

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, SINGAPORE
65-874-2982

Maryam Nazri

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

Symposium Support

Chevron Texaco Ovonic Company
Toyota Motor Sales USA, Inc.
U.S. DOE/Hydrogen & Fuel Cells

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

TUTORIAL

FT BB: Hydrogen Storage Materials-Science and Technology
Sunday November 30, 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 emphasis on three main classes of compounds. The fundamentals of 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 be also reviewed. This tutorial does not include hydrogen storage in gas and liquid tanks.

Instructors:

Gholam-Abbas Nazri, General Motors R&D Center
Rosa Chiang Young, Chevron Texaco Ovonic
Chen Ping, National University of Singapore

SESSION BB1: Hydrogen Storage Program and Technology

Chairs: Gholam-Abbas Nazri and Rosa Young
Monday Morning, December 1, 2003
Fairfax B (Sheraton)

NOTE EARLY START

8:25 AM INTRODUCTORY REMARKS - G. ABBAS NAZRI

8:30 AM *BB1.1

USDOE's National Hydrogen Storage Project: Addressing Critical Technology Barriers. Carole J. Read, A. Bouza, L. Cataquiz, J. Milliken, J. Petrovic and S. Satyapal; Office of Hydrogen, Fuel Cells, and Infrastructure Technologies, U.S. Department of Energy, Washington, District of Columbia.

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 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 microspheres, self-assembled nanocomposites, metal-organics, 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 is 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

New Science And Technology: The Basis Of The Hydrogen Economy. Stanford R. Ovshinsky, Energy Conversion Devices, Inc., Rochester Hills, Michigan.

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 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 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 of revolutionary import not only for its societal impact but for the new materials science that it absolutely requires in all of its aspects. New science and new technologies build much needed new industries, which provide not only jobs but feedback on our educational system. Recall that 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 so necessary to make positive, realistic and productive this revolutionary transition of energy from its fossil fuel beginnings to the present.

10:00 AM *BB1.3

The Hydrogen Programs In China. Qidong Wang, Changpin Chen and Lixin 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 recovery, storage, purification and compression for processing hydrogen gas were quite active. For the use of hydrogen, hydrogen powered internal combustion engines and partial substitution of hydrogen for gasoline in IC engines for vehicles were systematically investigated, together with the on board storage of hydrogen in metal hydride hydrogen storage containers. In early nineteen nineties, the attention and interest 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 were 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 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 economy 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. And the development from the more easily and readily carried out projects to more sophisticated and difficult ones are also emphasized.

10:30 AM *BB1.4

Recent Advances in Solid Hydrogen Storage Systems.

B. S. Chao, R. C. Young, V. Myasnikov, Y. Li, B. Huang, F. Gingl, P. Ferro, V. Sobolev and S. R. Ovshinsky; Texaco Ovonic Hydrogen Systems, Rochester Hills, Michigan.

Hydrogen energy offers great promise as an energy alternative in the near future. Additionally, hydrogen technologies 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 states. Solid hydrogen storage systems also have features of low-pressure operation, compact, safe, tailorable deliverable pressure, excellent absorption /desorption kinetics, modular design for easy scalability, and long cycle life. In this paper, solid hydrogen storage systems (such as portable power canisters, lightweight fiber wrapped vessels, and aluminum tubular vessels, developed by Texaco Ovonic Hydrogen Systems LLC) will be discussed. For example, three canisters, 85 g of reversible hydrogen stored in each canister, interfaced with a 1 kW PEM fuel cell can sustain more than 150 min full power run time. The canister showed no plastic deformation after completing 500 charge/discharge cycles. The strain gages 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 APU applications. The lightweight fiber wrapped vessel combined with the high performance metal hydride targets on-board applications. On a system level, the vessel has a volumetric energy density of 50g hydrogen per liter and a gravimetric density of 1.6 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 @ 1500 psig. 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 transportation and shipment, 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 Au, Savannah River Technology Center, Aiken, South Carolina.

In this paper, amorphous/nanostructured composite materials Mg-Ni, Mg-Ni-La, Mg-Ni-Ce, Mg-Mg₂Ni, 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 Pd, 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 compositions, crystal structure, grain size, and the distribution of the catalyst 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%-LaNi₅ 20% 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 controls of the process of dehydrogenation.

11:30 AM **BB1.6**

Hydriding Behaviour of Mg-C Nanocomposites.

Marco Vittori Antisari¹, Amelia Montone¹, Jasmina Grbovic¹, Ennio Bonetti², Luca Pasquini², Alex Bassetti² and Anna Lisa Fiorini²; ¹Materials and Technology, ENEA, Rome, Italy; ²Department of Physics, University of Bologna, Bologna, Italy.

Recently, we can notice an increasing interest in modifying the microstructure of materials for hydrogen storage toward a nanocrystalline structure in order to improve material performances in this kind of application. Nowadays these materials often are 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 characterised by high volume fraction of surfaces-interfaces and a high defects density. Moreover hydrogen sorption can be further accelerated by catalyst addition and easier activation could be observed on nanocomposite Mg-based system. We have investigated magnesium carbon materials for hydrogen storage obtained by mechanical milling for different times graphite and magnesium with different amount 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. 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 BB2: Hydrogen Storage Alloys
Chairs: Ping Chen and Maryam Nazri
Monday Afternoon, December 1, 2003
Fairfax B (Sheraton)

2:00 PM **BB2.1**

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

Arc-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 carriers 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 unfunctionalized 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. Rougier¹, R. Janot¹, X. Darok¹, L. Aymard¹, G. A. Nazri² and J. M. Tarascon¹; 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 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**

Infrared Screening of Combinatorially Prepared Hydrogen Sorbing Metal Alloys. Charles H. Olk, Materials & Processes Lab, General Motors Research Development & Planning, Warren, Michigan.

The investigation of many stoichiometric variations involving large numbers of combinations of elements offers a means to discover a hydride 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 sorption related emissivity changes 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 Nanoparticulates. S. Kishore¹, J. A. Nelson², J. H. Adair², D. E. W. Vaughan² 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 sub-surface. 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 in the pressure range from zero to 20 atmospheres over a range of temperatures from 40C to 100C. 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 these particles at high temperatures, Pd nanoparticles were also studied, that were supported on nanoporous 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-metal hydrides.

4:30 PM **BB2.5**

Properties of the Magnetic Hydride YFe₂H_x From First Principles Calculations. David 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 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 YFe_2 and YFe_2H_x with $x \approx 4$ 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 moments. The mechanism for the moment increase is shown to be related to d band narrowing with the H potential pulling s,p 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 Technology
Chairs: Ping Chen, Maryam Nazri and Rosa Young
Monday Evening, December 1, 2003
8:00 PM
Exhibition Hall D (Hynes)

BB3.1

Hydrogenation of Nanocrystalline Mg-based Alloys.

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

Environmental protection and pollution control will restrict increasingly the use of polluting fossil energy fuels long before their depletion; thus alternative energy sources and devices for high-capacity energy storage must be developed. Metal hydrides are a clean 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 kWh/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 sorption temperatures and unknown cycling life. Recently it was published that the design of improved nanocrystalline Mg alloys can proceed by metal oxides, e.g. V_2O_5 [1] as catalysts. The aim of this paper is to present results on the influence of V_2O_5 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 desorption are still unclear and should be clarified by microstructural investigations in detail. This research focuses on investigating the microstructural/chemical properties relationship in regard to the hydrogenation behavior of nanocrystalline Mg with and without V_2O_5 . [1] W. Oelerich, T. Klassen, R. Bormann, J. Alloys and Comp. 315 (2001), 237 This work was supported by the EU RTN-Network Project HPRN-CT-2002-00208.

BB3.2

Hydrogen absorption of C14 Laves NiTiZr-NiVnNb pseudo-binary alloys. Kazuhiro Ishikawa¹, Shintaro Noda¹, Kiyonori Suzuki² and Kiyoshi Aoki¹; ¹Kitami Institute of Technology, Kitami, Hokkaido, Japan; ²Monash University, Melbourne, Victoria, Australia.

The C14 Laves alloys are attractive candidates for hydrogen storage alloys. In this work, the crystal structures and the hydrogen absorption properties of C14 Laves NiTiZr-NiVnNb 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 $\text{NiTi}_2\text{-NiZr}_2$ 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 $\text{Ni}(\text{TiZr})_{1-x}(\text{VnNb})_x$, the hydrogen desorption temperature remains high with increasing x, although the hydrogen capacity is decreased. However, the hydrogen desorption temperature of the $\text{Ni}(\text{Ti}_{1-x}\text{V}_x)\text{Zr}$ 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. Lioba Jastrow¹, Lyudmila Lyubenova¹, Janez Dolinsek² 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 application. In order to understand kinetics of hydrogen absorption and desorption in more detail, data on hydrogen diffusion are necessary. The aim of this paper is to present hydrogen diffusivities in melt-spun amorphous $\text{Zr}_{69.5}\text{Cu}_{12}\text{Ni}_{11}\text{Al}_{7.5}$ alloys. Hydrogen charging was performed electrochemically in a 2:1 glycerin-phosphoric acid electrolyte. Hydrogen contents were measured by a microbalance with accuracy of $\pm 1 \mu\text{g}$ 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 destruction of the spin echo signal. The analysis of the echo damping allows a model-independent determination of the hydrogen self-diffusion constant, with the low limit of sensitivity $D > 10^{-10} \text{ cm}^2/\text{s}$. 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 $\text{H/M} = 0.2$ 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

$\text{Gd}(1-x)\text{Sr}(x)\text{Co}(1-y)\text{Fe}(y)\text{O}(3-\delta)$ 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 ($\sim 900\text{C}$) 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 500C and 700C. 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. $\text{Gd}(1-x)\text{Sr}(x)\text{CoO}(3-\delta)$ 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, $\text{Ce}(0.8)\text{Gd}(0.2)\text{O}(2-\delta)$ (CGO). $\text{Gd}(0.8)\text{Sr}(0.2)\text{CoO}(3-\delta)$ (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 close to that of the electrolyte ($\sim 13 \text{ ppm/C}$). 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 GSC/CGO composite cathodes resulted in thermal matching with the electrolyte material up to the IT-SOFC operating temperature of approximately 600C with the maintenance of high electrical conductivity. Composite GSC/CGO cathodes reduce the problems associated with poor GSC thermal matching to the electrolyte without compromising other important cathodic properties.

BB3.5

Ab-initio Modeling of Interstitial Mg:H Solid Solutions. Manlio Messina^{1,2}, Fabrizio Cleri¹ and Manuela Volpe¹; ¹Unita' Materiali e Nuove Tecnologie, ENEA, Centro Ricerche Casaccia, Roma, Italy; ²Dipartimento di Fisica, Universita' 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 10⁻⁶at., the enthalpic contribution is negative 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 electron DOS upon H insertion reveals the upward shift of the Fermi level and the creation of deep hydrogen-like states below the metallic

band. The volume local deformations due to H insertion were studied in details.

BB3.6

Preparation and characterization of Pt/IrO₂/YSZ electrodes by MOCVD. Aide Minerva Torres-Huerta² and Jorge Roberto Vargas-García¹; ¹Metallurgical Eng., National Polytechnic Institute, Mexico, D. F., Mexico; ²Metallurgical, National Polytechnic Institute, Mexico, D. F., Mexico.

Ionic/electronic 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 electrode 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 agglomeration of Ni 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 metal/acetylacetonates were used as a source materials. They were mixed and evaporated together. The size of each component calculated from the XRD line/broadening 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 are about 1.0 μm thick. The electrochemical performance of the Pt/IrO₂/YSZ nano-composite electrodes indicate 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 non-ferrous 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-T plateau extends, but the slope of plateau increases. Through SEM, EDS and XRD analysis, it was found that the crystal parameters and cell volume increases, 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/atom of the alloys.

BB3.8

Hydrogen Storage in Carbon Nanostructures.

Baljinder Singh Ghoman and Alan H. Windle; Materials Science & Metallurgy, Cambridge University, Cambridge, Cambridgeshire, 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 costs 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 repeatable, and thus reliable, results. In particular, calibration techniques and standard materials have been used to achieve this confidence. Physical adsorption 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.

SESSION BB4: Hydrogen Storage in ABH₄ and Nitrides
Chairs: Maryam Nazri and Rosa Young
Tuesday Morning, December 2, 2003
Fairfax B (Sheraton)

NOTE EARLY START

8:00 AM *BB4.1

Borazane BH₃NH₃ – a promising hydrogen source. Gert Wolf, Inst. fuer Physikalische Chemie, TU Bergakademie Freiberg, Freiberg/Sachsen, Germany.

Borazane seems to be an interesting material for the use as a hydrogen source. Several properties appear favourable 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 Borazane 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 melting process of BH₃NH₃ residuals 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 also. A controlled hydrogen evolution from BH₃NH₃ 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, Royal Society of Chemistry, Cambridge, UK, 1997, p. 514 [3] G. Wolf, J. Baumann, F. Baitalow, F. P. Hoffmann, Thermochimica Acta 343, 2000, 19-25

8:30 AM BB4.2

Rietveld refinement and ab initio studies of Ti-Doped NaAlD₄ and Na₃AlD₆. 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 compared to structural parameters for undoped NaAlD₄ and NaAlH₄. The refined lattice parameters for the tetragonal NaAlD₄ structure are found to be a=5.010 angstroms and c=11.323 angstroms. Results of ab initio calculations of the lattice parameters are within a few per cent 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 alanates. The Rietveld refinement, LDA, and GGA results for the Al-H bond length in NaAlD₄ are 1.626, 1.634, and 1.631 angstroms, respectively. Refined values of the Al-H bond lengths in Na₃AlD₆, are in agreement within 2% of earlier work on undoped Na₃AlD₆. The calculated GGA formation energies for the decomposition reactions of NaAlD₄ and Na₃AlD₆ are 33.5 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 NaAlH₄ by solid-state NMR. Julie Lynn Herberg¹, Robert S Maxwell¹ 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 Ti-doped NaAlH₄ as a hydrogen storage material has gained attention because of its large weight percentage of hydrogen (~5 %), compared to traditional interstitial hydrides. The addition of transition-metal dopants, in the form of Ti-halides, such as TiCl₃, dramatically improve the kinetics of the absorption and desorption of hydrogen from NaAlH₄. X-ray diffraction studies of Sun et al. [1] have suggested that Ti may be substituting into bulk NaAlH₄. These authors, as well as others, have suggested that the Ti is present as Ti³⁺. Desorption kinetics studies by Majzoub et al. [2] have further suggested that the resultant Ti valence state is independent of the precursor Ti-halide used for doping. However, the role that Ti plays in enhancing the absorption and desorption of H₂ is still unknown. In the present study, ²⁷Al, ²³Na, and ¹H MAS NMR have been performed to understand the structural impact that Ti has on the bulk NaAlH₄ material. All experiments were performed with pure NaAlH₄ and NaAlH₄ doped with Ti to fully understand how the Ti impacts this complex network. ²⁷Al-¹H and ²³Na-¹H double resonance experiments were performed to understand structural changes that occur with the addition of the

Ti-precursor. Also, T1, T2, and multiple quantum ^1H NMR experiments were performed to gather insight into the structure and dynamics of ^1H within Ti-doped NaAlH_4 . [1] D. Sun, T. Kiyobayashi, H.T. Takeshita, N. Kuriyama, C.M. Jensen, *J. Alloys Comp.* 337 (2002) L8-L11 [2] E. H. Majzoub, K.J. Gross, *J. Alloys Comp.*, 1 (2003) in press This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

9:30 AM *BB4.4

Study of Thermophysical Properties of NaAlH_4 .

Bouziane Yebka and G. Abbas Nazri; GM R&D, Warren, Michigan.

Complex metal hydrides of general formula, ABH_4 (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 gaseous hydrogen at suitable temperature and pressure. The initial steps of thermal decomposition of NaAlH_4 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 30-500°C showed that the initial evolution of hydrogen occurred at a slow rate at ~80°C, prior to fast decomposition at 190°C and at 260°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 was obtained for the various steps in the decomposition process including the formation of intermediate phases Na_3AlH_6 , and NaH . We also found that the decomposition of NaH is highly pressure dependent probably due to the high compressibility of the diffuse H^- anion. The crystal-chemistry of NaAlH_4 during decomposition has been established using X-ray diffraction analysis.

10:30 AM BB4.5

Transition Metals Modified Lithium Nitride for Hydrogen Storage. Xiong Zhitao and Chen Ping; Physics, National University of Singapore, Singapore, Singapore.

As a new candidate for hydrogen storage, lithium nitride (Li_3N) 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 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 Li_3N -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 appraised with Pressure-Composition (P-C) isotherms 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 on 9/5/03 LW

11:00 AM BB4.6

Metal Nitrides and Imides as Viable Hydrogen Storage Materials. Ping Chen, Zhitao Xiong and Kuang Lee Tan; 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 Li-N-H system, up to 11.5wt% of hydrogen can be absorbed, in which more than half is reversible at temperature above 250 Celsius when operating under ambient pressure (1.0 bar). 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. 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 Hydrogen Storage Materials By Temperature Programmed Reaction. T. S. Rufael, 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 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, heats of absorption and desorption 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 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 PCT or Sieverts method. Examples of analysis with 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-Abbas Nazri
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. Parilla, Jeffery L. Alleman, A. Harv Mahan, Kim M. Jones, Katherine 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), 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 (1). 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% (2,3). 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 purified to ~99.5 wt% with minimal structural damage and with a 75 wt% yield. Hydrogen adsorption is observed at near ambient temperatures on the 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 nano-particles 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.; Bekkedahl, T. A.; Kiang, C. H.; Bethune, D. 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.; Parilla, P. A.; Gennett, T.; Alleman, J. L.; Hornyak, 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.; Mahan, A. H.; Parilla, P. A.; Alleman, 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. Hisashi Kajiura¹, Shigemitsu Tsutsui¹, Koji Kadono¹, Yousuke Murakami², Mitsunao Kakuta¹ and Masafumi Aya¹; 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 volumetric method, with an error less than 0.04wt% per gram [1]. The measured samples were (1) activated carbon fibers, (A-20, Osaka Gas Chemicals Co., Ltd. and FT300-20, Kuraray Chemical Co., Ltd.), (2) single-walled carbon nanotubes (purified HiPco[®] SWNTs, Carbon Nanotechnologies, Inc. and 20-40% purity, as-produced SWNTs, MTR Ltd.), (3) multi-walled carbon nanotubes (ground core, Strem Chemicals, Inc.), (4) graphite powder (99.997% purity, max. particle size 200mm, Goodfellow Cambridge Ltd.), and (5) vitreous carbon (99.5% purity, particle size 80-200mm, Goodfellow Cambridge Ltd.). The measurements were carried out on the samples of over 1 gram. The highest storage capacity of 0.43wt% was obtained for purified HiPco[®] 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. Issues in the development of carbon-based hydrogen storage media will be discussed at the meeting. [1] H. Kajiuura et al., Appl.Phys.Lett. 82(2003)1105.

3:00 PM BB5.3

A Molecular Dynamics Simulation Study Towards Understanding the Effects of Diameter and Chirality on Hydrogen Adsorption in Singlewalled Carbon Nanotubes. Hansong Cheng², Milen K. Kostov³, Alan C. Cooper¹, Guido P. Pez¹, Steven J. Stuart⁴ and Milton W. Cole³; ¹Corporate Science and Technology Center, Air Products and Chemicals, Inc., Allentown, Pennsylvania; ²Computational Modeling Center, Air Products and Chemicals, Inc., Allentown, Pennsylvania; ³Department of Physics, The Pennsylvania State University, University Park, Pennsylvania; ⁴Department of Chemistry, Clemson University, Clemson, South Carolina.

A force field methodology has been developed for the description of carbon-carbon and carbon-molecular hydrogen interactions that is ideally suited to modeling hydrogen adsorption on single-walled carbon nanotubes (SWNT) [1]. The method makes use of existing parameters of potential functions developed for sp² and sp³ hybridized carbon atoms and allows accurate representation of molecular forces on curved carbon surfaces. This approach has been used in molecular dynamics (MD) simulations for hydrogen adsorption in SWNT. The results reveal significant nanotube deformations, consistent with ab initio MD simulations [2], and the calculated energies of adsorption at room temperature are comparable to the reported experimental heats of adsorption for H₂ in SWNT [3,4]. The efficiency of this new method has permitted the MD simulation of hydrogen adsorption on a wide range of SWNT types, varying such parameters as nanotube diameter and chirality. The results show that these SWNT physical parameters have a substantial effect on the energies of adsorption and hydrogen capacities. [1] M. K. Kostov, H. Cheng, A. C. Cooper, G. P. Pez, Phys. Rev. Lett. 89, 6105 (2002). [2] H. Cheng, G. P. Pez, A. C. Cooper, J. Am. Chem. Soc. 123, 5845 (2001). [3] A. C. Dillon, K. M. Jones, T. A. Bekkadal, C. H. Kiang, D. S. Bethune, M. J. Heben, Nature 386, 377 (1997). [4] M. Shiraishi, T. Takenobu, M. Ata, Chem. Phys. Lett. 367, 633 (2003).

4:00 PM BB5.4

Using nanoporous carbon membranes in Fuel cells. Ramanathan Ramanarayanan¹, Ramakrishnan Rajagopalan², Henry Foley² and Thomas E Mallouk¹; ¹Chemistry, Pennsylvania State University, University Park, Pennsylvania; ²Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania.

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 working 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. Eugen Rabkin¹, Vladimir M Skripnyuk¹, Yuri Estrin² and Rimma Lapovok³; 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 the commercial 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 alloy processed by a combination of ECAP and HEBM was found to exhibit 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 further efforts are needed to lower the hydrogen desorption temperature as well as to apply ECAP method to other hydride forming alloys and intermetallic, 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 Nazri and Rosa 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 Baraton¹ and Lhadi Merhani²; ¹SPCTS UMR CNRS 6638, University of Limoges, Limoges, France; ²CERAMEC R&D, Limoges, 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. Indeed, 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 wide 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 10-10,000 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 the device with emphasis on the fundamental gas-surface interactions. This work has been partially funded by the European Commission (contract No. BRPR-CT95-0002).

8:45 AM BB6.2

Ruthenium as Schottky Metal for SiC-based High Temperature Hydrogen Sensors. Sukumar Basu, Somenath Roy and Chacko Jacob; Materials Science Center, Indian Institute of Technology, Kharagpur, West Bengal, India.

Fast and precision detection of hydrogen leakage, much before the onset of its lower explosion limit, is imperative. Schottky diodes and MOS capacitors have been explored for leak detection and for monitoring 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 and Pt start reacting with SiC substrate causing a drift in the sensor parameters and leading to the unreliable operations. 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 temperature. Ruthenium (Ru), a member of the platinum metals in group VIII of the periodic table, has the advantage of its lower reactivity with SiC and hydrogen gas during high temperature operations. This report presents the sensor response behaviour of the Ru/3C-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

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 potential barrier at the SiC/Si heterointerface, due to a band-offset of ~ 1.2 eV, precludes high injection of thermally generated electrons in Si substrate into the SiC epilayer. So, the performance of the Ru/3C-SiC Schottky devices at high temperature (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 Pd/3C-SiC junctions, the Ru/3C-SiC Schottky sensors showed higher resolution and better reversibility in the hydrogen concentration range 10,000 and 20,000 ppm. The SIMS, RBS and glancing incidence XRD studies indicated that up to 400°C there was no formation of ruthenium silicide at the Ru/3C-SiC interface. Moreover, the formation of ruthenium hydride is not known to be thermodynamically feasible. So, the two major problems associated with the Pd/SiC Schottky sensors could be overcome by using the Ru/SiC structure. Table 1 presents the state of metal/SiC interfaces in the as-deposited and in different annealing conditions.

9:00 AM BB6.3

The Electrical Characteristics and Hydrogen Response Mechanism of a Pd/AlN/Si Thin Film Gas Sensor.

Erik F McCullen^{1,2}, H.E. Prakasam², Wenjun Mo³, Jagdish Thakur², R Naik¹, L Rimai², K.Y.S. Ng³ and G.W. Auner²; ¹Physics, Wayne State University, Detroit, Michigan; ²ECE, 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 gates 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 AlN, 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 AlN/Si interface. Our previous investigations on 500 Å AlN did show the presence of interface traps, with an estimated surface density between 8×10^{14} and 1.5×10^{15} m⁻²eV⁻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 barrier height due to the hydrogen adsorption at the Pd surface and Pd/AlN interface. The amount of adsorption is determined from coupled rate kinetic equations, which depend on the hydrogen partial pressure and other parameters of the device. We have found a very good agreement between the simulated and experimental results for the conductance.

9:15 AM BB6.4

Abstract Withdrawn

10:00 AM BB6.5

Designing A New Generation Of Fuel Cells Using Layer-By-Layer Deposition Of Polyelectrolytes.

Tarek Rafic 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 thickness, structural morphology and catalyst loading. Performance plots characterizing the physical properties of the LBL-fuel cell assembly will be presented and discussed.

10:15 AM BB6.6

The influence of surface reconstruction and C-impurities on photocatalytic water dissociation by TiO₂. Xiliang Nie and Karl Sohlberg; Chemistry Department, Drexel University, Philadelphia, Pennsylvania.

TiO₂ is well known as a prototype photocatalyst for water dissociation. To understand the mechanism of its photocatalytic water dissociation we performed first-principles calculations. We find that the surface reconstruction of the catalytically favorable (TiO) termination is very different from the physically favorable (oxygen) termination. We also find that carbon impurities decrease the band-gap 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 band-gap, are key to understanding the photocatalysis of water dissociation. Possible avenues to improve the efficiency of water dissociation will be discussed based on our calculations.

10:30 AM BB6.7

Structural studies on the perovskite-based La₄Sr_{n-4}Ti_nO_{3n+2}. Jesus Canales, John T. S. Irvine and Wuzong Zhou; School of Chemistry, University of St Andrews, St Andrews, United Kingdom.

Perovskite titanates with nominal stoichiometry ABO_{3+δ} are frequently reported in SOFC literature as having O₃ stoichiometry. Such phases often exhibit quite interesting properties, but are not stoichiometric and the structural characterisation 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 La₄Sr_{n-4}Ti_nO_{3n+2} 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 parental ABO₃ perovskite in crystallographic shears (CS planes). The layered structure was lost for the n=12 member (La₂Sr₄Ti₆O_{19-δ}), a good candidate to substitute Ni/YSZ cermet as anodes in SOFCs due to its high total conductivity under reducing conditions. In this structure, excess oxygen is accommodated within the perovskite framework in randomly distributed short-range linear defects.

10:45 AM BB6.8

Novel Metal-Ceramics Composite Membrane for High Temperature Hydrogen Separation. Caiji Su, Koji Kuraoka, Tetsuro Jin and Tetsuo Yazawa; Special Division for Green Life Technology, National Institute of Advanced Industrial Science and Technology, Kansai center, Osaka, Japan.

Palladium membrane that possesses a thickness of 100 micrometer or several ten micrometers is selective to hydrogen transportation, but its low permeance, hydrogen embrittlement and instability to sulfur limit 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 colloid 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 electroless plating. The membrane had a high hydrogen permeance at 773K (0.7Kmol per hour and per m² at a pressure difference of 1atm) and the selectivity of PH₂/PN₂ was above 300. The preparation process shows that SiO₂ layer has a unique property compared with ZrO₂ for palladium adhering. This was probably due to the formation of Pd₂Si between the SiO₂ and Palladium layers. The seeding process by chemical vapor deposition was significant for the preparation of a defect-free membrane. A novel electroless plating process was also applied using a both of pH=6, which is different with the usually used basic ones containing N2H₄.

11:00 AM BB6.9

Neutron Metrology for Fuel Cell Technology.

Charles F. Majkrzak, Terrence J Udovic, Muhammad Arif and David L Jacobson; NCRN, NIST, Gaithersburg, Maryland.

There are a number of neutron measurement techniques which are particularly well-suited for studying materials of relevance to hydrogen fuel cell membranes 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 can provide direct visualization of water transport through the electrode assembly in operating fuel cells. Complementary refraction 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), respectively. 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 and storage materials can be obtained by neutron diffraction and inelastic scattering methods. Theoretical analysis of these results can contribute to a detailed understanding of

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 AM BB6.10

Ionic Conductivity Enhancement of Solid Oxide Fuel Cell Electrolytes by Heavy Ion Implantation. Jeremy Cheng, Rojana Pornprasertsuk, 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 Xe³⁺ ions over a range of doses from 10¹³ to 10¹⁶ 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 10¹² / 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 a/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 AM BB6.11

Ab initio study of adsorption of molecular hydrogen on microporous metal-organic frameworks. Sebastien Hamel^{1,2} and Michel Cote^{1,2}; ¹Physics, Universite de Montreal, Montreal, Quebec, Canada; ²Regroupement Quebecois de Materiaux 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. 300, 1127 (2003)