SYMPOSIUM GG
Materials and Technology for Hydrogen Storage and Generation
March 28 - 31, 2005

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* Invited paper
Hydrogen storage and production are critical issues for the 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, carbons, and organic and inorganic systems, composite and hybrid materials. Recent discoveries and new approaches will also 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

8:30 AM *GG1.1
Casole Reed1, Sunita Satyapal1, Antonio Bozaz1 and John Petrovic2

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 traditional 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 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)2(H2O)2: A NbO Type Microporous Metal-Organic Framework with High Hydrogen Sorption (BPTC = 3,3',5,5'-Biphenyltetracarboxylate). Banglin Chen1, Nathan W. Cocker1, Andrew R. Millward2, Duane W. S. Cuttrell3 and Omar M. Yaghi4
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 (MOF) has been deliberately designed, synthesized and 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 area of 1580 m²/g which can store hydrogen up to 2.5 wt% at 77K and 1 bar.

9:30 AM *GG1.3
1LANSCAPE-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 (1-200 bar) for the first time. We found that hydrogen occupancy in the (32+X)H2136H2O, 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 solid 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 50K. We have discovered a 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 3.5 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.

10:00 AM *GG1.4

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 ammine-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. Ammoniaborane (H3BNH3) is the simplest stable AB with the highest hydrogen content (about 19.6 wt%), having a volumetric energy density of about 9.44 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 thermal stability begins at temperatures below 140 degrees centigrade and the overall process is exothermic but heat needed to be supplied to activate the material. We are studying two ammoniaborane-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. Polyborazine is the product of NH3BH3 thermolysis. Polyborazine is the product of borazine thermolysis. Prior studies have shown that polyborazine consists of a combination of linear, 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 Arac1 and Gholam-Abbas Nazri2
1Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada; 2Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois.

Hydrogen storage in complex chemical hydrides is an approach in which hydrogen storage involves the formation of hydrogen-metal complexes of the general type ABH4, where A and B represent metal atoms, and H represents hydrogen atoms. These compounds are known to form strong hydrogen-metal bonds, allowing hydrogen to be stored in a variety of solid-state materials. A key challenge in the development of hydrogen storage materials is to find compounds that can store hydrogen at or near room temperature and pressure, making them suitable for use in fuel cell applications. The storage density of hydrogen in these materials is typically much lower than that of liquid hydrogen, but the development of efficient methods to store and release hydrogen is an active area of research. Recent studies have focused on the characterization of hydrogen storage materials using Raman spectroscopy and X-ray diffraction. These techniques are valuable tools for understanding the structure and phase transitions of hydrogen storage materials, as the changes in hydrogen content lead to distinct changes in the material's vibrational and diffraction properties. The use of Raman spectroscopy and X-ray diffraction in the study of hydrogen storage materials is crucial for designing and optimizing materials for use in fuel cell applications.
Complex chemical hydrides with general ABH₄ formula (where A=alkaline and alkaline earth metals, and B is usually group IIII 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 can also 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 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 with respect to the solid state are identified, and the vibrational 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 Destabilized Metal Borohydrides for Reversible Hydrogen Storage. Ming An; 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 anhydrous (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 re-hydriding 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, we destabilized LiBH₄ releases 9 wt% hydrogen starting from less than 100°C. The materials are also reversible in dehydriding and rehydriding cycling tests. The destabilized borohydrides absorb 9 wt% hydrogen after dehydriding. About 6 wt% hydrogen was reclaimed from rehydried 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 thermodynamic 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

NaAIH₄ is a reversible hydrogen storage material, the reversibility is achieved by doping NaAIH₄ with ~2% 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 rehydriding reaction, for evidence of the probable surface catalytic role of the Ti dopant. Rehydriding 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 of 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 XPS and diffractometry evidence that will be discussed in light of our theoretical results.

2:00 PM GG2.2
Hydrogen Absorption & Desorption over Alkali Metal Amide-Hydride Systems. Zhtiao 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 amide and Li₂MgN₂H₂ ternary amide systems, we found that after hydrogenation the solid products comprises of amide and hydride of corresponding metal hydrides. Hydrogen desorption and 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, 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 80°C with 2wt% capacity. Further exploration of a broader range of amide-hydride system is necessary to filter suitable materials for hydrogen storage.

2:30 PM GG2.3

In recent years, the high performance complex chemical hydrides have been developed as hydrogen storage media. Most attention has been given to catalyzed NaAIH₄ reaction, 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 (Cr, 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 NaAIH₄. 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.

2:30 PM GG2.4
Electron Microscopy Studies of Lithium Aluminium Hydrides With and Without Ti and V-Based Additives. Carmen M. Andreu1,2, John C. Walmsley3, Hendrik W. Brinks2, Randi Holmestad1, Dieter Blanchard2, Bjorn C. Houback2, 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 the work, the microstructure of LiAlH₄ with and without TiCl₄, 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 thin 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 form a single phase. 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

Warren, Michigan.
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 kinetics of hydrogen release are 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. $\text{Al}_2\text{O}_3$ 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 $\text{H}_2$ Sorption at Al-Ti Alloy Surfaces in Aluminate H Storage Materials. Roland Stumpf; Sandia National Laboratories, Livermore, California.

The rates of ad- and desorption of $\text{H}_2$ at metal surfaces and the effect of $\text{H}$ on mass transport at these surfaces are critical for the uptake and release kinetics of the hydride storage materials like Ti-doped NaAlH$_4$. Simple metals (e.g. Li, Mg, Al) are the main constituent of light complex hydride storage materials. However, they do not by themselves readily react with $\text{H}_2$. Transition metals (e.g. Ti, Ni, Pd) on the other hand are known to catalyze $\text{H}$-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 $\text{H}_2$ differently than either metal alone. At exposed Ti in an Al matrix we find very low barriers for $\text{H}_2$ dissociative adsorption and recombinative desorption, in part caused by a novel molecular chemisorption state for $\text{H}_2$. The 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 second layer split $\text{H}_2$ more readily and bind H more strongly than pure Al. We will also discuss how high $\text{H}_2$ pressures typical for storage operations affect the stability of Al-Ti surface structures, which will in turn affect the catalytic activity of these Ti-Ti surface alloy. Finally, I show how $\text{H}_2$ facilitates Al mass transport through the formation of mobile AlH 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 Janes 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 Refueling Station. Xinluna 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 ABA$_x$ type hydride LaNi$_5$ (M= $\text{Mg}, \text{Mn}, \text{Fe}$) 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 Nm$^3$ and product hydrogen pressure in the range of 13-40MPa. With boiling water as the heating media the compressors can produce hydrogen with pressure of 12-15MPa and purity of 99.9996% 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 49 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 Abdul', Hasen Atiyeh, Brant Peppley; Philip Jessop and Boyd J. Davis; Chemical Engineering, Queen, Kingston, 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 complexes 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 will be known from a known sample of sodium borohydride 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 hydrates 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 concentrations of the reactants, 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. Sanjnan Kumar Dash, Gohul Yashin 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 m$^2$/g and up to 80% open pore volume available to hydrogen storage. The structure and the porous 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 BiC, 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 a quartz balance. The amount of hydrogen sorbed 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 NiOYSZ 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, Yonin, South Korea.

Modified Ni/YSZ cathodes 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 nanosstructures and electrical conductivity of powders ball-milled in dry atmosphere and in ethanol were investigated by XRD, 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 800 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 Kumar1, Michael U. Janezyik2, Ashok Kumar3, Seshu S. Srinivasan4, Matthew T. Smith5, and Elena I. Stefanakos6; 
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, novel nanocomposites can be made by direct synthesis. The tube orientation includes 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 carbon nanotubes with carbon nanotubes as well as fullerenes. Carbon nanotubes as well as fullerenes have been shown to absorb as much as 60 wt% hydrogen and 28 g 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 magnetic field. The effects of carbon nanotube alignment in nanocomposites on hydrogen adsorption and desorption are investigated, and both critical desorption and adsorption processes aligned in specific directions were characterized with SEM, TEM, and FTR. 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-FC36-96GO14224.

GGG8.6
Fabrication of Nano Oxides by Ball Milling to be used as Additives for Magnesium Based Mixtures for Hydrogen Storage Application. Jean-Louis Bellet, Jean-Francois Silvain and Jean-Marc Heintz; ICMCB-CNRS, Pessac, France.

In order to be able to use magnesium as hydrogen storage, kinetic, energetic and structural properties have improved. Magnesium is a light metal 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 RGM 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 shown that ball milling is an interesting alternative route to produce such nano particles. For nano Cr2O3, a new technique has been presented: 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 interesting method. Even approach that SCF process allow to obtain a more pure and fine product. However the drawback of the SFC method is the cost of both the initial product and the experiment itself. All results will be discussed in term of morphology, crystallinity and size. The obtained results are in good agreement with experiments. Results of the hydrogen adsorption/desorption reaction (hydriding/dehydriding kinetics).

GGG8.7

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 diode properties in metal-diode-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(V) 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 intercalation of hydrogen into layer spaces of the basic semiconductor.

GGG8.8
Novel Metal-Organic Frameworks: Microwave Crystallization and Structure. Nevenka Rajic, Matyas Bakubogor, Sanja Sajic, Djordje Stojakovic and Venceslav Kaucic; 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 frameworks, while inorganic ones, 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 RGM 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 shown that ball milling is an interesting alternative route to produce such nano particles. For nano Cr2O3, a new technique has been presented: 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 interesting method. Even approach that SCF process allow to obtain a more pure and fine product. However the drawback of the SFC method is the cost of both the initial product and the experiment itself. All results will be discussed in term of morphology, crystallinity and size. The obtained results are in good agreement with experiments. Results of the hydrogen adsorption/desorption reaction (hydriding/dehydriding kinetics).
exotic materials or tailoring the known hydride systems. On the other hand, transition metal complex hydrides, TMH₃, T₄ = Mg ≈ Fe, Co, Ni), have not been identified as potential candidates for hydrogen storage. These hydrides especially Mg₂FeH₆ have shown excellent cyclic capacities (more than 500 cycles) even without a catalyst. Besides, Mg₂FeH₆ possesses the highest volumetric and gravimetric hydrogen storage densities of kg/m³ and g/m³ and has a high melting point. 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 catalytic kinetics and reduction in the operating temperature is very much possible by using a distorted nanoscale Mg₂FeH₆ structure, catalyst doping and/or lattice substitution. Keeping these facts in view, the present investigation aims to improve the sorption kinetics and thermodynamics of Mg₂FeH₆, by 1) preparing nano-scale Mg₂FeH₆ 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 Mg²⁺ by incorporating Na⁺/Li⁺. The synergistic behavior of the tailored nano-scale transition metal complex for hydrogen storage is outlined.


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 stored hydrogen 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. This 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 Na₂AlH₆ 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.


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 rate of desorption is highly 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 are 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 surface components and hence the overall hydrogen cycling efficiency are needed to 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 reaction spectroscopy (DRS). Both LEIS and DRS are low-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 atoms 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 Carbocarboxylates TiC(CH₃CO)L₆. Sulavanev S. Khakidin, Jagadeesh N. R. and Brian J. Ullrich; Department of Chemistry, New Mexico State University, Las Cruces, New Mexico.

In the present work the TiC(CH₃CO)L₆ of a number of compositions at the lower limit of the carbon homogeneity region (TiC₀.₄₇H₀.₂₂, TiC₀.₄₇H₀.₁₉, TiC₀.₄₇H₀.₀₇, TiC₀.₅₀H₂.₁₁) were studied by means of powder neutron diffraction (λ = 1.085 nm) and X-ray (λ = 0.15418 nm) techniques. Samples of TiC(CH₃CO)L₆ were prepared from titanium powder by adding both of given quantity of titanium hydride TiH₂ with known concentration of H (y = 0.17; 2) and also of stoat of the trade-mark "very pure". Before sintering, the initial powders were carefully mixed up in an agate mortar, and the cylindrical briquettes were prepared under pressure of 3x10⁶ N/m². Then the briquettes were annealed in evacuated and sealed quartz ampoules from 500-700 °C to 1000 °C with the step of 100 °C. At 500-700 °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 Ti₂C(H₂) were observed, the sintering process being very active. With increasing temperature up to 800-1000 °C pressure 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 have hexagonal and monoclinic phases. In the present paper we will describe two techniques that are applicable to a wide range of system types. Using this approach, the models should be useful to develop 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 Na₂AlH₆ 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.

SESSION GG5: Hydrogen Storage Materials: Carbonaceous Systems

Chairs: Ping Chen and Golam-Abbas Nazri

Wednesday Afternoon, March 30, 2005
Room 3018 (Moscone West)

1:30 PM GG5.1 Hydrogen Diffusion Within Crystalline C₁₀₀. Stephen FitzGerald₁, Ryn Hannachi₂, Dorab Sethna₁, Marie Rinkoski₁, David Sholl³ and Ken Sieber; 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 C₁₀₀(Dullerite). Although pure C₁₀₀ will never be a practical storage medium, it does offer an ideal opportunity to study the interaction of hydrogen within a well-characterized curved graphite matrix. Our results are based on infrared spectroscopy and loading isothermal data 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 H₂ molecules briefly occupy the same octahedral site [2]. This surprising prediction has now been confirmed by experimental data in which we have dramatically increased the diffusion constant with hydrogen concentration. This leads to a good agreement between simulated desorption curves we are experimentally observing data. 1. S. A. FitzerGerald, S. Firth and M. Rinkoski, Phys. Rev. B 60,
4:00 PM *GG5.5 Kinetic Study of Hydrogen Generation from Sodium Borohydride and Reactive Solvent Mixtures. Chih-ting Plera Lo¹, Kunn Karon² 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 + NaOC(CH₃)₄. Hydroborohydride 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 hydride 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 sources 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 has shown that methanolysis of borohydride has better kinetics than that of hydrolysis at low temperatures. Also, 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 +90°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 AED 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.


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 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 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 straightforward to produce a stable powdered material that likely contains a stable mixture of stoichiometry NaSi, together with a glassy SiO₂. The product, while stable in dry air, also 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.
A large number of studies for development of the fuel cell vehicles are currently being made 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 property of organic hydrides will be discussed with special reference to organic compounds, catalyst supports, and so on and the hydrogenation and dehydration, and crystallite size closely related with the nanostructural 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 in situ X-ray diffraction will be presented. The focus will be on the occupation in the crystal lattice and change of occupation with the amount of hydrogen in the hydride phase will be discussed based on in situ neutron diffraction study.

10:30 AM **GG6.4**

High-Pressure Metal Hydride Tank for Fuel Cell Vehicles.


Toyota introduced the world’s first fuel cell vehicles, the FCHV, into the market in 2002. Although mass production of three types of cars has greatly improved the 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 high-pressure metal hydride 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, 7.3 kg 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 phase. Its dissociation pressure is at 243K is 0.6MPa 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 5-4 mass% and 1600-2400 times as volumetric density.

11:00 AM **GG6.5**


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 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 TixCr2yMn (x=0.11 (1.08≤x≤1.16), y=0.1 (0.95≤y≤1.08)) exhibited the maximum value of 1.8% in the pressure range of 33 MPa and 0.1 MPa at 269K (dissociation pressure; 5-11 MPa), and the alloy improved over 10% more capacity than conventional one (T1.2CrMn: 1.6 wt%, T1.2Cr1.9Mn0.1: 1.3 wt%). Effective hydrogen capacity increased to 1.9 wt% at 332 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 1.8 at 296K. According to the van’t Hoff plots, the standard enthalpy differences (heat of formation) of the T1.16Cr0.92Mn0.18 and T1.08Cr0.14Mn0.16 hydrides were -21 and -22 kJ /molH2, respectively. These absolute values were about 10 kJ/molH2 smaller than that of LiNi5. 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 In1-xGaxN and GaAsxN1-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 In1-xGaxN can be made with bandgaps spanning nearly the entire solar spectrum. Specifically, spontaneous water splitting should occur in In0.4G0.6N, which has a direct bandgap of 2.0 eV. In the case of GaAsxN1-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 H2O 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).