

SYMPOSIUM GG

Materials and Technology for Hydrogen Storage and Generation

March 28 - 31, 2005

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TUTORIAL

Materials for Hydrogen Storage and Production
Monday March 28, 2005
2:00 PM - 5:00 PM
Room 2008 (Moscone West)

Hydrogen storage and production are critical issues for hydrogen economy. This tutorial will cover fundamentals of materials design for hydrogen storage and hydrogen production technology. The emphasis will be on solid state hydrogen storage materials including complex chemical hydrides, metal hydrides, carbonaceous materials, porous organic and inorganic systems, composite and hybrid materials. Recent discoveries and new approaches also will be discussed. New analytical tools for characterization of hydrogen storage materials will be discussed. A brief description of government programs and international activities on solid-state hydrogen storage will be covered.

1. A Critical Overview of Hydrogen Storage Materials
2. Government Programs and Approaches toward Hydrogen Storage and Production
3. New Frontiers in Hydrogen Storage Materials
4. Applications of Hydrogen Storage Systems

Instructors:

Gholam-Abbas Nazri, General Motors RD Center
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SESSION GG1: Hydrogen Storage Materials: Metal - Organic Frameworks

Chairs: Gholam-Abbas Nazri and James Wang
Tuesday Morning, March 29, 2005
Room 3018 (Moscone West)

8:30 AM *GG1.1

Hydrogen Storage for Fuel Cell Vehicles: DOE's View on Key Technical Issues. Carole Read¹, Sunita Satyapal¹, Antonio Bouza¹ and John Petrovic²; ¹Office of Hydrogen, Fuel Cells and Infrastructure Technologies, US Department of Energy, Washington, District of Columbia; ²Los Alamos National Laboratory, Los Alamos, New Mexico.

Hydrogen storage systems that enable greater than a 300-mile driving range are critical to the success of the hydrogen economy and hydrogen fuel cell vehicles. At the present time, there is no known hydrogen storage technology that meets all the challenging performance requirements to make hydrogen-powered automobiles competitive with conventional vehicles. Breakthrough and innovative new ideas are needed to meet the system gravimetric and volumetric capacities, fill and discharge rates, and cost targets. To address these critical needs, The Department of Energy has formed a National Hydrogen Storage Project, to be launched in October 2004 (Fiscal Year 2005), with approximately \$150 million in DOE funding over 5 years, subject to congressional appropriations. A summary of the activities of the National Hydrogen Storage Project will be presented, including: Focus areas in metal hydrides, chemical hydrogen storage and carbon-based materials with multiple university, industry, and national lab partners Independent projects on new materials and concepts for hydrogen storage These projects are designed to address the key issues that impact the potential success of hydrogen fuel cell vehicles namely, driving range and technical performance characteristics. Key requirements include discovery and development of materials with both high gravimetric and volumetric capacity, system packaging for optimum conformability, capability for hydrogen re-fill times expected by tomorrow's customers, transient response capability needed when integrated with fuel cell and hybrid fuel cell engines and storage system durability and cycle lifetime. Finally, data will be presented on current DOE hydrogen storage projects and the respective technology's status relative to the DOE system performance targets.

9:00 AM *GG1.2

Cu₂(BPTC)(H₂O)₂(DMF)₃(H₂O): A NbO Type Microporous Metal-Organic Framework with High Hydrogen Sorption (BPTC = 3,3',5,5'-Biphenyltetracarboxylate). Banglin Chen¹, Nathan W. Ockwig², Andrew R. Millward², Damacio S. Contreras¹ and Omar M. Yaghi²; ¹Department of Chemistry, The University of Texas-Pan American, Edinburg, Texas; ²Department of Chemistry, The University of Michigan, Ann Arbor, Michigan.

A NbO type microporous metal-organic framework Cu₂(BPTC)(H₂O)₂(DMF)₃(H₂O)(MOF-504) has been deliberately designed, synthesized and structurally characterized. The X-ray single crystal structure reveals that there exist 1D channels along *c* axis, with alternate cages of about 10.5 and 3.5 Å. The evacuated MOF-504 has a surface areas of 1580 m²/g which can store hydrogen up to 2.5 wt% at 77 K and 1 atm.

9:30 AM GG1.3

Hydrogen Clathrate Hydrate - Novel Hydrogen Storage Material: Crystal Structure, Kinetics, and Phase Diagram. Konstantin A. Lokshin¹, Yusheng Zhao¹, Duanwei He¹, Wendy L. Mao^{3,2}, Ho-Kwang Mao², Russell J. Hemley², Maxim V. Lobanov⁴ and Martha Greenblatt⁴; ¹LANSCE-12, Los Alamos National Laboratory, Los Alamos, New Mexico; ²Geophysical Laboratory, Carnegie Institution of Washington, Washington, District of Columbia; ³Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois; ⁴Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, New Jersey.

The detailed crystal structure information for the hydrogen clathrate hydrate was determined by neutron diffraction as a function of temperature (10-300 K) and pressure (1-2000 bar) for the first time. We found that hydrogen occupancy in the (32+X)H₂*136H₂O, x=0-16 clathrate can be reversibly varied by changing the large (hexakaidecahedral) cage occupancy between 2 and 4 molecules, but keeping single occupancy of the small (dodecahedral) cage in the sII structure. Above 130-160K the guest hydrogen molecules were found in the delocalized state, rotating around the centres of the cages. Decrease of temperature results in the rotation freezing followed by a complete localization below 50 K. We have discovered an extremely fast method of the clathrate synthesis, which allows the complete hydrogen hydrate formation in minutes. The influence of substitutions of different entities for hydrogen on the clathrate structure and stability was studied. High hydrogen capacity (up to 3.77 mass % at ambient pressure), fast kinetics, and readily accessible P-T range are the features that make hydrogen clathrate an excellent candidate for a hydrogen storage material.

10:30 AM *GG1.4

Regeneration of Ammonia-Borane Complexes for Hydrogen Storage. Nahid Mohajeri and Ali T-Raissi; Florida Solar Energy Center, University of Central Florida, Cocoa, Florida.

With funding from the National Aeronautics and Space administration - Glenn Research Center, a research program is underway at the Florida Solar Energy Center that aims to develop a high-density hydrogen storage system based on amine-borane (AB) complexes. Due to their high hydrogen capacity, these hydrides have been employed, in the past, as disposable hydrogen sources for fuel cell applications. However, to meet the requirements for on-board hydrogen storage, it is essential that cost effective and energy efficient methods for the regeneration (i.e. hydrogenation) of the spent (dehydrogenated) AB complexes can be found that utilize only hydrogen and/or electricity (i.e. acceptable hydrogen economy energy currencies) for their regeneration and reuse. Ammonia-borane (H₃BNH₃) is the simplest stable AB with the highest hydrogen content (about 19.6 wt%), having a volumetric energy density of about 4.94 kWh/L vs. 2.36 kWh/L for liquid hydrogen. At room temperature and atmospheric pressure, it is a white crystalline solid, stable in water and ambient air. Its thermolysis begins at temperatures below 140 degrees centigrade and the overall process is exothermic but heat needs to be supplied to activate the material. We are studying two ammonia-borane-based systems with high hydrogen storage capacity. One system employs borazine-cyclotriborazane cycle. Borazine is a product of NH₃BH₃ thermolysis. Cyclotriborazane is the inorganic analog of cyclohexane. Cyclotriborazane is stable in both solid state and in solution, and does not dehydrogenate unless heated to above 100 degrees centigrade. Second system involves polymeric AB complexes such as poly-(aminoborane) and polyborazylene. Poly-(aminoborane), an inorganic analog of polyethylene, is also a product of NH₃BH₃ thermolysis. Polyborazylene is the product of borazine thermolysis. Prior studies have shown that polyborazylene consists of a combination of linear; chain branched, and fused cyclic segments. For these systems, we are investigating two regeneration (i.e. reduction of borazine, poly-(aminoborane) and polyborazylene) approaches. They are: 1) catalytic hydrogenation and 2) indirect (multi-step) synthesis. Results obtained to-date will be presented and discussed.

11:00 AM *GG1.5

Hydrogen Storage in Complex Chemical Hydrides (ABH₄) for Fuel Cell Application: Structural Studies by Raman Spectroscopy and X-ray Diffraction. Daniel Ross¹, Maryam Nazri¹, Ricardo Aroca¹ and Gholam-Abbas Nazri²; ¹Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada; ²GM Research and Development Center, General Motors Corporation,

Warren, Michigan.

Complex chemical hydrides with general ABH₄ formula (where A = alkaline and alkaline earth metals, and B is usually group III such as B, Al or Ga) are potential hydrogen storage materials. Some of the advantages of this class of compounds are high hydrogen sorption capacity and tolerance to compositional modification, particularly substitution on the A and B sites. Thermophysical properties of ABH₄ can be tuned to generate hydrogen at the desired temperature-pressure ranges by elemental substitution on the A and B sites. The kinetics of this class of compounds also can be improved by doping the materials with early transition metals. In order to understand the nature of bonding and detail mechanism of hydrogen sorption, we have studied the local structure of this class of compounds by vibrational spectroscopy and their long range order was explored using x-ray diffraction. In this study, we report elemental substitution and formation of new phases in ABH₄ type compounds. Results of temperature dependent vibrational spectroscopy (Raman) will be presented. The spectroscopic data are complemented with x-ray diffraction data for full structural characterization. The interpretation of the spectroscopic information and x-ray diffraction data are aided by cluster-based density functional theory calculations, to obtain energetic, structural, and vibrational data, with attention given to the relative energies during decomposition of ABH₄ compounds. Characteristic assignment of the vibrational bands of all the states is made. Internal modes due to the solid state are identified, and the vibration data is used to track changes during the hydrogen sorption process. An attempt is made to identify the effect of Ti doping in new materials as can be extracted from spectroscopic data, crystallographic simulation, and computational studies, allowing for the use of spectroscopic probes for future physicochemical studies.

11:30 AM **GG1.6**

The Study of the Destabilized Metal Borohydrides for Reversible Hydrogen Storage. Ming Au, Savannah River National Laboratory, Aiken, South Carolina.

Alkali metal borohydrides such as LiBH₄ and NaBH₄ hold large amounts of hydrogen (18.5wt% and 10.6wt%) more than alanates (7.5wt%) and other conventional metal hydrides (1.4~1.8 wt%). Unfortunately, heating above 400°C is required to release the hydrogen, which is over its melting point. The feasibility of rehydrogenation has also not adequately been studied and demonstrated. Currently, these hydrides have been used as on-demand hydrogen sources through an irreversible catalyzed hydrolysis and are marketed commercially. However, there is a promising opportunity that the alkali metal borohydrides can be destabilized to release hydrogen at lower temperature and then be recharged at moderate condition. In our investigation, the destabilized LiBH₄ releases 9 wt% hydrogen starting from less than 100°C. The materials are also reversible in dehydrogenating and rehydrogenating cycling tests. The destabilized borohydrides absorb 9 wt% hydrogen after dehydrogenating. About 6 wt% hydrogen was reclaimed from rehydrogenated borohydrides. This paper will present our results in the effort to reduce the thermodynamic stability and improve the kinetics of borohydride dehydrogenation. To understand the mechanism of the destabilization, the theoretic simulation of the thermodynamics and bonding energy of the modified LiBH₄ and corresponding data of the materials characterization will be discussed in this paper.

SESSION GG2: Hydrogen Storage Materials: Metal:
Complex Chemical Hydrides
Chairs: Ping Chen and Rosa Young
Tuesday Afternoon, March 29, 2005
Room 3018 (Moscone West)

1:30 PM **GG2.1**

A Density Functional Theory Study of the Catalytic Role of Transition Metal Atoms in Reversible Hydrogen Storage in the Complex Metal Hydride, NaAlH₄. Santanu Chaudhuri and James T. Muckerman; Chemistry, Brookhaven National Laboratory, Upton, New York.

NaAlH₄ is a reversible hydrogen storage material. The reversibility is achieved by doping NaAlH₄ with ~2 wt.% Ti. Despite the heightened interest in the role of Ti in this complex multi-step process, the mechanism is still unclear. We have looked at the reverse reaction, i.e., the rehydrogenation reaction, for evidence of the probable surface catalytic role of the Ti dopant. Rehydrogenation starts from a mixture of nanoscale particles of metallic Al and NaH, and neither of these phases has an affinity for reacting with molecular hydrogen. Our Density Functional Theory (DFT) calculations show dissociation of molecular hydrogen aided by a particular arrangement of Ti atoms on the surface of Al-metal. The Al(001) surface is found to be ideally suited for a reaction of this kind. The molecular hydrogen is first

dissociated to form an Ti-H-Al-H-Ti bridge bond followed by migration of the atomic hydrogen. The overall reaction is exothermic and spontaneous. The energetics of the reverse reaction on the doped Al(001) surface and the mechanism of hydride formation will be discussed using DFT and first principles molecular dynamics simulation results. The particular arrangement of Ti atom required for this process is also supported by experimental EXAFS and diffraction evidence that will be discussed in the light of our theoretical results

2:00 PM **GG2.2**

Hydrogen Absorption & Desorption over Alkali Metal Amide-Hydride Systems. Zhitao Xiong, Jianjiang Hu, Guotao Wu and Ping Chen; Physics, National University of Singapore, Singapore, Singapore.

In the recent investigations of hydrogen storage in lithium nitride, lithium imide and Li₂MgN₂H₂ ternary imide systems, we found that after hydrogenation the solid products comprises of amide and hydride of corresponding metal(s). Hydrogen desorption from the mixture of amide and hydride could take place at temperatures much lower than those for the dissociation of the pure amide and hydride. In this presentation, interaction between varieties of amides and hydrides, such as Mg(NH₂)₂-NaH, Mg(NH₂)₂-CaH₂ and Mg(NH₂)₂-MgH₂, will be examined. It shows that hydrogen desorption occurs very easily over the above three systems. Mg(NH₂)₂-MgH₂ system, as an example, even releases substantial amount of hydrogen near room temperatures. However, certain barrier exists in the re-hydrogenation of post-desorbed Mg(NH₂)₂-CaH₂ and Mg(NH₂)₂-MgH₂ samples. Mg(NH₂)₂-NaH system, on the other hand, can be reversible. Hydrogen absorption occurs at temperatures as low as 60°C with 2wt% capacity. Further exploration into a broader range of amide&hydride system is necessary to filtrate suitable materials for hydrogen storage.

2:30 PM **GG2.3**

Effect of Molecular Mixing on Hydrogenation Process of Complex Chemical Hydrides. Bouziane Yebka and Gholam-Abbas Nazri; Energy Storage System, General Motors Corporation, Warren, Michigan.

In recent years, the high performance complex chemical hydrides have been developed as hydrogen storage media. Most attention has been given to catalyzed NaAlH₄ system, because of its high hydrogen sorption capacity. The improved hydrogenation dehydrogenation of this class of compounds has been reported by effective doping of various catalysts, particularly the early transition metals (Sc, Ti, V). However, the hydrogenation reaction still requires long time and high pressure. We report the positive effect of new mixing technique to enhance the kinetics of hydrogenation-dehydrogenation process for NaAlH₄. Results of improved hydrogenation dehydrogenation cycles using the new mixing technique will be reported. The effect of mixing on various phases formed during decomposition will be discussed.

3:30 PM **GG2.4**

Electron Microscopy Studies of Lithium Aluminium Hydrides With and Without Ti- and V-Based Additives.

Carmen M. Andrei^{1,3}, John C. Walmsley⁴, Hendrik W. Brinks², Randi Holmestad¹, Didier Blanchard², Bjorn C. Hauback² and Gianluigi A. Botton³; ¹Physics, Norwegian University of Science and Technology, Trondheim, Norway; ²Institute of Energy Technology, Kjeller, Norway; ³Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada; ⁴SINTEF Materials and Chemistry, Trondheim, Norway.

Complex hydrides of aluminium (alanates) are one of the most promising compounds for hydrogen storage due to their low weight and high hydrogen storage capacity. Addition of transition metals improves the hydrogen release and may also provide reversibility of the decomposition process. The role of the transition metal in the reaction kinetics as a catalyst or a dopant is not yet understood. In this work, the microstructure of LiAlD₄ with and without TiCl₃·1/3(AlCl₃) and VCl₃ additives has been studied in different steps of the decomposition process using electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS) in a scanning transmission electron microscope (STEM). Energy filtered transmission electron microscopy (EFTEM) was used to show elemental distributions in the samples. The spatial distribution of the additives and the main elements within the alanate particles was examined with a resolution of a few nanometers. The analysis of the electron energy loss spectra reveals the chemical state of Al, O and the additives. Ti and V do not appear to mix chemically with Al to significant degree. For all the Ti additive conditions studied, it was found that Ti was distributed relatively uniformly between the particles. However, in the samples containing V, most of the additive was in the form of VO or V₂O₃ and it was found highly concentrated in just a few particles. EELS and EDS mapping suggest that Ti is distributed preferentially at particle surfaces. In high V containing

particles, the transition metal was present in a significant proportion of the particle bulk. It is difficult to say whether the opportunities to enhance the decomposition kinetics are better for V than for Ti because V is highly concentrated in the particles. All the samples showed evidence of oxidation, in spite of procedures being adopted to avoid exposing the material to air. Al₂O₃ forms a thin layer at the surface of the particles. The different types of oxides may influence the kinetics of the process, particularly where the oxide form preferentially at the sample surface and where the additive has different oxidation state.

4:00 PM GG2.5

Promotion of H₂ Sorption at Al-Ti Alloy Surfaces in Al₃Al₂ Storage Materials. Roland Stumpf, Sandia National Laboratories, Livermore, California.

The rates of ad- and desorption of H₂ at metal surfaces and the effect of H on mass transport at these surfaces are critical for the uptake and release kinetics of complex hydride storage materials like Ti-doped NaAlH₄. Simple metals (e.g. Li, Mg, Al) are the main constituent of light complex hydride H storage materials. However, they do not by themselves readily react with H₂. Transition metals (e.g. Ti, Ni, Pd) on the other hand are known to catalyze H-chemistry, but we need to understand how to transfer this property to alloys with simple metals. Our first principles calculations indicate that alloys of Al and Ti bind H differently than either metal alone. At exposed Ti in an Al matrix we find very low barriers for H₂ dissociative adsorption and recombinative desorption, in part caused by a novel molecular chemisorption state for H₂. Ti atoms also activate neighboring Al atoms for bonding with H. We find for example that pure Al surfaces that have Ti atoms substitutionally incorporated in the 2nd layer split H₂ more readily and bind H more strongly than pure Al. We will also discuss how high H₂ pressures typical for storage operations affect the stability of Al-Ti surface structures, which will in turn affect the catalytic activity of the Al-Ti surface alloy. Finally, I show how H facilitates Al mass transport through the formation of mobile AlH_x species. Some of the concepts suggested by theory are investigated by our UHV and high pressure experiments.

4:30 PM GG2.6

Abstract Withdrawn

SESSION GG3: Poster Session: Hydrogen Storage
Materials: General

Chairs: Gholam-Abbas Nazri and James Wang

Tuesday Evening, March 29, 2005

8:00 PM

Salons 8-15 (Marriott)

GG3.1

Hydride Hydrogen-Compression Alloys and High-Pressure Hydrogen Compressors for Hydrogen Refuelling Station.

Xinhua Wang and Changpin Chen; Department of Materials Science and Engineering, Zhejiang University, Hangzhou, China.

It is well known that metal hydrides can be used to compress hydrogen. In the present study, the rare earth based AB₅ type hydrogen storage alloys (Mm-MI-Ca)(Ni-M)₅, (M=Mn,Al,Fe,Zr), have been studied for the purpose of high-pressure hydrogen compression and two alloys with favorable hydrogen storage properties have been selected. Some techniques to improve the heat and mass transfer of the metal hydride bed were investigated and several types of metal hydride high-pressure compressors were designed and built with the hydrogen capacity from 20 L to 24 Nm³ and product hydrogen pressure in the range of 12-40MPa. With boiling water as the heating media the compressors can produce hydrogen with pressure of 12-15 MPa and purity of 99.9999% hydrogen from the hydrogen source at initial pressure of 3-5 MPa and purity of 98% hydrogen. With oil as the heating media the developed compressors can compress hydrogen from initial hydrogen pressure of 3-5 MPa to product pressure of 40 MPa. Each of these metal hydride hydrogen compressors is a combination of a compressor and a hydrogen purifier. They are competent for hydrogen refueling for the on board hydrogen storage units of fuel cell vehicles, including high-pressure hydrogen tanks and metal hydride hydrogen storage units, and will become a prospective key apparatus for hydrogen refueling station.

GG3.2

Alternative Solvents for Chemical Hydrogen Storage

Compounds. Mohamed Abdul¹, Hasan Atiyeh², Brant Peppley³, Philip Jessop⁴ and Boyd R. Davis^{1,2}; ¹Chemical Engineering, Queen's University, Ontario, Canada; ²Kingston Process Metallurgy, Kingston, Ontario, Canada; ³Chemistry and Chemical Engineering, RMC, Kingston, Ontario, Canada; ⁴Chemistry, Queen's University, Kingston, Ontario, Canada.

Currently, experiments are under way to determine the following criteria of sodium borohydride in the non-aqueous medium: solvability of sodium borohydride; reaction kinetics of the sodium borohydride hydrolysis reaction; and the potential formation of complex species. Boron NMR and H NMR are used to determine the presence of new complex species formed in the non-aqueous medium, as well as to determine the degree to which sodium borohydride solvates. The kinetics of the hydrolysis reaction will be determined using the hydrogen evolution method, in which the rate of hydrogen produced would be known from a known sample of non-aqueous medium containing sodium borohydride. These experimental results would establish the viability of using non-aqueous compounds as inert solvents to facilitate the rapid release of hydrogen from sodium borohydride. The use of a non-aqueous solvent means that hydrated compounds will not be formed upon release of hydrogen, and it is likely that a catalyst will not be required. The hydrolysis reaction would be conducted in the inert non-aqueous medium in which the concentration of the reactants - for example, water and sodium borohydride - would be controlled. Since the reactants are not pre-mixed, the hydrogen storage density could be expected to be significant, since solid feed could be used.

GG3.3

Hydrogen Sorption Measurements on Carbide Derived

Carbons. Ranjan Kumar Dash, Gleb Yushin and Yury Gogotsi; Department of Materials Science and Engineering and A.J. Drexel Nanotechnology Institute, Drexel University, Philadelphia, Pennsylvania.

Carbide derived carbons (CDCs) represent a new class of porous carbons produced by thermo chemical etching of metal atoms from carbides. CDCs have BET specific surface area of up to 2000 m²/g and up to 80% open pore volume available to hydrogen storage. The structure and the porosity of the resultant carbon can be controlled by the structure of the carbide precursor as well as the process parameters including synthesis temperature and environment. These properties, combined with very low cost, make CDC a potential candidate for hydrogen storage. In this work, CDCs produced from B₄C, ZrC and other carbides were evaluated according to their hydrogen storage capacity. Hydrogen sorption measurements were performed at 77K up to a pressure of 1 atm by a volumetric method using Quantachrome Autosorb-1. The amount of hydrogen adsorbed at atmospheric pressure reached 2 wt.%. The influence of carbon structure, pore size and surface termination on the efficiency of hydrogen sorption will be discussed.

GG3.4

Development of Ni-YSZ and NiO-YSZ Composites for a Cathode in High Temperature Electrolysis by Mechanical Alloying. Hyun Seon Hong, Ui-Seok Chae and Soo-Tae Choo; Institute for Advanced Engineering, Yongin, South Korea.

Modified Ni/YSZ cermets for a cathode that can be used in high temperature electrolysis were synthesized by the ball milling of Ni and YSZ powder and by the ball milling of NiO and YSZ powder followed by the reduction of NiO. Effects of milling time and environment on microstructures and electrical conductivity of powders ball-milled in dry process and in ethanol were investigated by XRD, SEM, TEM and 4-point probe. XRD patterns for both the dry and wet ball-milled powder showed that the Ni/YSZ composite was composed of crystalline Ni (NiO in case of NiO/YSZ composite) and YSZ particles up to 72-h millings. Dry-milling increased the average particle size in both the composites while wet-milling reduced the average size. As the milling time increased, little change in the particle size was observed in the dry-milled powder whereas the particle size decreased in the wet-milled powder. Especially, very fine particles less than 0.1 micrometer were observed in the wet-milling condition. From the TEM analysis, these fine particles were revealed to be YSZ particles. After annealing at 900 oC in air for the Ni/YSZ composite and in hydrogen for the NiO/YSZ composite, the electrical conductivities of the composites were enhanced. Particles became denser and more closely contacted after sintering, creating better electron migration paths.

GG3.5

Nanocomposites with Carbon Nanotubes Aligned in High Magnetic Field for Hydrogen Storage Applications.

Arun Kumar^{1,2}, Michael U. Jureczyk^{1,2}, Ashok Kumar^{1,2}, Sessa S. Srinivasan², Matthew T. Smith² and Elias K. Stefanakos²; ¹Nanomaterial and Nanomanufacturing Research Center, University of South Florida, Tampa, Florida; ²Clean Energy Research Center, University of South Florida, Tampa, Florida.

Carbon nanotubes (CNT) possess exceptional mechanical, electrical and thermal properties due to their nanoscale dimension and unique chemical structure. Particularly, SWNTs are considered the most promising reinforcement materials for high performance and

multifunctional nanocomposite development. However, due to the nanoscale dimension and intensive van der Waals interactions of the nanotubes, nanocomposites made by directly and randomly mixing SWNTs with a polymer resin have poor tube dispersion, low tube loading and lack in nanotube orientation. SWNT suspensions were made under high magnetic fields stacked in multiple layers and cured to make nanostructured materials with desirable tube orientation. The resultant composites have controlled in-plane tube orientation and high tube loading. In the present approach polyaniline based conducting nanocomposites were prepared with a metal oxide such as SnO₂, and then doped with carbon nanotubes as well as modified fullerenes. Carbon nanotubes as well as fullerenes have been shown to absorb as much as 60 wt% hydrogen and 28g of hydrogen per mole of fullerene, respectively. This is due to the high surface to volume ratio of these carbon structures. Using a high magnetic field, the carbon nanotubes are aligned in the conducting nanocomposite in the direction of the magnetic field. The effects of carbon nanotube alignment in nanocomposites on hydrogen adsorption and desorption are investigated. The nanocomposites containing carbon nanotubes aligned in specific directions were characterized with SEM, FTIR and TEM to understand the effect of alignment. The hydrogen adsorption and desorption efficiency of aligned nanocomposite was compared with nanocomposites of the same chemical consistency without alignment. Additional experiments are under progress in our laboratory. This work is supported by DOE grant DE-FC36-04G014224.

GG3.6

Elaboration of Nano Oxides by Ball Milling to be used as Additives for Magnesium Based Mixtures for Hydrogen Storage Application. Jean-Louis Bobet, Jean-Francois Silvain and Jean-Marc Heintz; ICMCB-CNRS, Pessac, France.

In order to be able to use magnesium as hydrogen storage, kinetics properties have to be largely improved. Mechanical Grinding and especially Reactive Mechanical Grinding have been used for that purpose as well as introduction of many additives. After reviewing briefly the results of the literature, oxides appear as one of the most interesting additive family. Moreover, synthesis of nano objects are also becoming of first importance today regarding to the development of nano technologies. Therefore the processes presented in this communications RMG and supercritical fluid (SCF) are interesting. The aim of this work was to synthesize nano oxides to be used as additives in hydrogen storage applications. First we will show how the nano oxides Cr₂O₃ and CeO₂ could be synthesized directly by ball milling and second we will discuss the role of both ball milling conditions and initial product characteristics. In the case of nano CeO₂, the results obtained will be compared with that obtained with the classical co-precipitation method, usually used. It will be showed that ball milling is an interesting alternative route to produce such nano particles. For nano Cr₂O₃, a new technique has been used: the supercritical fluid (SCF) process. This method has been widely used to produce copper coated powders and to produce some metallic nano materials (especially Pd and Cu). It will be shown here that it is also a very suitable route to produce nano Cr₂O₃. It even appears that SCF process allow to obtain a more pure and fine product. However the drawback of the SCF method is the cost of both the initial product and the experiment itself. All results will be discussed in term of morphology (SEM, granulometric analysis and zeta potential), crystallinity (XRD including the determination of both lattice strains and crystallites size, TEM) and of efficiency on catalysing the hydrogen sorption reaction (hydriding/dehydriding kinetics).

GG3.7

The Influence of Hydrogen on the Electrical and Photoelectric Properties of Photodiodes Based on Indium Monoselenide. Stepan Drapak, Vasyl Kaminskii, Zakhar Kovalyuk and Victor Netyaga; The National Academy of Sciences of Ukraine, Frantsevich Institute of Material Sciences Problems, Chernivtsi, Ukraine.

Electrical and photoelectric characteristics of photosensitive structures based on layered p-InSe are investigated depending on degree of the intercalation with hydrogen of the basic semiconductor. It is found that the increase of hydrogen amount in indium selenide leads to the improvement of diodic properties in metal-dielectric-semiconductor structures whereas in Mott diodes the rectification becomes worse and even vanishes. The reasons of such changes of the electrical characteristics for the investigated structures are discussed on the base of their band diagrams. The spectral noise density $S(f)$ was measured at low frequencies. It is established that that in the investigated structures the $1/f$ noise is dominating one but the $S(V)$ dependence on bias voltage V differs from the initial samples. The obtained results are discussed from the point of view of the insertion of hydrogen into interlayer spaces of the basic semiconductor.

GG3.8

Novel Metal-Organic Frameworks: Microwave Crystallization and Structure. Nevenka Rajic^{1,2}, Natasa Zabukovec Logar¹, Sanja

Sajic², Djordje Stojakovic² and Venceslav Kaucic^{1,3}; ¹Inorganic Chemistry, National Institute of Chemistry, Ljubljana, Slovenia; ²Faculty of Chemical Technology and Metallurgy, University of Belgrade, Belgrade, Yugoslavia; ³Biotechnical Faculty, University of Ljubljana, Ljubljana, Slovenia.

Recently, a considerable interest has been directed towards the synthesis of hybrid organic-inorganic solids, which exhibit an enhanced structural versatility, original electronic, magnetic and optical properties. Also, some of these crystalline metal-organic frameworks can reversibly occlude large amounts of gases, which makes them suitable for gas storage materials for hydrogen-fueled vehicles and portable electronics. Rigid aromatic dicarboxylates have been explored as appropriate building units for construction of organic backbone, while zinc ions because of their ability to accommodate various coordination modes, have usually been selected to generate open architecture. Here we report the synthesis and structures of two metal-organic frameworks ZnBDC-I and ZnBDC-II (BDC - 1,4-benzenedicarboxylate). Both compounds have been isolated after crystallization of a mixture containing zinc nitrate, Na₂BDC and water. The crystallization was performed under microwave heating for 1 hour at 180 deg. C. The structure of I consists of metal-organic zigzag chains in which tetrahedral Zn centres are linked by BDC acting as bridging bidentate ligands. The structure of II is a 3-D network arising through interconnection of the square-pyramidal Zn units and BDC ions. Each BDC is coordinated to four Zn atoms. It seems likely that interactions between zinc centres and the terminal C=O groups of the chains in I lead to the formation of the 3-D open framework II. This structural relationship between I and II gives an insight into the possible pathways in the building process of metal-organic networks. In accord with this observation it includes a transformation of 1-D chain to 3-D open framework. (Crystal data for I are as follows: monoclinic system, C 2/c, a=1.50262(6), b=0.50422(2), c=1.21132(6) nm, beta=103.900(2)deg.; for II - monoclinic system, C 2/c, a=1.79978(5), b=0.63647(1), c=0.72657(2) nm, beta=91.467(1)deg.).

SESSION GG4: Hydrogen Storage Materials: Complex Chemical Hydrides

Chairs: Ping Chen and Maryam Nazri
Wednesday Morning, March 30, 2005
Room 3018 (Moscone West)

8:30 AM GG4.1

Atomic and Electronic Structure of Alkali Borohydrides: An Ab Initio Study. W. Gempel¹, Nicholas Kiousis¹ and Dimitrios

Papaconstantopoulos²; ¹Physics, California State University Northridge, Northridge, California; ²Center for Computational Materials Science, Naval Research Laboratory, Washington D.C., District of Columbia.

Alkali borohydrides MBH₄ (M = Na, K) have attracted great interest recently due to their potential applications as hydrogen storage materials and energy carriers for fuel cells due to the extremely large gravimetric capacity. At low temperature the compounds crystallize with a tetragonal structure having P4₂/nmc symmetry in which the [BH₄]- complexes are ordered. We have carried out total-energy ab initio electronic structure calculations based on the Projector Augmented Wave (PAW) method to calculate the atomic and electronic structure of this series. The lattice constants and various bond lengths are in good agreement with experiment. Results of the trend of the heat of formation for the hydriding/dehydriding reactions, the band structure, the density of states, and bonding properties of the [BH₄]- complexes will be discussed. *Supported by NASA grant award, NCC5-513

9:00 AM GG4.2

Synthesis and Characterization of Nanoscale Transition Metal Complex for Hydrogen Storage. Sessa S. Srinivasan¹, Matthew

T. Smith¹, Elias K. Stefanakos¹, Deepak Deshpande², Yogi Goswami², Michael Jurczyk^{1,3}, Arun Kumar^{1,3} and Ashok Kumar^{1,3}; ¹Clean Energy Research Center, College of Engineering, University of South Florida, Tampa, Florida; ²Solar Energy and Energy Conversion Laboratory, College of Engineering, University of Florida, Tampa, Florida; ³Nanomaterials and Nanomanufacturing Research Center, College of Engineering, University of South Florida, Tampa, Florida.

The development of light weight hydrogen storage systems with high volumetric and gravimetric hydrogen densities is indeed essential for the on-board fuel cell vehicular applications. Among the different hydrogen storage systems designed and developed so far, Ti-doped sodium aluminum hydrides exhibit potential promise of reversible hydrogen storage capacity (4-5 wt.%) at moderate temperatures. However, the poor cyclic stability of these hydrides due to the partial reversibility of the two step reactions necessitates the development of

exotic materials or tailoring the known hydride systems. On the other hand, transition metal complex hydrides, TMH_x ($T = \text{Mg}$; $M = \text{Fe}$, Co , Ni) have also been identified as potential candidates for hydrogen storage. These hydrides especially Mg_2FeH_6 , have shown excellent cyclic capacities (more than 500 cycles) even without a catalyst. Besides, Mg_2FeH_6 possesses the highest volumetric and gravimetric hydrogen densities of 150 kg/m^3 and $5.6 \text{ wt.}\%$ respectively. However, at low temperatures, the rate of release of hydrogen and the effective reversible hydrogen capacity seems poor. Recent reports declared that the enhancement in the cycling kinetics and reduction in the operating temperature is very much possible by using a distorted nano-scale Mg structure, catalyst doping and/or lattice substitution. Keeping these facts in view, the present investigation aims to improve the sorption kinetics and thermodynamics of Mg_2FeH_6 , by 1) preparing nano-scale Mg-Fe-H system using mechano-chemical synthesis process and chemical formulation approach, 2) surface localized catalyst (Ti-species) doping and 3) cationic substitution of Na^+/Li^+ for Mg^{2+} by incorporating NaH/LiH . The synergistic behavior of the tailored nano-scale transition metal complex for hydrogen storage is outlined.

9:30 AM GG4.3

Beyond Weight Percent - The Influence of Material Characteristics on Hydrogen Storage System Performance.
Daniel A. Mosher and Donald L. Anton; UTC Fuel Cells Program, United Technologies Research Center, East Hartford, Connecticut.

The attribute of solid state hydrogen storage materials that is most commonly the focus of evaluations is reversible hydrogen weight percent. Other material characteristics, including density, charging pressure, enthalpy and conductivity can strongly influence the weight of storage system components and hence the overall hydrogen weight percent that is ultimately of interest. However, accounting for these effects involves some level of storage system representation that typically is not undertaken when making material assessments and comparisons. The current paper will present a number of simplified models that represent system elements and trade-offs on a high level so that overall system performance can be estimated without the burden of detailed design studies. These models should be useful to evaluate novel materials in a more complete manner for a better assessment of their potential when implemented in a storage system. While the models have been derived during the design of a particular NaAlH_4 system, the key attributes are sufficiently general to be applicable to a wide range of system types. Using this approach, the properties of materials can be related more precisely to goals for overall system performance with modest additional effort.

10:30 AM GG4.4

Practical Sorption Kinetics of Several NaAlH_4 Compositions.
Xia Tang, Donald L. Anton and Daniel A. Mosher; UTC Fuel Cell Program, East Hartford, Connecticut.

Sodium alanate has been studied as a promising candidate for reversible hydrogen storage due to its intermediate temperature charge/discharge range and relatively high storage capacity. Its rates of desorption and absorption can be enhanced by the addition of Ti and many other transition metal cation catalysts. To date, the sorption kinetics, especially absorption, are not well understood due to its highly exothermic absorption properties. In this study, practical sorption kinetics of several sodium alanate compositions were investigated and compared. A sorption kinetic model has been developed which supported the design of a prototype hydrogen storage system. The kinetic model described can be used with many similar alanate compounds to motivate design modifications and predict system performance.

11:00 AM GG4.5

LEIS and DRS: Diagnostic Tools for Studying Hydrogen on Surfaces. Robert Bastasz and Josh Whaley; Sandia National Laboratories, Livermore, California.

Hydrogen adsorption, dissociation, association, and desorption at surfaces are controlling factors that determine the performance of hydrogen storage materials. Diagnostic tools that can characterize the details of these processes at the atomistic level are needed to better understand what makes existing hydrogen storage materials work and how to make improvements. We will describe two techniques that are especially well-suited to this task: (1) low-energy ion scattering (LEIS) and (2) direct recoil spectroscopy (DRS). Both LEIS and DRS are ion-beam probe techniques that can provide information about the composition and structure of surfaces. The special feature of the techniques for the study of hydrogen storage materials is their ability to detect and identify hydrogen isotopes on surfaces along with impurity and substrate atoms. They can be used to monitor hydrogen uptake, release, and exchange on surfaces, analyze the composition of the outer atomic layer on materials, and determine the local atomic structure of ordered surfaces. A description of the LEIS/DRS methods, required instrumentation, analysis of data, and examples of

LEIS/DRS measurements of hydrogen on the surfaces of various materials will be presented.

11:30 AM GG4.6

Neutron Diffraction and X-ray Study of Structural Transformations in Titanium Carbohydrides TiC_xH_y .
Sultanova Khakimjanovna Svetlana and Iralis Khidirov;
Composition Materials, INST of Nuclear Physics, Tashkent, Uzbekistan.

In the present work the TiC_xH_y of a number of compositions at the lower limit of the carbon homogeneity region ($\text{TiC}_{0.47}\text{H}_{0.22}$, $\text{TiC}_{0.47}\text{H}_{0.19}$, $\text{TiC}_{0.47}\text{H}_{0.07}$, $\text{TiC}_{0.50}\text{H}_{0.21}$) were studied by means of powder neutron diffraction ($\lambda = 0.1085 \text{ nm}$) and X-ray ($\lambda = 0.15418 \text{ nm}$) techniques. Samples of TiC_xH_y were prepared from titanium powder by adding both of given quantity of titanium hydride TiH_y with known concentration of H ($y = 0.17$; 2) and also of soot of the trade-mark "very pure". Before sintering, the initial powders were carefully mixed up in an agate mortar, and the cylindrical briquette was prepared under pressure of $3 \times 106 \text{ N/m}^2$. Then the briquettes were annealed in evacuated and sealed quartz ampoules from $500\text{--}700^\circ\text{C}$ to 1000°C with the step of 100°C . At $500\text{--}700^\circ\text{C}$ usually the formation of solid solution of carbon in the α -Ti hexagonal lattice, rapid absorption of hydrogen by this solution and formation of threefold solid solution $\text{Ti}_2\text{C}_x\text{H}$ were observed, the sintering process being very active. With increasing temperature up to $800\text{--}1000^\circ\text{C}$ pressured powder becomes well sintered, and hydrogen emission from the sample was prevented. The final product was obtained after the annealing at temperature of 1200°C during 4 h followed by quenching in water. According to X-ray and neutron diffraction data, the samples were homogeneous and monophase and had the NaCl-type structure (the space group-sp.gr.Fm3m) with the average lattice parameter $a=0.4283 \text{ nm}$. As a result of structural study of TiC_xH_y after by heat treatment using special regime for preventing exit of hydrogen out of the lattice, five temperature ranges of temperature of structural changes are found out: 1. $T \geq 1200^\circ\text{C}$, at which TiC_xH_y have disordered cubic structure, is described within the framework of sp. gr. Fm3m, where the carbon atoms occupy octahedral interstices and the hydrogen atoms - tetrahedral ones. 2. $1000^\circ\text{C} < T < 1100^\circ\text{C}$; the disordered cubic structure is still observed in which the hydrogen atoms statistically are arranged on both octahedral and tetrahedral interstices. 3. $800^\circ\text{C} \leq T \leq 1000^\circ\text{C}$; formation of long-range order is observed. Crystal structure of the ordered phase is described within the framework of sp.gr.Fd3m, where the carbon atoms occupy one type of octahedral interstices 16 (c) and the hydrogen atoms-the other type of octahedral interstices 16 (d). 4. $600^\circ\text{C} \leq T \leq 800^\circ\text{C}$: the decay of ordered cubic phase with segregation of α -Ti is observed. 5. $T < 475^\circ\text{C}$: the formation of metastable ordered cubic phase with the formation of periodic antiphase domains is observed, at these temperatures process of the decay is hindered. The formation of ordered periodic antiphase domains (long-period structure) in the interstitial phase is found for the first time.

SESSION GG5: Hydrogen Storage Materials:
Carbonaceous Systems

Chairs: Ping Chen and Gholam-Abbas Nazri
Wednesday Afternoon, March 30, 2005
Room 3018 (Moscone West)

1:30 PM GG5.1

Hydrogen Diffusion Within Crystalline C_{60} .

Stephen FitzGerald¹, Rym Hannachi¹, Dorab Sethna¹, Marie Rinkoski¹, David Sholl² and Ken Sieber²; ¹Physics, Oberlin College, Oberlin, Ohio; ²Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania.

Given the present interest in hydrogen storage within novel forms of carbon we have investigated the behavior of molecular hydrogen within crystalline C_{60} (Fullerite). Although pure C_{60} will never be a practical storage medium, it does offer an ideal system to study the interaction of hydrogen within a well-characterized curved graphitic matrix. Our results based on infrared spectroscopy and loading isotherms indicate that hydrogen binds preferentially within the lattice interstitial octahedral sites. The measured binding energy of 92 meV agrees quite closely with model calculations based on standard carbon-hydrogen van der Waals interactions [1]. Diffusion occurs by hydrogen hopping between octahedral sites via an energetically unstable tetrahedral site. Kinetic Monte Carlo simulations indicate that this process should be greatly enhanced by the presence of dimers in which two H_2 molecules briefly occupy the same octahedral site [2]. This surprising prediction has now been confirmed by experimental data in which we see a dramatic increase in the diffusion constant with hydrogen concentration. This leads to a good agreement between simulated desorption curves are experimental outgassing data. 1. S. A. FitzGerald, S. Forth and M. Rinkoski, Phys. Rev. B **65**,

140302 (2002). 2. B. P. Uberuaga, A. F. Voter, K. K. Sieber, and D. S. Sholl, Phys. Rev. Lett., **91**, 105901 (2003).

2:00 PM GG5.2

Effect of Physical State of Carbon Nanocomposites on Hydrogen Adsorption and Desorption. Michael U. Jurczyk^{2,1}, Arun Kumar^{1,2}, Ashok Kumar^{2,1}, Sessa S. Srinivasan², Matthew T. Smith² and Elias K. Stefanakos²; ¹Nanomaterial and Nanomanufacturing Research Center, University of South Florida, Tampa, Florida; ²Clean Energy Research Center, University of South Florida, Tampa, Florida.

The inclusion of multiwalled carbon nanotubes in a conjugated polymer matrix results in extensive alterations in the polymer morphology. When the physical state of a substance is changed, heat is either absorbed or liberated but the temperature remains constant. The flexibility of chain molecules arises from rotation around the saturated chain bond, moreover the potential energy barriers hinder this rotation. It is not surprising therefore that the flexibility of polymer chains is an important factor in determining their melting point and stability. If the substitution of carbon nanotubes is random the primary effect is a decrease in the degree of crystallinity. These microstructures are governed by the balance of interactions between hydrodynamic forces (both viscous and elastic) and the forces working to retain the integrity of the disperse particles, such as interfacial tension or, in the case of solid filler, their mechanical strength. Carbon materials have long been shown to absorb as much as 60 wt% hydrogen due to their large surface areas as well as their high surface to volume ratios. In the present approach conducting polyaniline was doped with a metal oxide, such as SnO₂, as well as carbon nanotubes. The resulting carbon nanocomposites were made in both in gel and solid-state form to study the effect of physical state on hydrogen adsorption and desorption by weight percentage. The morphology formation process and its impact on the rheological properties of complex polymer systems, i.e. polymer blends and composites, are being studied. The materials are also compared with regard to their thermal stability using DSC, and further characterized using various techniques such as FTIR, as well as conductivity using a four-point probe. Further experiments are in progress to better understand the nature of the hydrogen storage mechanism. This work was supported by DOE grant DE-FC36-04G014224.

2:30 PM *GG5.3

Conversion of Organic Streams in Supercritical Water. Eckhard Dinjus, Nikolaos Boukis, Johannes Abeln and Andrea Kruse; ITC-CPV, Forschungszentrum Karlsruhe, Karlsruhe, Germany.

Thermal treatment of aqueous streams loaded with organics can be efficiently performed at pressures and temperatures above the critical data for water (P_c = 22.1 MPa, T_c = 374°C). Two applications are under investigation using supercritical water (SCW) as solvent and reactant: supercritical water oxidation (SCWO) and gasification (SCWG). SCWO is typically operated at 25-35 MPa and 600-900 °C, because water, oxygen, CO₂ and most of the organics form a single fluid phase with fast oxidation kinetics. Thus, SCWO can be processed with high space-time yield and -in the case of higher concentrated streams- self-sustaining. Expensive off-gas treatment is prevented because NO_x formation is suppressed. Other heteroatoms form or their corresponding salts. However, acids may lead to corrosion, formation or presence of salts to plugs. To avoid these problems a transpiring wall reactor (TWR) has been developed and installed. Results of SCWO of different industrial effluents are very promising. Destruction of the organic waste compounds was close to 100 %, even for effluents containing solids and salts up to 5 wt. % each. The SCWG process of biomass is performed under SCW conditions. The aim of this work is to study the conversion of biomass (especially wet waste biomass) to fuel gas with high energetic value. At SCW conditions organic matter reacts with water to form a hydrogen containing gas. The feed carbon is converted preferentially to CO₂, which can be separated by e.g. stripping, and to methane, as a minor product. While the organic carbon is oxidized to CO₂, water is reduced to from hydrogen, e.g. for glucose: C₆H₁₂O₆ + 6 H₂O → 6 CO₂ + 12 H₂. In basic studies of the biomass gasification, the main reaction pathways were identified. In addition the influence of ingredients of biomass and additives / catalysts was investigated. The changes in selectivity of different reaction pathways observed, opens the possibility to manipulate the chemistry of biomass gasification in supercritical water. Therefore high gas yields with different feedstock of various compositions can be achieved. The SCWG process is performed using efficient heat exchangers at SCW conditions. Compression work is low since non-compressible water slurry is pressurized. The reaction of the organic substances with water proceeds fast and completely, with high space-time yield. At about 600°C and 25 MPa high gasification yield can be achieved. Formation of CO, tar and char is low enhancing the efficiency of the SCWG process. A 100 kg/h SCWG plant (acronym: VERENA) has been installed and is operated since 2003. A high thermal efficiency of

about 80% for diluted educt streams has been measured. Experimental results with the VERENA plant confirmed the production of a hydrogen rich gas and the high thermal efficiency of the process. The development efforts are focused on process optimisation particularly with respect to energy efficiency as well as applicability to different feedstock.

3:30 PM GG5.4

Alkali Metals Plus Silicon Form Convenient Pure Hydrogen Sources. Michael Lefenfeld and James L. Dye; SiGNa Chemistry, LLC, New York, New York.

A need exists to prepare a compound of sodium and silicon with the stoichiometry NaSi conveniently and inexpensively, so that it may be easily handled in air without a significant loss in its ability to reduce water. This reduction reaction of water with NaSi would be able to produce large amounts of hydrogen per unit mass of the solid. The yield would be 0.10 kg H₂/kg NaSi, more than double the Department of Energy (DOE) target for 2005 and larger than the 2015 target of 0.081 kg H₂/kg fuel. The Na-Si material of our invention reacts immediately with water to produce pure hydrogen and releases heat in the process. However, the material is completely unreactive toward dry oxygen over a period of several weeks, meaning that the powder can be weighed in air or transferred from one container to another. Our results demonstrate that it is straight forward to produce a stable powdered material that likely contains a silicide with the stoichiometry NaSi, together with a glassy SiO₂. The product, while stable in dry air and only slowly reactive in moist air, produces large yields of hydrogen when introduced into liquid water. The gaseous product is pure hydrogen, uncontaminated with anything except water vapor. Thus, the material is an excellent source of hydrogen for use in fuel cells.

4:00 PM GG5.5

Kinetic Study of Hydrogen Generation from Sodium Borohydride and Reactive Solvent Mixtures.

Chih-ting Flora Lo¹, Kunal Karan¹ and Boyd R. Davis²; ¹Chemical Engineering, Queen's University, Kingston, Ontario, Canada; ²Mining Engineering, Queen's University, Kingston, Ontario, Canada.

Sodium borohydride is a promising hydrogen storage material with high gravimetric storage density and rapid kinetics for hydrogen release from both hydrolysis and methanolysis reactions. Hydrolysis: NaBH₄ + 6H₂O → 4H₂ + NaBO₂·4H₂O Methanolysis: NaBH₄ + 4CH₃OH → 4H₂ + NaB(OCH₃)₄ Hydrolysis of borohydride has been well studied in the literature, however, its implementation via an aqueous solution is impeded by a number of factors. A controlled rate of reaction and long term stability can only be achieved in a very high pH environment which is corrosive to system components. Also, hydrated borate forms in the reaction and is difficult to handle and remove as it tends to precipitate on the surface of all elements in the system. Moreover, the hydrate results in a significant reduction in the storage density due to the 1:6 sodium borohydride to water ratio which gives a 5.5% gravimetric storage density. Furthermore, aqueous solution prevents operation of the system at temperatures much below 0°C. On the other hand, very few studies have investigated the methanolysis of sodium borohydride. Our previous study have shown that methanolysis of borohydride has better kinetics than that of the hydrolysis reaction at low temperatures. Also, the reaction by-product was observed to be completely soluble in methanol. A major advantage of methanolysis of sodium borohydride is the possibility to operate in cold conditions. However, as methanol is heavier than water and the reaction by-product is heavy, this system only has a 4.8 wt% gravimetric storage capacity. In this project, various compositions of water-methanol mixtures were prepared to study the hydrogen production mechanism and kinetics of sodium borohydride over wide range of temperatures (-40 to +60°C). The rates of hydrogen production were determined using volumetric displacement method. Experimental data indicated that the kinetics of hydrogen generation via methanolysis reaction were rapid compared to that from hydrolysis reaction at low temperatures. Expectedly, the activity of methanolysis decreased with decreasing temperature however the rate of reaction can be improved with additives. The hydrogen generation reaction products were analyzed using XRD and NMR to identify the mechanism of reaction(s). The kinetic study of hydrogen generation from water-methanol mixtures is also discussed. Preliminary results indicate that the individual advantages of hydrolysis and methanolysis may be realized in an appropriate mixture of water and methanol.

4:30 PM GG5.6

Improvement of Hydrogen Absorption-Desorption Property for Organic Hydride. Takashi Atsumi¹, Takahiro Hayashi¹, Ryuta Morishima¹, Hiroshi Suzuki¹, Shinya Hodoshima² and Yasukazu Saito²; ¹Material Engineering Div. 3, Toyota Motor Corporation, Susono, Shizuoka, Japan; ²Department of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo, Shinjuku-ku, Tokyo, Japan.

A large number of studies for development of the fuel cell vehicles are carried out as the means to an environmentally friendly future. Hydrogen storage is one of the biggest problems for developing the fuel cell vehicles. Important issues of hydrogen storage materials are for example weight, volume, safety, and energy efficiency. Organic hydride for liquid fuel is expected to be a candidate of hydrogen storage media because of its safety, high gravity density and low cost. In this talk, the hydrogen absorption-desorption properties of organic hydrides will be discussed with special reference to organic compounds, catalyst supports, metallic species and so on. Suitable materials and conditions made it possible to advance the hydrogen storage property.

SESSION GG6: Hydrogen Storage Materials: Metal - Alloy Hydrides

Chairs: Maryam Nazri and Rosa Young
Thursday Morning, March 31, 2005
Room 3018 (Moscone West)

8:30 AM *GG6.1

Effect of Carbon Addition on Hydrogen Storage Performances of Magnesium-Based Alloys: From Bulk Powders to Thin Films. Aline Rougier¹, Xavier Darok¹, Vinay Bhat¹, Luc Aymard¹, Gholam Abbas Nazri² and J. Marie Tarascon¹; ¹LRCs UMR6007, Amiens, France; ²GM R&D, Warren, Michigan.

In a recent study, we demonstrated that carbon addition proved to be as efficient as Pd coating, with the advantage of being of a much lower cost, to improve the hydrogen absorption/desorption performances of Mg-based alloys [1]. This beneficial effect, firstly observed on ball-milled powders, revealed to be also positive on thin film behavior. By optimizing the conditions of deposition, metallic or transparent Mg-based thin films were successively grown using the Pulsed Laser Deposition technique. The modification of the optical properties with hydrogen loading, making those Mg-based thin films suitable for switchable mirrors, were also accomplished by gas sorption. Mg-C thin films show faster and larger hydrogenation, illustrated by an increase in the optical transmittance ($TMgHx = 15\% < T(Mg-C)Hx = 30\%$) of hydrided thin films. In this paper, a further understanding of the fundamental origin of such enhancement in hydrogen absorption/desorption performance by carbon addition will be presented. Finally, the positive effect of carbon will be compared to the one of other additives considering both bulk and thin film approaches. [1] R. Janot, L. Aymard, A. Rougier, G.A. Nazri, and J-M. Tarascon. J. of Mater. Res., 18(8), 1749-1752 (2003).

9:00 AM *GG6.2

New Magnesium Based Ternary Compounds Derived from Laves Phases for Hydrogen Storage. Jean-Louis Bobet and Bernard Chevalier; ICMCB-CNRS, Pessac, France.

It is well established that hydrogen is probably the fuel of tomorrow. However, the problems of (i) mass production as well as (ii) storage still have to be solved. This work focuses on this second problem and the aim of it was the study of hydrogen storage in magnesium based ternary compounds. Magnesium is a light inexpensive and abundant material but the hydriding reaction takes place at rather high temperature (i.e. 287 C at 1 atm) and the kinetics is very low (few hours). It is well known that the improvements of the kinetics can be achieved by adding various elements (nano oxide for example) and by using reactive mechanical grinding. However, all these methods just allow to change kinetics while thermodynamic remain the same so that the sorption temperature remains too high. To modify the thermodynamic, new materials based on magnesium have to be prepared. The AB₅ and AB₂ compounds have been widely developed and offer good thermodynamic properties but the weight capacity is too low (<1.8%). The goal of this work was to elaborate new ternary compounds based on the AB₂ structure (i.e. Laves phase) containing magnesium. First, we will describe the synthesis method derived from the classical solid state chemistry method and then, we will present the results of the structural characterization. This first experiment was done with A = rare earth and B = Ni. The structure of the obtained compounds derived from the Laves phase where the A atom in the tetrahedral site are replaced by magnesium atom so that the formula of the compounds can be written as (RE_{0.5}Mg_{0.5})Ni₂. The sorption properties will also be discussed in term of both kinetics and thermodynamic (PCT curves). Finally, the results concerning the solid solution (RE_{0.5-x}Mg_{0.5+x})Ni₂ and (RE_{0.5}Mg_{0.5})Ni_{2-x}M_x (with M = Co and Al) will be presented. The effects of the substitution will be discussed in term of crystal structure and sorption properties. The effects of substitution will be compared with the previous results obtained on AB₅ and AB₂ compounds.

9:30 AM *GG6.3

Hydrogen Absorption-Desorption Mechanisms of Metal

Hydrides Studied by *insitu* Powder Diffraction.

Yumiko Nakamura and Etsuo Akiba; Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan.

Hydrogen absorption and desorption of metal hydrides are generally accompanied by phase transformation and significant volume change. In some cases, lattice defects are introduced as well. *Insitu* powder diffraction technique enables to directly observe phase transformation as crystal structure change. Analysis of diffraction data provides lattice strain introduced by hydrogenation and dehydrogenation, and crystallite size closely related with the nanoscopic reaction mechanisms. In this talk, introduction and relaxation of lattice strain and change in crystallite size in alloy and hydride phases that are observed by *insitu* X-ray diffraction will be presented. Hydrogen occupation in the crystal lattice and change of occupation with the amount of hydrogen in the hydride phase will be discussed based on *insitu* neutron diffraction study.

10:30 AM *GG6.4

High-Pressure Metal Hydride Tank for Fuel Cell Vehicles.

Daigoro Mori¹, Nobuo Kobayashi², Tamio Shinozawa³, Tomoya Matsunaga³, Hidehito Kubo⁴, Keiji Toh⁴ and Makoto Tsuzuki⁴; ¹Fuel Cell System Development Div., Toyota Motor Corporation, Susono, Shizuoka, Japan; ²Fuel Cell System Engineering Div., Toyota Motor Corporation, Toyota, Aichi, Japan; ³Material Engineering Div.3, Toyota Motor Corporation, Susono, Shizuoka, Japan; ⁴Corporate Technical Center, Toyota Industries Corporation, Obu, Aichi, Japan.

Toyota introduced the world's first fuel cell vehicles, the FCHV, into the market in 2002. Although those vehicles have great potential as future vehicles, it is also realized that further breakthrough technologies to solve essential problems, such as cost and cruising range, are needed for FCHV vehicles to be competitive with internal combustion engine (ICE) vehicles. We have developed a new type of hydrogen-absorbing alloy tank. The high-pressure metal hydride (MH) tank is designed, based on the 35MPa cylinder vessel. The heat-exchanger module including hydrogen-absorbing alloy is integrated in the tank. Its advantage over high-pressure cylinder vessel is large hydrogen storage capacity, for example, 7.3kg at the 180L tank volume. Cruising range is about 2.5 times longer than that of the same volume 35MPa cylinder vessel system. While the conventional hydrogen-absorbing alloy tank has problems in charge and discharge process, the hydrogen charging rate of this system is equal to 35MPa cylinder without external cooling facility. Furthermore, it can release hydrogen at 243K because of a hydrogen-absorbing alloy with high dissociation pressure. Ti-Cr-Mn alloy with AB₂ laves phase. Its dissociation pressure at 243K is 0.5MPa and we can use this alloy only in the high-pressure system. We think the high-pressure MH system is one of the realistic option to achieve cruising range over 700km. However, much increase in hydrogen storage capacity of alloys, is still expected to develop a thoroughly practical FCHV. Estimated target of hydrogen storage density is 3-4mass% and 1600-2400 times as volumetric density.

11:00 AM *GG6.5

Development of Hydrogen Absorbing Alloy with High Dissociation Pressure. Yoshitsugu Kojima¹, Yasuaki Kawai¹, Shin-ichi Towata¹, Tomoya Matsunaga², Tamio Shinozawa² and Masahiko Kimbara³; ¹Toyota Central R&D Labs., Inc., Nagakute, Aichi, Japan; ²Material Engineering Div.3, Toyota Motor Corporation, Susono, Shizuoka, Japan; ³Corporate Technical Center, Toyota Industries Corporation, Obu, Aichi, Japan.

A high-pressure MH tank containing a hydrogen absorbing alloy with high dissociation pressure and compressed hydrogen can improve various issues of hydrogen absorbing alloys and volumetric hydrogen density of a high-pressure hydrogen tank. Ti-Cr-Mn is a useful hydrogen absorbing alloy with high dissociation pressure. In this study, hydrogen absorption and desorption properties of Ti-Cr-Mn were measured by varying the contents of Ti, Cr and Mn to obtain the optimum composition. Ti-Cr-Mn had the hexagonal MgZn₂ (C14 Laves phase) structure and Ti_xCr_{2-y}Mn_y (1.02 ≤ x ≤ 1.41, 0.09 ≤ y ≤ 1.66) was easily activated at hydrogen pressure of 33 MPa and room temperature. The effective hydrogen capacity of Ti_xCr_{2-y}Mn_y [x ≥ 1.1 (1.08 ≤ x ≤ 1.16), y ≤ 1.0 (0.96 ≤ y ≤ 1.08)] exhibited the maximum value of 1.8 wt% in the pressure range of 33 MPa and 0.1 MPa at 296K (dissociation pressure: 5-11 MPa), and the alloy provided over 10% more capacity than conventional Ti-Cr-Mn (Ti_{1.2}CrMn: 1.6 wt%, Ti_{1.2}Cr_{1.9}Mn_{0.1}: 1.3 wt%). The effective hydrogen capacity increased to 1.9 wt% at 353 K. At the low temperature of 233 K, the alloy absorbed 2.0 wt% of hydrogen and the hydrogen desorption capacity at 0.1 MPa was 1.6 wt%. According to the van't Hoff plots, the standard enthalpy differences (heat of formation) of the Ti_{1.16}Cr_{0.92}Mn_{1.08} and Ti_{1.08}Cr_{1.04}Mn_{0.96} hydrides were -21 and -22 kJ/molH₂, respectively. These absolute values were about 10 kJ/molH₂ smaller than that of LaNi₅. The alloy

had sufficient hydriding and dehydriding kinetics. In the pressure range of 33 MPa and 0.1 MPa at 296 K, the alloy absorbed and desorbed 1.8 wt% of hydrogen in 60 sec and 300 sec, respectively. The hydrogen capacity changed gradually over many cycles and that the capacity after 1000 cycles was 94 % of the initial capacity. The handlings of the alloy were similar to compressed hydrogen. Thus the developed alloy can be utilized for the high-pressure MH tank.

11:30 AM GG6.6

Group III-Nitride Materials for High Efficiency

Photoelectrochemical Cells. Joel W. Ager¹, W. Walukiewicz¹, K. M. Yu¹, W. Shan¹, J. D. Denlinger² and J. Wu³; ¹Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; ²Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California; ³Department of Physics, Harvard University, Cambridge, Massachusetts.

Two ternary alloys based on the III-nitrides are explored as potential components of photoelectrochemical cells (PECs) for the direct generation of hydrogen using solar energy. We will show that $\text{In}_{1-x}\text{Ga}_x\text{N}$ and $\text{GaAs}_x\text{N}_{1-x}$ alloys represent fundamentally new opportunities for the development of inorganic PECs. More specifically, changing the alloy composition in these materials allows for independent adjustment of the energy band gaps and the location of the conduction and the valence band edges relative to the water redox potentials. In addition, these nitride alloys have demonstrated superior corrosion resistance under PEC operating conditions compared to other semiconductors of similar energy gaps. Experimental data will be presented that show that high quality single phase $\text{In}_{1-x}\text{Ga}_x\text{N}$ can be made with bandgaps spanning nearly the entire solar spectrum. Specifically, spontaneous water splitting should occur in $\text{In}_{0.4}\text{Ga}_{0.6}\text{N}$, which has a direct bandgap of 2.0 eV. In the case of $\text{GaAs}_x\text{N}_{1-x}$ we will demonstrate that the replacement of a few percent of As in the N sublattice drives the bandgap down from the GaN value (3.4 eV) into a range that is attractive for PEC cells [1]. This band gap reduction is explained by a valence band anticrossing interaction that pushes the valence band maximum up initially by 0.5 eV. From the point of view of a PEC cell, this reduces the gap (desirable for efficiency) without compromising the desired overpotentials for the H_2O redox potentials. [1] J. Wu, W. Walukiewicz, K. M. Yu, J. D. Denlinger, W. Shan, J. W. Ager III, A. Kimura, H. F. Tang, and T. F. Kuech, Phys. Rev. B **70**, 115214 (2004).