SYMPOSIUM BB

BB: Materials and Technologies for a Hydrogen Economy

November 30 - December 3, 2003

Chairs

Gholam-Abbas Nazri
General Motors R&D and Planning Ctr
MC 480-102-RCEL
30500 Mound Rd.
Warren, MI 48090-9055
586-986-0737

Rosa C. Young
Hydrogen Systems
Chevron Texaco Ovonic
2983 Waterview Dr.
Rochester Hills, MI 48309
248-293-8772 x-7030

Chen Ping
Dept. of Physics
National University of Singapore
10 Kent Ridge Crescent
Singapore, SINAGPORE
65-874-2982

Maryam Nazri
Dept. of Mechanical Engineering
Massachusetts Institute of Technology
77 Massachusetts Ave.
Cambridge, MA 02139
248-761-0096

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*Invited paper
TUTORIAL

PT BB: Hydrogen Storage Materials - Science and Technology
Sunday November 20, 2003
1:30 PM - 5:00 PM
Room 204 (Hynes)

The tutorial will cover a general overview of the field of solid-state hydrogen storage materials with an emphasis on three main classes of compounds. The fundamental changes in energy storage as a 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 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 of revolutionary import not only for its societal impact but also for the new science that will arise from it. The present age of civilization is 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 necessary to make possible the revolutionary transition of energy from its fossil fuel beginnings to the present.

10:00 AM *BB1.3
The Hydrogen Programs In China. Qidong Wang, Changbin Chen and Linxin Chen, Department of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang, China.

Hydrogen programs in China since 1980 are reviewed. Back in nineteen eighties, the studies on metal hydride hydrogen storage, storage, purification and compression for processing hydrogen gas were quite active. For the use of hydrogen, hydrogen powered internal combustion engines and partition distribution of hydrogen for IC engines for vehicles systematically investigated, together with the on board storage of hydrogen in metal hydride hydrogen storage containers. In early nineteen nineties, the attempts 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 initiated by some bicycle factories in view of the expected market together with the study of small sized hydrogen hydrogen storage tanks for the application. Immediately followed, 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 firing based 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 hydrogen infrastructure and the effective and profitable applications of hydrogen are stressed. And the development from the more easily and readily carried out projects to more sophisticated and difficult ones are also emphasized.

NOTE EARLY START

8:25 AM INTRODUCTORY REMARKS - G. ABBAS NAZRI

8:30 AM *BB1.1

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 on-board hydrogen 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 while meeting the constraints of volume, weight, 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 microphases, self-assembled nanostructures, metal-organic frameworks, carbon nanoporous, 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 *BB1.2

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 hydride batteries and hydrogen fueled fuel cells. In 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 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 of revolutionary import not only for its societal impact but also for the new science that will arise from it. The present age of civilization is 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 necessary to make possible the revolutionary transition of energy from its fossil fuel beginnings to the present.

10:30 AM *BB1.4

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 systems. Solid hydrogen storage systems also have features of low-pressure operation, compact, safe, desirable deliverable pressure, excellent stability and design for easy scale-up and long cycle life. In this paper, solid hydrogen storage systems (such as portable power containers, lightweight fiber wrapped vessels, and aluminum tubular vessels, developed by Texaco Ovonic Hydrogen Systems, Inc.) will be discussed. For example, three containers, 85 g of reversible hydrogen stored in each container, interfaced with a 1 kW PEM fuel cell can sustain more than 50 min full power run time. The container showed no plastic deformation after completing 500 charge/discharge cycles. The strain gauges instrumented on the surface of the cylinders all were in compliance with the DOT approved range. The cylinders are in the early commercialization stage for UPS and AHV applications. The lightweight cylinders are combined with the high performance metal hydride targets on-board applications. On a system level, the vessel has a volumetric energy density of 84 g hydrogen per liter and a gravimetric density of 1.65 wt %. 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 at 1500 psi. The vessel can easily release the hydrogen at 500 slpm at
70°C. The aluminum tubular vessels, flexible in length and diameter, target bulk storage and infrastructure applications, such as stationary power, hydrogen storage and transport, 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, Mg-Ni-Zr, and Mg-Ni-Ln55, Mg-Ni-Zr have been synthesized using the mechanical alloying process. To increase the hydrogenation and dehydrogenation kinetics, the small amount of catalytic elements Pb, Ni, Pt, and V have been coated on the surface of materials by using of surface alloying. The new materials produced have been investigated by X-ray diffractometer, TEM, SEM and EDS for their phase analysis, crystal structure and grain size, and the distribution of the catalytic elements. Hydrogen storage capacities and the hydriding/dehydriding kinetics of the new materials have been measured at different temperature using an automatic Sieverts 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 250°C respectively. The composite material Mg80%-Ni20% absorbs 1.96 wt %, but releases 0.55 wt % hydrogen only at 250°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 now in control of the process of dehydrogenation.

11:30 AM BB1.6 Hydriding Behaviour of Mg-C Nanocomposites. Marco Vittori Antonini1, Amelia Montone,1 Jasmina Grbovic,1 Emico Bonetti2, Luca Puspanzi1, Alex Rassetti3 and Anna Lisa Fiorini1

1Materials nanochemistry, ENEA, Rome, Italy; 2Department of Physics, University of Bologna, Bologna, Italy.

Recently, we can notice an increasing interest in modifying the microstructure 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 the high volume fraction of surfaces-interfaces and a high defects density. Moreover hydrogen sorption can be further accelerated by the addition of carbon, and its absorption-desorption 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 magnesium 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 capability has been tested by a hot wall reactor. The results show that the microstructure after milling depend on the amount of additives and its hydrogenation capacities of the material. The particular ratio of Carbon to Benzene seems to play a major role.

SESSION BB2 Hydrogen Storage Alloys

Chair: Ping Chen and Maryam Nazir
Monday, afternoon, December 1, 2003
Fairfax B (Sheraton)

2:00 PM BB2.1 Electrocally-Induced Hydrogen Absorption in Mg-Functionalized Single Wall Carbon Nanotubes. Zafar Iqbal and Yuking Wang; Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, New Jersey.

Argon-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 thermogravitmetric 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 change capacitance and molecular dynamics of the hydrogen trapped in the nanotubes, respectively. Weight uptake in the 2.4 weight % range has been observed and evaluated of the chemistry of the process studied by in-situ Raman scattering [1]. These results will be compared with similar data for undoped carbonized SWNTs of the same diameter. [1] Also see: C.P. An, Z.V. Vardeny, Z. Iqbal, G. Spinks, R.H. Baughman and A.A. Zakhidov, Synth. Metals, Vol. 116, 411 (2001).

2:30 PM BB2.2 Surface Treatments for Improved Hydrogen Storage Properties of Nanocrystalline Magnesium Based Alloys. A. Hansger1, R. Janco1, X. Durek1, E. Ayvand1, G. A. Nueri2 and J. M. Tharanon3; 1Laboratoire de Reactivite et Chimie des Solides, Amiens, France; 2General Motors R&D, Warren, Michigan.

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 sorption-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.


The investigation of many stoichiometric variations involving large numbers of combinations of elements offers a means to discover a hydrogen storage material with optimal properties. We introduce the use of synchrotron 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 powders and 32 Mg-Ni or Mg-Fe binary powders. Hydrogenation of the powders observed indicate a substantial decrease in hydriding temperatures, which sensitively depends on composition.

4:00 PM BB2.4 Morphological Effects on Hydrogen Storage in Palladium Nanoparticles. S. Kishore1, J. A. Nelson1, J. H. Adair2, D. E. W. Vaughan3 and P. C. Eklund1; 1Physics, Pennsylvania State University, University Park, Pennsylvania; 2Materials Science, Pennsylvania State University, University Park, PA 16802, Pennsylvania.

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 the surface and/or subsurface. In this paper, the morphological aspects of improved hydrogen storage are addressed at the nanoscale. Both spherical and nanotubular 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 100nm were measured gravimetrically from the pressure range from zero to 20 atmospheres over a range of temperatures from 400C to 1000C. These results were compared to those from nanotubular 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 the particles at high temperatures, Pd nanoparticles were also studied, thus were supported on monoporous zeolite and zirconia matrices [sponges] to understand the improvements in the hydrogen uptake performance. The results will be compared to bulk palladium and other recent findings in nano-metal hydrides.

4:30 PM BB2.5 Properties of the Magnetic Hydride YFe2Hx. From First Principles Calculations. Daisuke Joseph Singh1 and M. Gupta2; 1Center for Computational Materials Science, Naval Research Laboratory, Washington, District of Columbia; 2Institut des Sciences des Matériaux, Université Paris-Sud, Orsay, France.

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 trilanthides, 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 YFe₂ and YFe₃H₄ with x ≈ 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 to be highly sensitive to the H positions, which we calculate from first principles. Using the calculated positions, good agreement with experiment is obtained for the moment. The mechanism for the moment increase is shown to be related to d band narrowing with the H potential pulling up a 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 Materials and Technologies

**BB3.1** Hydrogenation of Nanocrystalline Mg-based Alloys. Daniel Zander, Lyudmila Lyubchenko 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 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, metal/hydride batteries, thermal engines, air-conditioning systems etc. Mg-based metal hydrides with volumetric energy density of 1.5–1.6 kW/l, low cost and high abundance are the best candidate for safe energy storage and transport material. On the other hand, commercialization in mobile storage systems, metal/hydride batteries and other clean applications have been slowed down due to high sputtering temperatures and unknown cycling life. Recently it was published that the design of improved nanocrystalline Mg hydrides 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 behavior of nanocrystalline Mg. The mechanisms by which metal oxides improve hydrogen absorption as well as description are still unclear and should be clarified by microradiographical structures in detail. This research focuses on investigating the structural/functional properties relationship in regard to the hydrogenation behavior of nanocrystalline Mg with and without V₂O₅.[1] W. Oelerich, T. Klussn, R. Bornmann, J. Alloys and Comp. 315(2001). 237 This work was supported by the EU HTN-Network Project HPRN-CT-2002-00298.

**BB3.2** Hydrogen absorption of Cl₂ Laves NiTiZr-NiVNb pseudo-binary alloys. Kazumaro Ishihara, Shiharo Noda, Kyomori Suzuki and Kiyoshi Aoki; Kitami Institute of Technology, Kitami, Hokkaido, Japan; Monash University, Melbourne, Victoria, Australia.

The Cl₂ Laves alloys are attractive candidates for hydrogen storage alloys. In this work, the crystal structures and the hydrogen absorption properties of Cl₂ Laves NiTiZr-NiVNb pseudo-binary alloys are investigated by XRD measurement and hydrogen analysis. The hydrogen capacity and the hydrogen desorption temperature of the NiTiZr ternary compound, formed in NiTi₃Zr, 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 NiTi[V]₀.₅[Zr]₀.₅(Nb)₀.₅, the hydrogen desorption temperature remained high with increasing x, although the hydrogen capacity was increased. However, the desorption temperature of the NiTi[V]₀.₅[Zr]₀.₅ alloy decreased to 250 K with V content without serious decrease of the hydrogen capacity.

**BB3.3** Hydrogen Diffusion in Zr-Cu-Ni-Al Metallic Glasses. Liubasha Jastrzembska, Lyudmila Lyubchenko, Irene Dolbelek and Uwe Koester; 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 real detail, on a microstructure and defect diffusion are necessary. The aim of this paper is to present hydrogen diffusivities in metastable amorphous Zr₆₅Cu₇Ni₁₃Al₂₅ alloys. Hydrogen charging was performed electrochemically in a 2.1 glycerol-phosphoric acid solution. Hydrogen content was 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 this dephasing allows a model-independent determination of the hydrogen self-diffusion constant, with the low limit of sensitivity D = 10⁻⁹ 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 content, density and structural models.

**BB3.4** Synthesis and Characterization of Gd(0.05)(Co(1-x)Zr(x))(L-y)(Fe(y)) as a Cathode Material for Intermediate Temperature SOFC Solid Oxide Fuel Cells. Chris Dyck and Vladimir Krast; 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 550°C and 750°C. Currently, the availability of IT-SOFC cathode materials with low overpotentials (high catalytic activity for oxygen), high conductivity, and thermal matching to the electrolyte material, is limiting the advance of the technology. Gd(0.05)Co(1-x)Zr(x)O(3-d) (GSC) was determined to provide the best balance of properties as a base composition for further study. Manipulation of the Co-site in GSC resulted in a dramatic decrease in the thermal expansion coefficient to a level comparable to 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 Gd(0.05)Co(1-x)Zr(x)Gd(0.5)y(Co(3-d) (GCG) 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 GCG/SCG cathodes reduce the problems associated with poor GSC thermal conductivity without compromising other important cathode properties.

**BB3.5** Ab-initio Modeling of Interstitial Mg H Solid Solutions. Mario Mazzini1,2, Fabrizio Cleri1 and Manuel Volpe1; 1Unina Materiali e Nuove Tattologie, ENEA, Centro Ricerche Ciaccio, Roma, Italy; 2Dipartimento di Fisica, Università La Sapienza, Roma, Italy.

We studied the thermodynamics of interstitial Mg H solid solutions by means of ab-initio electronic structure calculations. Soft pseudopotential [Troullier-Martins] 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 Gibbs free energy is known to be positive at any H concentration above 0.1 H/M, the enthalpy contribution to 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 shift of the Fermi level and the creation of deep hydrogen-like states below the metallic.
Boronane 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. First of all we have 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 thermodynamic and kinetic description of the decomposition and of the effectiveness of the chosen catalysts. A controlled heating rate in solutions near room temperature seems possible. [1] J. Baumann Dissertation 2003, TU-Bergakademie Freiberg, Germany [2] F. P. Hoffmann, G. Wolf, L. D. Hansen, Advances in Boron Chemistry. Rolf H. Grigera, Ed. Wiley-VCH. Berlin, UK. 1997. p. 514 [3] G. Wolf, J. Baumann, F. Baitalow, F. P. Hoffmann, Thermochimica Acta 343, 2000. 18-25.

8:30 AM BB4.2
Rietveld refinement and ab initio studies of Ti-Doped NaA ID4 and Na3AID6. Eric H Majzoub1 and Vidvuds Ozolins2
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 ab-initio calculations. Ti-doped NaAID4 and NaAID6. The refined lattice parameters for the tetragonal NaAID4 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-refined values. 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 inhomogeneous distribution of electronic density in the alloys. The Rietveld refinement, LDA, and GGA results for the AlH bond length in NaAID4 are 1.626, 1.634, and 1.681 Å, respectively. Refined values of the AlH bond lengths in NaAID6, are in agreement within 2% of earlier work on undoped NaAID6. The calculated GGA formation energies for the reaction decompositions of NaAID4 and Na3AID6 are 33.5 and 49.9 kJ/mole of H₂, respectively. The corresponding LDA values are significantly higher: 44.6 and 76.3 kJ/mole of H₂. GGA results are in closer agreement with the measured enthalpy.

9:00 AM BB4.3
Investigation of Ti-doped NaAID4 by solid-state NMR. Julie Lynn Herberg1, Robert S Maxwell2 and Eric H Majzoub2
1Chemistry and Material Science, Lawrence Livermore National Laboratory, Livermore, California. 2Engineered Materials Department, Sandia National Laboratories, Livermore, California.

In recent years, the development of doped NaAID₄ as a hydrogen storage material has gained attention because of its large weight percentage of hydrogen traditional metal hydrides. The addition of transition-metal dopants, such as TiCl₄, dramatically improves the kinetics of the absorption and desorption of hydrogen from NaAID₄. X-ray diffraction studies of Sun et al. [1] have suggested that Ti may be substituting into bulk NaAID₄. These authors, as well as others, have suggested that the Ti is present as Ti₃H₈. Desorption kinetics studies by Majzoub et al. [2] have further suggested that the rate limiting step is independent of the presence of Ti-hydrides as a result of Ti-doping. However, the role that Ti plays in enhancing the absorption and desorption of H₂ is still unknown. In the present study, ²³⁵Na, and ²³⁴H MAS NMR have been performed to understand the structural impact that Ti has on the bulk NaAID₄ material. All experiments were performed with pure NaAID₄ and NaAID₄ doped with Ti to fully understand how the Ti impacts this complex network. Al₂H₄ and Na₂H₂ double resonance experiments were performed to understand structural changes that occur with the addition of the

## SESSION BB4: Hydrogen Storage in AH₄ and Nitriles

**Chairs:** Miriam Nam and Ron Yoej

**Fairfax B (Sheren)**

### NOTE EARLY START

**8:00 AM *BB4.1**


The volume local deformations due to H insertion were studied in detail. BB3.6 Preparation and characterization of Pt-IrO₂/YSZ electrodes by MOCVD. A. Álvarez-Monserrate-Heuza and Jorge Roberto Vargas-García, Metallurgical Eng., National Polytechnic Institute, Mexico, D. F., Mexico; 2Metallurgical, National Polytechnic Institute, Mexico, D. F., Mexico.

Ionic/electrochemical composites have wide applications as electrodes in zirconia/based solid electrolyte devices. These materials increase the length of the triple phase boundary (gas/electrode/electrolyte), where electrochemical reactions take place. Both the length of the triple phase boundary and the microstructure of porous electrodes play a significant role for the oxygen reduction reaction. Nowadays, Ni/YSZ cermet and (La, Sr)MnO₃ materials are the most used porous electrodes in zirconia/based devices, however, the main drawback is the poor adhesion of the cermet particles. In this work, we report the use of MOCVD technique to produce Pt-IrO₂/YSZ composite in the form of thin film useful for electrodes to YSZ cells and their structural and electrochemical characterization. Pt and IrO₂ represent the electronic conductor components while YSZ is the ionic conductor component. To obtain the composite film only metallic/ceramic inclusions were used as a source materials. They were mixed and evaporated together. The size of each component calculated from the XRD line broaden of the first peak was in the range of 15 to 35 nm in diameter. The particle sizes were confirmed by TEM. The EDS analysis indicated a uniform distribution of components. Cross-sectional SEM images revealed that the composite films about 1.0 μm thick. The electrochemical performance of the Pt-IrO₂/YSZ microcomposite electrodes indicates a superior electrocatalytic activity than conventional Pt paste porous electrodes.

BB3.7 Effect of heat treatment on properties of Ti-Mn based Laves phase hydrogen storage alloys. Lijun Jiang, research center of energy material and technology, general research institute for nonferrous metals, Beijing, China.

Effects of heat treatment on the properties and microstructure of non-stoichiometric Ti-Mn based hydrogen storage alloys were investigated. The results show that the hydrogen storage capacity increases and the width of P-C-P plateau extends but the slope of plateau increases. Through SEM, EDS and XRD analysis, it was found that the crystal parameters and cell volume increase, the composition homogeneity effectively enhances and the content of C15 phase decreases after heat treatment. The accretion of slope of plateau may be related to the ratio of valence electron/s of the alloys.

BB3.8 Hydrogen Storage in Carbon Nanostructures.

Baljinder Singh Ghoman and Ahn H. Wible, Materiink Science & Metallurgy, Cambridge University, Cambridge, Cambridgehire, United Kingdom.

The drive towards renewable energy sources capable of displacing our current need for fossil fuels has led research communities to investigate the potential use of hydrogen. Substantial cost and formidable scientific challenges have hindered such a transition, the storage of hydrogen being one area of concern. Carbon nanostructures are a potential storage medium, however the reported results vary greatly. This project has developed the equipment and experimental procedure required to obtain reproducible, and thus reliable, results. In particular, calibration techniques and standard materials have been used to achieve this confidence. Physical absorption of hydrogen on carbon surfaces is widely acknowledged as the storage mechanism but the strength of the carbon-hydrogen interaction, storage sites and the amount of hydrogen that can be stored have yet to be established. Therefore, a variety of tailored carbon nanostructures have been studied, with the structure-property relationships and the influence of sample geometry allowing a greater understanding of where hydrogen is stored.

Complex metal hydrides of general formula, AlH₄ (A = alkali metals, B = third group elements such as B, Al, Ga) are potential candidates as hydrogen storage media for transportation. Decomposition of complex hydrides生成氢气 at elevated temperatures. The hy-products of the dehydrogenation process can be regenerated using gases or hydrogenation 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 35-850°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 200°C. Four regions of weight loss and five major endothermic peaks were measured during the thermal analysis. The effect of heating rate on the thermal analysis response showed that a high resolution of the thermal processes could be achieved at higher heating rates. Thermodynamic data were obtained for various 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 probably due to the high compressibility of the diffused H₂. 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 Zhaixi 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, such properties as chemical stability, thermodynamic and kinetic properties etc. have to be improved and strengthened. The formation of ternary nitride of Li₆M-N, where M represents first row transition elements, was reported recently. The replacement of Li₄+ with transition metal ions creates unique properties quite different from those observed in the parent nitride. In this study, standard high temperature ‘ceramic’ method was employed to synthesize a variety of Li₆M₃N-type ternary nitrides, Li₆M-N (M=Ti, V, Mn, Fe, Co, Ni, Cu). Subsequently, the hydrogen storage properties of these ternary nitride have been analyzed with a powder X-ray diffraction and Temperature-Programmed-Desorption (TPD). Powder X-ray diffraction measurement also revealed the phase and composition changes during the hydrogen absorption and desorption processes. Presented paper #BB4.4 to BB4.5 5/9/03/10 LW

11:00 AM #BB4.6 Metal Nitrides and Imides as Viable Hydrogen Storage Materials, Ping Hui, Zhijun Xiao, Koong Lean Tsai, 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 11.6wt% of hydrogen can be absorbed, in which more than half is reversible at temperature above 250 Celsius when operating under a hydrogen pressure ~1.0MPa. 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 progresses in material exploration. Serials of metal nitrides and imides have been synthesized and their hydrogen storage properties have been evaluated. About 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.


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 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 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/nitrogen 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 desorption as well as extent of activation can be extracted from TPR curves. In addition, multiple absorption and desorption steps can be identified from the number absorption or desorption 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. In the near future, 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

Chair: Ping Chen and Gholam-Abbas Nazari

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. Pirillo, Jeffery L. Allemann, A. Huy Mabon, Kim M. Jones, Katherine E.H. Gilbert and Michael J. Heben; Basic Sciences, NREL, Golden, Colorado.

The hydrogen storage properties of carbon single-walled and multi-wall nanotubes (SWNTs and MWNTs), graphitic nanofibers, 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. More recently, incorporation of a metal alloy into pure single-wall nanotubes resulted in carbon/metal composite materials showing capacities of up to ~7 wt% (23). Unfortunately, samples exhibiting high hydrogen storage capacities cannot 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 (HWCVD) 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 150 torr with reactor temperatures of 400 and 550 C for static and flowing gases, respectively. Ferrocene 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 purifed to ~95.5 wt % with minimal structural damage and with a 75 wt % yield. Hydrogen adsorption is observed at near ambient temperatures on as-synthesized MWNTs containing iron nanoparticles. No hydrogen adsorption, however, is observed at near ambient conditions 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. M., Békedah, T. A.; Kim, H. S.; Heben, M. J. 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.; Pirillo, P. A.; Bennet, T.; Allemann, J. L.; Hennayak, G. L.; Jones, K. M. In AIP Proceedings for Hydrogen in Materials and Vacuum Systems: Newport News, VA, 671 (2002) 77. (4) Dillon, A. C.; Mabon, A. H.; Pirillo, P. A.; Allemann, 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, Shigeki Kajiyama1, Shigeruji Tatsuka1, Koji Kise2,1, Yosuke Murakuma2,1, Mutsuyoshi Aka2,1, and Masahumi Atsu1,2.

1Materials Laboratory, 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 volumetric method, with an error less than 0.005% [1]. The measured samples were (1) activated carbon fibers, (A-20, Osaka Gas Chemicals Co., Ltd. and FT30(B-20), Kuraray Chemical Co., Ltd.), (2) single-walled carbon nanotubes (purified HPCO™ SWNTs), Carbon Nanotechnologies, Inc. and 26-40% purity, as-produced SWNTs, MTR Ltd.), (3) multi-wall carbon nanotubes (ground core, Strem Chemicals Inc.), (4) graphite powder (99.997% purity, max. particle size 200nm, Goodfellow Cambridge Ltd.), and (5) vitreous carbon (99.9% purity, particle size 80-200nm, Goodfellow Cambridge Ltd.). The measurements were carried out on the samples of over 1 gram. The highest storage capacity of 0.42wt% was obtained for purified HPCO™ single-walled carbon nanotubes (SWNTs). In these SWNTs, the hydrogen density in pores with a diameter less than 1nm was estimated to be 0.022 g/ml, which corresponds to 31% of liquid hydrogen density in the development of hydrogen storage media was discussed at the meeting. [1] H. Kajjiri et al., Appl.Phys.Lett. 82(2003)1105.


4:00 PM BB5.4 Using nanoporous carbon membranes in fuel cells, Ramamohan Ramanarayanan1, Ramakrishna Rajagopalan1, Henry Foley2 and Thomas E Mallouk1, 2Chemistry, Pennsylvania State University, University Park, Pennsylvania. We have synthesized nanoporous carbon membranes that have monodisperse pores of 4-5 A. 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.

4:30 PM BB5.5 Improving the Hydrogen Absorption/Desorption Properties of Alloy ZK60 by Equal Channel Angular Pressing, Eugenio Smektala, Michael T. Waga, Mirko Freibach1, and Himma Lapidus2, 1Materials 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 same 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 improve the hydrogenation/magnesium niobium 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 alloy processed by an combination of ECAP and HEBM was found to have the highest rate of hydrogen desorption. An interesting feature associated with combined ECAP/HEBM processing is the disappearance of pressure hysteresis with regard to hydride formation/desorption. This hydrogenation behavior is explained in terms of the microstructure of bulk samples and the morphology of dehydrated powders as observed by transmission and high resolution scanning electron microscopies. While other efforts are needed to lower the hydrogen absorption rate 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 commercial ball milling warrant further research in this area.

SESSION BB6: Hydrogen Storage Materials and Applications
Chairs: Ghulam-Abbas Naqui and Ron Young
Wednesday Morning, December 3, 2003
Fairfax B (Sheraton)
8:30 AM BB6.1 Nanomaterials-Based Gas Sensors as Safety Devices for the Hydrogen Storage Industry, Marie-Isabelle Barson1 and Ladh Mertens2, 1SPCT’s UMR CNRS 6588, University of Liéges, Liéges, France; 2CERAMEC R&D, Liéges, France. 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. Many 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 nano-sized metal oxides, we have developed miniature hydrogen sensors using a finely tuned thick-film technology. Operated at 280°C, these low-cost devices are capable of selectively detecting hydrogen in the 10-10,000 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 these sensors with emphasis on the fundamental gas-surface interactions. This work has been partially funded by the European Commission (contract No. BRPR CT95 0092).

8:45 AM BB6.2 Ruthenium as Schottky Metal for Si-Based High Temperature Hydrogen Sensors, Sukiwo Ikeda, Somesh Roy and Chand Kochi, Materials Science Centre, Indian Institute of Technology, Kharagpur, West Bengal, India. Fast and precise detection of hydrogen leakage, much before the onset of its lower explosion limit, is imperative. Schottky diodes and Metal-oxide-glass capacitors have been extensively used to monitor the concentration of hydrogen at elevated temperatures. Palladium and platinum are used as catalytic metals for hydrogen sensors because of the high efficiency of dissociating H2 molecules on their surface. However, above a certain temperature Pd or Pt start reacting with SiC substrate causing a drift in the sensor parameters and leading to the unreliable operation. In addition, the hydrogen content augmentation above a certain concentration leads to the formation of metal hydrides. Therefore, replacement of Pd or Pt by an alternative suitable metal or alloy has been a key issue to the development of stable Schottky sensors for hydrogen detection at high temperatures. Ruthenium (Ru), a member of the platinum metal in group VIII of the periodic table of elements, has the advantage of reacting with SiC and hydrogen gas during high temperature operations. This report presents the sensor response behaviour of the Ru/Si/SiC (epilayer on Si substrate) Schottky junctions studied at different temperatures (200-400°C) in presence of varying concentrations of hydrogen from 5,000 ppm to 20,000 ppm. The output signal of the sensor, the response time and the reversibility were investigated from the transient response characteristics of the
The electrical characteristics and hydrogen response mechanism of a Pd/AIN/Si thin film gas sensor. Erik F. McCullough, H.E. Prinzmann, Wenzuo Mo, Jadhagish Thakur, R. Naik, L. Rimmel, K.Y. S. Ng, and G.W. Auner. Physics, Wayne State University, Detroit, Michigan; ECE, Wayne State University, Detroit, Michigan; Chemical Engineering and Materials Science, Wayne State University, Detroit, Michigan.

The electrical characteristics, sensitivity, and the response time of a hydrogen sensor utilizing a Pd/AIN/Si[Si] structure have been investigated. The AIN layer was deposited by plasma source molecular beam epitaxy (PSMBe), and the Pd and gases 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 ppm 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 AIN, from 250-2000 Å. The C(V) and G(V) measurements were utilized to investigate the presence of surface states within the Si gap at the AIN/Si interface. Our previous investigations on 500Å AIN did show the presence of interface traps, with an estimated surface density between 8x10^12 and 1.5x10^13 μm^-2 at 1.5 V. In our present work we have examined the effect of AIN thickness on the density of these interface traps. The density is strongly dependent on AIN thickness, with the thinner devices showing a density of interface states several orders of magnitude greater than the thicker AIN 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 barrier height, which is consistent with the observed conductance changes in devices.
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

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 10^16 ions/cm². 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 also a significant permanent increase in conductivity caused by the dense dislocation network. The microstructure was characterized with 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 170 nm thick measured from thickness fringes, following heat treatment. TEM taken with weak beam conditions confirms a surface layer about 150 nm thick that contains a high concentration of dislocations. The dislocation density is on the order of 10^5/ cm². 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 n/2(110) (100) 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 ZrO₂ 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. Sébastien Hamel1,2, and Michel Cote1,2. 1Physics, Université de Montréal, Montreal, Quebec, Canada; 2Regroupement Québécois 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 (pseudo-potentials, 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 H2 were obtained that could be compared to the experimental INS spectra. [1] Rosi et al., Science Vol. 308, 1127 (2005)