SYMPOSIUM N

Materials for Hydrogen Storage

December 1 - 2, 2004

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* Invited paper

SESSION N1: Materials for Hydrogen Storage: Metal Hydrides
Wednesday Morning, December 1, 2004
Independence E (Sheraton)

8:30 AM *N1.1
Basic Issues That Need to be Addressed to Enable use of Metal Hydrides. Howard K. Birnbaum, [1]Materials Research Laboratory, University of Illinois, Champaign, Illinois; [2]Materials Science and Engineering, University of Illinois, Urbana, Illinois.

As one of the material types under consideration for hydrogen storage for vehicular applications, it is worth reviewing some of the major issues in the metal-hydrogen systems that require understanding prior to any successful application. This paper will address such issues and briefly describe what is known about them as well as indicating the author's views as to the directions needed for further progress. I will discuss H storage capacity in the metal hydrides and what determines the amount of H that can be absorbed; the relationship between the thermodynamics of absorption and desorption and the bonding of H in the lattice; factors affecting the kinetics of adsorption and desorption and the role of surface oxides and catalysts; structural changes in absorption and desorption of H and how these are related to the changes observed on repeated cycling. It is hoped that this necessarily brief overview, one that is based on reported results, will be of some assistance in focusing future fundamental studies,

9:00 AM N1.2
In-situ Observation of Hydride Stability of Vanadium Alloys in Electron Microscope. Kohsuke Takase, Katsuaki Aoyagi, Somei Ohnuki, Takanori Suda and Seiichi Watanabe; Materials Engineering, Hokkaido University, Sapporo, Japan.

High-resolution microscopy was applied for surveying hydride stability in Vanadium alloys, which are candidate for hydrogen storage materials of advanced hydrogen energy systems and core component materials of fusion reactors. Hydride of V2H in Vanadium alloys was stable at room temperature under the vacuum condition in microscope, but it was decomposed during electron-irradiation up to 100 C. It was confirmed from the lattice image and FFT that V2H has a BCT structure, where hydrogen atoms locate at octahedral sites. Crystal orientation was <110>beta // <110>mat., and lattice mismatch was about 10 %. After the decomposition of the hydride, relatively large lattice expansion was observed in the matrix, which suggests that hydrogen atoms should be trapped by lattice defects and included in the matrix. Intensive electron beam accelerated the hydride decomposition, which is a radiation-enhanced diffusion process. For clarify the effect of hydrogen pressure, some results from the environmental cell will be also discussed.

9:15 AM N1.3
Nano-Columnar Mg and MgAl Thin Films Created by Plasma Sputter Deposition for Improved Hydrogen Kinetics and Storage Properties. S.W.H. Eijt, M. W. Zandbergen, H. Schut and W. J. Legerstee; Delft University of Technology, Interfaculty Reactor Institute, Delft, Netherlands.

Nanostructuring of metal hydrides can have a strong impact on the time scale of hydrogen uptake and release. This is in particular important for Mg-alloys when considered as hydrogen storage materials, since bulk diffusion is notoriously slow and the kinetic rather than thermodynamic properties are dominant in the hydrogen uptake and release processes. In this study, sputter deposition was found to be a good method to create nanostructured Mg and MgH_2 μm thin films using Ar or mixtures of 50% Ar and 50% H_2 as a sputter plasma. Transmission electron micrographs show that the films develop a columnar structure with grain sizes of typically 120 nm wide with the μm-long columnar axes extending throughout the thickness of the films. Application of a substrate bias voltage up to -100 V during film growth leads to a gradual reduction in columnar widths, down to $\sim$50 nm at a bias voltage of -100 V. This reduction in grain sizes correlates with a clear reduction in hydrogen desorption temperatures from 410 °C to 360 °C. This stems from the shorter hydrogen diffusion pathways through the MgH_2 grains. Also, XRD and TEM studies show that grains in films prepared under a bias voltage are more randomly oriented with more defects in the grains and at the surfaces. The presence of these defects is expected to contribute to a faster recombination at the surface of hydrogen into hydrogen molecules, and consequently to lower hydrogen desorption temperatures. Despite the advantage of these better desorption properties, hydrogen storage capacities were found to decrease by more than an order of magnitude for samples prepared at a -100 V substrate bias voltage relative to those prepared without bias voltage. Capping of the Mg films with $\sim$200 nm thin Pd films by sputter deposition leads to reduced hydrogen desorption temperatures around 200 °C, which is caused by the catalytic activity of the Pd top layer. Optimum hydrogen loading conditions of these films were obtained just above $\sim$200 °C at 2.5 bar hydrogen pressure, resulting in hydrogen capacities in the range of 5-7 wt%. Finally, by proper co-sputtering of Mg and Al and subsequent hydrogen loading, thin films of nano-columnar $Mg(AlH_4)_2$, a promising metal hydride for future hydrogen storage purposes, could be produced.

9:30 AM N1.4
Hydrogen Storage in Li and Mg Hydrides Destabilized by Alloy Formation with Si. John J. Vajo[1], Florian Mertens[2], Channing C. Ahn[3], Robert C. Bowman, Jr.[3] and Brent Fultz[3]; [1]HRL Laboratories, LLC, Malibu, California; [2]General Motors Research and Development Center, Warren, Michigan; [3]Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California.

Light element metal hydrides contain large amounts of hydrogen by weight but often decompose at temperatures too high for reversible storage applications. Lithium hydride, which contains 12.5 weight percent (wt.%) hydrogen but does not decompose appreciably below 900 °C, i s an extreme example. Magnesium hydride, which contains 7.6 wt.% hydrogen and has an equilibrium pressure of 1 bar at approximately 280 °C, decomposes under more moderate conditions but is still considered too stable for most applications. We show that S i can significantly destabilize these hydrides through formation of the alloys $Li_{2.35}Si$ and Mg_2Si upon dehydrogenation. Inclusion of Si does, however, reduce the gravimetric density to 5.0 wt. % for both systems. Alloy formation stabilizes the dehydroge na ted states, thereby increasing the equilibrium hydrogen pressure and effectively destabilizing the hydrides. For the LiH/Si system, the equilibrium pressure at 490 °C increases from $5x10^{-5}$ to 1 bar, a factor of $>10^4$. Isotherms were obtained at 400 to 500 °C and x-ray diffraction was used to characterize several lithium silicides that form during hydrogenation and dehydrogenation. Van't Hoff plots give a hydrogenation/dehydrogenation enthalpy of 120 kJ/mol-H_2. In contrast, the enthalpy for pure LiH is 19 0 k J/mol-H_2. For the MgH_2/Si system, the dehydrogenation pressure at 300 °C was >7.5 bar, which is >4 times the pressure for pure MgH_2. Calculations for this system give equilibrium pressures of 1 bar at approximately 20 °C and 100 bar at approximately 150 °C, which represent an i n crease of more than a factor of 1000 over the pressure for pure MgH_2. The MgH_2/Si system was not readily reversible. Hydrogenation of Mg_2Si appears to be kinetically limited due to the relatively low temperature, <150 °C, required for hydrogenation at 100 bar. The two systems described show how hydride destabilization through alloy formation upon dehydrogenation can be used to design and control equilibrium pressures of strongly bound hydrides. pp

9:45 AM N1.5
Hydrogen Permeation Alloys Consisting of Pseudobinary NbTi-NiTi. Kunihiko Hashi, Kazuhiro Ishikawa, Takeshi Matsuda and Kiyoshi Aoki; Kitami Institute of Technology, Kitami, Japan.

V, Nb and Ta showing large hydrogen solubility and high hydrogen diffusivity are promising for hydrogen permeation membranes. However, these metals suffer from severe hydrogen embrittlement and are pulverized spontaneously during hydrogenation. In addition to hydrogen permeability, mechanical properties are also one of the most important characteristics for hydrogen permeation membranes, because membranes have to endure the large pressure difference between upstream and downstream sides. In general, a metal having the large hydrogen permeability is susceptible to hydrogen embrittlement. Thus, it is difficult to improve the resistance of V, Nb and Ta-based alloys to hydrogen embrittlement without the much loss of hydrogen permeability. We have paid attention to the B2-NiTi intermetallic compound having good mechanical properties. In this paper, we present new hydrogen permeation alloys consisting of pseudobinary NbTi-NiTi, in which eutectic phases play a major role in prevention of hydrogen embrittlement, while the NbTi phase contribute mainly to the hydrogen permeation.

10:30 AM *N1.6
The Use of Hydrogen Driven Metallurgical Reactions (HDMR) to Produce Reactive, Nano- Scale And Nano-Composite Materials. James Joseph Reilly[1], Jason Graetz[1], John Johnson[1], Robert Klie[3], Gary Sandrock[4], Tom Vogt[2] and Jim Wegrzyn[1]; [1]Energy Sciences and Technology, Brookhaven National Laboratory, Upton, New York; [2]Physics Dept., Brookhaven National Laboratory, Upton, New York; [3]Materials Science Dept., Brookhaven National Laboratory, Upton, New York; [4]SunaTech Inc., Ringwood, New Jersey.

The cyclic reactions involved in the formation and decomposition of alloy hydrides almost invariably result in the pulverization of the alloy. This hydrogen decrepitation (HD) process was exploited some years ago to produce rare earth alloy powders for fabrication into magnets. More recently the HDDR (hydrogen decrepitation, disproportionation, recombination) process was introduced, which

exploits the thermodynamic instability of many alloys at high temperatures in the presence of H2 gas and is used to produce alloys with improved magnetic properties. We have exploited this process to produce reactive nanoscale and nanocomposite materials. The latter can be readily produced by introducing a third component which can undergo a metathesis reaction with the original alloy, thereby greatly increasing the number of possible reactions and process versatility. Such solid state reactions fall into a wide class which may be designated as hydrogen driven metallurgical reactions (HDMR). After a brief overview of the chemistry involved, examples will be given of the application of HDMR to produce novel Li nanoscale and nanocomposite materials for use as anodes in Li ion batteries. This will be followed by a discussion of its potential application to prepare improved hydrogen storage compounds.

11:00 AM N1.7
Structure and stability of complex metal hydrides: theoretical approach. Zbigniew Lodziana and Tejs Vegge; Depatrment of Physics, Technical University of Denmark, Lyngby, Denmark.

The complex metal hydrides are one of the most promising candidates for fulfilling the hydrogen storage requirements for the automotive industry. A novel systematic approach to study the phase stability of LiBH4 and alanates, based on ab initio calculations is presented. LiBH4 is particularly interesting, since it has a gravimetric hydrogen density of 18.5% and a volumetric hydrogen density of 121 kg/m3. By combining simulated annealing and ab initio lattice dynamics calculations, the Helmholtz free energy F(T) of the hydrides can be determined. This allows to find not only the most stable ground state structure and compare temperature dependence of stability, but also to rule out structures unstable at finite temperatures. As an example we show that for the LiBH4 three thermodynamically stable phases can be identified and a new phase of Cc symmetry is proposed for the first time for a complex hydrides. At low temperatures it becomes unstable with respect to structure with Pnma symmetry in agreement with experimental observations. The XDR pattern and vibrational spectra of the Cc structure agrees well with recently reported experimental data on LiBH4. Calculations of the free energy at finite temperatures yield, that the previously postulated structure with P63mc symmetry turns out to be unstable at finite temperatures with respect to lattice vibrations. For alanates we provide insight into the equilibrium thermodynamics by calculating temperature dependence of the free energy for LiAlH4, Li3AlH6 and LiH. Free energy of solids combined with thermodynamics of hydrogen gives reasonable description of the observed phase transition and hydrogen release. A stable structure of Li3AlH6 with R-3c symmetry is also provided. Presented approach shows great predictive potential of ab initio calculations applied to complex metal hydrides.

11:15 AM N1.8
In Situ X-ray and Neutron Powder Diffraction Study of $LaNi_{5-x}Sn_x$-H Systems. Yumiko Nakamura[1], Robert C. Bowman[2] and Etsuo Akiba[1]; [1]National institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan; [2]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

$LaNi_{5-x}Sn_x$ alloys have been reported as good candidates for a heat pump or sorption compressor material in space flight applications since they show a wide and flat plateau region and also exhibit excellent stability during repeated absorption-desorption cycles. From the viewpoint of the relationship between strain formation and stability of the hydride phase with repeated cycling, any structural changes and introduction of lattice strain in the $LaNi_{5-x}Sn_x$-H system are of great interest. We have studied the structural change and lattice strain formation during absorption and desorption of hydrogen (deuterium) by high purity $LaNi_{5-x}Sn_x$ alloys (x = 0.22, 0.25) using *insitu* X-ray and neutron diffraction along with simultaneously measuring the P-C isotherms. From the profile analysis of X-ray diffraction data, lattice parameter and lattice strain in each hydriding state are evaluated. *Insitu* neutron diffraction data provide hydrogen occupation changing with hydrogen content. The hydriding properties and the stability are discussed in relation to the structural data.

11:30 AM *N1.9
First Principles Computations to Predict and Understand H Storage in Metals, Complex Hydrides and Metal-Organic Frameworks. Gerbrand Ceder and Tim Mueller; MIT, Cambridge, Massachusetts.

Hydrogen is expected to play an important role in the future distribution of energy. While hydrogen fuel cells have seen significant improvements, the problem of hydrogen storage remains the limiting problem. First principles computations can be used to explore the potential of new materials for hydrogen storage (1,2). Key properties, such as reaction enthalpy, absorption sites, and hydrogen diffusion can all be computed with modern first principles methods. We use Density Functional Theory to evaluate the properties of metal hydrides, alanates and metal-organic framework structures. In metal hydrides, the reaction enthalpy can be tailored to any desired value, but the variation of hydrogen potential with hydrogen content, will limit the amount of hydrogen that can be stored in a reasonable pressure range. In the metal-organic framework MOF-5 we have investigated the potential adsorption sites, and the influence of the framework on the nature of the organic linkers. We find that there is only a minor change in the electronic structure of the organic linkers when they are placed in a framework. The implications of this for the hydrogen storage mechanism in this materials and others will be discussed. We will also present a more general framework within which to understand the limits of hydrogen storage in a wide range of materials, whether the hydrogen is stored as adsorbed H2, or through chemical reaction with other materials. (1) Arroyo y de Dompablo ME and Ceder G. First principles investigations of complex hydrides AMH4 and A3MH6 (A=Li, Na, K, M=B, Al, Ga) as hydrogen storage systems. Journal of Alloys and Compounds 2004; 364:6-12. (2) Smithson HJ et al. First Principles Study of Stability and Electronic Structure of Metal Hydrides. Phys. Rev. B 2002; 66:144107.

SESSION N2: Hydrogen for Materials Storage: Complex Metal Hydrides
Wednesday Afternoon, December 1, 2004
Independence E (Sheraton)

1:30 PM *N2.1
Properties of Advanced Hydrogen Storage Materials. Karl J. Gross and Weifang Luo; Sandia National Laboratory, Livermore, California.

The use of hydrogen for transportation presents technical challenges that require the development of novel hydrogen storage materials. The discovery that hydrogen can be reversible absorbed and desorbed from Ti-doped NaAlH4 has created an entirely new prospect for lightweight hydrogen storage [1]. This includes complex hydrides and the broader class of materials that store hydrogen reversibly through decomposition / recombination reactions. An example of which is the Li-N-H system with a theoretical reversible capacity of 6 wt% hydrogen in the temperature range of 255-285°C [2]. Modifications of this system are showing significant improvements in changing the operating temperature and pressure conditions [3]. The latest results on complex hydrides and modified amides are presented including cycle life properties and in situ X-ray diffraction studies. 1. Bogdanovic and Schwickardi, J. Alloys and Compounds Vol. 253,1, 1997. 2. Nature vol.420, p302, Nov. 21, 2002. 3. W. Luo, accepted, J. Alloys and Compounds, 2004.

2:00 PM N2.2
Raman Spectroscopy of Single Crystal Sodium Aluminum Hydride. Eric Majzoub[1], Kevin McCarty[1] and Vidvuds Ozolins[2]; [1]MS 9403, Sandia National Laboratories, Livermore, California; [2]University of California, Los Angeles, Los Angeles, California.

Sodium aluminum hydride, a complex ionic hydride has gained attention due to a high hydrogen weight content (about 7.5 wt.%) and its reversibility upon doping with a few mol.% Ti, as shown by Bogdanovic and coworkers in 1997. The role of Ti in the reversibility of this material is not yet understood. However, it is necessary to understand the mechanism of enhanced kinetics in this system, if the higher wt.% candidates in this class of materials are to be exploited for hydrogen storage. NaAlH4 can be viewed as an ionic solid with Na+ cations and AlH4- anions. A study of the lattice dynamics is useful in understanding the role of dopants and possible decomposition pathways. We will present a full polarization analysis of Raman spectra from single crystal NaAlH4, and in-situ spectra up to the melting point of approximately 180C. In-situ Raman spectroscopy indicates that the AlH4- anion remains stable up to temperatures near the melting point of NaAlH4. The implications of a stable AlH4- anion and the role of Ti in the enhanced kinetics mechanism will be discussed.

2:15 PM N2.3
Characterization of the Titanium Catalyst in Sodium Aluminum Hydride. Job Rijssenbeek[1], Yan Gao[1], Seth T. Taylor[1], Matthew J. Banholzer[1], Sesha S. Srinivasan[2], Craig M. Jensen[2], Jonathan C. Hanson[3] and Xianqin Wang[3]; [1]GE Global Research, Niskayuna, New York; [2]Chemistry, University of Hawaii, Honolulu, Hawaii; [3]Chemistry, Brookhaven National Laboratory, Upton, New York.

The discovery that the dehydrogenation and rehydrogenation of $NaAlH_4$ can be catalyzed by addition of titanium-based compounds has catapulted complex hydrides to the forefront of hydride research. Only recently has the chemical state and local atomic environment of

the titanium catalyst become apparent from X-ray absorption spectroscopy performed by our group and others. Results of detailed in-situ powder x-ray diffraction experiments during both the dehydrogenation and the rehydrogenation reactions of $NaAlH_4$ will be presented. These novel data prove that both reactions occur in a stepwise fashion and agree well with pressure-composition isotherms of the same material. X-ray absorption spectroscopies (XANES/EXAFS) at the temperatures of interest reveal that the titanium is quickly reduced to a metallic state during ball milling and subsequent hydrogen desorption from $NaAlH_4$. We will also present the first direct imaging of the Ti-containing nanoparticles by energy-filtered transmission electron microscopy. These studies begin to elucidate the chemical and morphological changes that accompany hydrogen sorption and desorption cycling.

2:30 PM N2.4
X-Ray Absorption Study of Ti-Doped Sodium Aluminum Hydride. Jason Graetz[1], Alexander Yu. Ignatov[2], Trevor A. Tyson[2], James J. Reilly[1] and John Johnson[1]; [1]Energy Sciences and Technology, Brookhaven National Lab, Upton, New York; [2]Physics, New Jersey Institute of Technology, Newark, New Jersey.

The discovery of reversible hydrogen cycling in Ti-doped sodium aluminum hydride [1] has generated considerable interest in the sodium alanates and led to approximately 100 new publications on this system over the past seven years. Despite this tremendous effort, the mechanism by which $NaAlH_4$ is activated in the presence of a small amount of titanium is still not well understood. In part, this is because the location and valence of the activating species is unknown. X-ray absorption near-edge spectroscopy was used to explore the local titanium environment and valence in 2-4 mol% Ti-doped sodium alanate [2]. An empirical relationship between the titanium valence and the Ti *K*-edge onset, based upon known standards, was used to estimate oxidation states of the titanium catalyst in doped $NaAlH_4$. These results demonstrate that the formal titanium valence is zero in doped sodium alanate and nearly invariant during hydrogen cycling. We found no evidence of a tri-or tetravalent dopant ion, indicative of a bulk lattice substitution. Rather, the edge fine structure suggests that aluminum atoms coordinate the titanium in an environment similar to that of $TiAl_3$. This is not surprising since $TiAl_3$ is the most thermodynamically stable titanium product. However, the fine structure of the post-edge region indicates that the titanium lacks the long-range order that exists in crystalline $TiAl_3$ and is likely amorphous in this system. These results also demonstrate that the local titanium environments are nearly equivalent in the hydrided ($NaAlH_4$) and dehydrided (NaH +Al) states. [1] B. Bogdanovic and M. Schwickardi, J. Alloys Compd. **253 – 254**, 1 (1997). [2] J. Graetz, A.Y. Ignatov, T.A. Tyson, J.J. Reilly, J. Johnson, accepted to Appl. Phys. Lett., (2004).

3:15 PM *N2.5
Materials for Hydrogen Storage: Issues and Challenges. Puru Jena, Physics, Virginia Commonwealth, Richmond, Virginia.

The limited supply of fossil fuels, its adverse effect on the environment, and growing worldwide demand for energy has necessiated the search for new and clean sources of energy. The possibility of using hydrogen to meet this growing energy need has rekindled interest in the study of safe, efficient, and economical storage of hydrogen. Unfortunately, the current methods for storing hydrogen as a compressed gas or liquid do not meet the industry requirements. An alternate method for hydrogen storage involves metal hydrides. The conventional intermetallic hydrides store hydrogen at interstitial sites and are reversible at around room temperature. However, the relative weight of stored hydrogen in these materials is rather low (1-3 wt %) and do not meet the requirement of the transportation industry (10%). A novel approach for hydrogen storage is to combine the favorable kinetics and thermodynamics of conventional metal hydrides with that of the large hydrogen storing capacity of organic molecules such as CH4. This talk will deal with the issues and challenges in hydrogen storage materials. In particular, I will discuss the properties of a novel class of materials called alanates which have the chemical composition (Mn+ (AlH4)n-, M=Li, Na, K, Mg). Although these materials can store uo tp 18 wt % hydrogen, the temperature where hydrogen desorbs is rather high. It was recently discovered that doping of Ti-based catalyst in NaAlH4 can significantly lower the hydrogen desorption temperature, but why and how Ti acconplishes this task remains a mystery. Using first principles calculations we will provide a molecular level understanding of the role of Ti in lowering the hydrogen desorption temperature in NaAlH4 and LiBH4. It is hoped that the understanding gained here can be useful in designing better catalysts as well as hosts for hydrogen storage.

3:45 PM N2.6
Destabilized Alkali Metal Borohydrides for Hydrogen Storage. Ming Au, Jeffrey Holder and Ted Motyka; Savannah River National Lab, Aiken, South Carolina.

Alkali metal borohydrides such as LiBH4 and NaBH4 hold large amounts of hydrogen (18.5wt% and 10.6wt%) more than alanates (5.6wt%) and other conventional metal hydrides (1.4 1.8 wt%). Unfortunately, heating above 470°C is required to release the hydrogen, which is close to its melting point. The feasibility of rehydrogenation has also not adequately been studied. Currently, these hydrides have been used as on-demand hydrogen sources through an irreversible catalyzed hydrolysis and are marketed commercially. However, there is a possibility that the alkali metal borohydrides can be destabilized to release hydrogen and then be recharged at acceptable low temperature. In our investigation, the modified LiBH4 releases 9 wt% hydrogen starting from 150°C. The materials are also reversible in dehydriding and rehydriding tests. The destabilized borohydrides absorb 9 wt% hydrogen after dehydriding. About 6 wt% hydrogen was reclaimed from rehydrided borohydrides. This paper will present our initial results in the effort to reduce the thermodynamic stability and improve the kinetics of borohydride dehydrogenation. The crystalline structure, bonding feature, catalysts distribution, particle size and morphology will be discussed in this paper.

4:00 PM N2.7
Computational Studies of NHxBHx Materials for Hydrogen Storage. Maciej Gutowski, Pacific Northwest National Laboratory, Richland, Washington.

The NHxBHx (x=1-4) offer very attractive gravimetric densities of hydrogen. For instance, NH4BH4 stores 24wt% of hydrogen. The NB unit is isolectronic to the CC unit and the NHxBHx materials may be viewed as inorganic variants of hydrocarbons. The N and B atoms differ, however, in electronegativity resulting in polarity of the NHxBHx molecules. The electrostatic interactions among polar NHxBHx species are responsible for the solid-state nature of the NHxBHx compounds under standard conditions, whereas the analogous hydrocarbons are gaseous. In consequence, the NHxBHx compounds offer also attractive volumetric density of hydrogen. Density functional theory calculations with gradient corrected exchange-correlation functionals were performed for solid NHxBHx (x=1-4) compounds and for BN. The four steps of hydrogen release were found thermoneutral to within 10 kcal/mol. Molecular dynamics simulations for clusters with a few tens of NHxBHx molecules were performed to characterize the role of surface effects and identify chemical pathways for hydrogen release and uptake.

4:15 PM *N2.8
Characterization and Mechanistic Studies of the Active Titanium Species in the Reversible Dehydrogenation of Ti-Doped Sodium Aluminum Hydride. Craig M. Jensen[1], Martin Sulic[1], Meredith Kuba[1], Klaus Yvon[3], Alberto Albinati[4], Sandra Eaton[2], Sesha Srinivasan[1], Sandrine Gomes[3], Hans Hagemann[3] and Guillaume Renauudin[3]; [1]Chemistry, University of Hawaii, Honolulu, Hawaii; [2]Chemistry and Biochemistry, University of Denver, Denver, Colorado; [3]Laboratoire de Crystallographie, Universite de Geneve, Geneve 4, Switzerland; [4]Department of Structural Chemistry, University of Milan, 1-20133 Milan, Italy.

In 1997, Bogdanovic and Schwickardi reported that the elimination of hydrogen from solid NaAlH4 is markedly accelerated and rendered reversible under moderate conditions upon mixing the hydride with a few mole percent of selected transition metal complexes. We found that doping the hydride through an alternative, mechanical milling method leads to considerable improvements in the practical hydrogen cycling performance of the hydride. It now appears that a variation of the doped hydride could possibly be developed as a viable means for the onboard storage of hydrogen. However, no dopant precursors have been found that give a greater kinetic enhancement than those cataloged in Bogdanovic's original, 1995 patent. Similarly, only the sodium and mixed sodium, lithium salts of the alanates have been found to undergo largely reversible dehydrogenation under moderate conditions upon doping. This lack of progress is surprising in view of the recent "gold rush" flurry of activity that has been directed towards the development of alanates as practical onboard hydrogen carriers. Clearly, these efforts have been handicapped by a lack of understanding of the nature and mechanism of action the dopants. We have therefore initiated efforts to elucidate the fundamental basis of the remarkable hydrogen storage properties of this material. Our efforts have pointed to a model of the material in which the dopants are substituted into the bulk hydride lattice. A detailed version of this model has emerged from our recent studies of the doped hydride by electron paramagnetic resonance and infrared spectroscopy as well as X-ray diffraction. The results of these studies will be presented and discussed in terms of their relationship to our "substitutional" model of the doped hydride.

SESSION N3: Poster Session: Materials for Hydrogen Storage
Wednesday Evening, December 1, 2004
8:00 PM
Exhibition Hall D (Hynes)

N3.1
Ab Initio Study on the Miscibily Between Titanium and Sodium Alanate. Eung-Kyu Lee[1,2], Young Whan Cho[2] and Jong-Kyu Yoon[1]; [1]School of Materials Science and Engineering, Seoul National University, Seoul, South Korea; [2]Nano-Materials Research Center, Korea Institute of Science and Technology, Seoul, South Korea.

As hydrogen storage materials, sodium alanate (NaAlH4) has high theoretical capacity (7.5wt%), relatively low dehydrogenation temperature, and cheap materials cost. Until mid 1990, however, the dehydrogenation of sodium alanate had been characterized by very slow kinetics and limited reversibility under severe conditions. Bogdanovic in 1997 was the first to report that sodium alanate could be made reversible at moderate temperature and pressure by doping with Ti. Although many researchers have studied, there is no clear understanding yet on the role of Ti in sodium alanate; whether Ti dissolves into the alanate structure and occupies a specific lattice site or exists as a separate phase such as free Ti or Ti-Al intermetallics. Moreover, it is quite difficult to characterize the state of Ti by experimental techniques. Therefore, a theoretical calculation of the hypothetical reaction enthalpy between Ti and sodium alanate would provide some insight about the possible state of Ti in sodium alanate. In this study, the total energy of the Ti doped sodium alanate has been calculated by ab initio calculations based on the projector-augmented plane wave method. We calculated the total energy of (Na1-x,Tix)AlH4, Na(Al1-x,Tix)H4, (Na1-x,Tix)3AlH6, Na3(Al1-x,Tix)H6, Na, Al, Ti, and Al3Ti using the ultrasoft pseudopotential method with exchange correlation energy by general gradient approximation. To investigate the miscibility between Ti and alanate, the reaction enthalpies were calculated which determine whether the reactions will go or not. From these information, we may be able to explain where Ti atom locates in sodium alanate and obtain optimized lattice structure of Ti-doped sodium alanate.

N3.2
Hydrogenated Aluminum Clusters for Hydrogen Storage: A DFT Study. Alexander Goldberg[1] and Irene Yarovsky[2]; [1]Materials Science, Accelrys Inc., San Diego, California; [2]Applied Physics, RMIT University, Melbourne, Victoria, Australia.

Hydrogen storage is one of the crucial issues in fuel cell technology. Light metal clusters, such as aluminum, have recently attracted researchers' attention since such clusters represent a promising material for hydrogen storage devices. Hydrides of Al clusters and nanowires offer an advantage of high storage densities, relatively low cost and high safety potential as the hydrogen release is endothermic. Al7 and Al13 have been especially promising since they have been identified as particularly stable of all Al clusters. In this work adsorption of hydrogen on Al13 clusters has been investigated theoretically using the Density Functional Theory. We have performed geometry optimization of atomic and molecular hydrogen in the proximity of Al13 and calculated the binding energy and electronic properties of the stable Al13+H assemblies. We have also calculated the energy barrier for the hydrogen atom transition between different adsorption sites on Al13 cluster as well as the activation energy for the dissociation and adsorption of molecular hydrogen. The hydrogen atom adsorbs on the surface of Al13 cluster, preferably the atop position, without an energy barrier. A small barrier for H atom transition from one adsorption site to another together with the minor energy difference between the most stable isomers points towards high mobility of the hydrogen atom on the surface. Up to twelve H atoms can be adsorbed on the cluster resulting in the less distorted cluster geometry. We have calculated a dissociation-adsorption barrier for the hydrogen molecule to be about 14 kcal/mol. It can be concluded that the Al13 clusters have a large hydrogen storage capacity while requiring some additional (but not very high) energy to release the adsorbed hydrogen.

N3.3
An in-situ X-ray Diffraction Study of the Desorption of $TiCl_3$-Doped Sodium Alanate. Scott A. Speakman, Joachim H. Schneibel and Dewey S. Easton; Metals and Ceramics Division, Oak Ridge National Lab, Oak Ridge, Tennessee.

Sodium alanate ($NaAlH_4$) is a reversible hydrogen storage medium when catalyzed with $TiCl_3$. In this study, commercially obtained sodium alanate was ball-milled with and without $TiCl_3$, as well as left in its as-received state. The hydrogen release and uptake was measured during temperature-programmed absorption and desorption, as well as by isothermal charging and discharging, using a Sievert-type apparatus. These data were supplemented by in-situ X-ray diffraction studies of hydrogen desorption. In-situ X-ray diffraction allowed the contribution of $NaAlH_4$ decomposition to the hydrogen release rate to be separated from that of Na_3AlH_6 decomposition, as well as the identification of resulting phase products. The decomposition of Na_3AlH_6 produced not only the expected products, such as NaH and Al, but also minor phase(s) that have not yet been matched to any phase in the ICDD Powder Diffraction File. The as-received sodium alanate consistently displayed deviations from the published phase, demonstrated by significant peak splitting. Significant lot-to-lot variations of the as-received alanate were also observed. Ball-milling in an inert atmosphere produced a homogeneous crystal structure consistent with previously published results. The addition of $TiCl_3$ produced an average lattice parameter increase of 400 ppm; however, Rietveld analysis could not distinctly confirm the presence of Ti substitution on the Al site. This work is progressing towards a description of the role of $TiCl_3$ and of micro-alloying in the charging/discharging kinetics of sodium alanate. This research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy under Contract No. DE-AC05-00OR22725.

N3.4
Local Atomic Structure for Dopants in Complex Metal Hydrides. Edward Bruster[1], Tabbetha A. Dobbins[1] and Roland Tittsworth[2]; [1]Institute for Micromanufacturing/ Physics, Louisiana Tech University, Ruston, Louisiana; [2]Center for Microstructes and Devices, Louisiana State University, Baton Rouge, Louisiana.

Research has shown that dopant additions to complex metal hydrides can enhance hydrogen desorption kinetics. The atomic-scale location of Ti dopants in NaAlH4 has not been fully described. As well, a mechanism for the kinetic enhancement has not been fully developed. Recently, published works have shown that dopant ion size may largely influence hydrogen desorption kinetics. We propose to study the local bonding environment of the dopant atoms using extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES). Using these techniques, we will provide details of the local bonding environment of Ti dopants in NaAlH4. Knowledge of the atomic-scale interactions between the dopant atoms and host lattice will aid in a broader understanding of the mechanism for improved hydrogen desorption. Dopant atoms are typically added via mechanical milling. We will examine the preferred valence state for dopants and the preferred bond length and orientation with respect to the other metallic cations in the system. Once completed, the proposed studies, coupled with existing information regarding the kinetics of hydrogen desorption and storage capacity, will aid in information regarding the mechanisms for desorption enhancements. We will perform XANES and EXAFS at the synchrotron source at J. Bennet Johnston Center for Advanced Microstructures and Devices (CAMD) located in Baton Rouge, LA using the DCM beamline which is capable of attaining x-ray energies from 2 keV to 14 keV. The hydroscopic nature of these materials complicate powder handling during transport to the x-ray beamline. At CAMD, we have developed a protocol for handling samples which includes the use of controlled atmosphere sample holders which will be loaded inside of a nitrogen glove box. Ti-doped NaAlH4 powders will be prepared at Louisiana Tech University- Institute for Micromanufacturing via mechanical milling. After XANES/EXAFS measurement, we will use the WINXAS package for XANES/EXAFS data extraction and the FEFF8.0 package for atomic structure model fitting. The proposed research will yield crystallographic information about the dopant location within the host structure. Information such as coordination environment of the dopant atom and bond length between the dopant atom and metal host atoms will be obtained. This data will give the hydrogen storage research community a basic understanding of dopant atomic local structure and provide information regarding which experimental factors control this structure (i.e. milling time/rate, valence state of precursor salts).

N3.5
Hydrogen Absorption and Desorption by Magnesium-Based Nano-Composite Materials. Yoshitsugu Kojima, Yasuaki Kawai and Tetsuya Haga; Toyota Central R&D Labs., Inc., Aichi, Japan.

Magnesium Mg has a high hydrogen H2 storage capacity of 7.6 wt%. However, the high work temperature (573 K), slow reaction kinetics (high activation energy) limit the practical application of MgH2 system. In this study, Mg-based nano-composite materials were prepared by high-energy planetary ball milling of MgH2 and a catalyst (metal oxides, transition metals, metal chlorides). The H2 absorption and desorption properties of these materials were investigated with a Sieverts-type apparatus and a temperature-programmed desorption analysis. The nano-composite materials containing Ni-based catalysts (LiNiO2, Ni nano-particles) exhibited the rapid absorption and desorption kinetics. The nano-composite materials desorbed H2 below

498 K, while the composite materials (MgH2 and catalysts) and the ball-milled MgH2 could not desorb H2 at the temperature. After H2 desorption, high H2 pressure and the catalysts accelerated the H2 absorption. The H2 absorption capacities of the nano-composite materials exhibited 5.0 wt% at 9 MPa and 296K. Formation enthalpy and entropy of MgH2 were not altered by milling with these catalysts. It was considered that the activation energy of the H2 absorption and desorption was reduced drastically.

N3.6

NMR and X-ray Diffraction Studies of Phase Transformations in the Destabilized LiH-Si System. Robert C. Bowman[1,3], S.-J. Hwang[2], C. C. Ahn[3] and J. J. Vajo[4]; [1]Jet Propulsion Laboratory, Pasadena, California; [2]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California; [3]Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California; [4]HRL Laboratories, LLC, Malibu, California.

The novel approach of destabilizing hydrogen rich but strongly bound hydrides such as LiH via alloying with Si has been recently shown to be feasible and to improve substantially their potential as hydrogen storage materials in fuel cell powered vehicles. A reversible hydrogen storage capacity totaling around 5.0 wt.% was measured with mixtures of LiH and silicon powders where this LiH+Si system produces a 4-to-5 order-of-magnitude increase in the equilibrium pressure compared to just LiH alone for temperatures below 800 K. Volumetric measurements of the hydrogen absorption and desorption isotherms in the 650 K - 780 K temperature range revealed two and three plateau regions on lightly ballmilled mixtures of 2.5LiH+Si and 4.4LiH+Si, respectively. The phase compositions at the various stages of reaction for these samples have been examined by Magic Angle Spinning-nuclear magnetic resonance (MAS-NMR) of the ^{7}Li, ^{1}H, and ^{29}Si spins and powder x-ray diffraction (XRD). The initial mixtures of LiH and Si were found from the NMR and XRD results to convert into at least two of the known Li-Si silicide intermetallics (i.e., $Li_{12}Si_7$ and $Li_{13}Si_4$) as well as providing evidence for a previously unknown ternary Li-Si-H phase as hydrogen was first desorbed and then absorbed. While the absorption reactions are certainly reversible over portions of the Li-Si-H composition range, incomplete recovery of the original LiH + Si phases was also observed under some test conditions. The distributions of the silicide and hydride phases for various stages of reaction are reported.

N3.7

Cyclic Behavior of Hydrogen Absorption and Microstructural Change in V-Cr-Ti Alloy. Kohta Washio[1], Takanori Suda[1], Somei Ohnuki[1], Seiichi Watanabe[1], Hironobu Arashima[2], Hideaki Ito[2] and Toshiki Kabutomori[2]; [1]Materials Engineering, Hokkaido University, Sapporo, Japan; [2]Muroran Res. Inst., Japan Steel Works, Muroran, Hokkaido, Japan.

BCC type V-Cr-Ti alloys has high hydrogen-storage capacity, but after repeating the hydrogenation-dehydrogenation cycles, it shows degradation of effective storage capacity, which is the difference of the absorption and desoption. To clarify the degradation, in this work, crystal structural and microstructural observation was carried out by means of XRD and crosscut TEM. (1) Crystal structural change: From XRD analysis the hydrogenation caused diffraction- peak shifting to low angle side, and then showed broadening slightly after 100 cycles. The results mean that lattice planes should be expanded and included internal stress. (2) Microstructural change: Before hydrogenation, it showed typical annealed structures including a limited number of planner dislocations. The hydrogenation induced irregular cracks and tangled dislocations. With increasing of cycles, the width of the crack was expanded, and the dislocations were accumulated with high density. (3) Degradation due to cyclic charging: The crystal structural and microstructural changes indicated that the decreasing of effective storage capacity may depends on the increasing of immobile hydrogen trapped by dislocation, as well as decreasing of hydrogen-stored sites in interstitial positions.

N3.8

Synthesis and characterization of doped magnesium alanate. Yoonyoung Kim[1,2], Young Kwan Kim[1], Young Whan Cho[1] and Kyung Byung Yoon[2]; [1]Nano-material Research Center, Korea institute of Science and Technology, Seoul, South Korea; [2]Department of Chemistry, Sogang University, Seoul, South Korea.

Some complex hydrides which can reversibly absorb and desorb hydrogen have recently been discovered. These discoveries have prompted many experimental and theoretical works on light metal complex hydrides which have high theoretical hydrogen capacities up to 10 wt%. However, the dehydrogenation temperature is relatively high and the hydrogen uptake process is very slow and can only be realized under severe conditions. Fortunately, doping with some transition metals such as Ti has been known to improve both thermodynamics and kinetics. Magnesium alanate, $Mg(AlH_4)_2$, is one of the promising materials that has high theoretical hydrogen content (9.3 wt%) and relatively low decompose temperature around 140^0C. However, it has not been confirmed yet whether it can be rehydrogenated at moderate temperature and pressure. Magnesium alanate has been synthesized by metathesis reaction of sodium alanate and magnesium chloride in THF. $Mg(AlH_4)_2$, in the reaction product was separated from NaCl by filtration using the solubility difference in THF. The phase composition and crystal structure of purified magnesium alanate have been characterized by XRD, FT-IR and elemental analysis. The thermal decomposition behavior of $Mg(AlH_4)_2$ has also been investigated by TGA/MS. To improve thermodynamics and kinetics, magnesium alanate was doped with $TiCl_3$ or $Ti(OBt)_4$ in appropriate organic solvent. The decomposition temperature and reversibility of the doped magnesium alanate were measured by TGA/MS and a Sievert-type apparatus.

N3.9

Multinuclear NMR on Ti-doped $NaAlH_4$. Julie Lynn Herberg[1], Robert S. Maxwell[1] and Eric Majzoub[2]; [1]Chemistry and Material Science, Lawrence Livermore National Laboratory, Livermore, California; [2]Sandia National Laboratories, Livermore, California.

Ti-doped NaAlH4 has gained attention because of its large weight percentage of hydrogen (5 %), compared to traditional interstitial hydrides making it an excellent candidate for hydrogen storage materials. The addition of transition-metal dopants, in the form of Ti-halides, such as $TiCl_3$, dramatically improves the kinetics of the absorption and desorption of hydrogen from$NaAlH_4$. New results from ^{1}H, ^{27}Al, and ^{23}Na MAS (Magic Angle Spinning) NMR (Nuclear Magnetic Resonance), ^{1}H Multiple Quantum NMR, and ^{1}H NMR variable temperature will be presented. All experiments were performed with pure $NaAlH_4$ and $NaAlH_4$ doped with Ti to fully understand how the Ti impacts this complex network to gather insight into the structure-properties relationships necessary to engineering advanced H_2 storage materials. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

N3.10

Metal Nanocable Systems for Hydrogen Storage. Jesse Thomas McCann[1], Yugang Sun[1], Jun Chen[2] and Younan Xia[1]; [1]Department of Chemistry, University of Washington, Seattle, Washington; [2]Institute of New Energy Material Chemistry, Nankai University, Tianjin, China.

Engineering the nanostructure of materials with good hydrogen storage characteristics provides an excellent route to enhancing their storage performance. We have recently demonstrated controlled synthesis of large quantities of well-defined one-dimensional silver nanostructures by the reduction of metal salts in the presence of a polymeric capping reagent. Galvanic replacement with a palladium salt can be used to synthesize nanotubes or functionalize the surface of the nanowires, as palladium can catalyze the decomposition of dihydrogen into hydrogen atoms, which can then be stored in the lattice interstices of silver. This approach was used to prepare a new class of nanostructured materials for hydrogen storage with hydriding/dehydriding characteristics and hydrogen uptake capacity comparable to pure palladium. These nanostructured interstitial storage media display a number of advantages over bulk crystalline systems, such as mitigation of crystal strain with their high surface-to-volume ratio, leading to excellent cycle stability. The synthesis methods used allow a good degree of flexibility, and this talk will focus on methods and possibilities for the fabrication of higher performance one-dimensional hydrogen storage materials.

N3.11

Hydrogen in and from Different Boron-Nitrogen Compounds. Gert Wolf, Inst. fuer Physikalische Chemie, TU Bergakademie Freiberg, Freiberg/Sachsen, Germany.

Different BNH-compounds have a high hydrogen content per mass unit (up to 18 mass% of hydrogen) and unusual hydrogen exchange properties also. They could be therefore interesting and suitable materials for the use as a hydrogen source or for storage. The compounds are isosteric to well known aliphatic or aromatic hydrocarbons (CH-compounds). Since the bonding conditions and with it the state of the hydrogen are not comparable for the BNH- and in the CH-compounds, respectively, we observed for the decomposition and formation of BNH-compounds completely other properties. The thermodynamic and kinetic properties of thermal activated processes and of reactions in solutions are unexpected. Similar statements are follow from the comparison of the thermophysical properties for the BNH-compounds with the corresponding values for complex hydrides (alkali alanates or boranates). The basis for all of these considerations are our extensive experimental investigations of the thermophysical

and structural properties of selected BNH-compounds [1 to 4]. By use of different calorimetric, gravimetric, volumetric and spectroscopic measurements we determined process parameter for the decomposition and formation. The sequence of the thermal events is strongly controlled kinetically. The influence of high hydrogen pressure (up to 5kbar) on the decomposition of solids and solutions with different solvents seems to be negligible. [1] J. Baumann Dissertation 2003, TU-Bergakademie Freiberg, Germany [2] F. P. Hoffmann, G. Wolf, L. D, Hansen, Advances in Boron Chemistry, Royal Society of Chemistry, Cambridge, UK, 1997, p. 514 [3] G. Wolf, J. Baumann, F. Baitalow, F. P. Hoffmann, Thermochimica Acta 343, 2000, 19-25 [4] J.Baumann, F. Baitalow, G. Wolf Ztschr. Anorgan.Allgem. Chemie 2004 in press

N3.12

Hydrogen Existing States and Degradation of Type 316L and Alloy 625 for High-Pressure Hydrogen Storage Tank.

Kenichi Takai, Kota Murakami and Nobuyuki Yabe; Mechanical Engineering, Sophia University, Tokyo, Japan.

High-resistance metals to hydrogen degradation have been required since hydrogen pressure in tank for fuel cell vehicle varies from 35 MPa to 70 MPa, and that in hydrogen storage tank increases to above 100 MPa. Austenitic metals used under the high-pressure hydrogen for fuel-cell constituent materials such as Type 316L and Alloy 625 were prepared, because of the low susceptibility to hydrogen degradation. Three principal aspects regarding the austenitic metals are present here: (1) to find out the condition of hydrogen cathodic charging safer than high-pressure hydrogen charging method since the charging under high-pressure hydrogen is much danger and more expensive than the cathodic charging, (2) to analyze hydrogen existing states in the metals by measureing hydrogen trap activation energy (Ea) obtained by thermal desorption spectrometry (TDS), and (3) to clarify the relationship between the hydrogen existing states and the degradation. The both metals were solution heat treated, charged under cathodic polarization and high-pressure hydrogen, then analyzed hydrogen content and existing states. The cathodic charging enable us to be comparable with charging under high-pressure hydrogen because of same hydrogen content and same hydrogen desorption profile without the surface damage ,when the specimens are charged under a condition of 50mA/m2 in pH 2.5 H2SO4 solution added to 0.06 mass ppm NH4SCN. The hydrogen desorption peak temperature of Type 316L is 433 K and that of Alloy 625 is 411 K. The peak temperature increases with specimen thickness because of rate-determining in hydrogen diffusion. The saturated hydrogen content in Type 316L is 280 mass ppm, and that in Alloy 625 is 80 mass ppm. Ea values of both metals are approximately 45 kJ/mol, which is close to an activation energy of hydrogen diffusion in fcc metals. Hydrogen content desorbed below 473K from these specimens increases with degree of plastic deformation. Thus the hydrogen desorbed below 473K is trapped at lattice defects such as dislocations and vacancies created by the deformation. Whereas Ea value is held constant in spite of increasing in degree of plastic deformation. This means that the activation energy of hydrogen diffusion is larger than binding energy between hydrogen and trapping sites during hydrogen desorption process.

N3.13

Photoelectrochemical Properties of Titania Nanotubes.

Craig A. Grimes, Karthik Shankar, Gopal K. Mor and Oomman K. Varghese; Penn State University, University Park, Pennsylvania.

N-type nanocrystalline titania has attracted significant attention in the scientific community for its unique properties such as size quantization effects, large specific surface area and the possibility of large-scale use in high-efficiency semiconducting photoelectrochemical cells. In this study we examine the photochemical properties of titania nanotube arrays fabricated by anodization of a starting Ti foil in a fluoride ion containing electrolyte. While the nanocrystalline titania typically used in photoelectrochemical cells is prepared from a colloidal sol of nanoparticles, the titania nanotubes in the present study are robust immobilized structures grown anodically upright from the basal plane to form a compact non-particulate film. The average pore size, wall thickness and the length of the nanotubes are about 22 nm, 12 nm and 200 nm respectively for samples anodized at 10 V, and 76 nm, 27 nm and 400 nm respectively for a 20V sample. Diffuse reflectance UV-Vis spectroscopy is used to investigate the absorption properties of the titania nanotube samples. A broadening of the absorption spectra is seen as a function of material phase, nanotube diameter, and Pd sensitization. The photoelectrochemical behavior of the titania nanotubes are examined under bandgap UV illumination, and correlated with the nanotube size and crystallinity. The magnitude of the anodic photocurrents obtained from the polycrystalline nanotube samples appears to be significantly higher than that reported for any other form of nanocrystalline titania. Upon illumination by a 365 nm UV light source, anodic photocurrent densities as high as 25 mA/cm2 were obtained in 3-electrode photoelectrochemical cell with a film of titania nanotubes used as the photoanode, platinum mesh as the counter electrode and 1 M KOH the electrolyte. It is shown that for different nanotube sizes, the photoelectrochemical activity can be significantly enhanced by the appropriate annealing treatment, and by the addition of a non-continuous thin layer of Pd nanoparticles atop the surface of the nanotubes by evaporation.

N3.14

Carbon Nanofibrous Materials Prepared from Electrospun Polyacrylonitrile Nanofiber for Hydrogen Storage.

Seong Mu Jo[1], Wha Seop Lee[1], Dong Young Kim[1], Sun Ho Park[2,1] and Byung Chul Kim[2]; [1]Polymer Hybrid Research Center, Korea institute of Science and Technology, Seoul, South Korea; [2]Division of Applied Chemical Engineering, Hanyang University, Seoul, South Korea.

Hydrogen storage in carbon materials is a very attractive because high gravimetric storage capacities may be possible due to the low specific weight of carbon. Since the first report of hydrogen storage using nanocarbon materials by Dillon et al., lots of works for hydrogen storage using SWNT, MWNT, GNFs, etc., have been done. However, they showed low storage capacity in the range of 0.04-4 wt% at room temperature. Typical carbon materials such as active carbon, active carbon fiber, and graphite powder were also investigated as potent materials for hydrogen storage. They have very low capacities ranging from 0.04-0.4 wt% at room temperature because the effective pore volume for hydrogen storage in them is too low although they generally have very high surface area. Recently, there has been growing interest in electrospinning process of polymer solution or melt. Electrospinning is one of the powerful tools producing polymeric ultra-fine fibers in range of a few nanometer to a few hundreds nanometer in diameters, which cannot easily obtained by traditional methods for making fibers. In this study we prepared carbon nanofibers from carbonization of the electrospun polyacrylonitrile (PAN) nanofibers precursors. Electrospun PAN nanofibers were carbonized without or with iron acetylacetonate for induction of catalytic graphitization at the range of 900-1500 oC in nitrogen atmosphere, resulting in ultra-fine carbon fibers in the range of 90-300 nm. Structural properties and morphology of the resulting carbon nanofibers were investigated XRD, Raman IR, FE-SEM, TEM, and surface area/nanopore analysis (BET). The PAN based carbon nanofibers carbonized without catalyst have amorphous structure with d002 0.37 nm and smooth surface with very low surface area of 16-18 m2/g. The PAN based carbon nanofiber carbonized with catalyst showed the graphite structure around the catalyst particles on their surface. The graphite nanofibers with the average fiber diameter of 150-300 nm have about d002 0.341 nm indicating turbostrate structure. The graphite structure supported by raman spectra and XRD was grown with increase of carbonization temperature and catalyst contents. The hydrogen storage capacities of the above carbon nanofiber materials measured using gravimetric method by Magnetic Suspension Balance (MSB) at room temperature and 100 bars. The storage data were obtained after the buoyancy correction. The hydrogen storage capacity of the PAN based carbon nanofibers with the average fiber diameter of 90 nm, which were carbonized at 1000 oC, 1300 oC, and 1500 oC, showed 1.6 wt%, 1.8 wt%, and 0.2 wt%, respectively. The hydrogen storage capacity increased with increasing carbonization temperature but that of the sample at 1500 oC was low due to densification of pore structure in carbon nanofiber. In the case of graphitic nanofiber, the hydrogen storage capacities were 0.9 wt%. We discuss the effect of pore properties on hydrogen storage in the carbon nanofibers.

N3.15

Electrospun Poly(vinylidene fluoride) Based Carbon Nanofiber for Hydrogen Storage.

Seong Mu Jo[1], Wha Seop Lee[1], Dong Young Kim[1], Hye Jin Chung[2,1] and Do Woon Lee[2]; [1]Polymer Hybrid Research Center, Korea institute of Science and Technology, Seoul, South Korea; [2]Department of Chemical Engineering, University of Seoul, Seoul, South Korea.

Because physical adsorption of hydrogen gas at the interface of carbon materials due to the Van der Waals interactions will be higher than the bulk, enormous research works for hydrogen storage using SWNT, MWNT, GNFs, active carbon, active carbon fiber, and graphite powder etc., have been done. These data showed a large scatter and low storage capacity in the range of 0.04-4 wt% at room temperature. In the case of active carbon materials with very high surface area, they have very low capacities at room temperature because the effective pore volume for hydrogen storage in them. The hydrogen storage of saran carbon was higher than those of other active carbon materials. Recent carbonization of polyacetylene materials resulted in unique structured carbon material comprising graphite layered hollow sphere. The chemically or thermally dehydrochlorination of saran polymer and polyvinylchloride, etc., may produce polyacetylene or carbyne structure. The nanopore (< 1 nm) in porous carbon materials is expected to be more effective in hydrogen storage. The

carbonization of poly(vinylidene fluoride) (PVdF) can also produce polyacetylene or carbyne structure. It will be carbon material with smaller pore than saran carbon due to small atom size of fluorine. Recent electrospinning process of polymer solution is one of the powerful tools producing polymeric ultra-fine fibers in range of a few nanometer to a few hundreds nanometer in diameters, which cannot easily obtained by traditional methods for making fibers. Especially PVdF nanofiber with high surface area could not make by conventional extruding. In this study we prepared PVdF nanofiber with 200-300 nm in diameter by electrospinning process. Partial dehydrofluorination of PVdF nanofibers were carried out using DBU to make infusible fiber and then the infusible PVdF nanofibers were carbonized at 280 oC, 900 oC, 1000 oC, 1200 oC and 1300 oC. Structural properties and morphology of the PVdF based carbon nanofibers were investigated XRD, Raman IR, FE-SEM, TEM, and surface area/nanopore analysis (BET). The PVdF based carbon nanofibers had granular surface composed of carbon particles of 20-30 nm sizes, indicating their high surface area. They showed amorphous structure with d002 =0.37 nm. In the case of highly dehydrofluorinated PVdF fiber, the carbon fiber had more smooth granular surface with d002 = 0.34-0.36 nm. The hydrogen storage capacities of the above carbon nanofiber materials measured using gravimetric method by Magnetic Suspension Balance (MSB) at room temperature and 100 bars. The storage data were obtained after the buoyancy correction. The hydrogen storage capacity of the PVdF based carbon nanofibers with d002 = 0.34-0.36 nm showed 0.35 wt%. In this study the hydrogen storage capacities of carbon fibers prepared using different dehydrofluorination and carbonization temperatures conditions were investigated.

N3.16
Porous Silicon Nanostructures as Hydrogen Reservoirs.
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Enormous internal specific surface (up to 1000 m2/cm3) of porous silicon (PS) nanostructures is well-known to be covered by SiHX bonds. However, no detailed quantitative study on hydrogen amount in PS nanostructures as a function of their nanoscale morphologies was carried out up to now. In our work, we analyze PS nanostructures as hydrogen reservoirs. In particular, the nanoscale morphology dependent hydrogen concentration is evaluated by means of attenuated total reflection infrared spectroscopy. In particular, influence of porosity, nanocristallites geometry and dimension of the PS layers on the hydrogen concentration value is analyzed. Reproducibility of PS filling with hydrogen, natural and thermally stimulated hydrogen desorption will be reported. Conversion of the experimentally detected hydrogen concentration into electrical energy via fuel cells is theoretically estimated. Completely safe character of the hydrogen storage at ambient temperature and pressure, original technological approaches ensuring extremely low fabrication cost and possibility of PS mass production are believed to be the most important advantages for application of porous nanostructures as hydrogen reservoirs.

N3.17
Abstract Withdrawn

N3.18
Hydrogen Adsorption Mechanism in Carbon Nanotubes and the Role of Metal Catalyst.
Yong-Won Lee[1], Rohit Deshpande[2], Anne Dillon[3], Michael Heben[3], Hongjie Dai[4] and Bruce Clemens[1]; [1]Materials Science & Engineering, Stanford University, Stanford, California; [2]Chemical engineering, University of Tulsa, Tulsa, Oklahoma; [3]Center for Basic Sciences, National Renewable Energy Laboratory, Golden, Colorado; [4]Chemistry, Stanford University, Stanford, California.

Since carbon nanotubes (CNTs) were discovered in early 1990's, they have been extensively studied in many research areas. One promising application is to use CNTs as a hydrogen storage nanostructure due to their light mass and high surface area. However, the study of hydrogen storage in CNTs has been characterized by a wide range of reported storage densities. The role of metal catalyst in hydrogen adsorption in CNTs has not been clearly understood. For example, it has been reported that a small weight fraction of hydrogen can be stored in as-synthesized multi-walled nanotubes (MWNTs) with iron catalyst particles at their tips at near ambient temperature. In contrast, only weak hydrogen physisorption by van der Waals attractive forces is observed from purified nanotubes from which the iron has been completely removed or from iron nanoparticles themselves. Single-walled nanotubes (SWNTs) show a similar hydrogen adsorption behavior in terms of the existence of catalyst particles. In order to understand the mechanism of hydrogen uptake in CNTs with metal catalyst particles, a monolayer (ML) of Fe has been deposited onto as-synthesized and purified CNT samples from a pure iron target via sputter-deposition. MWNTs were initially grown by the hot-wire CVD (HWCVD) and SWNTs were produced by the arc-discharge method. Both samples are initially formed with iron catalyst particles at their tips that can be completely removed during purification. Prepared CNTs were characterized by transmission electron microscopy (TEM) and metal catalyst particles were analyzed by alternating gradient magnetometer (AGM). Hydrogen storage capacity of CNTs was determined with temperature-programmed desorption (TPD) and volumetric measurement using Sieverts type apparatus. Hydrogen charging was performed at near ambient conditions. The CNT samples that have been exposed to atmosphere contain atomic iron oxide and show deteriorating hydrogen capacity. After in-situ reduction of Fe oxide in hydrogen, hydrogen adsorbed in the CNT samples increased significantly. The role of metal catalyst in hydrogen uptake and adsorption mechanism is discussed.

N3.19
Molecular Modeling Studies on a Series of Metal-Organic Frameworks.
Seung Hoon Choi[1], Daejin Kim[1], Tae Bum Lee[1], Eunsung Lee[2], Youjin Oh[2], Jihye Yoon[2] and Jaheon Kim[2]; [1]Insilicotech Co. Ltd., Seongnam, Gyeonggi-Do, South Korea; [2]Dept. of Chemistry, Soongsil University, Seoul, Seoul, South Korea.

In order to find out rational design and synthetic strategies toward efficient hydrogen storage materials, quantum mechanical calculation and grand canonical Monte Carlo simulation have been carried out on a series of the MOFs(Metal-Organic Frameworks) having various organic linkers. The calculation results about specific surface areas and the shape of frontier orbitals for various frameworks indicated that the capacity of the hydrogen storage is largely dependent on effective surface area rather than the free volume. Based on the iso-electrostatic potential surface from density functional calculation and the amount of adsorbed hydrogens from grand canonical Monte Carlo calculation, it was also found that the electron localization around organic linker plays an important role in hydrogen capacity of MOFs. The prediction of the modeling study could be supported by the hydrogen adsorption experiments using IRMOF-1 and -3, which showed more enhanced hydrogen storage capacities of IRMOF-3 compared with the IRMOF-1's at 77 K and H2 1 atm.

N3.20
Polymeric Carbon Nanocomposites for Hydrogen Storage.
Arun Kumar, Michael U. Jurczyk, Ashok Kumar, Sesha S. Srinivasan and Lee Stefanakos; Clean Energy Research Center, University of South Florida, Tampa, Florida.

Currently, several classes of materials are being pursued as possible candidates for hydrogen storage including conventional and complex metal hydrides (both bulk and nanoscale), and carbon nano-structures. Due to their large surface area with relatively small mass, single wall carbon nanotubes have been considered as potential systems for high capacity hydrogen storage. However, it is evident from the recent reports that, more systematic evaluation of the synthesis and hydrogen storage property in these materials are necessary to achieve consistent reproducibility. Nanomaterials have diverse tunable physical properties as a function of their size and shape due to strong quantum confinement effect and large surface/volume ratio. In the present work, we have developed a carbon based polymeric nanocomposite for hydrogen storage. Polyaniline were synthesized and functionalized using chemical methods. The modifications of these polyanline structures were carried by doping with metal oxides such as SnO2 and TiO2. Further, the polymeric nanocomposites doped with carbon nano tubes are designed and developed to increase the porous structure and the number of binding sites which in turn improve the hydrogen storage capacity. The as-synthesized and doped polymeric nanocomposite material is characterized with various techniques like Raman, FTIR, UV-visible spectroscopy, DSC and SEM. Further experiments are in progress to understand the hydrogen storage mechanism.

N3.21
Generalized Kubas Complexes as a Novel Means for Room-Temperature Molecular Hydrogen Storage.
Yong-Hyun Kim, Yufeng Zhao, M. J. Heben and S. B. Zhang; National Renewable Energy Laboratory, Golden, Colorado.

Kubas complexes of dihydrogen, i.e., molecular hydrogen, are known as non-traditional chemical binding configurations of dihydrogen with transition metal atom, e.g. W, complexes. The intact dihydrogen molecule in the Kubas complexes can be regarded as being similar to oxygen molecules bound to iron in hemoglobin, the conveyer of oxygen in blood. In searching for a novel means for hydrogen storage to meet the DOE goals for high storage density and room-temperature operation, we have studied the generalized Kubas complexes of dihydrogen molecules with light metal elements such as B and Be embedded in a carbon nanostructure such as fullerenes based on first-principles local density-functional calculations. We found that,

whereas pure carbon nanostructures can bind molecular hydrogens only via a weak van der Waals interaction, B- and Be-doped carbon nanostructures are capable of forming stable Kubas complexes with hydrogen molecules with significantly increased binding energy suitable for room-temperature storage. In this case, the hydrogen molecular bond lengths are stretched by up to 20% when compared to H_2 in free space. The enhanced binding can be attributed to the Coulomb interaction between holes near the B and Be sites and σ electrons of the hydrogen molecules. Because Be is a double acceptor whereas B is only a single acceptor, the binding energy is larger in Be-doped carbon nanostructures. In general, charge transfer plays the pivotal role in the molecular H storage. In the case of B, about 0.2 electrons are transferred from H_2 to B. This number increases when replacing B by Be. However, when charging the carbon system negatively by doping, the Kubas binding diminishes. Our detailed study of doped fullerenes shows that for a fullerene-like $C_{48}B_{12}$-$12H_2$, the calculated storage capacity is 3.3 wt. %. This number can be increased to 4.2 wt. % if a 25% B doping of the fullerene can be achieved. Very recently we found that BeB_2, which has the same structure to MgB_2, can also form stable Kubas complexes with molecular hydrogen. For nanotubes made of BeB_2, a maximum 6.5-wt. % hydrogen storage capacity can be achieved. These results suggest that the generalized Kubas complexes of hydrogen with light metal dopants could be an ideal means for room-temperature and high-capacity hydrogen storage. Supported by the U. S. DOE/EERE and BES under contract No. DE-AC36-99GO10337.

N3.22
Hydrogen Adsorption Properties of Single Wall Carbon Nanotube-Organometallic Hybrid Materials. Calvin Curtis[2], Jeffrey L. Blackburn[2], Kim Jones[2], Jeffrey Alleman[2], Anne Dillon[2], Michael Heben[2] and Thomas Gennett[1,2]; [1]Chemistry, Rochester Institute of Technology, Rochester, New York; [2]National Renewable Energy Laboratory, Golden, Colorado.

The hydrogen sorption properties of a new genre of bucky-metallocene and bucky-metal carbonyls of 3-d transiton metals were characterized. In this project, various types of purified single wall carbon nanotube materials (SWNT); CVD, Arc and Laser Generated, were derivatized to organometallic-SWNT hybrid materials via ultraviolet photolysis reactions. Photolysis reactions were carried out in quartz apparatus using a Rayonet Photochemical Reactor equipped with twelve 254 nm bulbs. The reactions were performed in a nitrogen or argon atmosphere using standard Schlenk techniques. Air sensitive materials and products were manipulated and stored in an argon-filled Vacuum Atmospheres glove box. A series of metal carbonyls, cyclopentadienyl metal carbonyls and metal chlorides were utilized as starting materials where the metals included iron, cobalt, chromium, nickel and titanium . Preliminary investigations have demonstrated that the UV photolysis reaction conditions do produce functionalized carbon nanotube materials. In fact the hydrogen sorption properties of the air-stable, non-purified materials demonstrated an apparent second-order hydrogen desorption process that is highly reversible. The activation energy was determined to be approximately 30 kj/mol with a hydrogen desorption temperature from 30-70 C. The entire spectrum of materials produced, their purification, characterization and hydrogen storage properties will be described.

N3.23
Interaction of Hydrogen with Carbon Based Molecules through Transition Metal Atoms. Yufeng Zhao, Yong-Hyun Kim, Anne C. Dillon, Michael J. Heben and Shengbai Zhang; National Renewable Energy Laboratory, Golden, Colorado.

Carbon based materials and metal alloys are among the most competitive media for hydrogen storage. However, neither satisfies all of the Department of Energy volumetric and gravimetric goals for on-board vehicular storage. The former has the advantage in weight but suffers from a weak interaction and thus an impractically low temperature for operation. The later interacts strongly with hydrogen but has a low weight percentage capacity. Here, we show that, by combining the two in an organo-metallic complex, a promising new storage medium emerges. The technical feasibility is based on the fact that both hydrogen molecule (H2) and cyclopentadiene (Cp) may be ligands for transition metals (TM). Although each side is historically important in chemistry [1], the combination of the two has not yet been sufficiently appreciated, particularly from a viewpoint of fundamental physical interactions. In fact, there is much space to proceed in this direction considering that carbon nanoparticles such as fullerenes could be used as ligands in place of the Cp ring. Understanding the interplay between H2 and carbon molecules in a variety of transition metal complexes also creates new opportunities in hydrogen catalysis. The Cp ring is a good acceptor for the d-orbital electrons of a TM atom, and perfect coordination has been observed in ferrocene. Here, we replace one of the Cp rings in the ferrocene with H2 molecules. The other Cp ring may also be replaced with the pentagonal ring of a buckyball (C60). We investigate systematically the interactions with different TM atoms ranging from Sc to Ni in the third row of the Periodic Table. The maximum number of H2 molecules that bind depends critically on the number of empty d-orbitals of the metal atom, ranging from 5 in Sc to 2 in Ni. Not surprisingly, magic CpTM(H2)n clusters with close electronic shells, i.e., satisfying the 18-electron rule, are found to be the most stable. The calculated binding energy, e.g., 0.5 eV per H2 for a "close shell Sc", is weaker than a typical hydride of about 3 eV per H, but substantially stronger than the van der Waals interaction of less than 0.1 eV per H2. This could be ideal for room temperature (RT) operation. Also, none of the adsorbed H2 molecules dissociates. In analogous to the 3-center 2-electron coordination in the Kubas complex [1], the (2n+1)-center, 2n-electron coordination can be considered as a generalized Kubas complex (GKC). Our calculation shows that the GKCs can form on all twelve pentagonal rings of a C60, with a retrievable weight percentage as high as 8.7% at RT. [1] G.J. Kubas, J. Organometallic Chem. 635, 37 (2001)

N3.24
Dehydrogenation Kinetics and Long Term Cycling Behavior of Titanium Doped $NaAlH_4$. Sesha Srinivasan[1,2] and Craig M. Jensen[2]; [1]Clean Energy Research Center, College of Engineering, University of South Florida, Tampa, Florida; [2]Chemistry, University of Hawaii, Honolulu, Hawaii.

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. Titanium doped $NaAlH_4$ is right now considered as the potential hydrogen storage system, which satisfies the said criteria. The dehydrogenation of $NaAlH_4$ consists of two consecutive steps of decomposition at 220 and 250^o C with the total hydrogen release of 5.6 wt.%. However, doping a few mole concentrations of selected transition metal complexes to the host hydride reduces significantly the decomposition temperatures to 100 and 185^o C respectively. This breakthrough has been followed by a great deal of effort to develop $NaAlH_4$ as a practical hydrogen storage material. For an ideal hydrogen storage material, the dehydrogenation kinetics and the cycling stability are important properties to be evaluated. Keeping these points to ponder, we have studied the dehydriding kinetics of the Ti-doped $NaAlH_4$ over a number of dehydrogenation and rehydrogenation cycles. Besides, the Ti-doped $NaAlH_4$ has been prepared from the hydrogenation of NaH and Al using the solvent mediated milling method. Comparing the initial and final cycling stages of Ti doped (NaH + Al), the synchrotron powder x-ray diffraction profiles exhibit, a growing resistance to the hydrogenation of Na_3AlH_6 to $NaAlH_4$.

N3.25
Abstract Withdrawn

N3.26
Abstract Withdrawn

N3.27
Modified Self Assembly Approach for Fabrication of Carbon Nanotube Electrodes. Ramasudhakar Babu Dhullipudi[1], Yuri Lvov[1,2], Alfred R. Gunasekaran[1] and Tabbetha A. Dobbins[1,3,4]; [1]Institute For Micromanufacturing, Louisiana Tech University, Ruston, Louisiana; [2]Chemistry, Louisiana Tech University, Ruston, Louisiana; [3]Physics, Louisiana Tech University, Ruston, Louisiana; [4]Physics, Grambling State University, Grambling, Louisiana.

The challenges that currently prevent the use of carbon nanotubes (CNTs) for solid state hydrogen storage applications are mainly due to the insufficient hydrogen storage capacity and the slow adsorption/desorption kinetics1. As improvements are made to the storage capacity and kinetics, many researchers are employing electrochemical methods to test the storage capacity of hydrogen in CNT electrodes2. The electrochemical charge discharge experiments are typically done on compressed pellets of CNTs combined with heavy metals such as Nickel or gold. Self assembly techniques have been used for making multilayered films of polycation and polyanions and for the deposition of nanoparticles for sensor applications and drug delivery systems3. The present work highlights the utilization of the self assembly combined with electrodeposition for fabricating thin film electrodes. A novel method to form CNT electrodes comprising of surface modified thin film of carbon nanotubes and conducting polymeric layers is demonstrated. The electrodes are formed by alternating the electrophoretic deposition (EPD) of CNTs with layer-by-layer self assembly of a polyion monolayer. Figure 1 shows the deposition scheme to produce CNT electrode. Early data suggests that SWNTs have an isoelectric point near 7. Polystyrene sulfonate (PSS) is known to have an isoelectric point of 1 Therefore, at a pH of 3, one could possibly induce a negative surface charge onto the PSS layer while inducing a positive surface charge onto the CNTs. The electrostatic force between these particles with opposite surface charges will bind them together forming a nanocomposite thin film

electrode. The results obtained from the preliminary experiments for the electrode fabrication are presented. The sequence of steps followed to fabricate the nanocomposite thin film electrode are listed below. 1.Si substrate 2. Dipped into solution containing PSS to form a monolayer of PSS 3. Rinse in DI water and Dry in N2 gas 4. Deposit CNTs using EPD and then Rinse and Dry References 1. Hydrogen, Fuel Cells, and Infrastructure Technologies, FY 2003 DOE Progress Report. 2. C. Nutzenadel, A. Zuttel, D. Chartouni, L Schlapbach, Electrochemical and Solid State Letters 2, Iss. 1 (1999), pp. 30-32 electrochemical storage of hydrogen in nanotube materials 3. P. Grant, Y. Lvov, M. McShane, SPIE-Proceedings, (SPIE International Biomedical Optics Conf.) 2002, v.4624, 47-54 Nanostructured Fluorescent Particles for Glucose Sensing.

SESSION N4: Materials for Hydrogen Storage: Carbon Based Systems
Thursday Morning, December 2, 2004
Independence E (Sheraton)

8:30 AM *N4.1
Molecular Dynamics Simulations on Hydrogen Adsorption and Storage in Single Walled Carbon Nanotubes.
Hansong Cheng[1], Alan Cooper[1], Guido Pez[1], Milen Kostov[3], Pamela Piotrowski[2] and Steven Stuart[2]; [1]Computational Modeling Center, Air Products and Chemicals, Inc., Allentown, Pennsylvania; [2]Department of Chemistry, Clemson University, Clemson, South Carolina; [3]Department of Physics, Pennsylvania State University, University Park, Pennsylvania.

We present systematic molecular dynamics simulation studies of hydrogen storage in single walled carbon nanotubes of various diameters and chiralities using a recently developed curvature-dependent force field. Our main objective is to address the following fundamental issues: 1. For a given H2 loading and nanotube type, what is the H2 distribution in the nanotube bundle? 2. For a given nanotube type, what is the maximal loading (H2 coverage)? and 3. What is the diameter range and chirality for which H2 adsorption is most energetically favorable? Our simulation results suggest strong dependence of H2 adsorption energies on the nanotube diameter but less dependence on the chirality. Substantial lattice expansion upon H2 adsorption was found. The average adsorption energy increases with the lowering of nanotube diameter (higher curvature) and decreases with higher H2 loading. The calculated H2 vibrational power spectra and radial distribution functions indicate a strong attractive interaction between H2 and nanotube walls. The calculated diffusion coefficients are much higher than what has been reported for H2 in microporous materials such as zeolites, indicating that diffusivity does not present a problem for hydrogen storage in carbon nanotubes.

9:00 AM *N4.2
Discovering the Mechanism of Hydrogen Adsorption on Aromatic Carbon Nanostructures to Develop Adsorbents for Vehicular Applications. Anne Catherine Dillon, Y. Zhao, Jeffrey L. Blackburn, Philip A. Parilla, Y.-H. Kim, S. Zhang, J. L. Alleman, A. H. Mahan, Kim M. Jones, K.E.H. Gilbert and M. J. Heben; National Renewable Engergy Laboratory, Golden, Colorado.

The hydrogen storage properties of carbon single-wall and multi-wall nanotubes (SWNTs and MWNTs), graphitic nanofibers, and other nanostructured carbons have become the subject of considerable debate. Reported capacities range from 0-60 wt%(1). For on-board vehicular storage a binding energy between 20-50 kJ/mol is necessary to allow for near-room temperature operation at reasonable pressures. This binding energy range likely dictates that molecular hydrogen be stabilized via enhanced physisorption or by complexing di-hydrogen with a transition metal atom. Early experiments on impure SWNT samples containing cobalt nanoparticles indicated that 5 - 10 wt% hydrogen storage on a SWNT weight basis might be achieved with a hydrogen binding energy of 20 kJ/mol(2). More recently, hydrogen adsorption was observed with a binding energy of 50 kJ /mol on as-synthesized MWNTs containing iron nanoparticles at their tips but virtually free of non-nanotube carbon impurities(3). No hydrogen adsorption, however, is observed at near ambient temperatures for purified SWNTs or MWNTs that do not contain cobalt or iron nanoparticles. Neither cobalt nor iron is a metal hydride and should not store hydrogen under the room temperature charging conditions employed here. Further, the incorporation of metal nanoparticles into purified nanotube materials via simple sonication processes did not result in hydrogen storage at near ambient conditions. These results imply that a special synergy occurs when small metal particles or atoms are in highly intimate contact with sp^2-hybridized aromatic carbon. Understanding this unique interaction could facilitate the economical engineering of a hydrogen storage material that meets United States Department of Energy targets for vehicular fuel cell applications. Recent theoretical studies have shown that an iron adatom forms a complex with a C_{36} fullerene and shares charge with four carbon atoms of a bent five-membered ring. Three di-hydrogen ligands also coordinate with the iron forming a stable 18-electron organo-metallic complex. Here the binding energy of the molecular hydrogen ligands is 43 kJ /mol. Iron has also been predicted to complex with all twelve of the five-membered rings in C_{60} with a binding energy of 42 kJ/mol and a hydrogen capacity of 4.9 wt.%. These results as well as experimental and theoretical findings of other promising carbon-based nanostructures for vehicular hydrogen storage will be discussed in detail. (1) Dillon, A. C.; Heben, M. J. *Appl.Phys.A* **2001**,72, 133. (2) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethune, D. S.; Heben, M. J. *Nature* **1997**, 386, 377. (3) Dillon, A. C.; Mahan, A. H.; Parilla, P. A.; Alleman, J. L.; Heben, M. J.; Jones, K. M.; Gilbert, K. E. H. *NanoLetters* **2003**, 3, 1425.

9:30 AM *N4.3
Hydrogen Storage in Graphite Nanofibers. Anthony J. Lachawiec, Angela D. Lueking and Ralph T. Yang; Dept. of Chemical Engineering, University of Michigan, Ann Arbor, Michigan.

Hydrogen storage in graphite nanofibers (GNFs) is studied by measuring the desorption amounts after equilibrating the samples with hydrogen at pressures up to 100 atm and ambient temperature. GNFs are grown by catalytic decomposition of ethylene on binary metal alloys. A number of factors that significantly affect the storage have been found, including the structure of the GNF, the remaining catalysts, the sample pretreatment conditions, and doped catalysts. A summary of reported observations will be given and our current results will be discussed.

10:30 AM N4.4
Hydrogen Sorption/Desorption in Surface-Modified Single Wall Carbon Nanotube Sheets. Yubing Wang and Zafar Iqbal; New Jersey Institute of Technology, Newark, New Jersey.

Self-assembled, thermally annealed sheets of single wall carbon nanotube (SWNT) bundles with individual tube diameters below 1 nm and 1.3 nm to 1.4 nm prepared by chemical vapor deposition and carbon-arc techniques, respectively, have been used in this study. Mg and Co nanoparticles were deposited on the SWNT-sheets from nitrate solutions by using them as the working electrode in an electrochemical cell. Hydrogen adsorption and desorption on the surface-modified SWNT sheets have been studied using electrochemical charging and discharging, as well as by gravimetry as a function of temperature and pressure using a microbalance set up. Characterization has been carried out in detail by a combination of in-situ Raman spectroscopy, and ex-situ fourier transform infrared (FTIR) spectroscopy, thermogravimetric analyses (TGA), thermopower and prompt gamma neutron measurements. Electrochemical sorption of up to 3% by weight is observed in the Mg-modified SWNTs, which is desorbed at temperatures below 150oC as indicated by TGA. Strong chemisorption with the appearance of C-H modes in the FTIR spectra and the absence of low temperature desorption is observed for Co-modified SWNTs. Details regarding the adsorption/desorption process obtained from in-situ Raman spectroscopy of the SWNT vibrations as a function of electrochemical charging will be discussed and compared with results on measurements on SWNT sheets modified by electrodeposition of the conducting polymer, polyaniline.

10:45 AM *N4.5
Hydrogen Storage in Metal-Organic Frameworks.
Omar M. Yaghi, University of Michigan, Ann Arbor, Michigan.

Reticular synthesis (logical construction of networks from molecular building blocks) has yielded a new class of crystalline porous materials commonly referred to as metal-organic frameworks (MOFs) in which metal ions and clusters are linked by organic units. The ability to prepare MOFs in high yield and with adjustable pore size, shape and functionality has led to their study as gas sorption materials. We have demonstrated that systematic variation of the organic component in isoreticular metal-organic frameworks (IRMOFs) has a marked effect on their capacities for methane. More recently, we discovered that IRMOFs are also capable of storing significant amounts of H2, and inelastic neutron scattering studies of molecular hydrogen adsorbed in IRMOF-1 pointed to the organic unit as one of the important adsorption sites. Thus, there is an acute need to collect and analyze more hydrogen uptake measurements on these materials in order to establish the favorable factors for its storage. Hydrogen adsorption isotherms measured at 77 K show a distinct dependence of uptake on the nature of the link for a set of five MOF materials containing the Zn4O(CO2)6 cluster. At 1 atm, the materials sorb between 4.2 and 9.3 molecules of H2 per formula unit. The results imply a trend in hydrogen uptake with the number of rings in the organic moiety.

11:15 AM N4.6
Hydrogen at High Potential Sites: Desorption in

Metal-Organic-Framework (MOF-5) and K-modified Carbon. Anne Dailly[1], John J. Vajo[2], Joanne Yim[1] and Channing Ahn[1]; [1]Caltech, Pasadena, California; [2]HRL Laboratories, LLC, Malibu, California.

Effective hydrogen physisorbents will require high adsorption potentials. Two types of material have requisite components. MOF structures, with large surface and edge areas due to organic linkers, were first claimed to display immediate uptake behavior but subsequently shown to display isotherm behavior more typical of Type 1 adsorption. We have synthesized MOF-5 (also denoted as IRMOF-1), as verified by x-ray diffraction, performed prescribed activation procedures for this class of materials, and taken volumetric isotherm measurements at 77K. For one sample, we performed a desorption isotherm at 5 bar and reached 3 wt% gravimetric density, with lower pressure results behaving similar to published values. A higher pressure run to around 50 bar reached a gravimetric density of 3.5 wt%, but displayed Langmuir type behavior up to 20 bar, before rising nearly linearly between 20 and 50 bar. Because the isotherm slopes have not leveled off at these pressures, we expect that higher sorption values can be reached and we will present data on higher pressure runs on these materials. Single point isotherm measurements of K-modified carbons have also displayed improvements in the ratio of RT/77K behavior over unmodified material. We will present complete RT and 77K isotherm data on these materials including activated carbon and nanotubes.

11:30 AM N4.7
Ab-initio Study of Metal-Organic Frameworks for Hydrogen Storage: MOF5, Be-MOF5, and Mg-MOF5.
Miguel Fuentes-Cabrera[1,2], Don Nicholson[1], Mike Widom[2] and Yang Wang[3]; [1]Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Department of Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania; [3]Pittsburgh Supercomputing Center, Pittsburgh, Pennsylvania.

Porous Metal-Organic Frameworks (MOFs) represent a new and exciting option for hydrogen storage materials because the size and chemical functionality of their pores can be changed to increase the hydrogen uptake. In particular, MOF5 takes up 1.32 hydrogen weight percent at 77 Kelvin. Theoretical Modeling can help to identify candidate MOFs for hydrogen storage. We used ab-initio modeling to study MOF5, Be-MOF5, and Mg-MOF5; we are interested in Be-MOF5 and Mg-MOF5 because they could have a higher hydrogen weight percent uptake than MOF5. We have analyzed the structural and electronic properties, the hydrogen binding energies, and barriers to hydrogen diffusion. Structural properties can be used to generate accurate atomic potentials that will serve to carry on precise atomistic simulations of hydrogen absorption. Electronic properties provide information on how to modify the materials to increase their hydrogen uptake. Hydrogen binding energies and barriers to hydrogen diffusion provide information on the interaction of the framework with the hydrogen molecules.

SESSION N5: Materials for Hydrogen Storage: Chemical Hydrides
Thursday Afternoon, December 2, 2004
Independence E (Sheraton)

1:30 PM N5.1
Modelling of hydride-forming materials characteristics.
Peter H.L. Notten[1,2], Alexander V. Ledovskikh[2], Evgeny Verbitskiy[1] and William Rey[3]; [1]Philips Research Laboratories, Eindhoven, Netherlands; [2]Eindhoven university, Eindhoven, Netherlands; [3]Eurandom, Eindhoven, Netherlands.

Two independent approaches are presented to describe the hydrogen intercalation and deintercalation processes in hydride-forming materials. Both pressure-composition isotherms and corresponding electrochemical Open-Circuit-Voltage (OCV) characteristics are addressed. The first approach is based on the thermodynamics and includes a lattice gas model based on the principles of statistical thermodynamics. To describe second order phase transitions and two-phase coexistence regions a binary alloy approach is considered. The second approach is based on equilibrium kinetics, describing the kinetics of all stages in the hydrogen (de)intercalation process, including the charge transfer reaction, hydrogen adsorption and absorption. A complete set of equations describes the main characteristics of the hydride forming material, i.e. the equilibrium pressure and equilibrium potential. Both models are adopted to simulate pressure-composition isotherms of model-type of non-stoichiometric, hydride-forming, materials (LaNixCu1.0-type), extensively studied in the literature [1,2], "standard" Mischmetal-based hydride-forming materials (MnNi3.9-xMn0.4AlxCo0.7-type) nowadays widely applied in commercial Nickel MetalHydride (NiMH) batteries [3,4] and a new class of high energy density hydrogen storage materials recently proposed; this latter class of materials were reported to occlude close to 6 wt.% in both bulk [5] and thin film [6] compounds. Excellent agreement between experimental and theoretical results has been found in all cases over a wide temperature range. The contribution of the entropy and the volumetric crystal lattice expansion to the pressure composition isotherms will be outlined. Advantageously, using the kinetic model opens the possibility to simulate the overall behaviour of the MetalHydride electrode during NiMH battery operation [7]. References [1] P.H.L. Notten, R.E.F. Einerhand and J.L.C. Daams,J. Alloys Comp., 210 (1994) 221. [2] P.H.L. Notten, R.E.F. Einerhand and J.L.C. Daams,J. Alloys Comp., 210 (1994) 233. [3] H. Senoh, K. Morimoto, H. Inoue, C. Iwakura and P.H.L. Notten, J. Electrochem. Soc., 147 (2000) 2451. [4] P.H.L. Notten, "Rechargeable nickel-metalhydride batteries: a successful new concept", "Interstitial intermetallic alloys", Chapter 7 in NATO ASI Series E 281 (1995) 151, Edts. F. Grandjean et al., ISBN 0-7923-3299-7. [5] P.H.L. Notten, M. Ouwerkerk, H. van Hal, D. Beelen, W. Keur, J. Zhou, H. Feil, J. Power Sources, 129 (2003) 45. [6] R. Niessen and P.H.L. Notten, J. Alloys Comp., submitted (2004). [7] A. Ledovskikh, E. Verbitski, A. Ayeb and P.H.L. Notten, J. Alloys Comp., 356-357 (2003) 742.

1:45 PM *N5.2
Energetics, Electronic Structure, Vibrational Properties, and Diffusion Processes in the Sodium Aluminum Complex Hydrides. Amra Peles, Yan Wang and Mei-Yin Chou; School of Physics, Georgia Institute of Technology, Atlanta, Georgia.

We present a first-principles investigation of the structural properties, electronic structure, and vibrational properties of the complex hydrides NaAlH4 and Na3AlH6. The calculations are performed within the density functional framework, employing norm-conserving pseudopotentials. The structural properties of both hydrides compare well with experimental data. A detailed study of the electronic structure and the charge-density redistribution reveal the features of an ionic covalent bonding between Al and H in the AlH4 and AlH6 anionic complexes embedded in the matrix of Na+ cations. The orbital hybridization and the characteristics of bonding orbitals within the complexes are identified. The calculated reaction energies of these complex hydrides are in good agreement with the experimentally determined values. These total-energy calculations are used to understand the atomistic processes associated with the catalytic reactions in sodium aluminum hydrides, a promising hydrogen-storage material. It is found that the substitutional geometry of the Ti catalyst in NaAlH4 is not particularly favorable. Examinations of the crystal structures and various diffusion energies suggest that AlH3 may be the mobile species in the dehydrogenation reaction. The effect of Ti is likely to facilitate the extraction of AlH3 from the hydrides and its subsequent decomposition on the surface.

2:15 PM N5.3
Decomposition Kinetics of Lithium Amide and its Implications for Hydrogen Storage. Frederick E. Pinkerton, Materials and Processes Laboratory, General Motors Research and Development Center, Warren, Michigan.

The kinetics of the $LiNH_2$ decomposition reaction 2 $LiNH_2 \rightarrow Li_2NH + NH_3$ were determined using thermogravimetric analysis (TGA). While not itself a hydrogen storage material, lithium amide is a primary component of the hydrided state of Li-N-H storage materials based on Li_3N or Li_2NH. Its decomposition by ammonia release, and the resulting degradation of hydrogen storage capacity, has important implications for the durability of Li-N-H storage systems. Fine powders were prepared from commercial lithium amide (Aldrich 95% purity) by ball milling for 20 min. Kinetic parameters were extracted from sets of TGA weight loss curves taken at different heating rates between 2.5 and 30°C/min. The reaction rate k(T) was found to depend on the TGA sample size as a consequence of the very low NH_3-$LiNH_2$ equilibrium vapor pressure at temperatures below 300°C. Larger samples produce a local concentration of ammonia high enough to inhibit further reaction, shifting the weight loss curves toward higher temperature (i.e. higher equilibrium NH_3 partial pressure). k(T) increased by about an order of magnitude as the samples size was reduced from 7 mg to 1.5 mg. The activation energy E_a was determined to be about 124 kJ/mole independent of the sample size. Direct isothermal measurements of k(T) at temperatures between 200°C and 300°C agree well with the k(T) values calculated from the heating rate-derived kinetic parameters. The value of E_a independently derived from the isothermal data is 125 kJ/mole. Although decomposition occurs slowly below 300°C, its cumulative effect could be large in real Li-N-H systems, where $LiNH_2$-containing hydrided material is held at elevated temperature under dynamic gas flow. The durability of Li-N-H for hydrogen storage was estimated from the measured kinetic parameters by calculating the time required to decompose 20% of the initial $LiNH_2$, as a function of the

operating temperature. The predicted lifetime falls below 10^5 min for operating temperatures in excess of about 160°C. For comparison, unmodified Li-N-H storage materials require temperatures near 200°C to release hydrogen into vacuum or inert gas at reasonable rates, and dehydriding in the presence of 100 kPa H_2 gas requires temperatures above 280°C.

2:30 PM N5.4
Hydrogen Storage in the B-H-Li-N System.
Alexandra Torgersen, R&D, General Motors, Warren, Michigan.

The B-H-Li-N system has been studied in the temperature range of 20-200°C using thermal analysis coupled with mass spectrometry, as well as with X-ray diffraction. This system contains four distinctly different crystallographic phases, at least two of which decompose releasing hydrogen below 200°C. Thermal decomposition is seen between 80 and 150°C, with hydrogen being released during the decomposition. A maximum of 10 wt% hydrogen loss is seen. The gas phase above the solid decomposition-residue contains in addition to hydrogen, very small amounts of ammonia, diborane and borazine, the BN equivalent of benzene.

2:45 PM N5.5
Chemical Hydride Systems Based on Metal Hydride/Hydroxide Reactions. John J. Vajo[1], Sky L. Skeith[1], Florian Mertens[2] and Scott W. Jorgensen[2]; [1]HRL Laboratories, LLC, Malibu, California; [2]General Motors Research and Development Center, Warren, Michigan.

We have studied hydrogen generation in solid-state metal hydride/hydroxide reactions as possible irreversible hydrogen sources for small-scale fuel cell applications. These reactions are exothermic but kinetically stable near room temperature. Thus, stoichiometric reactant mixtures can be prepared by mechanical milling without significant reaction. Hydrogen generation occurs upon heating and produces nearly theoretical amounts of hydrogen, up to 10 weight percent (wt. %) in the reactions studied thus far. We illustrate this class of reactions using the examples LiH + LiOH (6.2 wt.% H_2), 2LiH + NaOH (3.4 wt.% H_2), $LiBH_4$ + 4LiOH (6.8 wt.% H_2), and $3LiBH_4$ + $4LiOH{\cdot}H_2O$ (10.2 wt. % H_2) where the total hydrogen contents are given in parenthesis. Experimentally, for the LiH/LiOH system we obtained 5.3 to 5.7 wt. % H_2 by heating to 250 °C, with hydrogen production beginning at approximately 60 °C. Reactant purity and small amounts of hydrogen generation during mixing can account for the difference from the theoreti cal yield. The kinetics can be enhanced by addition of 2 to 10 mole percent $TiCl_3$. The $TiCl_3$ may function either as a catalyst facilitating the diffusion and desorption of hydrogen or as a dispersant promoting finer mixing of the reactants. The $LiBH_4$/LiOH system generated 6.6 wt. % H_2 with reaction beginning at 250 °C. The $LiBH_4/LiOH{\cdot}H_2O$ system generated >10 wt. % H_2 beginning at approximately 50 °C with >5.5 wt. % H_2 generated at temperatures <100 °C. The kinetics and products of these reactions will be il lustrated. Although exothermic, these reactions generate less heat, ΔH = -23 to 45 kJ/mol-H_2, than comparable hydrolysis reactions such as LiH + H_2O (ΔH = -109 kJ/mol-H_2) and $NaBH_4$ + $2H_2O$ (ΔH = -75 kJ/mol-H_2). Since the exothermic heat produced must be re moved to keep the hydrogen source isothermal, reduced heat generation reduces cooling requirements. In addition, reduced exothermicity during hydrogen generation, at least in theory, implies less necessary energy input during recycling. Thus, these irreversible chemical hydride systems offer the possibility of high hydrogen contents, reduced cooling requirements during hydrogen generation, and increased energy efficiency during recycling.

3:30 PM N5.6
Reversible Hydrogen Storage in Destabilized Lithium Borohydride. John J. Vajo[1], Sky L. Skeith[1] and Florian Mertens[2]; [1]HRL Laboratories LLC, Malibu, California; [2]General Motors Research and Development Center, Warren, Michigan.

Lithium borohydride ($LiBH_4$) contains >18 weight percent (wt. %) hydrogen but the hydrogen is strongly bound and complete dehydrogenation is highly endothermic. Partial dehydrogenation to LiH + B yields 13.6 wt. % hydrogen but is also quite endothermic with a standard enthalpy change of 67 kJ/mol-H_2. If reversible, an equilibrium pressure of 1 bar hydrogen would require a temperature of > 400 °C. Recently, we have focused on increasing the equilibrium hydrogen pressure of strongly bound hydrides, such as LiH, MgH_2, and $LiBH_4$, by stabilizing the dehydrogenated state. Stabilizing the products of $LiBH_4$ dehydrogenation can be accomplished by combining $LiBH_4$ with $1/2MgH_2$. During dehydrogenation, MgB_2 is formed which lowers the reaction enthalpy thereby stabilizing the dehydrogenated state. This effectively destabilizes the $LiBH_4$. With the addition of $1/2MgH_2$, dehydrogenation to LiH + $1/2MgB_2$ can yield 11.2 wt. % hydrogen. We have found that mechanically milled mixtures of $LiBH_4$ + $1/2MgH_2$, that included 2 to 10 mole percent $TiCl_3$ added as a catalyst, can be dehydrogenated to yield > 10 wt. % hydrogen. In addition, under 100 bar hydrogen the dehydrogenated mixture, or an initial mixture of LiH + $1/2MgB_2$ can be hydrogenated with absorption of 8 to 10 wt. % hydrogen. In temperature-ramp experiments conducted at 2 °C/min, dehydrogenation begins at approximately 300 °C and is complete and < 450 °C. Rehydrogenation begins at approximately 250 °C and is complete at 300 °C. X-ray diffraction measurements have been used to determine the dehydrogenation reaction products and demonstrate the reversible formation of $LiBH_4$. Isotherms were obtained at 300 to 400 °C. The isotherms had relatively flat plateaus from 2 to 8 wt. % and maximum capacities of 8.5 to 9.5 wt. %. Equilibrium pressures varied from 5.5 bar at 330 °C to 12.8 bar at 400 °C. A preliminary van't Hoff plot yielded a reaction enthalpy of 40 kJ/mol-H_2 and an estimated temperature of 225 °C for an equilibrium pressure of 1 bar. The measured enthalpy, which is approximately 25 kJ/mol-H_2 lower than the enthalpy estimated for pure $LiBH_4$, demonstrates that $LiBH_4$ is destabilized by MgH_2. Current work is focused on improving the kinetics and achieving further destabilization.

3:45 PM N5.7
Magnesium-Hydride Slurry Technology for Hydrogen Storage. Ajay Krishnan[2], Xionggang Lu[2], Srikanth Gopalan[2], Uday B. Pal[2] and Andrew W. Mcclaine[1]; [1]Safe Hydrogen LLC, Lexington, Massachusetts; [2]Manufacturing Engineering, Boston University, Brookline, Massachusetts.

Magnesium hydride-based slurry has great potential for hydrogen production and storage. Hydrogen is stored as a stable and pumpable slurry and generated whenever needed by mixing with water. The byproduct is stable Magnesium hydroxide (milk of magnesia). This slurry can be stored, transported and pumped using the existing transportation infrastructure. Thus, the magnesium hydride slurry lends itself well for automotive applications in conjunction with fuel cells. For such large-volume applications, the success and long term economic viability of this process depends on an effective recycling system for the by-products. The Solid-Oxide-Oxygen-Ion-Conducting-Membrane (SOM) process is being investigated for converting the by-product magnesium hydroxide to magnesium. The magnesium will then be used to produce the hydride slurry. The SOM process in principle utilizes a tubular yttria-stabilized-zirconia-based solid-oxide-fuel-cell as an anode in the temperature range 1100 to 1300 degree C. The magnesium hydroxide is dissolved in a molten ionic flux and with the application of an electrical potential between an inert cathode in the flux and the anode, the oxygen ions are pumped out of the flux through the zirconia membrane and are oxidized at the anode. Magnesium vapor evolves at the cathode and is condensed in a separate chamber (condenser). Performing in-situ reforming of gaseous hydrocarbons within the tubular anode minimizes the electrical power required for the electrolysis. The paper discusses the key features of the magnesium hydride slurry preparation process and means for hydrogen generation. The SOM process for magnesium production is analyzed in terms of power consumption, process efficiency, zirconia-anode stability, and energy balance. Important thermo-physical properties of the ionic flux, critical to the process, are also discussed. Finally, the paper includes a preliminary cost comparison of the overall process with existing state of the art technologies.

4:00 PM N5.8
Hydrogen Storage by Physisorption: Concept and New Class of Materials Beyond Carbon. Jean-Christophe P. Gabriel, Keith Bradley, Seung-Hoon Jhi, Young-Kyun Kwon and George Gruner; Nanomix, Emeryville, California.

Hydrogen storage using physisorption requires higher desorption temperatures than those possible using conventional adsorbents such as carbon. Using computational design, we explored several materials and identified some that have extremely strong physisorption interactions with hydrogen, including 12 kJ/mol heat of adsorption for hydrogen on some sites. Experimental adsorption isotherms on materials such as boron oxide has confirmed the calculations, and large coverage is observed at temperatures as high as the boiling point of methane, 115 K [1]. Considering the complexity of boron oxide chemistry, these results open a totally new and broad avenue for the research for new hydrogen storage materials [2]. We will also present our technical analysis of the feasibility of storing hydrogen by physisorption [3]. [1] Hydrogen storage by physisorption: beyond carbon Strong hydrogen adsorbents for hydrogen storage. S.-H. Jhi, Y.-K. Kwon, K. Bradley, J.-C. P. Gabriel, Solid State Commun. 129, 769-773, 2004 (Ranked within the five most downloaded article from SSC in first quarter 2004). [2] Hydrogen Storage in Nanostructure with Physisorption, K. Bradley, P. Collins, J.-C. P. Gabriel, Y.-K. Kwon, S.H. Jhi, G. Grüner, Patent US 6,672,077 B1. [3] Hydrogen Storage and Supply System, K. Bradley, J. D. Wyatt, J.-C. P. Gabriel, G. Grüner, Patent US 6,748,748 B2.