SYMPOSIUM BB
BB: Materials and Technologies for a Hydrogen Economy

November 30 - December 3, 2003

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Symposium Support
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Proceedings to be published in both book form and online
(see ONLINE PUBLICATIONS at www.mrs.org)
as Volume 801
of the Materials Research Society
Symposium Proceedings Series

*Invited paper
The tutorial will cover a general overview of the field of solid-state hydrogen storage materials with emphasis on three main classes of compounds. The fundamental change in hydrogen storage in complex chemical hydrides and their potentials and limitations will be reviewed. The science and technology of hydrogen storage in metal and alloy hydrides and their applications will be presented. The physics and chemistry of hydrogen storage in light-metal nitrides will be discussed. The latest progress in the area of hydrogen storage in nanotubes, and the role of nano-particles in kinetics and thermodynamics of hydrogen storage, will also be reviewed. This tutorial does not include hydrogen storage in gas and liquid tanks.

Instructors:
Gholam Abbas Nazri, General Motors R&D Center
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SESSION B1: Hydrogen Storage Program and Technology
Chair: Gholam Abbas Nazri and Rosa Young
Monday, December 1, 2003
Fairfax B (Sheraton)

NOTE EARLY START
8:25 AM INTRODUCTORY REMARKS - G. ABBAS NAZRI

8:30 AM *B1.1

In his January 2003 State of the Union address, President Bush announced an initiative to accelerate the development of hydrogen and fuel cell technologies for use in stationary, transportation and portable power applications. To that end, the U.S. Department of Energy’s Hydrogen, Fuel Cells, and Infrastructure Technologies Program is pursuing the vision of a hydrogen economy by conducting research and development for producing, delivering, storing and utilizing hydrogen. On-board hydrogen storage is a key enabling technology for the advancement of hydrogen and fuel cell power technologies. This paper describes the challenges of storing hydrogen on-board a vehicle and the progress made through the DOE program. The key technical challenge for hydrogen storage is how to store the necessary amount of hydrogen fuel required for a driving range of over 300 miles within the constraints of weight, volume, durability, efficiency and total cost. DOE is establishing a National Hydrogen Storage Project. Four key study areas are summarized below.

- Advanced Metal Hydrides - Carbon-Based Materials - Chemical Storage - New Materials: Examples include crystalline nanoporous materials (e.g. zeolites), polymer microspheres, self-assembled nanocomposites, metal-organic, boron nitride nanotubes, bulk amorphous materials and hydrogenated amorphous carbon. The DOE Program has collaborated with automotive companies to establish metrics that are based on the needs of the "end-user", not on what the storage technology can deliver. Program-sponsored projects address technical barriers, and progress will be measured against these specific technical targets. This paper will discuss the current Storage Program targets and current performance of leading on-board technologies. Program efforts will be highlighted that enable storage technologies to fulfill customer requirements in 2010 and 2015.

9:00 AM *B1.2

Hydrogen is called the "ultimate fuel." It is also the ultimate element. It was born in the Big Bang and almost all of known matter is composed of it. Its condensation into a star, our sun, through fusion, provides us the energy and the photons which power our earth and which we can utilize in the form of photovoltaics to break apart water and generate hydrogen as an energy source on earth. The hydrogen economy is here. It has been initiated by the electric and hybrid vehicles which depend upon it for their operation through nickel metal hydrides batteries and hydrogen for fuel for the internal combustion engine and by outwitting the Carnot cycle for use as a fuel cell. I will discuss the complete system needed for the hydrogen economy from generation to storage to infrastructure and use. Any one part of this loop is necessary but not sufficient. Our global economy is based upon energy and the societal needs for a nonpolluting, non-climate change fuel which does not require strategic military defense as does oil. The transition from fossil fuels to hydrogen is revolutionary import not only for its societal impact but for the development of a new star for what it absolutely requires in all of its aspects. New science and new technologies build much needed new industries, which provide not only the feedback on our current research but also, it is believed, the ages of civilization are known by their materials. Truly, the present age will be known by the materials that make up the twin pillars of our global economy – energy and information. Therefore I will address the new science, technology and atomic engineering of the materials that are necessary to make possible a revolutionary transition of energy from its fossil fuel beginnings to the present.

10:00 AM *B1.3
The Hydrogen Programs In China, Qidong Wang, Changxin Chen and Lixin Chen, Department of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang, China.

Hydrogen programs in China since 1980 have been reviewed. Back in nineteen eighties, the studies on metal hydride hydrogen recovery, storage, purification and compression for processing hydrogen gas were quite active. For the use of hydrogen, hydrogen powered internal combustion engines and part utilization of hydrogen for fueling IC engines for vehicles were systematically investigated, together with the on-board storage of hydrogen in metal hydride hydrogen storage containers. In early nineties, the attention of the scientists on metal hydride technology were diverted to the hydrogen storage electrode alloys for Ni-MH batteries. In late nineteen nineties, as the potential application of hydrogen fueled PEMFC was realized, research and development on PEMFC powered scooters and bicycles was initiated by some bicycle factories in view of the expected market together with the study of small sized hydride hydrogen storage tanks for the application. Immediately following, several big projects sponsored by the National Department of Science and Technology and many automobile companies on the R & D of PEMFC powered cars and buses were initiated together with the R & D on the hydrogen storage alloys with higher hydrogen storage capacities. In the 21st century, a program for transforming the coal fired electric power system into a renewable energy based electricity and hydrogen power system (or a hydrogen power system) in Zhejiang Province has been proposed and initiated. In this project the simultaneous building of an hydrogen infrastructure and the effective and profitable applications of hydrogen are stressed. As a result, the development from the more easily and readily carried out projects to more sophisticated and difficult ones are also emphasized.

10:30 AM *B1.4

Hydrogen energy offers great promise as an energy alternative in the near future. Additionally, hydrogen technology can significantly reduce and eventually eliminate the massive release of carbon dioxide from fossil-fuel combustion, the main cause of the global warming. One of the main challenges is how to safely store and use hydrogen. Storing hydrogen in the solid-state hydride form holds a significant volumetric advantage over compressed and liquid hydrogen storage. Solid hydrogen storage systems also have features of low-pressure operation, compact, safe, tolerable deliverable pressure, excellent heat of reaction /decomposition values, and extended shelf life. In this paper, solid hydrogen storage systems (such as portable power controllers, lightweight fiber wrapped vessels, and aluminum tubular vessels, developed by Texaco Ovonik Hydrogen Systems LLC) will be discussed. For example, three canisters, 8g of reversible hydrogen stored in each canister, interfaced with a 1 kW PEM fuel cell can sustain more than 50 min full power run time. The canister showed no plastic deformation after completing 500 plug-in/charge/discharge cycles. The strain gauges instrumented on the surface of the canisters all were in compliance with the DOT approved range. The canisters are in the early commercialization stage for UPS and AHV applications. The lightweight hydride canisters are combined with the high performance metal hydride targets on-board applications. On a system level, the vessel has a volumetric energy density of 56 kg hydrogen per liter and a gravimetric density of 1.6 w %. The vessel is capable of storing 3 kg of hydrogen with a fast refueling capability. 90% of stored hydrogen can be refueled in 10 min @ 1500 psig. The vessel can easily release the hydrogen at 500 slpm at
70°C. The aluminum tubing vessels, flexible in length and diameter, target bulk storage and infrastructure applications, such as stationary power, hydrogen production and purification, and hydrogen service stations. A tubular vessel with 6" in diameter and 62" in length can store up to 1 kg of hydrogen.

11:00 AM BB1.5
Hydrogen Storage Properties of Magnesium Based Amorphous/Nanostructured Composite Materials. Ming An, Savannah River Technology Center, Aiken, South Carolina.

In this paper, amorphous/nanostructured composite materials Mg-Ni, Mg-Ni-La, Mg-Ni-Ge, Mo-MgNi, Mg-LaNi5, Mg-Ni-Zr have been synthesized using the mechanical alloying process. To increase the hydrogenation and dehydrogenation kinetics, the small amount of catalytic elements Ni, Pt, and V have been coated on the surface of materials by using surfactant alloying. The new materials produced have been investigated by X-ray diffractometer, TEM, SEM and EDS for their phase composition, crystal structure and grain size, and the distribution of the catalyst elements. Hydrogen storage capacities and the hydrodrying/dehydrodrying kinetics of the new materials have been measured at different temperature using an automizer Severts apparatus. The results show that amorphous/nanostructured composite material Mg50%Ni50% absorbs 5.89 wt% within 5 minutes and desorbs 4.46% hydrogen within 50 minutes at 25°C respectively. The composite material Mg80%Ni20% absorbs 1.96 wt%, but releases 0.45 wt% hydrogen only at 25°C. It is believed that the mechanical alloying accelerates hydrogenation kinetics of the magnesium base materials at low temperature, but a high temperature is still required to liberate the hydrogen. The main product of the hydrogenation of various magnesium base materials, either amorphous or nanostructured, is same as MgH2. The stable thermodynamics of MgH2 is still in control of the process of dehydrogenation.

11:30 AM BB1.6
Hydrodrying Behaviour of Mg-C Nanocomposites. Marco Vittori Antoni, Amelia Montone, Jasmina Grbovic, Ennio Benetti, Luca Passini, Alex Bassetti and Anna Lisa Fiorini; 1Materials University, ENEA, Rome, Italy.

Recently, we can notice an increasing interest in modifying the microstructure of materials for hydrogen storage by nanocrystalline structure in order to improve material performances in this kind of application. Nowadays these materials are often magnesium based, owing to the low cost, low weight and high potential hydrogen capacity. However magnesium is hard to activate, its temperature of operation is high and the hydrogenation/dehydrogenation kinetics are slow. The mechanical processing of magnesium powders by ball milling has been shown to improve most of such properties. The absorption-desorption kinetics result faster, due to the peculiar metastable microstructure characterized by high volume fraction of surfaces-interfaces and a high defects density. Moreover hydrogen sorption can be further accelerated by some alloying addition and nanocrystalline Mg nanoparticle in particular, could be observed on nanocomposite Mg-based system. We have investigated magnesium carbon materials for hydrogen storage obtained by mechanical milling of different graphite and magnesia with different amounts of benzene, acting as a lubricant. These materials have been characterized by X-ray diffraction, SEM observations and DSC. The hydrogen sorption capacity has been tested by a hot wall reactor. The results show that the microstructure after milling depends on the amount of additives affecting the hydrogenation capabilities of the material. In particular the ratio of Carbon to Benzene seems to play a major role.

SESSION BB12: Hydrogen Storage Alloys
Chair: Ping Chen and Maryam Nazri
Monday Afternoon, December 1, 2003
Fairfax B (Sheraton)

2:00 PM BB2.2
Electrochemically-Induced Hydrogen Absorption in Mg-Functionalized Single Wall Carbon Nanotubes. Zafar Iqbal and Yubing Wang; Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, New Jersey.

Aro-prepared single wall carbon nanotube (SWNT) sheets with an average single tube diameter of about 1.2 nm were used as the working electrode in an electrochemical cell with 6M KOH as electrolyte, together with a reference electrode and nickel foil as the counter electrode. The SWNT sheets were sonicated in KOH to remove amorphous carbon layers on the sidewalls, electrochemically functionalized with Mg using aqueous Mg nitrate, and then charged in 6M KOH. Ex-situ thermogravimetric analysis, thermopower measurements and solid state proton nuclear magnetic resonance studies on the SWNT electrodes were carried out to determine weight uptake, sign of the charge carryon and structural and molecular dynamics of the hydrogen trapped in the nanotubes, respectively. Weight uptake in the 2-4 weight % range has been observed and evaluation of the chemistry of the process studied by in-situ Raman scattering [1]. These results will be compared with similar data for undoped and doped SWNTs of the same diameter. [1] Also see: C.P. An, Z.V. Vardeny, Z. Iqbal, G. Spinks, R.H. Baughman and A.A. Zhulidov, Synth. Metals, Vol. 116, 411 (2001).

2:30 PM BB2.2

Efficient and economical hydrogen storage material is essential for the future hydrogen economy. However, current materials have limited hydrogen capacity and slow kinetics for hydrogen sorption. Hydrogen sorption in practical high capacity alloys requires high temperature. The intermetallics Mg-based alloys exhibit a high hydrogen storage capacity [up to 7.6 wt. % for pure Mg]. However, their sorption kinetics remain slow below 250°C. In this work, we present the process to enhance the Mg-based alloys hydrogen absorption-desorption properties by modifying and monitoring the alloy surface composition and morphology. A further understanding on the fundamental origin of such an enhanced hydrogen adsorption/desorption characteristics will be discussed using a thin film approach.

3:30 PM BB2.3

The investigation of many stoichiometric variables involving large numbers of combinations of elements offers a means to discover a hydrogen storage material with optimal properties. We introduce the use of spatially resolved infrared imaging as a high throughput hydrogen storage candidate screening technique. Analysis is presented of a sample that consists of 16 separate Mg-Ni-Fe ternary pads and 32 Mg-Ni or Mg-Fe binary pads. Hydrogen capacity and de-hydriding kinetics were observed to indicate a substantial decrease in hydrodrying temperatures, which sensitively depends on composition.

4:00 PM BB2.4

Recently, several research groups have shown the benefits of hydrogen storage in metals such as nanocrystalline palladium. Benefits include faster kinetics implying reduced temperatures for efficient storage of hydrogen and, for nanoparticles, may include storage at new sites on this surface and sub-surface. In this paper, the morphological aspects of improved hydrogen storage are addressed at the nanoscale. Both spherical and nanocrystalline Pd particles were synthesized in self-assembly systems using reverse micelle and bilayer structures, respectively. Particle dimensions and shape were verified using TEM and AFM techniques. Hydrogen uptake properties of spherical particles with diameters from 2nm to 10nm were measured gravimetrically from the range of pressure zero to 20 atmospheres over a range of temperatures from 40C to 100C. These results were compared to those from nanocrystalline Pd particles with thickness in the range 2nm to 200nm and also as function of aspect ratio. To eliminate the effects of sintering and consequent loss of surface area of these particles at high temperatures, Pd nanoparticles were also studied, thus were supported on nanoscale zeolite and zirconia matrices [spacers] to understand the improvements in the hydrogen uptake performance. The results will be compared to bulk palladium and other recent findings in nano-metallic hydrides.

4:30 PM BB2.5

The incorporation of hydrogen into metallic lattices produces diverse, system dependent changes in properties that present important challenges to first principles theory. For example, in addition to distortions of the host electronic band structure, hydrogen may
behave as a cation or anion, effectively changing the band filling. Many of these effects are well described by density functional calculations, but some such as the insulating gaps in the rare-earth trihydrides, where hydrogen is an effective anion, are not. A sensitive test of the reliability of calculations is provided by systems that display magnetism as the description of magnetic properties is highly dependent on a correct description of the underlying electronic structure. Experimentally, it is known that both YFe₃ and YFe₃H₅ with n=4 are magnetic, with the moment increasing with H content. Here we report full potential density functional calculations for this system. We find the magnetic properties are highly sensitive to the H positions, which we calculate from first principles. Using the calculated positions good agreement with experiment is obtained for the magnetic moments. The mechanism for the moment increase is shown to be related to d band narrowing with the H potential pulling up character away from the metal sites. We also present electric field gradients which can be used as a test of our structure. We are grateful for helpful discussions with R. Gupta.

**SESSION BB3: Poster Session: Hydrogen Storage**

**BB3.1 Hydrogenation of Nanocrystalline Mg-based Alloys.**

**Daniele Zander, Lyudmila Lyubenova and Uwe Koester; Department of Biochemical Engineering, University of Dortmund, 44227 Dortmund, Germany.

Environmental protection and pollution control will restrict increasingly the use of polluting fossil energy fuel long before their depletion; thus alternative energy sources and devices for high-capacity energy storage must be developed. Metal hydrides are a clear medium for transmission and storage of hydrogen energy, which can be used in fuel cells, metalhydride batteries, thermal engines, air-conditioning systems etc. Mg-based metal hydrides with volumetric energy density of 1.5-1.6 kWh/l, low cost and high abundance are the best candidates for safe energy storage and transport material. On the other hand, commercialisation in mobile storage systems and metal/hydride batteries and other clean applications have been slowed down due to high temperature constraints and unknown cycling life. Recently it was published that the design of improved nanocrystalline Mg alloys can proceed by metal oxides, e.g. V2O5 [1] as catalysts. The aim of this paper is to present results on the influence of V2O5 on electrochemical hydrogenation in comparison with the improved gaseous hydrogenation method of nanocrystalline Mg. The mechanisms by which metal oxides improve hydrogen absorption as well as description are still unclear and should be clarified by microstructural investigations in detail. This research focuses on investigating the structural/electrochemical properties relationship in regard to the hydrogenation behavior of nanocrystalline Mg with and without V2O5 [1]. W. Oelerich, T. Klüsener, R. Borrmann, J. Alloys and Comp. 315 (2001), 237. This work was supported by the EU HTP-Network Project HPRN-CT-2000-00196.

**BB3.2 Hydrogen Absorption of Cl4 Loves Ni(Ti)Zr-NiV Nb pseudo-binary alloys.**

Kazuhiko Ishibashi1, Shinobu Noda1, Kyounori Suzuki2 and Kiyoshi Aoki1, 1Kitsum Institute of Technology, Kitami, Hokkaido, Japan; 2Monash University, Melbourne, Victoria, Australia.

The Cl4 Loves alloys are attractive candidates for hydrogen storage alloys. In this work, the crystal structures and the hydrogen absorption properties of Cl4 Loves Ni(Ti)Zr-NiV Nb pseudo-binary alloys are investigated by XRD measurement and hydrogen analysis. The hydrogen capacity and the hydrogen desorption temperature of the Ni(Ti)Zr ternary compound, formed in Ni4(Ti)Zr2 pseudo-binary section, are 2.4 wt % [1.5 H/M] and 850 K, respectively. In order to reduce the hydrogen desorption temperature, Ti and/or Zr of the compound were substituted by V and/or Nb. In the case of the Ni(Ti)Zr-V (Nb) alloys, the hydrogen desorption temperature remains high with increasing x, although the hydrogen capacity is decreased. However, the temperature of the Ni(Ti)Zr-V (Nb) alloys is decreased 250 K with V content without serious decrease of the hydrogen capacity.

**BB3.3 Hydrogen Diffusion in Zr-Cu-Ni-Al Metallic Glasses.**

Lisa Jastrzebski, Lyudmila Lyubenova1, Irena Dolosek2 and Uwe Koester1, 1Dept. Biochem. & Chem. Eng., University of Dortmund, Dortmund, Germany; 2J. Stefan Institute, University of Ljubljana, Ljubljana, Slovenia.

Zr-based metallic glasses are known to absorb high amounts of hydrogen, but exhibiting less severe embrittlement than their crystalline counterparts; therefore, they might be useful for hydrogen storage applications. In order to understand kinetics of hydrogen absorption and desorption of the in detail, an accurate model of the diffusion is necessary. The aim of this paper is to present hydrogen diffusivities in metastable amorphous Zr75Cu25-Ni10Al25 alloys. Hydrogen charging was performed electrochemically in a 2.1 M glycerophosphoric acid electrolyte. Hydrogen concentrations were measured by a microbalance with accuracy of ±1 µg as well as by LECO. Diffusivities of hydrogen atoms were measured at different temperatures by the technique of Nuclear Magnetic Resonance (NMR) diffusion in a static fringe field of a superconducting magnet. The diffusion of hydrogen nuclei in an inhomogeneous magnetic field is accompanied by the change of its NMR resonance frequency, which produces motional dephasing of the spin echo signal. The analysis of the spin echo decay allows a model calculation of the hydrogen self-diffusion constant, with the low limit of sensitivity D>10⁻¹⁷ cm²/s. In a number of metallic glasses hydrogen diffusion is known to depend on the hydrogen content; therefore diffusivities were also measured at different hydrogen contents between H/M = 0.2 and 1.2. The data will be compared with other measurements known for Zr-based metallic glasses (e.g., Zr-Pd or Zr-Ni) and discussed in regard to the Zr-content, density and structural models.

**BB3.4 Synthesis and Characterization of GdCo3(Fe-Co-(Ly)Fe3O4) as a Cathode Material for Intermediate Temperature Solid Oxide Fuel Cells.**

Chris Dyck and Vladimir Krstic, Mechanical Engineering, Queens University, Kingston, Ontario, Canada.

Solid oxide fuel cells (SOFCs) are electrochemical ‘engines’ that convert fuel and oxidant gases directly to electrical energy. The high operating temperature of SOFCs (~900°C) imposes severe constraints on the material systems that may be used for various cell components. Lowering the operating temperature allows for improved material choices, faster start-up times and improved longevity of components. Intermediate Temperature (IT) SOFCs are based on a doped-ceria electrolyte and operate between 500°C and 700°C. Currently, the availability of IT-SOFC cathode materials with low overpotential (high catalytic activity for oxygen), high conductivity, and thermal matching to the electrolyte material, is limiting the advance of the technology. Gd0.5(1-x)Fe2-xO3 (x=0.35) (GCO) is a promising cathode material system for use in IT-SOFCs due to its high catalytic activity for oxygen reduction and appreciable conductivity. However, it has a high thermal expansion coefficient that is unmatched to the common IT-SOFC electrolyte material, Ce0.8Gd0.2O1.95 (CGO). Gd0.5(1-x)Fe2-xO3 (x=0.35) has been developed to provide the best balance of properties as a potential composition for further study. Manipulation of the Cu-site in GCO resulted in a dramatic decrease in the thermal expansion coefficient to a level closer to that of the electrolyte (~13 ppm/C). However, the decrease in thermal expansion was accompanied by a large decrease in the conductivity as the iron content was increased in the system. Alternatively, formation of GCO/CGO composite cathodes resulted in thermal matching with the electrolyte material up to the IT-SOFC operating temperature of approximately 600°C with the maintenance of high electrical conductivity. Composite GCO/CGO cathodes reduce the problems normally associated with poor GCO thermal matching to the electrolyte without compromising other important cathode properties.

**BB3.5 Ab-initio Modeling of Interstitial MgH2 Solid Solutions.**

Maurizio Mussaron1, Fabrizio Cleri1 and Manuel Volpe1, 1Unima Materiali e Nuove Tecnologie, ENEA, Centro Ricerche Cinecittà, Roma, Italy; 2Dipartimento di Fisica, Università Sapienza, Roma, Italy.

We studied the thermodynamics of interstitial MgH2 solid solutions by means of ab-initio electronic structure calculations. Soft pseudopotential [Boullier-Martinet] with non-linear core correction and Perdew-Burke-Ernzerhof GGA exchange-correlation functionals were employed, in the framework of a DFT plane-wave scheme. We inserted increasing concentrations of interstitial H atoms in the hcp Mg lattice, in both tetrahedral and octahedral positions. We calculated the energy of solution and the volume variation as a function of H concentration, to obtain enthalpy vs concentration curves. The results show that, although the difference in Gibb's free energy is known to be positive at any H concentration above 1 H/M, the enthalpy contribution at any H concentration, thus locally favouring H clustering. This reflects the existence of a driving force for the subsequent formation of the metallic hydride. Examination of the changes induced in the Mg DOS upon H insertion reveals the upward movement of the Fermi level and the creation of deep hydrogen-like states below the metallic level.
Boron seems to be an interesting material for the use as a hydrogen source. Several properties appear favorable for such an application. The evolution of hydrogen takes place exothermically in different thermal decomposition steps at temperatures lower than 150°C and from solutions by the influence of a catalyst near room temperature already. Furthermore, all of the bulk has determined the fundamental thermodynamic properties of BH₃NH₃. The standard entropy was obtained from low temperature heat capacity measurements. During these investigations we could observe an interesting phase transition in the solid state. The formation enthalpy was derived from different types of calorimetric measurements. The thermal decomposition of solid Borane and the evolution of hydrogen was studied by use of different types of calorimetric investigations, combined with gravimetric, volumetric and spectroscopic measurements. The sequence of the thermal events is strongly controlled kinetically. Dependent on the heating rate we observed a well defined first decomposition step near 90°C with an evolution of one mole H₂, a merging process of BH₃NH₃ residues at high heating rates only and finally a second decomposition step with a hydrogen evolution comparable to the first one. The hydrogen evolution from solutions of BH₃NH₃ in different solvents was investigated by use of calorimetric arrangements for the process monitoring and for the determination of the most important parameters for a thermochemical and kinetic description of the decomposition and of the effectiveness of the catalysts also. A controlled heating rate experiments solutions near room temperature seems possible. [1] J. Baumann Dissertation 2003, TU-Bergakademie Freiberg, Germany [2] F. P. Hoffman, G. Wolf, L. D. Hansen, Advances in Boron Chemistry, Royal Society of Chemistry, Cambridge, UK, 1997, p. 514 [3] G. Wolf, J. Baumann, F. Baitolow, F. P. Hoffman, Thermochimica Acta 343, 2000, 18-25

8:30 AM BB4.2 Rietveld refinement and ab initio studies of Ti-Doped NaA1D4 and Na3A1D6. Eric H Majzoub1 and Vldvuds Ozolina2
1Analytical Materials Science, Sandia National Laboratories, Livermore, California, 2Materials Science and Engineering, University of California Los Angeles, Los Angeles, California.

The structure of Ti-doped sodium aluminum deuteride has been determined using Rietveld refinement of x-ray and neutron powder diffraction data and comparison with experimental results of undoped NaA1D4 and NaA1D. The refined lattice parameters for the tetragonal NaA1D4 structure are found to be a = 5.010 Å and c = 11.323 Å. Results of ab initio calculations of the lattice parameters are within a few percent of the Rietveld refinement. The generalized gradient approximation (GGA) is found to produce significantly better agreement with the experimental data than the local-density approximation (LDA), which is attributed to a very important contribution of electronic density in the bonds. The Rietveld refinement, LDA, and GGA results for the Al-H bond length in NaA1D4 are 1.626, 1.634, and 1.681 Å, respectively. Refined values of the Al-H bond lengths in NaA1D6 are in agreement within 2% of earlier work on undoped NaA1D6. The calculated GGA formation energies for the decomposition reactions of NaA1D4 and Na3A1D6 are 33.8 and 49.9 kJ per mole of H₂, respectively. The corresponding LDA values are significantly higher 44.6 and 70.3 kJ per mole of H₂. GGA results are in closer agreement with the measured enthalpy.

9:00 AM BB4.3 Investigation of Ti-doped NaA1H₄ by solid-state NMR. Julie Lynn Herberg1, Robert S Maxwell2 and Eric H Majzoub3
1Chemistry and Material Science, Lawrence Livermore National Laboratory, Livermore, California, 2Engineered Materials Department, Sandia National Laboratories, Livermore, California.

In recent years, the development of Ti-doped NaA1H₄ as a hydrogen storage material has gained attention because of its large weight percentage of hydrogen using traditional methodologies. The addition of transition-metal dopants, such as TiCl₄, dramatically improves the kinetics of the absorption and desorption of hydrogen from NaA1H₄. X-ray diffraction studies of Sun et al. [1] have suggested that Ti may be substituting into bulk NaA1H₄. These authors, as well as others, have suggested that the Ti present is Ti³⁺. Desorption kinetics studies by Majzoub et al. [2] have further suggested that the resultant Ti vapor pressure is independent of the presence of Ti³⁺-doped NaA1H₄. However, the role that Ti plays in enhancing the absorption and desorption of H₂ is still unknown. In the present study, ⁴⁰Ti, ⁴⁰N, and ³¹P MAS NMR have been performed to understand the structural impact of Ti on the bulk NaA1H₄ material. All experiments were performed with pure NaA1H₄ and NaA1H₄ doped with Ti to fully understand how the Ti impacts this complex network. All ¹H and ³¹P-H MAS NMR experiments were performed to understand structural changes that occur with the addition of the

9:30 AM *BB4.4
Study of Thermophysical Properties of NaAlH4

Complex metal hydrides of general formula, AlH2A [A = alkali metals, B = third group elements such as B, Al, Ga] are potential candidates as hydrogen storage media for transportation. Thermal decomposition of complex hydrides generates hydrogen at elevated temperatures. The by-products of the dehydrogenation process can be regenerated using excess NaAlH4 at suitable temperature and pressure. The initial steps of thermal decomposition of NaAlH4 may be more complicated from the decomposition pathway reported in the literature. Close examination using thermal analysis by TGA, DSC and IR measurements over the temperature range 35-550°C showed that the initial evolution of hydrogen occurred at a slow rate at ~80°C, prior to fast decomposition at 180°C and at 260°C. Four regions of weight loss and five major endothermic peaks were measured during the thermal analysis. The effect of initial rate on the thermal analysis response showed that a high resolution of the thermal processes could be achieved at higher heating rates. Thermodynamic and kinetic studies obtained through several steps in the decomposition process including the formation of intermediate phases NaAlH4, and NaH. We also found that the decomposition of NaH is highly pressure dependent and due to the high compressibility of the diffusive H2, NaH has the higher pressure. The crystal chemistry of NaAlH4 during decomposition has been established using X-ray diffraction analysis.

10:30 AM *BB4.5
Transition Metals Modified Lithium Nitride for Hydrogen Storage
Xiong Zhaixue and Chen Ping, Physics, National University of Singapore, Singapore, Singapore.

As a new candidate for hydrogen storage, lithium nitride (Li3N) possesses remarkable storage capacity (up to 11.4 percent of its own weight). For the practical applications, however, aspects such as chemical stability, thermodynamic and kinetic properties etc. have to be improved and strengthened. The formation of ternary nitride of Li-M-N, where M represents first row transition elements, was reported 50 years ago. The replacement of Li+ with transition metal ions creates unique property quite different from those observed in the parent nitride. In this study, standard high temperature ‘ceramic’ method was employed to synthesize a variety of Li3M-type ternary nitrides, Li-M-N (M=Ti, V, Mn, Fe, Co, Ni, Cu). Subsequently, the hydrogen storage properties of these ternary nitrides have been performed with Thermal Analysis and Temperature-Programmed-Desorption (TPD). Powder X-ray diffraction measurements also revealed the phase and composition changes during the hydrogen absorption and desorption processes. Changed paper #BB4.4 to BB4.5 5/9/03 LW

11:00 AM *BB4.6
Metal Nitrides and Irides As Viable Hydrogen Storage Materials
Ping Lu, Zhiqian Xiong, Kyoung Lee, Physics Department, National University of Singapore, Singapore, Singapore.

Strong interaction between hydrogen and lithium nitride and imide was reported in last November. Such interaction reveals that metal nitrides and imides could be hydrogen storage media. In Li3N system, up to 11.5 wt% of hydrogen can be absorbed, in which more than half is reversible at temperature above 250 Celsius when operated at high pressure [1]. To reduce the operating temperature and to enhance materials’ performance, metal nitrides or imides with proper thermodynamic and chemical properties have to be developed. Here, we report the recent progress in material exploration. Serials of metal nitrides and imides have been synthesized and their hydrogen storage properties have been evaluated. Above 5.5 wt% hydrogen storage capacity has been achieved. The operating temperature has been largely reduced to 150 Celsius, quite close to the practical target.

11:30 AM *BB4.7
Old Technique For New Materials Characterization Of Solid State Hydrides By Thermodynamic Programmed Reaction
T. S. Rufaid, ChevronTexaco Energy Technology Company, Houston, Texas.

The most common diagnostic tools in studying reversible solid-state hydrogen storage materials involve volumetric or gravimetric approaches. Here, we present Temperature Programmed Reaction (TPR) approach which can provide a fast, simple and complementary technique to obtain hydrogen storage capacity, thermodynamic and kinetic information from a wide range of solid materials. The very high thermal conductivity of hydrogen compared to other gases provides the basis for TPR, which is routinely used to characterize the reduction behavior of metal oxide and sulfide catalysts. TPR employs a constant heating rate of a powder sample in a dynamic and non-equilibrium environment with a constant flow of a hydrogen/inert gas mixture, while monitoring the rate of hydrogen absorption and desorption by a sensitive thermal conductivity detector. A slight change in hydrogen concentration is reflected by significant changes in the thermal conductivity signal. Hydrogen storage materials exhibit fingerprint type TPR spectrum, unique to their composition and structure. Specific rates of hydrogen intake, hents of absorption and description as well as extent of activation can be extracted from TPR curves. In addition, multiple absorption and desorption states can be identified from the number absorption or description peaks. Material stability and potential phase changes can also be inferred indirectly. The simplicity and the highly sensitive thermal conductivity measurement provide a number of advantages over the traditional volumetric or gravimetric techniques. Metal hydride alloys will be presented to demonstrate the effectiveness of the TPR technique in characterizing hydrogen storage materials.

SESSION BB5: Hydrogen Storage in Carbonaceous Materials
Chairs: Ping Chen and Gholam-Ahmad Nazar
Tuesday Afternoon, December 2, 2003
Fairfax B (Sheraton)

2:00 PM BB5.1
Enhancing Hydrogen Adsorption by Metal Incorporation in Carbon Multi-wall Nanotubes Produced by Continuous Hot Wire Chemical Vapor Deposition
Anne Catherine Dillon, Phillip A. Perillo, Jeffery L. Allemen, Aaron Hey Milam, Kim M. Jones, Kerherin E.H. Gilbert and Michael J. Heben; Basic Sciences, NREL, Golden, Colorado.

The hydrogen storage properties of carbon single-wall and multi-wall nanotubes (SWNTs and MWNTs) and their graphitization, metal nanowires, and other nanostructured carbons have recently become the subject of considerable interest. Reported capacities range from ~0-60 wt%. Early experiments on highly impure SWNT samples indicated 5 to 10 wt% hydrogen storage on a SWNT weight basis [1]. More recently, incorporation of a metal alloy into pure single-wall nanotubes resulted in carbon/nanotube composite material showing capacities of up to ~7 wt% [2]. Unfortunately, samples exhibiting high hydrogen storage capacities can not be straightforwardly fabricated, and it is believed that a greater understanding of the metal-nanotube interaction and adsorption mechanism is needed. Hot wire chemical vapor deposition (HCWVD) has recently been adapted for a continuous growth process for high-density carbon MWNTs. (4) Multi-wall nanotube growth is optimized in 1.5 methane argon at 1500 tor with reactor temperatures of 400 and 550 C for static and flowing gases, respectively. Periconc is employed to provide a gas-phase catalyst. Highly graphitic nanotubes can be continuously deposited with iron content as low as 15 wt% and carbon impurities below thermal gravimetric analysis detection limits. The MWNTs are simply purified to ~95.5 wt % with minimal structural damage and with a 75 wt% yield. Hydrogen adsorption is observed at near ambient temperatures in as-synthesized MWNTs containing iron nanoparticles. No hydrogen adsorption, however, is observed at near ambient temperatures for the purified MWNTs or for purified MWNTs that were subsequently combined with iron nanoparticles via sonication. From these results, we obtain a greater understanding of the nature of the metal-graphitic carbon interaction. This information can be used to aid in the design of effective adsorbents for hydrogen storage. (1) Dillon, A. C., Jones, K., G. Beckedahl, T. A.; Kiiro, S., C. H.; Behrend, D. V. Nature 386 (1997) 377. (2) Dillon, A. C., Heben, M. J. Appl. Phys. A 72 (2001) 133. (3) Heben, M. J.; Dillon, A. C.; Gilbert, K. E. H.; Perillo, P. A., Gennett, T.; Allemen, J. L.; Hornyk, G. L.; Jones, K. M. In AIP Proceedings for Hydrogen in Materials and Systems: Newport News, VA, 671 (2002) 77. (4) Dillon, A. C.; Milam, A. H.; Perillo, P. A.; Allemen, J. L.; Heben, M. J.; Jones, K. M.; Gilbert, K. E. H. NanoLetters (in press).

2:30 PM BB5.2
Hydrogen Storage Using Carbon Materials At Room Temperature
Hashim Kajiyama, Shigematsu Takeuchi, Koji Kato, Yosuue Nakamura, Mitsuomi Kukutsu, and Masafumi Ata
1Materials Laboratories, Sony Corporation, Yokohama, Japan; 2Technical Solutions Center, Sony Corporation, Yokohama, Japan.

The hydrogen storage capacity of five types of commercially available
carbon materials with different nano-structures was measured up to 8MPa at room temperature using an apparatus, based on the volume of displaced air measured by an error less than 0.0005% [1]. The measured samples were (1) activated carbon fibers, (2) Osaka Gas Chemicals Co., Ltd. and TS100-20, Kuraray Chemical Co., Ltd. (2)

(3) single-walled carbon nanotubes (purified HPco® SWNTs, Carbon Nanotechnologies, Inc. and 2-4% purity, as-produced SWNTs, MTR Ltd.), (4) multi-walled carbon nanotubes (ground core, Synth Chemica Inc.), (4) graphite powder (99.97% purity, max. particle size 200nm, Goodfellow Cambridge Ltd.), and (5) 95% nanoparticle prepared by a chemical route at 1 gram. The highest storage capacity of 0.42wt% was obtained for purified HPco® single-walled carbon nanotubes (SWNTs). In these SWNTs, the hydrogen capacity in pores with a diameter less than 1nm was estimated to be 0.022g/ml, which corresponds to 31% of liquid hydrogen density. In the development of hydrogen storage media will be discussed at the meeting. [1] H. Kajjara et al., Appl. Phys. Lett. 82 (2003) 1105.


Using nanoporous carbon membranes in fuel cells, Ramamohan Ramamurthy, Nilakantha Rajagopalan, Henry Foley and Thomas E Mallouk

We have synthesized nanoporous carbon membranes that have monodisperse pores of 4-5 Å. These membranes have excellent size and shape selectivity that makes them an ideal candidate for use as separators in fuel cells. The selectivity of these membranes to gases such as air and water gas (carbon monoxide and hydrogen) were measured using a permeation testing unit. The performance of the membranes in fuel cells will be discussed. This talk will describe a method to improve tolerance of fuel cells to catalyst poisons using the carbon membranes.

Improving the Hydrogen Absorption/Desorption Properties of Alloy ZK60 by Equal Channel Angular Pressing, Eugene Chiklin, Oleg Ovsyannikov, Vladimir Vlassov, Konstantin G. Himmels, Seiji Igarashi, Minoru Igarashi, Supriya Loprov, M. Materials Engineering, Technion, Haifa, Israel, 2Institut fuer Werkstoffkunde und Werkstofftechnik, TU Clausthal, Clausthal-Zellerfeld, 3School of Physics and Materials Engineering, Monash University, Clayton, Victoria, Australia.

Magnesium alloys are popular candidate materials for hydrogen storage. While their hydrogen storage capacity is sufficiently high for automotive applications, the hydrogen desorption kinetics are too slow for the purpose. An enhancement of the desorption rate is commonly achieved through microstructure refinement by means of high energy ball milling (HEBM). In the present work, an attempt was undertaken to reach the goal by using equal channel angular pressing (ECAP). Route A (eight passes through a 120 deg die, followed by a room temperature pressing through a 90 deg die) was employed. The ECAP treatment was also applied in combination with HEBM. The object of the study was to compare the high nitrogen magnesium alloy ZK60 (Mg-4.95 wt. %Zn-0.71 wt. %Zr). ECAP was shown to have a significant accelerating effect on the hydrogen absorption/desorption kinetics exceeding that of HEBM. The nickel processed by a combination of ECAP and HEBM showed the highest rate of hydrogen desorption. An interesting feature associated with combined ECAP/HEBM processing is the disappearance of pressure hysteresis with regard to hydrogen absorption/desorption. This hydrogenation behavior is explained in terms of the microstructure of bulk samples and the morphology of dehydrogenated powders as observed by transmission and high resolution scanning electron microscopies. While other efforts are needed to lower the hydrogen desorption temperature as well as to apply ECAP method to other hydride forming alloys and intermetallics, the first results obtained with ECAP of a Mg alloy are encouraging. The prospects of obtaining larger amounts of material with good hydrogen storage and desorption potential within reasonable processing time and, notably, the possibility of avoiding health hazards associated with finely dispersed toxic powders in conventional ball milling warrant further research in this area.

SESSION BB6: Hydrogen Storage Materials and Applications

Chairs: Gholam-Abbas Nasri and Rosa Young

Wednesday Morning, December 3, 2003  Fairfax B (Sheraton)

8:30 AM BB6.1 Nonmetallic-Based Gas Sensors as Safety Devices for the Hydrogen Storage Industry, Marielle Barton and Hind Merhan

With the rapid development of hydrogen storage technology, concerns about safety issues must be addressed to improve acceptance of this environmentally-friendly technology by the public. Safety hazards pertaining to potentially explosive atmosphere in confined areas where hydrogen storage systems are located, call for early detection of leaks to effectively protect personnel and properties. While commercial hydrogen detection systems already exist, economic considerations preclude their widespread dissemination and installation on vehicles as well. Taking advantage of nanosized metal oxides, we have developed miniature hydrogen sensors using a finely tuned thick-film technology. Operated at 200°C, these low-cost devices are capable of selectively detecting hydrogen in the 10-100 ppm range with a sensitivity at least one order of magnitude higher than that reported for commercial devices. We will report on the fabrication, characterization and performance of the devices with emphasis on the fundamental gas-surface interactions. This work has been partially funded by the European Commission (contract No. BPRH CT95 0002).

8:45 AM BB6.2 Ruthenium as Schottky Metal for Si-Based High Temperature Hydrogen Sensors, Sukukuma, Sonameth Roy and Chinobby Jacob

Sodium and Potassium Sensitivity of Mica for Hydrogen Storage, Truong, Long, Bin Lang, Ben He, Xiaodong Cai, Yeqing Zhao and Jun Peng

First and precise detection of hydrogen leakage, much before the onset of its lower explosion limit, is imperative. Schottky diodes and Mott diodes have been extensively used as sensors for hydrogen in fuel cells. This talk will describe a method to improve tolerance of fuel cells to catalyst poisons using the carbon membranes.
sensors. The sensor parameters were found to improve with higher operating temperature, up to 400°C. It is important to note that up to about 400°C, the reaction barrier has not been determined, and the sensitivity of the Schottky diode is determined by adsorption and desorption processes, due to a band-offset of about 1.2 eV. Preheating injection of thermally generated electrons into the Si substrate, so the performance of the Ru/SC/Si Schottky device at high temperatures (up to 400°C) is not much influenced by the Si substrate. The sensitivity of the Schottky sensors was found to be a function of the applied bias and saturated at about 0.8 V. As compared with the Ru/SC junctions, the Ru/SC Schottky sensors showed higher resolution and improved reversibility in the hydrogen concentration range, 10,000 and 20,000 ppm. The SMS, RBS and glancing incidence XRD studies indicated that at about 400°C there was no formation of ruthenium silicide at the Ru/SC/Si interface. Moreover, the formation of ruthenium sulfide is not known to be thermodynamically favorable. So, the two major problems associated with the Ru/SC/Si Schottky sensors could be overcome by using the Ru/SC/Si structure. Table 1 presents the state of metal/Si interfaces in the unoxidized and in different annealing conditions.

**9:00 AM BBE.6 The Electrical Characteristics and Hydrogen Response Mechanism of a Pd/AlN/Si Thin Film Gas Sensor.**

Erik F. McCullen,2,3,4,5 H.E. Prinzmann,5 Wenzhou Mo,5 Jagdish Thakur,5 R Nau,5 R. Irmän,5 K.Y. S. Ng,6 and G.W. Aumer5 1Physics, Wayne State University, Detroit, Michigan; 2ECSE, Wayne State University, Detroit, Michigan; 3Chemical Engineering and Materials Science, Wayne State University, Detroit, Michigan.

The electrical characteristics, sensitivity and the response time of a hydrogen sensor utilizing a Pd/AlN/Si(111) structure has been investigated. The AlN layer was deposited by plasma source molecular beam epitaxy (PSMBE), and the Pd grids were deposited via mask using magnetron sputtering. The capacitance vs. bias voltage, C(V), and conductance vs. voltage, G(V), measurements were performed at several elevated temperatures, for different pppm concentrations of H2. The devices are found to be sensitive to hydrogen, down to 1 ppm concentration in the surrounding flow, with a response that is independent of the presence of oxygen, propane and CO. We have investigated the devices electrical characteristics for varying thicknesses of AlN, from 25 to 2000 Å. The C(V) and G(V) measurements were utilized to investigate the presence of surface states within the Si gap at the AlN/Si interface. Our previous investigations on 50 Å AlN did show the presence of interface traps, with an estimated surface density between 8×10^12 and 1.8×10^13 m^-2 V^-1. In our present work we have examined the effect of AlN thickness on the density of these interface traps. The density is strongly dependent on AlN thickness, with the thinner devices showing a density of interface states several orders of magnitude greater than the thicker AlN devices. We have also investigated the effect of hydrogen on the conductance. There is an enhancement in the conductance values when the device is exposed to hydrogen gas. Theoretically we explain it by proposing that there is a change in the behavior of the underlying junction, which is discussed in more detail in the discussion section.

**9:15 AM BBE.6 Abstract Withdrawn**

**10:00 AM BBE.6 Designing A New Generation Of Fuel Cells Using Layer-By-Layer Deposition Of Polyelectrolytes.**

Tarek R. Farhat, Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Most fuel cells utilizing the membrane-electrode assembly have their ion-conductive membrane sandwiched between bipolar plates. Unfortunately, applying conventional techniques to isolated polyelectrolyte membranes is challenging and difficult. A more practical alternative is to use the layer-by-layer technique to fabricate the membrane electrode assembly which, technologically, is relatively simple, economic, and robust. The process paves the way to fabricate ion-conductive membranes tailored for optimum performance in terms of controlled structural and catalytic loading. Performance tests characterizing the physical properties of the LBL-fuel cell assembly will be presented and discussed.

**10:15 AM BBE.6 The influence of surface reconstruction and impurities on photocatalytic water dissociation by TiO2.**

Xiuling Nie and Karl Schöllgen; Chemistry Department, Drexel University, Philadelphia, Pennsylvania.

There is a number of number measurement techniques which are primarily well-suited for studying materials of thin film solar cells and storage media. The neutron’s sensitivity to hydrogen and deuterium, as well as its great penetrating power, makes it possible to probe a variety of fuel cell properties over a wide range of length scales. At the micron scale, neutron tomography could provide direct visualization of water transport through the electrodes in operating fuel cells. Complementary refinement and phase contrast imaging can also be performed. On the nanometer scale, the concentration and distribution of water and hydrogen within a fuel cell membrane material, both normal to and in the plane of the film, can be obtained by specular neutron reflectometry (NR) and small angle neutron scattering (SANS). These measurements can be performed in situ, on properly prepared substrates, under conditions of temperature and humidity identical to those which exist in actual fuel cells. Finally, on the molecular level, the structure and dynamics of fuel cell membrane materials can be obtained by neutron diffraction and inelastic scattering methods. Theoretical analysis of these results can contribute to a detailed understanding of TiO2 is well known as a prototype photocatalyst for water dissociation. To understand the mechanism of its photocatalytic water dissociation, we designed and performed series of experiments. The surface reconstruction of the catalytically favorable (TiO2) termination is very different from the physically favorable (oxygen) termination. We also find that carbon impurities decrease the bandgap of TiO2, in agreement with previously reported experimental results. We suggest that these issues, the surface structure of the catalytically favorable termination and the magnitude of the bandgap, are key to understanding the photocatalysis of water dissociation. Possible methods to improve the efficiency of water dissociation will be discussed based on our calculations.

**10:30 AM BBE.7 Structural studies on the perovskite-based La0.87Sr0.13TiO3 thin films.**

John T. S. Irvine and Wuzong Zhou; School of Chemistry, University of St Andrews, St Andrews, United Kingdom.

Perovskite titanates with nominal stoichiometry ABO3±δ, B=Ti, are frequently reported in SOFC literature as having O2 stoichiometry. Such phases often exhibit quite interesting properties, but are not stoichiometric and the structural characterization is usually not rigorous. Here we demonstrate how excess oxygen can be incorporated in a titanate perovskite-based lattice. A new family of layered perovskites La0.87Sr0.13TiO3.08 has been investigated by means of XRD, neutron diffraction, TEM, TGA and density and magnetic measurements. Such layered perovskites are known for being capable of accommodating extra oxygen beyond the perovskite ABO3 perovskite in crystallographic sheets (C8 planes). The layered structure was lost for n=1 member (La0.87Sr0.13CoO3.08) due to Co3+ substitution by a Y2+ or Mg2+ site. High pressure and temperature (2.0 GPa and 300°C) were used to achieve a sufficient oxygen content in this perovskite framework in randomized distributed short-range linear defects.

**10:45 AM BBE.8 Novel Metal-Ceramics Composite Membrane for High Temperature Hydrogen Separation.**

Cuill Su, Koji Kurkac, Tetsuro Jin and Tetsuo Yurshin; Separation Division for Green Life Technology, National Institute of Advanced Industrial Science and Technology, Kanagawa center, Otsuka, Japan.

 Palladium membrane that possesses a thickness of 1.00 micrometer or several ten micrometers is selective to hydrogen transportation, but its low permeance, hydrogen enrichment and instability to sulfur make the membrane to be applied in practical processes. In this work, thin Palladium/SiO2 composite membrane supported on porous stainless steel has been fabricated by a novel preparation procedure. SiO2 colloid was applied to modifying the pore size of the substrate and an intermediate SiO2 layer was made by dip-coating using colloids with smaller particle size. Palladium nuclei were seeded by chemical vapor deposition using Pd(hfac)2, and then a 2.3 micrometer palladium layer was prepared by electrodeless plating. The membrane has a 72% hydrogen permeation and the Pd (99.96 wt%) and the Pd/SiO2 (99.96 wt%) have a 98.5% permeation and a 2.5% permeation at a pressure difference of 1 atm and the selectivity of Pd2/PN2 was above 300. The preparation process shows that SiO2 layer has a unique property compared with the Pd2/O2 palladium adhering. This work is probably due to the formation of Pd2Si between the SiO2 and Palladium layers. The seeding process by chemical vapor deposition was significant for the formation of a defect-free membrane. A novel electrodeless plating process was also applied using a bath of pH=6, which is different with the usually used basic ones containing NH4.
the fundamental transport mechanism of the hydrogen, thereby enabling rational design of improved fuel cell materials. Illustrative examples of the neutron metrology applicable to fuel cell research and development will be presented.

11:15 A.M. BB6.10
Ionic Conductivity Enhancement of Solid Oxide Fuel Cell Electrolytes by Heavy Ion Implantation. Jeremy Cheng, Rejana Pompmearsuk, Yuji Saito and Fritz B Prinz; Materials Science and Engineering, Stanford University, Stanford, California.

Yttria-stabilized zirconia (YSZ) is an important anionic conductor and the most common electrolyte material for solid oxide fuel cells (SOFC). The low ionic mobility of the material is one factor that restricts its use to high temperatures, typically 800-1000°C. However, the conductivity of the material is strongly affected by microstructural features such as grain boundaries and dislocations. Heavy ion irradiation will introduce a variety of point and line defects in the material. With high doses, isolated dislocation loops can interact and react to form complex dislocation networks. This ion irradiation damage can significantly increase the ionic conductivity of the material. Bulk single crystals of YSZ as well as thin film samples were modified using heavy ion implantation. Single crystals were tested to eliminate grain boundary effects, isolating the effects of irradiation. The material was irradiated with 320-450 keV Xe ions over a range of doses from $10^{13}$ to $10^{15}$ ions/cm$^2$. The conductivity was subsequently evaluated with various two point impedance spectroscopy methods. Following heat treatment, there is a large transient increase in conductivity which can be removed with the application of a voltage at moderate temperatures. This may be related to a non-equilibrium ion or point defect concentration following irradiation. There is a significant permanent increase in conductivity caused by the dense dislocation network. The microstructure was characterized using X-ray diffraction and cross sectional transmission electron microscopy. XRD indicates a lattice expansion as the point defect and dislocation concentration increases in the irradiated region. This recovers into a surface layer, about 150 nm thick, which contains a high concentration of dislocations. The dislocation density is on the order of $10^{15}$ /cm$^2$. To further understand the enhancement of oxygen diffusion, quantum chemistry simulations were performed using a cluster method. The oxide ion vacancy migration energy of a perfect YSZ was calculated to be approximately 1.4 eV, which correlates with experiments. The result was then compared with that of the dislocation cluster. Atomic positions in the $\frac{1}{2}$$\langle$110$\rangle$$\langle$100$\rangle$ dislocation cluster were calculated using the displacement equations of straight edge dislocations in an anisotropic media. The results reveal the reduction of the migration energy to half the value of the perfect crystal: 0.7 eV in pure ZrO$_2$ and 0.8 eV in YSZ dislocation clusters.

11:30 A.M. BB6.11
Ab initio study of adsorption of molecular hydrogen on microporous metal-organic frameworks. Sebastien Hamel$^{1,2}$ and Michel Cote$^{1,2}$; $^{1}$Physics, Universite de Montreal, Montreal, Quebec, Canada; $^{2}$Regroupement Quebecois de Matériaux de Pointe (RQMP), Montreal, Quebec, Canada.

In the ongoing search for promising compounds for the storage of hydrogen, novel microporous metal-organic frameworks (MOF) have been discovered recently [1]. Well defined binding sites were deduced from inelastic neutron scattering (INS) spectroscopy of the rotational transitions of the adsorbed molecular hydrogen. In light of this discovery we performed ab initio density functional theory (DFT) calculations of the adsorption of molecular hydrogen on this class of microporous MOF to compare different adsorption sites. The DFT code used (Abinit) is based on plane-waves and different approximations (pseudopotentials, exchange-correlation potentials) were accessed for a set of relevant properties (binding energy, energetically favored configuration, distance between the adsorbents and adsorbates). In particular, phonon spectra of the adsorbed H$_2$ were obtained that could be compared to the experimental INS spectra. [1] Rosi et al., Science Vol. 300, 1127 (2003)