content not over 0.01% assumes a so great importance. In the current technologies of separation of these gases, metal molecular palladium-based membranes are applied with a 500-600 C limitation for the gas mixture temperature. At the same time, the optimum temperatures of the steam or air-vapor reforming processes in the power generation solid polymer fuel cell-based plant reformers are ranging 700 to 900 C. Application of the palladium molecular membranes causes a need in reduction of the reformer operation efficiency. In this paper we present some results of design, manufacture and tests of a molecular ceramic membranes (MCM) using the alumo-magnesium spinel (AMS) as its support component. To build the molecular membrane the support are impregnated by a sol which is then convert to a gel leading to the formation inside the macro porous support to a nano porous structure. Hydrogen to CO permeability and selectivity test will be presented at temperature up to 1000 C.

A9.25
A Renewable Process of Hydrogen Storage and Generation using Sodium Borohydride in Automotive Fuel Cell Systems. Chih-ting Flora Lo¹, Kunal Karan¹ and Boyd Robert Davis²; ¹Chemical Engineering, Queen, Kingston, Ontario, Canada; ²Mining Engineering, Queen's University, Kingston, Ontario, Canada.

Sodium borohydride is a promising hydrogen storage material for automotive applications due to its high gravimetric storage density, safe handling characteristics and rapid hydrogen release kinetics from both hydrolysis and methanolysis reactions. In this work, a system combining a high temperature polymer electrolyte membrane (PEM) fuel cell with sodium borohydride as the hydrogen storage material is investigated. Hydrogen generation is obtained from a catalyzed hydrolysis reaction at normal operating conditions, or it is generated via the methanolysis reaction for sub-zero temperature start-ups. Water required for hydrogen generation is recycled from the fuel cell thus it does not need to be stored onboard. Methanol is stored onboard in a small container which needs to be refilled every few months like an oil change. Possibility of heat integration from the hydrogen generation unit and the fuel cell is discussed. Furthermore, if the spent fuel of hydrolysis and methanolysis reactions of sodium borohydride can be recycled electrochemically, then a complete renewable closed-loop cycle can be developed. This study showed that sodium borohydride can be a viable hydrogen storage option for automotive fuel cells.

A9.26
Kinetic Study of Hydrogen Generation via Methanolysis of Sodium Borohydride as a Low Temperature Start-up Mechanism for Automotive Fuel Cells. Chih-ting Flora Lo¹, Kevin Tsang¹, Kunal Karan¹ and Boyd Robert Davis²; ¹Chemical

Engineering, Queen, Kingston, Ontario, Canada; ²Mining Engineering, Queen's University, Kingston, Ontario, Canada.

Sodium borohydride is a promising hydrogen storage material for automotive applications with high gravimetric storage density and rapid kinetics for hydrogen release from both hydrolysis and methanolysis reactions. Hydrolysis: $\text{NaBH}_4 + 4\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ Methanolysis: $\text{NaBH}_4 + 4\text{CH}_3\text{OH} \rightarrow 4\text{H}_2 + \text{NaB}(\text{OCH}_3)_4$ Hydrolysis of sodium borohydride has been well studied in literature but has several major challenges. One of them is low-temperature start-up. A system using water as the solvent and reactant eliminates the possibility to operate at temperatures below zero. On the other hand, few studies have investigated the methanolysis of sodium borohydride while a major advantage of having methanol as a solvent and reactant is the capability to operate in cold conditions. In this project, the kinetics of hydrogen generation via the methanolysis reaction is investigated over a wide range of temperature between -20 to +50°C. It was shown that the methanolysis of sodium borohydride has better kinetics than that of the hydrolysis reaction at temperatures below 50°C. The activity of methanolysis decreased with decreasing temperature however the rate of reaction can be improved with catalysts, which were also studied in the lab. To demonstrate that methanolysis of sodium borohydride is a viable and compact start-up device for automotive applications, small pellets of sodium borohydride were used and showed minimal mass transfer issues under stirred conditions. The results of this work showed that methanolysis of sodium borohydride is a practical option for hydrogen generation at low temperatures.

A9.27

Hydrogen Purification using Nanoporous Carbide-Derived Carbon. Elizabeth N. Hoffman, Gleb Yushin, Michel W. Barsoum and Yury Gogotsi; Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Tunable porosity on the nanoscale has been achieved in carbide derived carbon (CDC), in which pore size and pore shape depends on structure, stoichiometry and chemistry of the carbide precursor, synthesis temperature and atmosphere. Nanoporous CDC has been synthesized via chlorination reactions from selected ternary carbides over the temperature range of 400 °C - 1200 °C. Hydrogen sorption isotherms were compared with sorption isotherms of common contaminant gases, showing considerable selective adsorption properties. The ability to finely adjust the porosity, carbon microstructure and surface termination in CDC offers a unique capability to synthesize adsorbent materials with increased selectivity for hydrogen gas contaminants, while allowing hydrogen to permeate with little adsorptive resistance. Based on sorption results, CDC exhibits tremendous potential as an adsorbent for hydrogen purification.

A9.28

Catalytic Decomposition of Methane into Hydrogen and Carbon without CO₂ Production. Hyun J. Kim, Dong S. Yun and Jung Whan Yoo; Material Team, Korea Institute of Ceramic Engineering & Technology, Seoul, South Korea.

Hydrogen is expected to become an important energy carrier for sustained energy consumption with reduced impact on the environment. A hydrogen-based energy system is regarded as a viable and advantageous option for delivering high-quality energy services. Traditionally, hydrogen is synthesized through steam reforming and/or partial oxidation of methane, which have significant effect on the global warming, since it releases CO₂ while producing hydrogen due to mixing methane with water and to increase of the reaction temperature. Direct catalytic decomposition of methane is regarded as a potential economical method to produce hydrogen. In the present study, we carried out methane decomposition over zeolite-supported metal catalyst under various conditions and investigated the factors which determined the catalytic activity and life for methane decomposition. In addition, the characterization of the carbon fibers formed at different conditions was described.

A9.29

Understanding the Mechanism of Hydrogen Adsorption into Metal-Organic Frameworks. Seung-Hoon Choi¹, Tae-Bum Lee¹, Daejin Kim¹, Ji Hye Yoon², Sang Beom Choi² and Jaheon Kim²; ¹Insilicotech Co., Ltd., Seongnam, Gyeonggi-Do, South Korea; ²Dept. of Chemistry, Soongsil University, Dongjak-Gu, Seoul, South Korea.

Hydrogen adsorption mechanism onto the porous metal-organic frameworks (MOFs) has been studied by density functional theory calculation. The selected functional and basis sets for the prediction of interaction energies between hydrogen and potential adsorption sites of MOF was utilized after the evaluation with the various functionals for interaction energy of H₂??C₆H₆ model system. Both the favorable adsorption sites and the orientational dependency of adsorption

energy were investigated at the same time with regard to the each set of adsorbed hydrogen molecules. According to these calculations, the metal sites are believed to play an important role that initiates hydrogen adsorption process and facilitates the propagation of the hydrogen adsorption to the whole frameworks. In addition, it was found that the aromatic ring incorporated as part of the framework showed very different interaction mode with the hydrogen from that of the gas phase benzene molecule. Based on these cumulative findings the rational design and synthetic strategies could be proposed to make MOFs very promising materials for the hydrogen storage.

A9.30

Carbide Derived Carbon Designed for Efficient Hydrogen Storage. Ranjan Kumar Dash¹, Gleb Yushin¹, Giovanna Laudisio³, Taner Yildirim², John Fischer³ and Yury Gogotsi¹; ¹Department of Materials Science and Engineering and A.J. Drexel Nanotechnology Institute, Drexel University, Philadelphia, Pennsylvania; ²National Institute of Standards and Technology, Gaithersburg, Maryland; ³Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

Inexpensive carbide derived carbons (CDCs) that have BET specific surface area (SSA) up to 2300 m²/g [1, 2] and open pore volume up to 80% represent a new class of porous carbons produced by thermo chemical etching of metal atoms from carbides. Tuning the pore size with high sensitivity [1] by using different starting carbides [1, 3-5] and synthesis temperatures allows the design of carbon materials with enhanced hydrogen storage capacity at ambient pressure. Despite substantial research in the field of hydrogen storage, the relationship between carbon porosity (SSA, pore size and pore volume) and hydrogen sorption capacity is not well understood. Our systematic study of the hydrogen sorption of carbon materials dispels the popular myth that hydrogen physisorption is directly proportional to SSA [6], and provides guidance for optimal design by demonstrating that a large volume of small pores with narrow size distribution is the key to high hydrogen uptake. While small pores (1 nm or below) are efficient for hydrogen sorption, mesopores (pores > 2 nm) do not contribute much to storage of hydrogen under these conditions. A higher SSA and larger pore volume increase the hydrogen uptake for a given pore size. Values up to 3 wt.% and 30 kg/m³ have been demonstrated in CDC; these are twice what can be stored in metal-organic frameworks (MOF-5) and several times higher than has been achieved in single or multi-walled carbon nanotubes at 77K and atmospheric pressure. References 1. Gogotsi, Y., et al., Nanoporous Carbide-Derived Carbon with Tunable Pore Size. *Nature Materials*, 2003. 2: p. 591-594. 2. Nikitin, A. and Y. Gogotsi, Nanostructured Carbide-Derived Carbon (CDC), in *Encyclopedia of Nanoscience and Nanotechnology*, H.S. Nalwa, Editor. 2004, American Scientific Publishers: CA. Vol. 7: p. 553-574 3. Dash, R.K., A. Nikitin, and Y. Gogotsi, Microporous Carbon Derived From Boron Carbide. *Microporous and Mesoporous Materials*, 2004. 72: p. 203-208. 4. Dash, R.K., et al., Synthesis and Characterization of Nanoporous Carbon Derived from Titanium Carbide. in preparation. 5. Dash, R.K., G. Yushin, and Y. Gogotsi, Synthesis, Structure and Porosity Analysis of Microporous and Mesoporous Carbon Derived from Zirconium Carbide. *Microporous and Mesoporous Materials*, in the press, 2005. 6. Schlappbach, L. and A. Zuttel, Hydrogen-Storage Materials for Mobile Applications. *Nature*, 2001. 414: p. 353-358.

A9.31

A Theoretical Study of Fe-Only Hydrogenase: Towards QM/MM Calculations. Steven Trohalaki^{1,2}, Soumya S. Patnaik^{1,2} and Ruth Pachter¹; ¹Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, Ohio; ²The Anteon Corporation, Dayton, Ohio.

The notion of H₂ production from metalloenzymes such as [NiFe]H₂ases and [FeFe]H₂ases in cyanobacteria or green algae, is promising. However, despite a number of experimental structural and spectroscopic studies, an understanding of the catalytic activity dependent on the protein environment is still lacking. In this study, we examine theoretically the Fe-only hydrogenase (CpI), and in particular the so-called 'H-cluster' [F₂S₂]_H active site at different oxidation states, applying density functional theory. Indeed, to enable investigation of the protein by combined quantum mechanics/molecular mechanics (QM/MM) methods, we first assess effects of the exchange correlation (x-c) functional and basis set. Our systematic study of model compounds related to [F₂S₂]_H reveals that, although the structural and electronic parameters using BP86 (within the generalized gradient approximation) and the hybrid B3LYP x-c functionals are similar, the BP86 functional, for example, predicts a structure where the CO bridges both Fe atoms for the oxidized form of [SCH₃(CO)(CN)Fe_p(μ-PDT))Fe_d(CO)₂(CN)], consistent with the x-ray CpI structure. Basis set effects are also notable. For example, in applying B3LYP/LACV3P**, we find a structure for the fully reduced species that is consistent with previous work (Bruschi et al., *Inorg.Chem.*, 2004) and the structure postulated for the active site of

the reduced enzyme. Finally, we discuss preliminary QM/MM results. Of particular interest is the effects of the binding pocket of the 'H-cluster,' the [4Fe-4S] subcluster of the active site, which is ligated to the protein through Cys300, Cys355, Cys499, and the subcluster bridging Cys499, as well as the two lobes of parallel beta strands, because the active site cluster is located in a cleft that makes a clear division between the lobes.

A9.32

Diffusion and Absorption/Desorption Kinetics of Hydrogen in TiV/MnCr H-storage bcc Alloys. Giovanni Mazzolai¹, Andrea Biscarini¹, Bruno Coluzzi¹, Fabio Massimo Mazzolai¹ and Ausionio Tuissi²; ¹Physics, University of Perugia, Perugia, Italy; ²Istituto per l'energetica e le interfasi, CNR-IENI, Lecco, Italy.

The chemical diffusion coefficient (D) of hydrogen has been measured in two alloys of the series 40Ti-xV-(50-x)Mn-10Cr, having a V content x equal to 32 and 36, by following the hydrogen absorption in the temperature range 273-1150 K. The isothermal pressure curves P(t) were fitted to a relationship [1] deduced from the second Fick equation under boundary conditions valid for the slab shaped samples used in these experiments. The Arrhenius plot of D gave the following values for the diffusion parameters: $W = 0.27 \pm 0.01 \text{ eV}$; $D_0 = (1.9 \pm 0.3) \times 10^{-7} \text{ m}^2/\text{s}$. Thermal desorption spectroscopy (TDS) data have shown that hydrogen emission from the pre-loaded samples started at 450 K for the 32 and 650 K for the 36 vanadium alloy, indicating a lower stability of the hydrides in the first alloy. An interesting feature of the 32V alloy at low H contents ($n\text{H}=\text{H}/\text{Me} \leq 0.09$) was an absorption process, which took place, on heating, between two desorption stages respectively due to the decomposition of the distorted bcc hydride and of the H solid solution α phase. [1] Elaborated from: P. G. Shewmon, Diffusion in solids, ed. Mc Graw Hill, N. Y. 1963, p. 18.

A9.33

Structure Analysis of Mg-based Super-laminates for Hydrogen Storage by TEM and in-situ XRD. Koji Tanaka¹, Nobuhiko Takeichi¹, Hideaki Tanaka¹, Tamotsu T. Ueda², Yoshihisa Kamiya², Makoto Tsukahara², Shiomu Kikuchi³ and Hiroshi Miyamura³; ¹Res. Inst. for Ubiquitous Energy Devices, Natl. Inst. of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan; ²IMRA Material R&D Co.Ltd, Kariya, Aichi, Japan; ³University of Shiga Prefecture, Hikone, Shiga, Japan.

Magnesium can absorb a large amount of hydrogen up to 7.6 mass%. Many Mg-based materials have been investigated to improve their kinetics of hydrogenation and dehydrogenation at elevated temperature. Recently, co-authors Ueda et al. reported that Mg/Cu super-laminates showed reversible hydrogenation and dehydrogenation at 473 K, which was lower than reaction temperatures of conventional Mg-based materials. The Mg/Cu super-laminates were prepared by fold and roll method using conventional two-high roll mill. Hydrogenation-dehydrogenation properties of the Mg/Cu super-laminate were investigated by PCT measurements. The Mg/Cu super-laminate absorbs hydrogen at 473 K after the hydrogenation and dehydrogenation at 573 K. It does not absorb hydrogen at 473 K without this pre-treatment process. We speculated that the reaction occurred at 473 K because of some phases and/or nano-structures formed during rolling process or pre-treatment process. In order to investigate the mechanism of hydrogenation and dehydrogenation at 473 K, the phase transformation was analyzed by in-situ XRD and the nano-structure of Mg/Cu super-laminate was observed by TEM. In-situ XRD results suggest that the reaction mechanism is as follows. In hydrogenation process at 573 K of the Mg/Cu super-laminate, Mg₂Cu phase is formed at the interface by interdiffusion between Mg and Cu layers. Mg₂Cu decomposes to MgH₂ and MgCu₂ by disproportionation. In dehydrogenation process at 573 K, MgH₂ returns to Mg, and Mg and MgCu₂ form Mg₂Cu. This Mg₂Cu phase absorbs and desorbs hydrogen reversibly through disproportionation and recombination process at 473 K. TEM observations revealed that as-rolled Mg/Cu super-laminate had the sub-micrometer-ordered laminate structure composed of Mg and Cu. The Mg and Cu layers have (0001) and (112) preferred-orientation respectively and dense lattice defects. Cu diffuses through grain boundaries into Mg layers and forms Mg₂Cu nano-grains. It is considered that this special structure leads to the phase transformation to Mg₂Cu at low temperature as 573 K and the nano-Mg₂Cu could be "a starting point" for the phase transformation. The Mg/Cu super-laminate after the pre-treatment process has uniformly distributed pores with a sub-micrometer diameter. It is considered that this structure enhances the diffusion of hydrogen and enables the hydrogenation and dehydrogenation at 473 K. NEDO supported this work under "Development of fundamental technologies in the safe utilization of hydrogen".

A9.34

Evolved Gas Analysis of Heat-Treated Carbon Nanomaterials. Yuri M. Shulga¹, Vyacheslav M. Martynenko¹, Alex

P. Moravsky² and Rouff O. Loutfy²; ¹IPCP RAS, Chernogolovka, Russian Federation; ²MER corporation, Tucson, Arizona.

Physical and chemical sorption of small molecules by high specific surface area carbon nanomaterials readily occurs during their synthesis, purification and storage. Trapped molecules can affect material properties. For example, gas desorption from carbon nanotube field emitters leads to inferior performance and shorter life time of vacuum electronic tubes. Adsorbates on carbon nanomaterials can reduce the capacity of hydrogen storage devices. Therefore, the gas composition and quantity evolved by carbon nanostructures at elevated temperatures merits critical evaluation. This paper presents data on evolved gas composition, which occurred upon heat treatment of fullerites, single-walled and multi-walled nanotubes. Upon prolonged storage in air and heating to 65 C the highly pure fullerite C60 mainly evolves oxygen gas while deuterofullerite C60D18 almost exclusively evolves water molecules. Above 400 C the deuterofullerites evolve CD4 and minor amounts of C2D4, and at 500 C some deuterobenzene C6D6 was also found in the gas phase. Purified SWNTs below 100 C evolve mainly diethyl ether and acetone molecules. Both solvents were used in purification. Hydrogen-containing molecules disappear from the mass-spectra upon heating the sample above 200 C. On heating SWNTs to 500-560 C the evolved gas is dominated by CO and CO₂ molecules. Purified SWNTs treated with 9 GPa of deuterium gas at 450 C contain more than 10 wt.% of deuterium when kept at these conditions. It was found that from RT to 400 C the mass-spectra of gases evolved from so-treated nanotubes show mainly hydrocarbons and at 500-550 C mainly D₂ and HD molecules. Lower temperatures for hydrocarbon evolution compared to deuterium molecules indicate weaker bonding of hydrocarbons or their precursors to the nanotube skeleton. Both hydrocarbons and deuterium are likely chemically bound to the tube before the thermal cracking of C-C and C-D bonds releases gas molecules. Of note, the hydrogenated SWNTs readily absorb water vapor from air, much in preference to molecular oxygen. The work was supported by ISTC (grant #2760).

A9.35

Structure and Thermal Conductivity of Silica Aerogels from Computer Simulations. Brian S. Good, Materials Division, NASA Glenn Research Center, Cleveland, Ohio.

Aerogels are of current interest in the aerospace community due to their light weight and low thermal conductivity, making them suitable for a variety of applications, notably cryotank insulation. These gels typically exhibit a complex structure; the smallest feature is a "primary" particle of amorphous silica, typically 2-5nm in diameter. The primary particles aggregate to form "secondary" particles, typically an order of magnitude larger, and these, in turn, form ropey structures, the details of which depend on the density. The gels appear to exhibit fractal dimensionality, at least over a small range of length scales. In this work, we investigate the relationship between the structure of the gels, their dimensionality and density, and their thermal conductivity. We model the secondary- particle aggregate structure using a modified Diffusion Limited Cluster Aggregation (DLCA) model. The model exhibits a qualitative difference in structure at low and high densities, and is consistent with experimental observation. At lower densities, we find evidence for a transition from fractal behavior at small length scales to approximately compact behavior at larger lengths. We model the thermal conductivity using a variant of the disordered resistor network approach that has been used to describe hopping electrical conduction in doped semiconductors. In our model, each secondary particle is assigned a thermal conductance that depends on the particle's size, and on the details of its contacts with neighboring particles; the conductivity of the gel network is obtained using standard numerical techniques. The scaling of the thermal conductivity with density and fractal dimension will be discussed.

A9.36

Hydrogen Uptake in Purified Multiwalled Carbon Nanotubes Synthesized using LaNi₅ as Catalysts. Ming Sheng Yu, Cheng Si Tsao, Kuei Sen Chang, Cheng Yu Wang, Tsui Yun Chung, Yan Hui Wu, Hsiu Pei Hsu and Kin Fu Lin; Institute of Nuclear Energy Research, Lungtan, Taoyuan, Taiwan.

We have synthesized a set of multi-walled carbon nanotubes (MWCNTs) by catalytically thermal decomposition of CH₄ on catalyst LaNi₅ powders with reaction temperatures at 670C. Fine powders of LaNi₅ were obtained by mechanical ball milling then followed by sonicating cutting with a high-energy probe. The size distribution of catalytic powders ranges from 40 to 1200 nm. Products obtained at reaction temperature mentioned above were characterized by HR-TEM, SEM and Raman Scattering, respectively. The yield was increased to around 300% when catalyst powders were evenly dispersed on quartz plate through the utilization of nickel network instead of confining in a ceramic crucible. Amorphous carbons, LaNi₅

catalyst and carbonaceous particles can be seen mixed or entangled with carbon nanotubes. The hydrogen capacity measured following general procedure for volumetric hydrogen adsorption measurement for the as-prepared products was around 0.15 wt%. Some samples then were carried out with various purified treatments and their hydrogen storage capacity thus jumped to 0.72~3.3 wt%. It was found that the purified CNTs revealed higher hydrogen storage capacity than that of as-prepared one, since the former has removed amorphous carbons and catalysts and induce higher surface area and larger micropore volume. In addition, the content of composed elements of residual catalysts for various purified treatment CNTs play an important role on hydrogen storage capacity. The hydrogen uptake increased with the decreasing of the amount of residual catalysts. However, the effect of hydrogen spillover mechanism for residual catalyst made of hydrogen adsorption alloy to enhance hydrogen storage for carbon nanotubes was not revealed in this study. The reason might be resulted from the physisorption of condensation of hydrogen inside the cavity of the tubes. Furthermore, the catalyst of hydrogen storage alloys does not show any expected synergistic effect to increase hydrogen storage for the composite CNT materials.

A9.37

Abstract Withdrawn

A9.38

NMR Investigations of Hydrogen Interaction with Metal-Containing Carbon Structures. Julie Lynn Herberg,

Robert S. Maxwell, Ted Baumann and Joe Satcher; Chemistry and Material Science, Lawrence Livermore National Laboratory, Livermore, California.

Carbon nanostructures, such as carbon nanotubes and carbon-based aerogels, have received significant attention as hydrogen storage materials due to their low molecular weight, tunable microporosity, and high specific surface areas. The National Renewable Energy Laboratory, for example, achieved 5 to 10 wt.% hydrogen storage using metal-doped (M=59Co and 57Fe) carbon nanotubes [1, 2]. Traditional detailed studies of the carbon nanotubes have shown that intimate mixing of metal particles with the sp²-hybridized carbon of the nanotube resulted in an unanticipated hydrogen adsorption at near-ambient conditions. Despite these promising results the exact mechanism of hydrogen adsorption and release in these materials has not yet been fully unraveled. Currently, two competing theories of the mechanism of hydrogen adsorption in these materials are in vogue. In the first, a lengthening of the molecular hydrogen bond occurs because the nanotube is in contact with a metal particle causing non-classical binding. In an alternate theory, molecular hydrogen dissociates when a metal particle is in contact with a nanotube because of the high degree of strain in this material. The lack of consensus regarding the initial stages of hydrogen adsorption, as a result, hampers efforts to engineer optimized hydrogen storage materials. Any effort to optimize the hydrogen storage properties of metal-doped carbon systems will need to be based on a more fundamental understanding of the carbon-metal, carbon-hydrogen, and metal-hydrogen interactions. NMR is an ideal method for determining the structure and dynamics of hydrogen within these materials. It is element specific, sensitive to structural and bonding motifs, capable of investigating disordered materials, and uniquely sensitive to a broad range of time scales. In the present study, the metal-carbon composites that will serve as the model systems for this work will be metal-doped carbon aerogels [3]. These materials are ideally-suited for these NMR studies as they can be prepared reproducibly in bulk, unlike other carbon-based materials, and possess many of the essential features important to the metal-nanotube composites, namely the intimate mixing of metals and graphitic carbon on the nanometer scale. ¹H and ¹³C NMR have been performed to develop a fundamental understanding of the carbon-metal, carbon-hydrogen, and metal-hydrogen interactions. 1. Dillion, A.C.; Jones, K.M.; Bekkedahl, T.A.; Kiang, C.H.; Bethune, D.S.; Heben, M.J. *Nature*, 1997. 386: p. 377. 2. Dillion, A.C.; Parilla, P.A.; Alleman, J.L.; Mahan, A.H.; Gilbert, K.E.H.; Jones, K.M.; Heben, M.J.; *Mat. Res. Soc. Symp. Proc.*, 2004 801: p167 3. Fu, R.; Baumann, T.F.; Cronin, S.; Dresselhaus, G.; Dresselhaus, M. S.; Satcher, Jr., J.H.; Langmuir 2005, 21, 2647-2651 This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory, under contract # W-7405-ENG-48.

A9.39

Optimization of Hydrogen Storage Containers.

Andrew Weisberg, Physics, Lawrence Livermore National Laboratory, Livermore, California.

Optimal macroscopic multiphase structures are determined by a rigorous theory adapted from a more general formalism which treats mechanical and thermal performance in arbitrary powered artifacts. This generalized formalism is a subset of Transport Theory applied to multi-graph connected networks, rather than to locally uniform

materials. Optima that validly combine the consequences of mass, volume, power, and cost are found with the Calculus of Variations by applying static optimization to an under-constrained artifact design. All investigations of such optima to date have probed parameterized families of macroscopic lattice containers suitable for storing hydrogen onboard motor vehicles. First-order-correct models of mass, power, and cost of pumping are introduced to enable optimization of actively powered transport that overcomes fluid drag in both heat-exchanging and mass-exchanging passageways. Heat transfer, mass transfer, and force balance combine to determine optimal fuel storage container geometry and phase ratios. Examples from the diverse possibilities for advanced hydrogen containers are optimized for plausible choices of vehicular cost function, fabrication processes, affordable materials, and hydrogen storage media.

A9.40

Direct Observation of Adsorption Sites and Hydrogen Nano-Cage Formation in Metal-Organic Frameworks.

Taner Yildirim and Michael R. Hartman; NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland.

Metal-organic framework (MOF) compounds, which consist of metal-oxide clusters connected by organic linkers, are a relatively new class of nanoporous material that shows promise for hydrogen storage applications because of their tunable pore size and functionality. Yet in spite of numerous experimental studies of hydrogen adsorption in MOF materials, the nature of the MOF-hydrogen interaction and the manner in which hydrogen molecules are adsorbed onto the structure are still unknown. Answers to these questions hold the key to optimizing these materials for practical hydrogen storage applications. Here we will report direct determination of the adsorption sites and hydrogen nano-cage formation within MOF-5, Zn₄O(BDC)₃ (BDC = 1,4-benzenedicarboxylate) using neutron scattering measurements along with first-principles calculations. The study utilized a deuterated BDC linker as well as deuterium gas to eliminate the high incoherent scattering cross section of hydrogen and permit the acquisition of high resolution neutron powder diffraction data using the BT-1 spectrometer at the NIST Center for Neutron Research. Deuterium loadings of 1, 2, 2.5, 6.5, 8.5, and 11.5 D₂ molecules per zinc atom were investigated. The Fourier difference analysis of the neutron data clearly show four different absorption sites, yielding D₂-uptake up to ~10 wt-% at low temperatures without any external pressure. The metal-oxide cluster is responsible for most of the adsorption while the organic linker plays only a secondary role. Equally important, we show that at high-concentration D₂ molecules form unique interlinked high-symmetry nano-clusters with intermolecular distances as small as 3.0 Ang. These results not only hold the key to optimize MOF materials for hydrogen storage applications but also suggest that MOFs can be used as templates to create artificial interlinked hydrogen nano-cages with novel properties. More information can be obtained at <http://www.ncnr.nist.gov/staff/taner/h2>.

A9.41

Long Term Hydrogen Storage as a Solid. Stephen C. Bates, Thoughtventions Unlimited LLC, Glastonbury, Connecticut.

A technique for passive, long-term storage of (para)hydrogen as a vacuum isolated solid is described and heat transfer magnitudes are calculated in detail. Heating of the solid is minimized by: 1) elimination of convection heating by vacuum isolation, 2) physical support of the solid by low thermal conductivity, high strength plastic cables, and 3) low optical emissivity of the vessel wall facing the transparent hydrogen solid that minimizes radiative heat transfer. The heat transfer to the cryosolid from the walls is greatly reduced compared to the same mass of material in contact with a wall for standard or possible future insulation materials, allowing decades-long storage of the hydrogen if necessary. Hydrogen is supplied by allowing the system to pressurize; storage mode can be resumed by vacuum pumping. Convective thermal conductivities on the order of 10⁻⁷ W/cm-K can be achieved by proper evacuation of the system. A 5 cm separation and a 300 K temperature difference implies an approximate heat flux of 0.15 W/m² Kevlar 29 cord embedded in the hydrogen solid is used for the solid support, with a tested low thermal conductivity of k = 21.5 x 10⁻⁶ Tl.58 W/cm-K. A typical cord setup is considered; a 5 cm separation, a cord diameter of 2 mm (area = 0.03 cm²), and 10 cable connections to the wall. Assuming one end is fixed at 300 K and the other at 10 K, the thermal gradient occurs closer to the solid hydrogen. An average of about 0.1 W per cable is estimated, resulting in 1 W total for all of the cables, lowered by a factor of 5 for insulated cable supports. Liquid filling followed by vacuum freezing results in the proper suspension of the solid after the solid melts next to the wall and evacuation removes this liquid layer, creating an insulating vacuum barrier. Radiant heat transfer is shown to be small. For a 273 K blackbody (the vessel wall), peak power is radiated at about 10 μm wavelength, and the total power is about 30

mW/cm² (0.03 W/cm²), or 300 W/m². Given a surface emissivity of at most 1% for proper used of materials (described), radiated power is 3 W/m². Peak power is radiated at about 10 μm wavelength, decreasing to 10% at 4.5 μm and 34 μm. The IR absorption bands for transparent solid hydrogen are not widely known, but at 4K they are from 4250 - 4700 cm⁻¹ (2.2 to 2.4 μm), where a 2 cm thick sample is fully absorptive, a weaker region at 8400-8800 cm⁻¹ (1.14 to 1.19 μm), and a narrow absorption at 1168 cm⁻¹ (8.6 μm). The major absorption wavelengths of solid hydrogen are outside the bandwidth of the heat radiation from the outer wall. Making a conservative estimate of the narrow absorption at 8.6 μm implies a 0.01 μm wide absorption. At this wavelength, the radiated power (assuming 1% emissivity) is about 1.5 x 10⁻⁵ W/cm²-micron, so the absorbed power would be on the order of 10⁻⁷ W/cm², or 10⁻⁵ W/m², a negligible amount compared with other sources.

A9.42

Abstract Withdrawn

A9.43

Abstract Withdrawn

A9.44

Abstract Withdrawn

A9.45

The role of film morphology on the photocatalytic efficiency of CdS film synthesized by CBD method. Tomoyuki Ishiyama¹, Takeo Arai², Yoshinori Sato¹, Kozo Shinoda¹, Balachandran Jeyadevan¹ and Kazuyuki Tohji¹; ¹Graduate School of Environmental Studies, Tohoku University, Sendai, Japan; ²Energy Technology Research Institute, National Institute Advanced Industrial Science and Technology, Tsukuba, Japan.

In recent years, global warming caused by the consumption of fossil fuel has become a serious problem and technologies to produce clean and environmental-friendly energy is urgently required. Under this context, hydrogen is considered as a form of clean energy. Though the technology to split water can be the ultimate goal, the splitting of the hydrogen sulfide (H₂S) should also be given serious consideration because the decomposition of H₂S requires only 25% of energy compared to that of H₂O. In this study, we used Cadmium sulfide (CdS) photocatalyst film to produce hydrogen gas through photo-splitting of H₂S. The band gap of CdS is 2.4eV and it can work under sun light irradiation. CdS film on a glass substrate is prepared by Chemical Bath Deposition (CBD) method. CBD is one of a technique to prepare chalcogenide film using dissociation of Cd complex ion in the chemical bath [1]. During CBD, deposition rate plays an important role in determining the film morphology [2, 3]. In this study, we used cadmium sulfate as Cd source, ammonia, as complex agent, and thiourea as the source of sulfur, respectively. To control the reaction rate, the concentrations of ammonia and thiourea were varied. When the concentration of ammonia complex agent was high or thiourea was low, the bath became metastable and the deposition reaction rate was low. Therefore, the CdS deposition on the glass substrate was through heterogeneous reaction. Consequently, the film consisted of small and dense CdS particles, which are two-dimensionally distributed on the substrate. On the contrary, when the concentration of ammonia is low or that of thiourea is high, the bath was unstable and CdS began to precipitate in the solution as clusters and later they are deposited on the substrate by adhesion. In this case, the film morphology was multiplicated and very porous. When the chemical bath was too unstable, most of CdS was precipitated in the bulk of the bath and little was deposited on the substrate. To improve the photocatalytic activity, the CdS film was supported with platinum by photo-reducing platinum ions of chloroplatinic acid. The photocatalytic activity of each film was estimated by measuring the amount of H₂ gas produced when it is dipped in Na₂S solution and exposed to Xe lamp radiation. As a result, hydrogen was successfully produced and photocatalytic activity of the films is influenced by their morphologies. In this presentation, we will report the detail about the relation between the morphology and photocatalytic activity of CdS films. Reference [1] J. M. Dona, J. Herrero, *J. Electrochem. Soc.*, **144**, 4081, 1997. [2] H. Zhang, X. Ma, D. Yang, *Materialletters*, **58**, 5, 2003. [3] M. Kostoglou, N. Andritsos, A. J. Karabelas, *ThinSolidFilms*, **387**, 115, 2001.

A9.46

Synthesis of Zn_xCd_{1-x}S photocatalyst thin film by dip-coating method and its photoreactivity. Masashi Hirayama¹, Takeo Arai², Yoshinori Sato¹, Kozo Shinoda¹, Balachandran Jeyadevan¹ and Kazuyuki Tohji¹; ¹Graduate School of Environmental Studies, Tohoku University, Sendai, Japan; ²Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Decomposition of hydrogen sulfide into hydrogen and sulfur using

either ZnS or CdS as photocatalyst is a beneficial reaction that could generate clean energy. However, ZnS could function only under ultraviolet light radiation, and CdS that could operate in the visible region needs rare metal such as Pt, as co-catalyst. It has been reported that the Zn_xCd_{1-x}S could extend the light response wavelength to visible range [1]. In this study, we focused our attention on the synthesis of film composed of Zn_xCd_{1-x}S solid solution. First, we synthesized Zn_xCd_{1-x}S particles with x varying between 0 and 1 by co-precipitation method and evaluated their photocatalytic activity. Then, based on these results, Zn_xCd_{1-x}S solid solution film was prepared. The coprecipitated Zn_xCd_{1-x}S particles were synthesized by introducing Na₂S solution into a mixed solution of Zn(NO₃)₂ and Cd(NO₃)₂. Five samples were prepared by varying the Zn/Cd ratio, while maintaining the total metal ion concentration constant. The sediment was filtered and dried in the oven at 333 K. The XRF analysis confirmed that the ratios between Zn and Cd of the particles were similar to the initial mole ratio. The XRD peaks shifted to higher angle with the increase in the value of x. From these results, it was inferred that while the crystal structure of the coprecipitated Zn_xCd_{1-x}S remained sphalerite type, the lattice constant expanded continuously from that of ZnS towards CdS for increasing Cd content. On the other hand, the UV-VIS reflection spectrum of Zn_xCd_{1-x}S fell between that of ZnS and CdS. Compared to Zn_{0.5}Cd_{0.5}S, the absorption edges of Zn_{0.67}Cd_{0.33}S and Zn_{0.33}Cd_{0.67}S shifted to lower and higher wavelengths, respectively. This suggested that the shift in band structure of Zn_xCd_{1-x}S with the change in the Zn/Cd ratio. The results of hydrogen generation reaction of all the Zn_xCd_{1-x}S showed higher reactivity than CdS, and the amount of hydrogen generated improved with increasing Zn/Cd ratio and the optimum was recorded for Zn_{0.33}Cd_{0.67}S. Zn_{0.33}Cd_{0.67}S thin film was made on Ti substrate by dip-coating method. Zn_{0.33}Cd_{0.67}S particles were dispersed in ethanol. The substrate was submerged in the slurry and removed slowly. After each dip-coat the substrate was dried at 333 K. The dip-coat/dry cycle was repeated till a film of specific thickness was obtained. Finally, the thin film sintered at specific temperature. Then their photocatalytic activity was evaluated by measuring the photocurrent. The detail results of this study will also be reported. [1] A. M. Roy et al. *PhotochemistryandPhotobiologyA : Chemistry*, **157**, 87, 2003.

A9.47

H₂ Formation by Zinc Hydrolysis in a Hot Wall Aerosol Flow Reactor. Brian Burg¹, Frank O. Ernst¹, Antonio Tricoli¹, Sotiris E. Pratsinis¹ and Aldo Steinfeld²; ¹Particle Technology Laboratory, ETH Zuerich, Zuerich, Switzerland; ²Institute of Energy Technology, ETH Zuerich, Zuerich, Switzerland.

Solar thermochemical processes, which make use of concentrated solar radiation as the energy source of high-temperature process heat, are considered for the production of solar fuels and H₂ in particular. Single-step thermal dissociation of water, although conceptually simple, has been impeded by the need of a high-temperature heat source for achieving a reasonable degree of dissociation, and by the need of an effective technique for separating H₂ and O₂ to avoid their recombination. Water-splitting thermochemical cycles bypass the H₂/O₂ separation problem and further allow operating at relatively moderate upper temperatures. Two-step water-splitting thermochemical cycles convert solar energy into chemical energy and H₂ fuel using energy carriers, in this case zinc. The first step reduces ZnO to Zn and O₂ by dissociation through solar irradiation. In the present study, the second exothermic step is investigated, where Zn is evaporated, carried by an Ar gas flow into a quartz aerosol jet flow condenser where it reacts with H₂O vapour to produce H₂ and ZnO nanoparticles in a temperature controlled reaction zone. A temperature dependency for the overall conversion between 673 K and 873 K was found with H₂ yields up to 81% with respect to Zn. Above and below these temperatures the conversion remained constant. Further, an inverse temperature dependency for effective particle yield was detected reaching as high as 27%, containing up to 80 wt% ZnO. From the XRD, BET and TEM analysed particles at the reactor exit, a maximum particle size of 350 nm at 723 K was observed. These particles were rod-like or spherically shaped with Zn and ZnO crystallite sizes in the order of 100 and 40 nm, respectively.

A9.48

Hydrogen Separation Using New Mixed Ionic and Electronic Conducting Membrane. Hengdong Cui, Annamalai Karthikeyan, Srikanth Gopalan and Uday B. Pal; Manufacturing Engineering, Boston University, Brookline, Massachusetts.

Mixed ionic and electronic conductors (MIECs) have potential applications in various gas separation applications. Hydrogen synthesis and segregation from water splitting and simultaneous partial oxidation of methane can be achieved using MIEC membranes conducting oxygen ions and electrons. Membranes used for such processes should be stable in the oxygen partial pressure gradient that exists across its thickness. A new dual-phase composite MIEC

membrane system comprising of one phase with high oxygen ion conductivity and a second phase with high electron conductivity, both individually stable in the gas atmospheres prevailing on both sides of the membrane during the hydrogen separation process has been developed. In such MIEC composites it is possible to tailor the ambipolar conductivity by compositional choice. In this work the composite MIECs system comprising of $Gd_xCe_{1-x}O_{2-x/2}$ (GDC) and $Gd_xSr_{1-x}Ti_{1-y}Al_yO_3$ (GSTA) has been studied. Electrical conductivity relaxation (ECR) experiments were conducted in the pO_2 range of $10^{-17} \sim 10^{-18}$ atm to evaluate the chemical diffusion coefficient of oxygen and surface exchange rates. The diffusion coefficient and surface exchange coefficient of this dual phase MIEC membrane in this pO_2 range were found to be $10^{-5} \text{ cm}^2/\text{s}$ and 10^{-4} cm/s respectively. The estimated critical thickness (L_c) of the membrane, defined as diffusion coefficient over surface exchange rate, is $\sim 1 \text{ mm}$. Oxygen permeation fluxes were measured across the MIEC composite membrane with a mixture of steam and argon as a feed gas and hydrogen and helium as a permeate gas. In this approach, oxygen split from water vapor permeates through the dense MIEC composite membrane leaving behind a hydrogen rich product on the feed side of the membrane (steam side). Electrons (or holes) also transport across the membrane to preserve electrical neutrality. The transported oxygen reacts with hydrogen on the permeate side to form H_2O vapor. Initial tests carried out at a reactor temperature of $900 \text{ }^\circ\text{C}$ shows that a hydrogen flux as high as $4 \mu\text{mol cm}^{-2}\text{s}^{-1}$ can be obtained using a 1mm thick membrane. Significant improvement in hydrogen flux can be obtained using thinner membrane, optimized membrane compositions and by feeding methane on the permeate side. These experiments are ongoing and results will be presented.

A9.49

Catalytic Decomposition of Methane over Cerium-Doped Ni Catalysts. Miguel A. Valenzuela, Jin An Wang and Oscar A. Gonzalez; Lab. Catalisis y Materiales, Instituto Politecnico Nacional, Mexico City, Mexico.

Recently, the catalytic decomposition of methane (CDM) has received extensive attention as a potential process for the production of high-purity hydrogen. The produced carbons, may be used as the substitutes of carbon black, fibers, graphite, composites, carbon fillers in tires and plastics or be used as catalyst supports. Deposited carbon also can be oxidized with CO_2 , H_2O and O_2 into CO , synthesis gas and CO_2 . The most studied catalysts for the CDM are nickel supported on: SiO_2 , TiO_2 , graphite, ZrO_2 , $SiO_2-Al_2O_3$, Al_2O_3 , $MgO-SiO_2$, MgO and $ZnAl_2O_4$ among others. The activity and life of the supported Ni catalysts for CDM strongly depend on the particle size of Ni metal and the textural properties of the support. Unfortunately, rapid deactivation of Ni-based catalyst results at temperatures in excess of $600 \text{ }^\circ\text{C}$, leading to a low yield of hydrogen. On the other hand, it is well known that the surfactant-assisted (SA) route provides finely tuned pore sizes, high surface areas and enhanced accessibility of the active surface sites. It is, therefore, a major challenge to develop a catalytic system that sustains its activity at high temperatures. In the present work, we report the synthesis, characterization and catalytic properties in the CDM of a new catalytic system prepared by the SA method. The Si-Ce-O mixed solids (50, 30, 10 and 5, Si/Ce molar ratio) were prepared by using $Ce(NO_3)_3$ as cerium source, tetraethyl orthosilicate (TEOS) as aluminum precursor and cetyltrimethylammonium bromide (CTABr) as synthesis template. The Ni catalysts were prepared by impregnation of the supports using Ni-acetylacetonate (30 wt.% Ni) as Ni source dissolved in toluene. The samples were characterized by: X-ray diffraction, nitrogen physisorption (BET area), FTIR, temperature-programmed reduction (TPR), TPO and TEM. Methane decomposition was carried out using in a continuous flow stainless steel fixed bed reactor operated at 853 K at atmospheric pressure. The feed stream was a mixture of high purity methane (20 mol % CH_4) diluted in argon. Under these operation conditions only hydrogen was obtained as a gaseous product over all the catalysts. The initial conversion of methane obtained for Ni/ SiO_2 catalyst was higher than that for the other catalysts. However, the Ni/ SiO_2 catalyst presented a lower stability, measured as the conversion at 90 min with respect to the conversion at 5 min. The Ni catalysts supported on SiO_2-xCeO_2 mixed supports were initially less active than the Ni/ SiO_2 catalyst and the initial activity depended of the amount of CeO_2 . A distinctive stability was shown by all Ni/ SiO_2-xCeO_2 catalysts, excepting for the one containing the major amount of CeO_2 which behaved similar to the Ni/ SiO_2 catalyst. These preliminary results indicated that CeO_2 addition improves the textural properties of SiO_2 , mainly pore structure, leading to a better distribution of deposited carbon and increasing the lifetime of Ni particles.

A9.50

Hydrogen generation from hydrogen sulfide using a two-compartment photoelectrochemical cell with the stratified CdS nanoparticles. Hiromichi Matsumoto¹, Takeo Arai³, Yoshinori Sato², Balachandran Jeyadevan² and Kazuyuki Tohji²;

¹Department of Resource Materials Development, Nittetsu Mining Co, Ltd., Tokyo, Japan; ²Graduate School of Environmental Studies, Tohoku University, Sendai, Japan; ³Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Hydrogen sulfide that generated by the industrial activity (petroleum processing, sewage treatment plants) and the natural activity (volcanic zone, natural hot springs) was so far processed using the great energy and the labor as the harmful one. We have paid attention to hydrogen-generation from hydrogen sulfide (H_2S) using photocatalyst. If the H_2S can be directly decomposed into hydrogen and sulfur, the environmental problem can be solved and become the useful technology that makes hydrogen energy produce. Up to now, we prepared a highly efficient photocatalytic stratified CdS nanoparticles possessing the form of a capsule with a layer constituted of CdS particle which can use solar energy in alkaline sulfide solution. This photocatalyst was prepared from alkaline sulfide solution by using hydroxide as a precursor. And the stratified CdS nanoparticles were supported with Pt by photo-deposition method. The photocatalyst were able to decompose hydrogen sulfide into hydrogen and polysulfide ion at high efficiency. This Pt-deposition stratified CdS nanoparticle shows higher activity than Pt-deposition CdS nanoparticles. In this report, we report highly effective hydrogen-generation approach using a two-compartment photoelectrochemical cell with the stratified CdS nanoparticles in an effort to generate hydrogen. A two-compartment photoelectrochemical cell [1], which consisting of CdS electrode immersed in alkaline sulfide solution, proton exchange membrane, platinum electrode and sulfuric acid solution, is constructed in an effort to generate hydrogen efficiently. This cell prevents the recombination of the electron and the hole and paves the way to attain high hydrogen conversion rates in order to facilitate the separation of reaction sites of photoexcited electron and the hole. CdS electrode was made from depositing a stratified CdS particle on a titanium electrode. By irradiating light (550 W Xenon lamp, the intensity of the light introduced at the side of the cell was measured to be 16 W) at a photocatalyst electrode, hydrogen sulfide is decomposed in the photocatalyst electrode side, and hydrogen is generated in the platinum electrode side. The structure, composition, morphology and light response of the deposited stratified CdS electrode were characterized by using XRD (X-ray Diffraction spectroscopy), XRF (X-ray Fluorescence Spectrometer), FE-SEM (Field Emission Scanning Electron Microscope) and UV-VIS (Ultraviolet-Visible spectroscope). We will discuss the relation of hydrogen-generation efficiency to photocurrent in irradiating light at a photocatalyst electrode. [1] G. Milczarek, A. Kasuya, S. Mamykin, T. Arai, K. Shinoda, K. Tohji, *Int. J. Hydrog. Energy*, **28**, 919, 2003.

A9.51

Transferred to A10.6

A9.52

Hydrogen States and Degradation of Fcc Metals for High-Pressure Hydrogen Storage Tank. Kenichi Takai, Mechanical Engineering, Sophia University, Tokyo, Japan.

High-resistance metals to hydrogen degradation have been required since hydrogen pressure in a storage tank for a fuel cell vehicle varies from 35 MPa to 70 MPa, and that in the tank for hydrogen refueling station increases to above 100 MPa. FCC metals used under the high-pressure hydrogen for fuel-cell constituent materials such as Type 316L, Alloy 625, and Aluminum were prepared, because of the low susceptibility to hydrogen degradation. Three principal aspects regarding the fcc metals are present here: (1) to analyze hydrogen desorption properties of fcc metals obtained by thermal desorption spectrometry (TDS), (2) to find out the condition of electrolysis hydrogen charging corresponding to various hydrogen pressures, since the charging under high-pressure hydrogen is much danger and more expensive than the electrolysis hydrogen charging, and (3) to clarify the relationship between the hydrogen state and the degradation properties using slow strain rate technique (SSRT). The fcc metals were solution heat treated, charged under the electrolysis and high-pressure hydrogen, then analyzed hydrogen content and the states. The electrolysis hydrogen charging enables us to substitute high-pressure hydrogen atmosphere such as hydrogen refueling station using Sieverts rule since hydrogen state absorbed by the electrolysis and high-pressure conform without the surface damage. The maximum hydrogen pressure on Alloy 625 surface achieves to approximately 600MPa by the electrolysis charging. The strain to failure of Alloy 625 is critically dependent on hydrogen content and decreases with increasing hydrogen content. The fracture surfaces transform from ductile to brittle with increasing hydrogen. In contrast, the strain to failure of Type 316L remains constant regardless of high hydrogen content. The fracture surfaces remain ductile up to 93.1 mass ppm hydrogen content.

A9.53

Advanced Composite Sandwich Structure Design for Cryogen Tanks. Monika Bubacz, David Hui and Leo Daniel; Mechanical Engineering, University of New Orleans, New Orleans, Louisiana.

Since hydrogen is one of the lightest elements and has very small molecules it can escape from tanks and pipes more easily than conventional fuels. A gram of hydrogen gas occupies about 11 liters (2.9 gallons) of space at atmospheric pressure, so for convenience the gas must be intensely pressurized to several hundred atmospheres and stored in a pressure vessel. In liquid form, hydrogen can only be stored under cryogenic temperatures. The paper aims at defining not only the cryogenic tank concept design, but to identify the state of the art in advanced materials and technologies applicable for tanks design. There is an increasing interest in replacing metal part with lightweight composite materials in space transportation industry. One potential source for significant structural weight reduction is a replacement of traditional metallic cryogenic fuel tanks with new design polymer matrix composite ones. Fiber reinforced plastics offer advantageous specific strength and stiffness compared to metals. Materials and technologies for cryogenic tanks design which is capable of meeting the flight requirements in harsh environment are still in developmental stage. The new tank design may take the form of thin-walled sandwich structures constructed with lightweight polymer core and composite laminate skins. Different solutions for preventing permeation of gases, such as oxygen and hydrogen, and debonding in composite sandwich structure for cryogenic tank wall are presented. The rate of gas leakage can be a function of material, tank fabrication method, mechanical load to the tank, internal damage-state of the material, and the temperatures at which the tank must operate. This paper addresses the inherent problems associated with gas permeation by developing a barrier made from DuPont aramid paper. Aramid paper is well known for its excellent resistance to gas permeability and impact loads. The structure incorporates nanoparticles for properties modifications and developing additional barrier agents, and resin systems compatible to laminate and core materials in order to improve adhesion. Helium permeability tests were performed on a specially built set-up with gaseous helium as a permeant using Alcatel ASM 142, a universal helium leak detector. Current helium permeability tests show that Kevlar and Nomex paper sheet coated with resin system compatible to laminate and core materials used as interleave in sandwich structure can improve mechanical properties of the whole sandwich structure and sustain high gas pressure. The best polyester resin coating was obtained by applying diluted resin with brush and roller and curing in press between release film and metal plates. Nomex T412 paper exhibits better permeability resistance than Kevlar N635.

A9.54

Transferred to A5.8

A9.55

A Novel Two-Step Hydrogen Cycled Methane Reforming Process. Richard Charles Breitung¹, Yardlyne Smalley¹, Zhong Lin Wang², Robert Snyder², Michael Haluska² and Andrew Hunt¹; ¹Nanomiser, nGimat, Atlanta, Georgia; ²Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

One of the major hurdles in the way of hydrogen economy implementation is cost effective production of the fuel gas. Most hydrogen in the United States is made using steam reforming, a fuel transformation process that suffers from high energy, purification and capital equipment costs. Here we report virtually carbon monoxide-free hydrogen using a promising low temperature (<400oC) two-step process. Hydrogen was generated from methane with an efficiency above 60% at space velocities of 500-1000 hr-1. We also observed hydrogen generation as low as 300oC using this process. This was achieved using novel nanomaterials ranging in particle size between 2 and 100 nm in combination with novel compositions, which improved methane decomposition kinetics. We attribute our hydrogen purity to selective reaction of steam with oxygen vacancy sites in the second step of the process and sequestration of CO found in syngas in the first step. Additionally, we observed low CO (<200 ppm) hydrogen production from methane at temperatures ranging from 400-600oC using steam reforming methods. We attribute this result to the presence of multiple processes along the packed bed column. Upstream, the hydrocarbon is cracked, while further downstream the resultant syngas undergoes a water gas shift reaction. The oxide nanomaterials, which were produced by nGimat's NanoSpray process and combustion chemical vapor condensation (CCVC) methods enabled superior low temperature performance due to enhanced surface area and associated retention of activity between cycling. NanoSpray/CCVC routes have been used to attain novel morphology and improved hydrogen generation performance as well as numerous other nanomaterials. During the process, chemical precursors containing the metal of interest, among others are dissolved in suitable solvents, which also act as a fuel for combustion. The

chemical precursor solution is atomized to a sub-micron level within nGimat's proprietary Nanomiser device and droplets are then mixed with the oxidizer and ignited to generate a premixed flame. The flame flash vaporizes the solvent and the precursors, which then decompose to yield reactive vapor intermediates that ultimately condense and form nanoparticles.

A9.56

Hydrogen Production by Water Splitting Using Dense Thin-Film Cermet Membranes. Sun-Ju Song, Tae H. Lee, Chen Ling, Stephen E. Dorris and Uthamalingam Balachandran; Ceramics Session, Argonne National Lab., Argonne, Illinois.

Since hydrogen is considered an ideal choice for next generation fuel due to its environmental benefits, hydrogen production technologies have been receiving considerable attention. Among these technologies, water splitting using oxygen transport membranes can meet environmental and economic goals. The oxygen potential gradient across the membrane is the driving force for hydrogen production from water in a membrane reactor. Oxygen can be separated through oxygen transport membranes, pushing the thermodynamic equilibrium of water dissociation to higher hydrogen yields. For cermet oxygen transport membranes, it has been reported that the oxygen flux is limited by bulk diffusion down to a membrane thickness of $\approx 90 \mu\text{m}$. To increase the oxygen permeation rate and thereby increase the hydrogen production rate, effort is underway to reduce the membrane thickness. In this talk, we will present the results of hydrogen production by water splitting using dense thin-film cermet membranes at moderate temperatures (500 to 900 oC).

A9.57

New Materials for Hydrogen Storage: Recent Development on Microporous Metal Organic Frameworks (MMOFs). Long Pan, JeongYong Lee, Xiaoying Huang and Jing Li; Chemistry and Chemical Biology, Rutgers University, Piscataway, New Jersey.

Production of storage materials with significantly improved hydrogen adsorption capability is an extremely important aspect in fuel cell technologies, especially for the commercialization of fuel cell vehicles (FCVs). While extensive efforts have been made to improve the hydrogen storage technologies currently being investigated, none is yet capable of meeting the gravimetric and volumetric targets required for large scale commercialization. There is, therefore, a strong need to explore new materials with enhanced sorption properties, in addition to continuing research in the more traditional technologies. This presentation describes our recent development on microporous metal organic frameworks (MMOFs), a subclass of MOFs that are characteristic of very small pores with pore dimensions in the range of several angstroms [1-3]. The design and synthesis, crystal structure analysis, low and high temperature/pressure hydrogen sorption studies, and pore properties of these materials will be discussed. References: [1] L. Pan, M.B. Sander, X.-Y. Huang, J. Li, M. Smith, E. Bittner, B. Bockrath, J. K. Johnson, J. Am. Chem. Soc., 126 (2004) 1308. [2] J. -Y. Lee, L. Pan, S.K. Kelly, T.J. Emge, J. Jagiello, J. Li, Adv. Mater. submitted. [3] J.Y. Lee, J. Li, J. Jagiello, J. Solid St. Chem. in press.

A9.58

High-Temperature Deformation Characteristics and Corrosion Susceptibility of Alloy 800H. Ajit K. Roy and Vinay Virupaksha; Mechanical Engineering, University of Nevada Las Vegas, Las Vegas, Nevada.

The structural materials to be used in the proposed nuclear hydrogen generation must withstand significantly high operating temperatures and hostile environmental conditions. While many thermochemical processes have been considered in generating hydrogen using nuclear source, the sulfur-iodine (S-I) process is currently being preferred by the United States Department of Energy as the leading process. The S-I cycle involves chemical reactions at temperatures upto 900oC in the presence of sulfuric acid and hydrogen iodide. Thus, the structural materials for applications in the S-I cycle must possess excellent corrosion resistance, and resistance to high-temperature plastic deformation. Alloy 800H, a leading candidate structural material, has been tested for its evaluation of tensile properties at temperatures upto 1000oC in an inert atmosphere. Further, the cracking susceptibility of this alloy has also been determined under constant-load, slow-strain-rate and self-loaded conditions in an environment relevant to the S-I cycle. An electrochemical polarization technique has been used to determine the localized corrosion susceptibility of Alloy 800H in a similar environment. The fracture characteristics of the tested specimens have also been evaluated by scanning electron microscopy as a function of the testing temperature. The results of the tensile testing, corrosion studies, and SEM evaluation will be presented in this paper.

A9.59
Transferred to A6.7

A9.60
Microstructural control and hydrogen permeability in the Nb-Ti-Ni system by a rolling-annealing technique. Sho Tokui¹, Kazuhiro Ishikawa² and Kiyoshi Aoki²; ¹Graduate Student, Kitami Institute of Technology, Kitami, Hokkaido, Japan; ²Department of Materials Science, Kitami Institute of Technology, Kitami, Hokkaido, Japan.

Hydrogen has been expected as a new energy source for fuel cells. Hydrogen permeation alloys are effective in a separation and a purification of hydrogen. Pd-based alloys are expensive and rare in resources, although they are commercially used for hydrogen production. Therefore, non-Pd based alloys have been strongly desired. Recently, the present authors reported high hydrogen permeability (Φ) and a good resistance to hydrogen embrittlement of Nb-Ti-Ni alloys in the as-cast state. This alloy consists of the primary (Nb, Ti) solid solution and the eutectic {TiNi+(Nb, Ti)} structure, and shows higher Φ than that of pure Pd. Furthermore, this alloy has more than 70 % of rolling reduction rate at R.T. In this paper, the microstructure of Nb-Ti-Ni alloys is controlled by rolling-annealing techniques and the relation between Φ and it is discussed. The value of Φ of the Nb₄₀Ti₃₀Ni₃₀ alloy is decreased with increasing the rolling reduction rate. Φ of this alloy remains low by annealing below 1273 K, while it is recovered at 1373 K. The eutectic structure of this alloy is disappeared and changes to small spherical (Nb, Ti) phase embedded in the TiNi phase. This experimental result shows a possibility of developing Φ by microstructural control using a rolling-annealing technique.

A9.61
High hydrogen permeability in Nb-Ti-Ni eutectic alloys containing much primary (Nb, Ti) phase. Kazuhiro Ishikawa¹, Weimin Luo² and Kiyoshi Aoki¹; ¹Department of Materials Science, Kitami Institute of Technology, Kitami, Hokkaido, Japan; ²Graduate Student, Kitami Institute of Technology, Kitami, Hokkaido, Japan.

We have demonstrated that the Nb₄₀Ti₃₀Ni₃₀ alloy shows higher hydrogen permeability (Φ) than that of pure Pd with a good resistance to the hydrogen embrittlement. This alloy consists of 40 vol. % of the primary (Nb, Ti) phase and 60 vol. % of the eutectic {TiNi+(Nb, Ti)} structure. In this paper, alloy compositions are optimized for further development of Φ in Nb-rich Nb-Ti-Ni alloys. The chemical compositions of the primary phase and the eutectic {TiNi+(Nb, Ti)} structure in the Nb₄₀Ti₃₀Ni₃₀ alloy are determined using an energy dispersive X-ray spectrometer (EDS), and is expressed as Nb₈₃Ti₁₃Ni₄ and Nb_{20.5}Ti_{38.5}Ni₄₁, respectively. The Nb₅₆Ti₂₃Ni₂₁ alloy, which lies on the line connecting these compositions, is chosen for microstructural observation and hydrogen permeation measurement. This alloy is constituted of the primary (Nb, Ti) solid solution and the eutectic structure of TiNi and (Nb, Ti) phases, and the volume fraction of the primary phase is about 62 vol. %. The value of Φ of this alloy is 3.47×10^{-8} (mol H₂ m⁻¹ s⁻¹ Pa^{-0.5}) at 673 K, which is 1.8 times larger than that of Nb₄₀Ti₃₀Ni₃₀ alloy. Furthermore, this alloy is not broken during hydrogenation even at 523 K. This experimental result suggests we can obtain high performance Nb-rich hydrogen permeation alloys by the suitable selection of alloy compositions.

A9.62
Decoration of Single-Walled Carbon Nanohorns with Platinum Nanoparticles. H. Hui, B. Zhao, A. A. Puzetzy, D. Styers-Barnett, H. Cui, Z. Liu, C. M. Rouleau, and D. B. Geoghegan

Single-walled carbon nanohorns (SWNHs) hold great potential in various applications due to their unique structure and properties. SWNH and the aggregates have large surface area, which can be used for metal catalyst supports and hydrogen storage. In this work we introduce the decoration of SWNHs with platinum by a convenient one-step chemical reaction. The decoration of SWNHs from two different sources was compared in this work. LA-SWNHs were synthesized by laser ablation of pure carbon targets using a high-power (600 W) industrial Nd:YAG laser facility at Oak Ridge National Lab. A variety of laser-processing parameters were used and analyzed through high-speed videography and time-resolved pyrometry at different background gas pressures and temperatures to determine the optimal conditions for SWNH production. Nanohorns produced by this technique were compared to EA-SWNHs synthesized by the electric-arc discharge method (purchased from Nanocraft Inc.). A mixture of SWNHs and hydrogen hexachloroplatinate (IV) in aqueous solution was reacted with sodium citrate to form Pt-decorated SWNHs (SWNHs/Pt) with 1-3 nm stabilized Pt nanoparticles on the SWNHs. High resolution TEM images show that the Pt nanoparticles uniformly decorate the SWNH aggregates. Thermal gravimetric analysis shows the weight percentage for the Pt

metal residue is ~20% for LA-SWNHs/Pt and ~15% for EA-SWNHs/Pt. SWNHs/Pt formed in this way can be easily dispersed in water via sonication producing a stable dispersion at room temperature. Nanohorns produced directly by laser ablation of Pt/C targets and the hydrogen storage efficiencies of these materials are currently under investigation. Research supported by the U. S. Department of Energy (EERE) through the Center on Carbon-Based Hydrogen Storage and by the U. S. Department of Energy, Division of Material Science, Basic Energy Sciences.

SESSION A10: Carbon-based Hydrogen Storage/H₂ Generation
Chairs: Anne Dillon and Constantina Filiou
Friday Morning, December 2, 2005
Room 311 (Hynes)

8:00 AM *A10.1
High Hydrogen Storage in Porous Carbide Derived Carbon. Giovanna Laudisio¹, Taner Yildirim², Ranjan K. Dash³, Gleb Yushin³, Yury Gogotsi³ and John E. Fischer¹; ¹Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; ²National Institute of Standards and Technology, Gaithersburg, Maryland; ³Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

One major barrier to the large-scale production of hydrogen powered vehicles is the absence of an efficient storage medium. Recent reviews^{1,2} show that none of the candidate materials currently meet the target fixed by the U.S Department of Energy (DOE). The new class of porous Carbide Derived Carbon (CDC) here presented seems to be promising in achieving the value of 6.5 wt% for reversible hydrogen uptake.³ Thermodynamic and kinetic parameters of the adsorption/desorption process were evaluated as a function of pore size and distribution for different CDCs with a Sieverts-type apparatus. High pressure measurements were also carried out to relate the loading/release of hydrogen to temperature and H₂ pressure with the ultimate aim of optimizing the hydrogen storage. The achieved gravimetric hydrogen uptake for CDCs is about twice than that of MOF-5 and several times higher than HiPCo or chemically modified SWCNT.⁴ The reproducibility of our results is demonstrated by the excellent agreement with the values of hydrogen sorption obtained from Quantachrome Auosorb-1, performed independently in two laboratories. Carbide derived carbons (CDC) are produced by extraction of the metal (and metalloids) from carbide precursors in halogen atmosphere.⁵ The resulting material has high surface area and pore size tunable with sub-Angstrom accuracy determined by the crystal structure of the starting material and the choice of process parameters.⁶ The atomic-level control on porosity in CDC porous carbon offers the unique opportunity to carry out a systematic study of gas adsorption phenomena and better understand hydrogen sorption in porous materials. This work was supported by the US DOE, Grant No. DE-FC36-04GO14280 *corresponding author fischer@seas.upenn.edu [1] Hirscher, M. et al., Journal of Nanoscience and Nanotechnology 2003, 3, 3-17. [2] Zuetzel, A., Mat. Today, 2003. [3] "DOE Hydrogen Program, FY 2004 Progress Report." [4] Kajjura, H. et al., Applied Physics letters 2003, 82, 1105-1107. [5] Nikitin, A. et al., Encyclopedia of Nanoscience and Nanotechnology 2004, X, 1-22. [6] Gogotsi, Y. et al., Nature mat. 2003, 2, 591-594.

8:30 AM A10.2
Porous Carbide Derived Carbons (CDC) Optimized for Hydrogen Storage: A SAXS Study. Giovanna Laudisio¹, Ranjan K. Dash², Jonathan P. Singer¹, Gleb Yushin², Taner Yildirim³, Yury Gogotsi² and John E. Fischer¹; ¹Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; ²Materials Science and Engineering Department, Drexel University, Philadelphia, Pennsylvania; ³National Institute of Standards and Technology, Gaithersburg, Maryland.

The development of efficient and cost-effective hydrogen storage materials is the key to success for hydrogen-based economy. Carbon-based nanomaterials represent the most promising candidates thanks to their low atomic weight and availability in different forms, allowing a wide range of pore size, shape and distribution. The chlorination of metal carbides at modest temperatures produces inexpensive carbide-derived carbons (CDC) with interesting properties that distinguish them from common porous carbons. Pore size and specific surface area (SSA) can be finely tuned in a wide range with sub-Angstrom accuracy by selection of the starting carbide and chlorination temperatures.^{1,2} Here we present a systematic Small Angle X-ray Scattering (SAXS) study of different CDC materials, before and after activation in CO₂ environment. Our results demonstrate that porosity in CDC materials can be tailor-made to fit the size of hydrogen molecule for efficient storage. Scattering techniques are non intrusive and allow a direct analysis of pore

dimensions and surface area. They are complementary to physical adsorption methods which indirectly evaluate the available pore volume through the adsorption isotherm equation. SAXS allows the determination of inhomogeneities in carbon samples over a wide size range (from few Angstroms to about hundreds of nm) and is especially required when the dimensions of the pores are the same order of magnitude as that of the probe molecules (N₂, CO₂) used in the adsorption measurements. This work was supported by the US DOE, Grant No. DE-FC36-04GO14280. [1] Gogotsi, Y. et al., W. Nature Mat. 2003, 2, 591-594. [2] Nikitin, A., et al., Encyclopedia of Nanoscience and Nanotechnology 2004, X, 1-22.

8:45 AM [A10.3](#)

Adsorption of H₂ on Carbon Based Materials and on Metal-Organic Framework: A Study by Raman Spectroscopy. [Andrea Centrone](#) and [Giuseppe Zerbi](#); [Chimica, Materiali ed Ingegneria Chimica "G. Natta"](#), Politecnico di Milano, Milano, Italy.

The lack of a suitable and cost effective means of storing hydrogen is one of the main unsolved challenges that prevents its use as a fuel on a global scale. Although several approaches for storing hydrogen are being pursued, the development of sorbent materials capable of reversible uptake and release offers key advantages if suitable gravimetric and volumetric uptake can be achieved. A promising new class of sorbing materials in this regard are Metal Organic Frameworks (MOFs), this class of extended solids possesses extremely high surface areas with tunable pore sizes. Understanding the intermolecular interactions responsible for gas sorption in solids is fundamentally important for the development of new materials with improved gas sorption properties and geometries. The perturbation of the intramolecular potential resulting from intermolecular interaction with an adsorbing material made Raman spectroscopy a useful technique to investigate the physical phenomena which take place because of these interactions. We have recorded the Raman spectra of adsorbed hydrogen on two carbon materials (obtained with two independent and chemically different processes) in a variety of different physical conditions. All observations are consistent with a physisorption as mechanism of adsorption due to Van der Waals interactions; no others mechanisms involving stronger interactions with the adsorbing materials (and that, hopefully, could give larger gas adsorption values) appear from the spectra. From the physics which derives, based on the data obtained in this work, the large values of hydrogen adsorption on carbon materials at ambient temperature reported in the previous literature should be subjected to a strong critical analysis and possibly the reproducibility of many experiments reported should be checked. We think that in spite of the many optimistic predictions spread in the literature no realistic steps toward a technologically useful absorption of hydrogen on carbonaceous materials have been yet experimentally found. We have also recorded the Raman Q-branch of deuterium adsorbed on MOF material (MOF-5) at various temperature and pressures. The lines of the adsorbed gas are broadened and structured probably because of different adsorption sites. The down-shifted lines suggest that the attracting potential is certainly stronger than for carbon based materials. The down-shifted lines are evidence of the existence of different interactions sites inside the materials with different chemical groups which are able to polarize and attract the guest molecule. Therefore, one promising approach in the effort of increasing the storage capacity of the adsorbing material should focus on sorbents able to strongly polarize hydrogen. This work has been supported by the European Commission, Fifth Framework Programme, Growth Programme (Research Project MAC-MES; Molecular Approach to Carbon Based Materials for energy Storage, G5RD-CT2001-00571).

9:00 AM [A10.4](#)

Study of Effect of Temperature and Pressure on the Hydrogen Sorption Capabilities of a Polyaniline-CNT Nanocomposite Material. [Michael Ulrich Jurczyk](#)¹, [Ashok Kumar](#)¹, [Elias](#)

[Stefanakos](#)², [Arun Kumar](#)² and [Sesha Shirinivasan](#)²; ¹Mechanical Engineering, University of South Florida, Tampa, Florida; ²Clean Energy Research Center, University of South Florida, Tampa, Florida.

It has been shown that carbon materials can be used for hydrogen storage to be used for clean energy fuel cells. Currently, materials such as single- or multi-walled carbon nanotubes demonstrate hydrogen adsorption rates of approximately 7 wt. %. This research work looks to combine polyaniline with carbon nanotubes to be used for hydrogen storage. The advantage of such a combination lies in the fact that hydrogen can be adsorbed in two different ways. Hydrogen can be stored via physisorption as well as via chemical bonding. Hence, the storage rate is increased above that of simple carbon structures. The effect of temperature and pressure on the polyaniline/carbon nanotube nanocomposite material during hydrogen sorption is studied by varying the pressure and temperature of the sample and the hydrogen during the sorption process. In addition, the nanocomposite is characterized using DSC, TGA, FTIR as well as Raman Spectroscopy.

9:15 AM [A10.5](#)

Thermomechanical Stabilities and Hydrogen Storage Capacities of Metal-Organic Frameworks. [Amit Samanta](#) and [Ju Li](#); Department of Materials Science and Engineering, Ohio State University, Columbus, Ohio.

Nanoporous metal-organic frameworks are promising hydrogen storage platforms. For this new type of materials, many physical properties such as the elastic constants are still unknown. We predict these properties and their thermomechanical stabilities under loading using density functional theory (DFT). We find that a simple spring-network model with angular interactions can be used to rationalize the results reasonably well. We then use DFT with local density functional (which tends to overestimate van der Waals binding) to calculate the physisorption energy of H₂ molecules at various sites. We find that the metal core sites tend to have the strongest attraction, which however is still significantly weaker (by simple thermodynamic estimates) from the DOE target for room-temperature on-board storage. We discuss physisorption energy trends for various possible chemical substitutions.

9:30 AM [A10.6](#)

In situ Investigations of Single Wall Carbon Nanohorn Synthesis by High Power Laser Vaporization.

[David B. Geohegan](#), [A. A. Puretzky](#), [D. Styers-Barnett](#), [H. Hu](#), [C. M. Rouleau](#), [H. Cui](#), [Z. Liu](#) and [B. Zhao](#); Condensed Matter Sciences Division and the Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Single-walled carbon nanohorns (SWNHs) and their aggregates provide a rich variety of possible adsorption sites for hydrogen storage and locations to support metal catalyst clusters against aggregation. Nanohorns are similar to single-walled carbon nanotubes (SWNTs), except they are shorter, closed structures containing numerous defect sites and different interstitial pore sizes within their flower-shaped aggregates. Optimizing the structure of nanohorns and their aggregates is complicated by the lack of knowledge regarding their formation. Unlike SWNTs, SWNHs are typically formed without the need for metal catalysts in high yield (up to 95% vs. amorphous carbon). Elucidation of the mechanisms for their formation, and for the formation of their flower-shaped, ultrafine (< 100 nm diameter) aggregates, is complicated by the complex dynamics and high temperatures of the long-lived plasma which is formed following ablation. In this study, single-walled carbon nanohorns (SWNHs) are synthesized using a high-powered (600 W) industrial Nd:YAG laser and metal-loaded either *in situ* or *ex situ*. High-speed videography and pyrometry are used to characterize the time scales and conditions for nanohorn growth following laser vaporization of carbon targets ranging from room temperature up to 1100C for a variety of laser pulse widths. Efficiencies for their production into room temperature and elevated temperature background gases are compared, and similarities between the conditions for SWNH synthesis with those of SWNTs are discussed. *Ex situ* transmission electron microscopy, scanning electron microscopy, optical absorption spectroscopy, Raman spectroscopy, thermogravimetric analysis, are used along with *in situ* diagnostic techniques to correlate the synthesis conditions with the resulting products and gain insight into their formation processes. Estimations of nanohorn purity and metal catalyst loading efficiencies are compared with arc-grown SWNH materials. Research supported by the U. S. Department of Energy (EERE) through the Center on Carbon-Based Hydrogen Storage and by the U. S. Department of Energy, Division of Materials Science, Basic Energy Sciences.

9:45 AM [A10.7](#)

Hydrogen Adsorption and Dynamics in Metallic-Organic Framework Materials. [Michael R. Hartman](#), [Taner Yildirim](#), [Terry J. Udovic](#) and [Craig M. Brown](#); National Institute of Standards and Technology, Gaithersburg, Maryland.

Metallic-organic framework (MOF) materials are nanoporous materials consisting of metal clusters linked by organic linkers and have been suggested as a potential hydrogen storage medium. The hydrogen adsorption characteristics of MOF-5, Zn₄O(BDC)₃ (BDC = 1,4-benzenedicarboxylate), were investigated using adsorption isotherms in conjunction with incoherent inelastic neutron scattering. The isotherm data were collected at temperatures ranging from 30 K to 100K for pressures up to 100 bar. The hydrogen uptake of MOF-5 at 30 K approached 10 wt. %, but rapidly decreased with increasing temperature to 1.2 wt % at 77 K and 1 bar H₂. The coupled translational-rotational dynamics of the adsorbed hydrogen were probed with incoherent inelastic neutron scattering using the filter analyzer neutron spectrometer (FANS) and the disc-chopper time-of-flight spectrometer (DCS) at the National Institute of Standards and Technology Center for Neutron Research. The inelastic neutron spectra were collected in both neutron energy loss and gain as a function of temperature and hydrogen loading. The variations in the

dynamical signature of the adsorbed hydrogen molecules were correlated with recent neutron powder diffraction work that located the adsorption sites within the MOF-5 structure. More information about this work can be obtained at <http://www.nsnr.nist.gov/staff/taner/h2>.

10:30 AM [*A10.8](#)

Biological Hydrogen Production via the Fermentation of Lignocellulosic Biomass. Pin-Ching Maness, Rohit Datar, Jie Huang, Ali Mohagheghi, Esteban Chornet and Stefan Czernik; National Renewable Energy Laboratory, Golden, Colorado.

Hydrogen is a clean fuel and its production from renewable resources will address both the environmental issues and energy security. Many bacteria harbor one or more the hydrogenase enzymes to catalyze H₂ production according to the equation $2H^+ + 2e^- \leftrightarrow H_2$. Microbial H₂ production via fermentation is a promising technology due to its fast rate of H₂ production, in darkness. However, one of the technical barriers is the high cost of glucose feedstock. Lignocellulosic waste biomass on the other hand is an abundant and renewable feedstock and its development for H₂ production will address the glucose cost barrier. Lignocellulosic biomass is comprised mainly of cellulose, hemicellulose, and lignin. Due to its heterogeneity and crystallinity, biomass has to be pretreated first to release its underlying monomeric sugars prior to bacterial fermentation. In this study, we chose steam explosion as the pretreatment technology and used corn stover as the model substrate. Steam explosion of corn stover under various severity parameters results in two fractions: an aqueous hydrolyzate derived mainly from the hemicellulose constituent, and a solid lignocellulose fraction containing cellulose and lignin. Using heat-treated sewage sludge as the microbial catalysts, we detected H₂ production from corn stover hydrolyzate with a carbon mass balance near 93 % and a H₂ molar yield (mol H₂/mol substrate) of 2.9. This finding indicates that the microbial consortium could ferment the 5- and 6-carbon monomeric sugars and their respective oligomeric sugars equally well, both of which are abundant in the hydrolyzate fractions. Fermentation of the solid lignocellulosic fraction was carried out using a thermophilic cellulolytic microbe *Clostridium thermocellum*, which efficiently breaks down the crystalline cellulose to H₂ with a carbon mass balance near 90% and a H₂ molar yield of 2.1. Collectively, our results indicate that lignocellulosic biomass is an ideal feedstock, in lieu of glucose, in support of fermentative H₂ production. Work is underway to further optimize the fermentation process in order to realize a H₂ economy.

11:00 AM [A10.9](#)

Non-Noble Nano-Catalysts for Hydrogen Production Using Microreactors. Debasish Kuila¹, Kriti Shetty¹, Wei Cao¹, Shihuai Zhao¹, Daniela Mainardi¹ and Naidu Seetala²; ¹IfM/Chemistry, Louisiana Tech University, Ruston, Louisiana; ²Grambling State University, Grambling, Louisiana.

The goal of this research is to investigate the activities of non-noble metal catalysts/supports using Si-microreactors for steam reforming of methanol to produce hydrogen for fuel cells. The non-noble catalysts/supports (Ni/SiO₂) were synthesized by sol-gel method using Ni (II) salts as a starting material and Si(C₂H₅O)₄ as a precursor of sol. EDX results indicate that the actual loading of Ni is lower than the intended loading of 40%, while SEM shows even coating of silica supported catalysts inside the microchannels. The specific surface area of the Ni nano-catalyst is 457.33 m²/g, which is considerably high and is preferred for catalysis. The magnetic properties of the catalysts were performed using a vibrating sample magnetometer (VSM) to study the activity of the catalysts before and after the steam reforming reactions. Initial experiments have been carried out over metal nano-catalysts in a microreactor with 50 μm channels in the temperature range of 473-573 K and atmospheric pressure. Preliminary results show 54% conversion of methanol with a selectivity of 88% to hydrogen. Computational studies are currently underway, using molecular dynamic modeling, to have a better understanding of the catalyst surface and mechanistic aspects of hydrogen production. * Supported by Louisiana Board of Regents

11:15 AM [A10.10](#)

Use of Refractory Materials for Hydrogen Generation using Nuclear Power. Ajit K. Roy, Ancila V. Kaiparambil and Radhakrishnan Santhanakrishnan; Mechanical Engineering, University of Nevada Las Vegas, Las Vegas, Nevada.

Three major chemical reactions are involved during a thermochemical process known as sulfur-iodine (S-I) cycle for generation of hydrogen using nuclear power. One such reaction is related to the decomposition of hydroiodic acid (HIx) at temperature ranging between 200-400°C. Two refractory materials namely Zr705 and Nb7.5Ta have been tested for evaluation of their metallurgical and corrosion characteristics under conditions relevant to the HIx decomposition process. The tensile properties of these alloys have been determined at

temperatures ranging from ambient to 400°C. Their susceptibility to stress-corrosion-cracking (SCC) has been determined under constant-load, slow-strain-rate (SSR) and self-loaded conditions. Further, the general and localized corrosion behavior has been studied at temperatures upto 400°C. An electrochemical polarization technique has also been used to determine the critical potentials at temperatures upto 90°C. The metallographic and fractographic evaluations of all tested specimens have been performed by optical microscopy and scanning electron microscopy respectively. The comprehensive test results will be presented in this paper.

11:30 AM [A10.11](#)

Properties of Carbon-doped Anatase TiO₂ Photo-Electrodes. Cristina S. Enache, Roel van de Krol and Joop Schoonman; Inorganic Chemistry, TUDelft University, Delft, Netherlands.

The use of anion dopants is a recent and exciting development in efforts to enhance the visible light absorption in metal oxide photo-electrodes for water splitting and other photochemical processes [1-2]. In the case of carbon-doped TiO₂, most work so far has been carried out on nano- and micro-sized powders. Recently, we reported the deposition of carbon-doped anatase TiO₂ thin dense films by spray pyrolysis of an ethanolic titanium-tetra-isopropoxide solution under a CO₂ atmosphere [3]. The use of thin dense films allowed us, for the first time, to determine donor densities and incident photon-to-current efficiencies (IPCE) of carbon-doped anatase. A donor density of $1.9 \times 10^{19} \text{ cm}^{-3}$ was found for oxidized C-doped TiO₂, compared to $2.5 \times 10^{16} \text{ cm}^{-3}$ for undoped TiO₂. While the IPCE at 330 nm was significantly higher than for comparable undoped TiO₂, no visible light photocurrent is observed due to the low carbon content. Here, we report on our efforts to increase the carbon concentration by subjecting TiO₂ to a post-deposition high-temperature treatment in a hexane-rich environment. By comparing the optical and photo-electrochemical characteristics for thin dense and nanoporous films, carbon is found to be mainly located at the surface of TiO₂. Only a small percentage is incorporated into the bulk of the material, which is confirmed by a small shift (~0.05-0.1 eV) of the absorption edge towards the higher wavelengths, and by an increase in the anatase-to-rutile transformation temperature. However, the carbon content obtained by our methods is still too low for a large absorption enhancement of TiO₂ in the visible part of the spectrum. In this respect oxidative annealing of TiC seems to be a more suitable method to enhance the visible light activity of TiO₂ [4]. One intriguing and yet unsolved question concerns the lattice site occupation of carbon in anatase TiO₂. Both cation (Ti) and anion (O) site occupations have been proposed [2,4]. However, the ionic radii for carbon at different valence states suggest that interstitial sites may be more favorable. A comparison between carbon-doped TiO₂ materials prepared using different methods will be presented. The influence of the various material's parameters on the photocatalytic activity will be discussed, and promising directions for future research will be indicated. References [1] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, *Science* 293 (2001) 269. [2] S. Sakthivel and H. Kisch, *Angew. Chem. Intl. Ed.* 42 (2003) 4908. [3] C.S. Enache, J. Schoonman, and R. van de Krol, *J. Electroceram.* 13, (2004) 177. [4] H. Irie, Y. Watanabe, and K. Hashimoto, *Chem. Lett.* 32 (2003) 772.

11:45 AM [A10.12](#)

Hydrogen Production using Sulfur Circulation.

Kazuyuki Tohji¹, Takeo Arai², Yoshinori Sato¹, Balachandran

Jeyadevan¹, Lin Hongfei¹ and Nakamichi Yamasaki¹; ¹Graduate School of Environmental Studies, Tohoku University, Sendai, Japan; ²Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

The direct conversion of solar energy into storable energy in the form of hydrogen is the dream of mankind. Realization of this will not only provide limitless clean energy, but also solve the environmental problems caused by CO₂ generated from the consumption of fossil fuel. The technology for the hydrogen generation from the electrolysis using solar cells is being intensively studied. However, this technology does not have the potential to substitute fossil fuel due to its high-energy consumption during the production of the same. On the contrary, the use of photocatalysts is considered to have the necessary potential to produce hydrogen at low cost and could become a viable substitute for fossil fuel energy. For this purpose, photosplitting of water is being considered. The effective splitting of water in practical conditions needs at least 2.0 eV and the photocatalyst that could provide the required energy is yet to be designed and developed. On the other hand, hydrogen sulfide (H₂S), which needs only around one half of the energy required to split water, is an potential candidate available in the realm of nature and is also generated as a by-product in large quantities from industrial processes. The efficiency of the photocatalyst depends on the prevention of recombination of electron and the hole. Therefore, it is important to design the same to facilitate the separation of reaction sites of photoexcited electron and the hole, which will pave the way to attain high conversion rates.

Recently, we have developed a metal sulfide semiconductor particle with a capsule like structure, which is called stratified particle. The wall of the capsule is composed of stratified layers formed of metal sulfide and metal nanoparticles. This structure effectively prevents the recombination of photoexcited electron and the hole during the production of H₂. This highly efficient photocatalyst has been proved to be efficient in splitting H₂S. However, when H₂S is split to generate H₂, polysulfide and elemental sulfur are produced. To realize a closed cycle, we should be able to generate H₂S from polysulfide and elemental sulfur. Thus, the objective of this work is to develop a new H₂S production process for the H₂ production system by hydrothermally reacting the recycled elemental sulfur and polysulfide S_n²⁻. A series of experiments have been carried out using batch type reactors to obtain the optimum reaction condition for high yield of S²⁻, and also to reveal the nature and reaction process or route for disproportionation of sulfur in aqueous solution. And then, a tube autoclave has been designed to study the possibility of producing H₂S continuously by using elemental sulfur and polysulfide S_n²⁻. Finally, the productivity of H₂ gas was evaluated by making use of the hydrothermal-treated solution of sulfur as reaction solution in a standard H₂ generation apparatus. Based on the above results, an integrated sulfur recycling process have been presented.

SESSION A11: H₂ Generation/Purification
Chair: Pin-Ching Maness
Friday Afternoon, December 2, 2005
Room 311 (Hynes)

1:30 PM *A11.1

Multicomponent Metal-Oxide Photocatalysts For Hydrogen Generation From Solar Energy. Paul Maggard, Digamber Porob and Junhua Luo; Chemistry, North Carolina State University, Raleigh, North Carolina.

Metal-oxide solids have been reported with up to a 50% quantum efficiency for H₂ production from the photocatalysis of H₂O, but only for a small fraction of solar energy that is ultraviolet light (~4%). We have recently synthesized new multicomponent metal-oxides which combine both strong visible-light absorption, which is the major component of the solar spectrum, and high photocatalytic activity for the production of H₂ from H₂O. In one method, hydrothermal synthetic techniques have been used to form nanocomposited materials consisting of visible-light-absorbing cores (e.g. Fe₂O₃ and BiFeO₃) that sensitizes photocatalytically-active shells (e.g. SrTiO₃ and NaTaO₃). In another approach, specific combinations of early and late transition metals were used to synthesize new metal-oxide solid solutions which achieve band energies that are appropriate for both visible-light absorption and H₂ production. These latter materials have shown remarkable potential for the photocatalytic production of H₂ (>1,000 μmol H₂ / h · g) from sunlight and water, and thereby providing a source of renewable energy for a future hydrogen economy. Both classes of materials have been found highly photocatalytically active under visible light and were characterized by a combination of XPS, SEM, XRD, UV-Vis DRS, and photocatalytic measurements. An interpretation of the calculated band structures which results in the high photocatalytic activities will also be presented.

2:00 PM A11.2

Synthesis and Characterization of Thin Film InVO₄ Photocatalysts. Roel Van de Krol, David A. Lloyd, Martijn R. Damen, Cristina S. Enache and Joop Schoonman; Delft Institute for Sustainable Energy, Delft University of Technology, Delft, Netherlands.

The prospect of a future Hydrogen Economy has revived interest in metal oxide photocatalysts for visible light-induced water splitting. Recent work suggests that InVO₄ may be a suitable material for this purpose [1]. We have prepared InVO₄ thin films by spray deposition of an ethanolic solution of 0.05 M In(NO₃)₃ and 0.05 M VCl₅. The films were deposited on F:SnO₂ coated glass and on fused silica (quartz) substrates, at temperatures between 300 and 400°C. X ray diffraction shows that all deposited films are polycrystalline with a crystal structure that corresponds to orthorhombic InVO₄, space group *Cmcm*. Depending on the deposition parameters, in particular the composition of the precursor solution, two types of orthorhombic InVO₄ films have been obtained which show different optical properties. The first type of film is optically transparent, with an indirect bandgap of ~3.4 eV as determined from UV-VIS spectroscopy. The i-V characteristics of these films in aqueous solutions (0.1 M KOH) show rectifying behavior, with leakage currents below 200 nA/cm² between -0.3 and +0.6 V vs SCE. In contrast, the second type of film has a yellowish color. Optical absorption spectra indicate that the yellow color is caused by a pronounced sub-bandgap absorption peak that starts at ~2.1 eV and is centered around ~2.9 eV. The bandgap of this material seems to be

similar to that of the transparent InVO₄. Ye et al. synthesized similarly colored orthorhombic InVO₄ by conventional solid state synthesis [1]. Although they reported a much lower bandgap of 1.9 eV, the shape of their optical absorption spectra seem to be more consistent with our interpretation of a sub-bandgap absorption. The i-V characteristics of the yellow films also show rectifying behavior, but now with a reduction peak at ~-0.15 V vs SCE and an oxidation peak at +0.20 V vs SCE. Integration of the oxidation peak yields an amount of charge that corresponds to ~10% of a monolayer. Hence, this peak is tentatively attributed to the presence of a surface state. This surface state is not observed for the optically transparent InVO₄ films, and there appears to be a relationship between this surface state and the bulk defects that are responsible for the sub-bandgap absorption. Electrochemical impedance analysis will be used to clarify the nature of these defects, and the implications for the use of InVO₄ as a visible light photocatalyst will be discussed. **References** [1] J. Ye, Z. Zou, H. Arakawa, M. Oshikiri, M. Shimoda, A. Matsushita, and T. Shishido, *J. Photochem. Photobiol. A* **148** (2002) 79.

2:15 PM A11.3

Core-shell nanorods for efficient photoelectrochemical hydrogen production. Zhi Gang Yu¹, C. E. Pryor², W. H. Lau³, M. A. Berding¹ and D. B. MacQueen¹; ¹SRI International, Menlo Park, California; ²Optical Science and Technology Center and Department of Physics and Astronomy, University of Iowa, Iowa City, Iowa; ³Center for Spintronics and Quantum Computation and Department of Physics, University of California, Santa Barbara, California.

We propose core-shell InP-CdS and InP-ZnTe nanorods as photocatalysts for efficient photoelectrochemical hydrogen production based on our systematic study of electronic structures and wave functions of these heterostructures using a strain-dependent k.p Hamiltonian. Our calculations indicate that in these heterostructures both energies and wave-function distributions of electrons and holes can be tailored to a considerable extent by exploiting the interplay of quantum confinement and strains. Consequently these nanorods with proper dimensions (height, core radius, and shell thickness) can simultaneously satisfy all criteria for effective photocatalysts in hydrogen production.

2:30 PM A11.4

Characteristics of H₂ Gas Generation Using GaN Photoelectrolysis. Katsushi Fujii¹, Masato Ono², Takashi Ito² and Kazuhiro Ohkawa^{2,1}; ¹Nakamura Inhomogeneous Crystal Project, Japan Science and Technology Agency, Tokyo, Japan; ²Department of Applied Physics, Tokyo University of Science, Tokyo, Japan.

Direct photoelectrolysis using a semiconductor by solar power is a promising method to generate H₂ gas from water. The major problems of a semiconductor electrode are the level of water splitting ability and its corrosion. We achieved H₂ gas generation using GaN photoelectrolysis for the first time. An n-type GaN was used as a working photoelectrode with 1 V extra bias. We also found that the characteristics of a GaN photoelectrode varied with the electrolyte. Photocurrent is a good indicator of the gas generation efficiency. Thus, we report the photocurrent dependence on the dopant concentration and the photo irradiation here. We used n-type Si-doped GaN grown by metalorganic vapor-phase epitaxy. The supplying ratios of the dopant and Ga during the growth were [Si]/[Ga] = 1.73, 4.31, 8.63 and 17.3×10⁻⁵. The onset voltage of photocurrent was approximately 0.4 V positive from each flatband potential in the dark except for the case of the highest Si-doped GaN. The onset for the highest Si-doped GaN was approximately 0.8 V positive from the potential. The positive shift of the onset voltage means reduction of photocurrent at the same voltage applied. The flatband potentials under illumination also shifted approximately +0.4 V from the initial potentials in the dark for all samples. This shift indicates that the minority carrier, which was generated by illumination, accumulated at the surface of the semiconductor to the electrolyte. Thus, this carrier accumulation is the reason why the onset voltage was different from the flatband potentials in the dark. The surface morphology of the highest Si-doped GaN was rough because of the over doped Si. This probably shows that the defects in GaN also suppressed the photocurrent. After the 2 h photoelectrolysis measurement, the flatband potentials in the dark for n-type GaN changed approximately +0.2 V. The onset voltage of photocurrent also increased 0.2 V for all samples. The surface characteristics of n-type GaN probably changed during illumination. In summary, the onset voltage of photocurrent was more positive than each flatband potential in the dark. We clarified that the minority carrier accumulation at the semiconductor surface shifts the onset voltage positive from the flatband potentials. The dopant concentration in GaN also affected the onset voltage. The flatband potential of GaN after the illumination shifted positive.

2:45 PM A11.5

Oxygen Flux And Process Analysis of Hydrogen Separation From Water Through Mixed Conducting Membrane.

Hydrogen synthesis and segregation from water splitting and simultaneous partial oxidation of methane can be achieved using MIEC membranes that conduct oxygen ions and electrons. The process offers hydrogen production on the feed side of the membrane (steam side) and syn-gas on the permeate side (methane side). The membrane process offers good control over product species since the oxygen flux can be controlled by changing external conditions. The oxygen flux and its dependence on driving force (partial pressure gradient across the membrane) are determined by the transport properties of the MIEC membrane. It is important to investigate chemical transport of oxygen and surface reaction rate of oxygen to understand and optimize the total flux through the membrane. In this work composite MIECs system comprising $Gd_xCe_{1-x}O_{2-x/2}$ (GDC) and $Gd_xSr_{1-x}Ti_{1-y}Al_yO_3$ (GSTA) have been studied for hydrogen separation process. The oxygen flux through the membrane determines the hydrogen production rate on the steam side and syn-gas composition on the methane side. Oxygen flux was obtained as functions of membrane thickness, fixed permeate and variable feed gas composition and vice versa. Theoretical analysis is being carried out to understand whether the oxygen flux is controlled by bulk or surface rates. Experimental results and theoretical analysis of oxygen permeation will be presented in this paper. Efficiency of the hydrogen and syn-gas production process is calculated based on the membrane properties, equilibrium compositions and the overall energy and balance of the products and reactants during various stages of the process. A brief analysis of the equilibrium composition of the gases under process conditions, their energy balance and cost analysis will be presented. Estimates for improved process control through optimization of membrane transport properties and design will also be presented.

3:00 PM A11.6

Proton Conductivity of Gamma-Irradiated Carbon Films.

Elvira Memetovna Ibragimova, Vladimir N. Sandalov, Makhmud U. Kalanov and Mukhtar I. Muminov; Radiation Solid State Physics, Institute of Nuclear Physics, Tashkent, Uzbekistan.

It is possible to obtain hydrogen by means of water radiolysis under direct transformation of nuclear energy, because the most of atom reactors are cooled with water. Nano-structured carbon have great prospects in confining hydrogen in safe bound state. The conductivity of isolated single-well nano-tubes was found to enhance after irradiation with electrons within the energy range of 75-400 keV. The goal of our experiment was to obtain and adsorb hydrogen on the surface of carbon film under water radiolysis in the course of gamma-irradiation both in the 60-Co gamma-source and in the stopped nuclear reactor. Electric conductivity of the samples was studied at 200-360 K prior and after various doses of irradiations in liquid nitrogen and in water at 300 K. The current measurements of dry and wet carbon film were compared, and the contribution from electronic, proton and oxygen transport into the current was separated. The $I(T)$ curve for the non-irradiated sample has a pronounced peak at 290 K, and a current in the temperature interval varies between 20-30 nA. The gamma-irradiation in liquid nitrogen resulted in smearing the peak and upon the highest dose of 50 kGy the current increases up to 50 nA and becomes non-depended on temperature in this interval. No thermal activation of conductivity is a strong evidence of its quantum character (proton conductivity). It was found, that 60-Co gamma-irradiation of carbon films at 77 K resulted in activation of the film surface and increase in the proton conductivity by desorption of 1.8 wt.% of hydrogen. The values of activation energy calculated from the experimental Arrhenius plots were 0.7457 eV for the non-irradiated C-film at a relative air humidity ~60 % and 0.0416 eV for the highest dose of gamma-irradiation, the both characteristic for proton conductivity. The activation energy of the conductivity was found to decrease significantly with the gamma-dose growth. The effective frequency factor, which characterizes oscillations of charge carriers at hopping conductivity, was also calculated and the hopping frequency was 1.343 THz, which is characteristic for protons. Thus, the most probable charge transfer mechanism is proton transfer over the network of H-bonds. Structure transformations were discovered in the C-films with the use of X-ray diffraction technique. The gamma-irradiation resulted in formation of nano-graphite precipitations, responsible for emerging the selective reflection from (002) plane at 27° . Besides, the diffuse band at $\sim 20^\circ$ became more intensive, which maybe attributed to nano-tubes. The growth of proton conductivity with the gamma-dose increase occurred because low conducting fullerene fraction transformed into higher conducting graphite and nano-tube phases under the irradiation. The work was supported by the grant F 2.1.2 from Uzbekistan Center for Science and Technology.