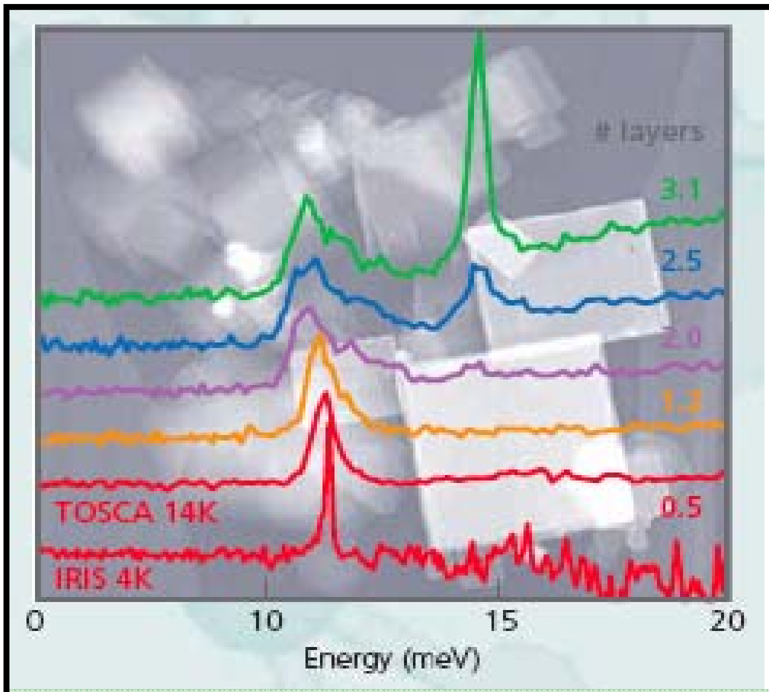

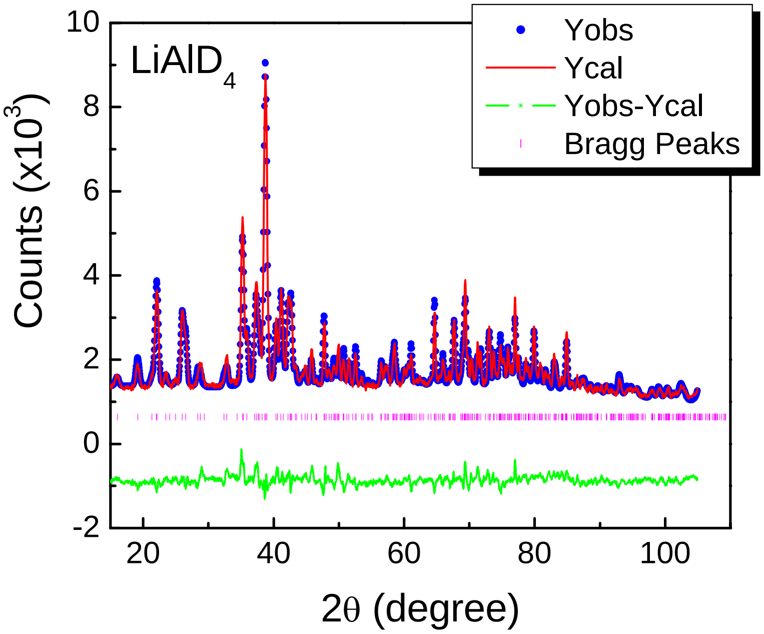

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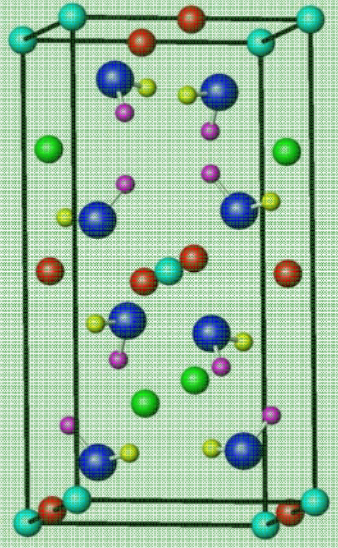
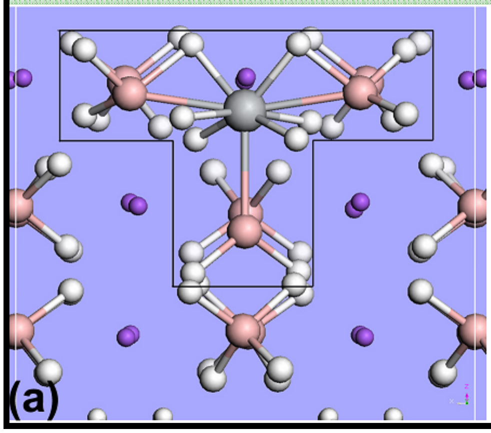
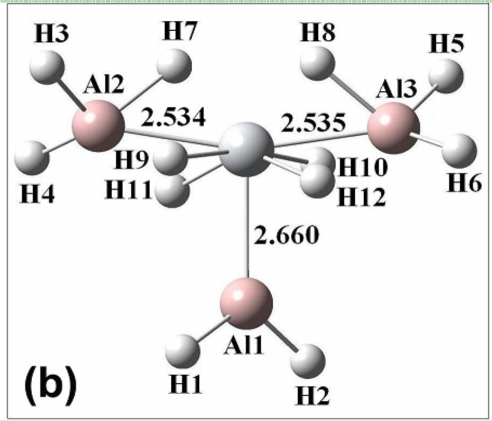
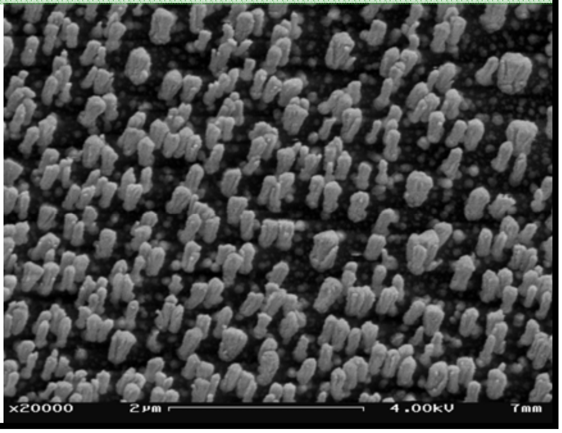


Hydrogen Contractors Meeting

May 16-19, 2006
Crystal Gateway Marriott Hotel
Arlington, Virginia







Cover

Top Left:

The para-ortho transition from a film of hydrogen adsorbed on MgO (100), as a function of coverage. Background: TEM image of the MgO nanocubes.
Courtesy: *John Larese, et al., ORNL and University of Tennessee.*

Top Right:

Neutron diffraction data from LiAlD4 at room temperature. The points in the upper frame are observed data; the solid line represents the best fit to the data. The lower curve shows the difference between observed and calculated diagrams. Tic marks show the position of the Bragg peaks for this structure.
Courtesy: *William Yelon, University of Missouri.*

Center:

The crystal structure of LiNH2, derived from room temperature neutron diffraction on non-deuterated powders. Appl. Phys. Lett. 88, (2006) 041914.
Courtesy: *William Yelon, University of Missouri.*

Bottom Left/Bottom Center:

A complex structure, TiAl3Hx, determined from DFT slab calculation with Ti occupying interstitial site and interacting directly with three neighboring (AlH4) groups, in a slab simulating NaAlH4(001), is believed to be a precursor state for the formation of TiAl3 binary phase observed experimentally and plays important role in hydrogen release/uptake in Ti-doped NaAlH4.
Courtesy: Qingfeng Ge et al., Southern Illinois University.

Bottom Right:

SEM top view of Au decorated Si nanorods.
Courtesy: Yiping Zhao, et al., University of Georgia.

This document was prepared under contract DE-AC05-06OR23100 between the U.S. Department of Energy and Oak Ridge Associated Universities.

Foreword

This volume highlights the scientific content of the 2006 Hydrogen Contractors Meeting sponsored by the Division of Materials Sciences and Engineering (DMS&E) on behalf of the Office of Basic Energy Sciences (BES) of the U. S. Department of Energy (DOE). This meeting is the second in a series of research theme-based Contractors Meetings sponsored by DMS&E held in conjunction with our counterparts in the Office of Energy Efficiency and Renewable Energy (EERE) and the first with the Hydrogen, Fuel Cells and Infrastructure Technologies Program. The focus of this year's meeting is BES funded fundamental research underpinning advancement of hydrogen storage. The major goals of these research efforts are the development of a fundamental scientific base in terms of new concepts, theories and computational tools; new characterization capabilities; and new materials that could be used or mimicked in advancing capabilities for hydrogen storage.

The purpose of the 2006 Hydrogen Contractors Meeting is to bring together researchers funded by BES together with their EERE funded counterparts in the area of hydrogen storage to facilitate the exchange of new results and research highlights, to foster new ideas and collaborations among the participants, and to identify needs of the research community. The meeting will also help DMS&E and BES in assessing the state of the program, charting future directions and identifying programmatic needs. Many of the BES Contractors Meetings are passing the quarter-century mark in longevity and are very highly regarded by their participants. It is hoped and indeed expected that the 2006 Hydrogen Storage Contractors Meeting will join the others in keeping with the long-standing BES tradition of excellence.

My colleagues and I wish to thank all of the speakers and meeting attendees for their active participation in sharing their ideas and research results. We also extend our thanks to Carole Read and Sunita Satyapal and their colleagues in the Office of Energy Efficiency and Renewable Energy (EERE) at DOE for the invitation to hold our meeting in conjunction with the 2006 Hydrogen Program Review and for their patient efforts in coordinating our activities. Thanks also go to Christie Ashton from DMS&E; Brian Herndon, Leslie Shapard and their colleagues from the Oak Ridge Institute of Science and Education; and Rich Bechtold and his colleagues from Alliance Technical Services for their assistance.

Tim Fitzsimmons
Division of Materials Sciences and Engineering
Office of Basic Energy Sciences
Office of Science
U.S. Department of Energy

Hydrogen Contractors Meeting

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Preliminary Agenda

Tuesday, May 16

Session I - Hydrogen Storage in Condensed Phases
Chair: Michael Trenary, University of Illinois, Chicago

5:35 pm Chemical Hydrogen Storage in Ionic Liquid Media
Larry Sneddon, University of Pennsylvania

5:55 pm Control of Hydrogen Release and Uptake in Condensed Phases
Tom Autrey, Pacific Northwest National Laboratory

Wednesday, May 17

Session II - Hydrogen Storage in Solids – I
Chair: Vijay John, Tulane University

5:35 pm From Fundamental Understanding to Predicting New Nanomaterials for High Capacity Hydrogen Storage and Fuel Cell Technologies
Jack Fisher, University of Pennsylvania

5:55 pm Metal-Organic Frameworks for Highly Selective Separations
Omar Yaghi, University of California, Los Angeles

Thursday, May 18

Session III - Poster Session (6:00 pm – 8:00 pm)

Elucidation of Hydrogen Interaction Mechanisms With Metal-Doped Carbon Nanostructures

Ragaiy Zidan, Steven Serkiz, Scott McWhorter, Polly Berseth, Jennifer Pittman, Savannah River National Laboratory; Puru Jena, Virginia Commonwealth University; and Apparao Rao, Clemson University

Characterization of Carbon Nanostructures in Pd Containing Activated Carbon Fibers Using Aberration-Corrected STEM

Klaus van Benthem, Xianxian Wu, Stephen J. Pennycook, Cristian I. Contescu, and Nidia C. Gallego, Oak Ridge National Laboratory

Theoretical Investigation of the Energetics of Hydrogen Interaction with Graphene Layers: The Effect of Interlayer Spacing on Hydrogen Storage

Rachel S. Aga, Maja Krcmar, James R. Morris, and Chong-Long Fu, Oak Ridge National Laboratory

Neutron Scattering Aided Studies of the Design, Synthesis and Thermodynamics of Molecular Hydrogen Adsorption Materials

J. Z. Larese, Lillian Frazier, Thomas Arnold, Michael Farinelli, Michael Hu, David Beach, A.J. Ramirez-Cuesta, and R.J. Hind, Oak Ridge National Laboratory and University of Tennessee, Knoxville

First-Principles Studies of Phase Stability and Reaction Dynamics in Complex Metal Hydrides

Mei-Yin Chou, Georgia Institute of Technology

Crystal and Electronic Structures of $LiNH_2$ and Related Compounds

J.B. Yang, X.D. Zhou, W.J. James and W.B. Yelon, University of Missouri-Rolla; Q. Cai, University of Missouri, Columbia

Understanding the Role (and Controlling the Behavior) of Transition Metal Dopants in $NaAlH_4$ Systems

Tabbetha A. Dobbins, Daniela Mainardi, Yuri Lvo, Institute for Micromanufacturing, Louisiana Tech University; Amitava Roy, Center for Advanced Microstructures and Devices, Louisiana State University

Integrated Nanoscale Metal Hydride – Catalyst Architectures for Hydrogen Storage

Yiping Zhao, The University of Georgia; Jin Z. Zhang, University of California, Santa Cruz; and Matthew D. McCluskey, Washington State University

The Molecular Design Basis for Hydrogen Storage in Clathrate Hydrates

Vijay T. John, Henry L. Ashbaugh, Gary L. McPherson, Tulane University; and Camille Jones, Hamilton College

First Principles Based Simulation of Hydrogen Interactions in Complex Hydrides

Qingfeng Ge and Jianjun Liu, Southern Illinois University

Dehydrogenation of Boron-Nanoclusters

Michael Trenary, University of Illinois at Chicago

NMR Studies of Metal-Hydrides: $MgScH_x$

Mark S. Conradi, Robert C. Bowman, Jr., Timothy Ivancic, Michael P. Mendenhall, Peter H. Notten, and W. P. Kalisvaart

Friday, May 19, 2006

Session IV - Plenary Speaker and Structural Characterization Focus

Chair: Tabbetha Dobbins, Louisiana Tech University

8:00 am Addressing Grand Challenges Through Advanced Materials
M .S. Dresselhaus, Massachusetts Institute of Technology

8:25 am Atomistic Transport Mechanisms in Revisible Complex Metal Hydrides
Peter Suter, Brookhaven National Laboratory

8:50 am *In-situ* Neutron Diffraction Studies of Novel Hydrogen Storage Materials
William Yelon, University of Missouri

9:25 am *In Situ* NMR Studies of Hydrogen Storage Systems
Mark Conradi, Washington University, St. Louis

9:50 am Break

Session V - Hydrogen Storage in Solids – II

Chair: Ragaiy Zidan, Savannah River National Laboratory

10:10 am High Throughput Screening of Nanostructured Hydrogen Storage Materials
Gang Chen, Massachusetts Institute of Technology

10:30 am Complex Hydrides – A New Frontier for Future Energy Applications
Vitalij Pecharsky, Ames Laboratory

10:50 am Molecular Hydrogen Storage in Novel Binary Clathrate Hydrates at Near-Ambient Temperatures and Pressures
Dendy Sloan, Colorado School of Mines

11:20 am Atomistic Mechanisms of Metal-Assisted Hydrogen Storage in Nanostructured Carbon
Nidia Gallego, Oak Ridge National Laboratory

11:50 am A Synergistic Approach to the Development of New Classes of Hydrogen Storage Materials
Jeff Long, Lawrence Berkeley National Laboratory

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Peter H. Notten, and W. P. Kalisvaart

Abstracts

Chemical Hydrogen Storage in Ionic Liquid Media

Grant No. DE-FG02-05ER15719-AO

Larry G. Sneddon (Penn), Tom Baker (Los Alamos) PIs,
Chang Yoon (student), Martin Bluhm, (postdoctoral) and Vincent Pons (postdoctoral)
Department of Chemistry, University of Pennsylvania, Philadelphia PA 19104-6323
Phone: 215-898-8632; Fax: 215-573-6743; email: lsneddon@sas.upenn.edu

Program Scope and Objectives

The development of efficient and safe methods for hydrogen storage is a major hurdle that must be overcome to enable the use of hydrogen as an alternative energy carrier. Although many molecular hydride complexes have certain features that might be attractive for chemical hydrogen storage, the high hydrogen capacities needed for transportation applications exclude most compounds. Amineboranes such as ammonia borane, NH_3BH_3 (19.6 wt% H_2), are thus unique in their potential ability to store and deliver large amounts of molecular hydrogen through dehydrogenation reactions.

Partial dehydrogenation of ammonia borane can be thermally induced in the solid-state,[1-4] but to be useful for hydrogen storage, milder conditions and more controllable reactions are required. Such reactions could in principle be attained in solution, but practical applications of chemical hydrogen storage will need a replacement for the volatile organic solvents that have traditionally been employed for reactions of molecular chemical hydrides. The goal of this project is to use the unique advantages of ionic liquid solvents[5] to develop new ways of inducing amineborane dehydrogenations at lower temperatures and to elucidate the important controlling factors in these reactions.

Recent Progress

Our intial work has now shown that ionic liquids provide advantageous media for ammonia borane dehydrogenation in which both the extent and rate of dehydrogenation are significantly increased.

Comparisons of ammonia borane dehydrogenation reactions in the solid-state versus in 1-butyl-3-methyl-imidazolium chloride (bmimCl) solvent are summarized in Fig. 1. Reactions in the solid-state were conducted in sealed, evacuated glass vessels that were heated in a thermostatically controlled oven. The bmimCl/NH_3BH_3 reactions were carried out by adding equal weights of bmimCl (dried) and NH_3BH_3 together in evacuated 250 mL flasks equipped with a vacuum adapter and then immersing the body of the flasks into an oil bath at the desired temperature. At the conclusion of each reaction, the sealed vessels or flasks were opened to a vacuum line and the evolved hydrogen passed through a liquid nitrogen trap in order to isolate any volatile non-hydrogen products, such as borazine. The evolved hydrogen was then quantitatively measured in calibrated volumes using a Toepler pump.

As seen in Fig. 1a, for the reactions carried out in the solid-state at 85ºC, there was negligible hydrogen production after 3 h, but after 17 h, 0.9 equivalents of H_2 were produced. Even with prolonged heating (67 h) at this temperature, no further H_2 release was observed. Similar results were observed at 95ºC, but with a shorter initial induction period. Thus, while there was no H_2 evolution after 1 h, 0.8 equivalents were obtained after 3 h. Again, as with the 85°C sample, prolonged heating at 95°C (48 h) yielded a total of only 0.9 equivalents of H_2.

In contrast to the results of the solid-state reactions, when ammonia borane dehydrogenation was carried out in bmimCl, no induction period was observed (Fig. 1b). Thus, separate samples heated for only 1 h at 85°, 90° and 95°C evolved 0.5, 0.8 and 1.1 equivalents of H_2, while samples heated at the same temperatures for 3 h produced 0.95, 1.2 and 1.5 equivalents. Heating for 22 h gave a total of 1.2, 1.4 and 1.6 equivalents of H_2, respectively, which are values significantly greater than the 0.9 equivalents ultimately obtained in the solid-state reactions.

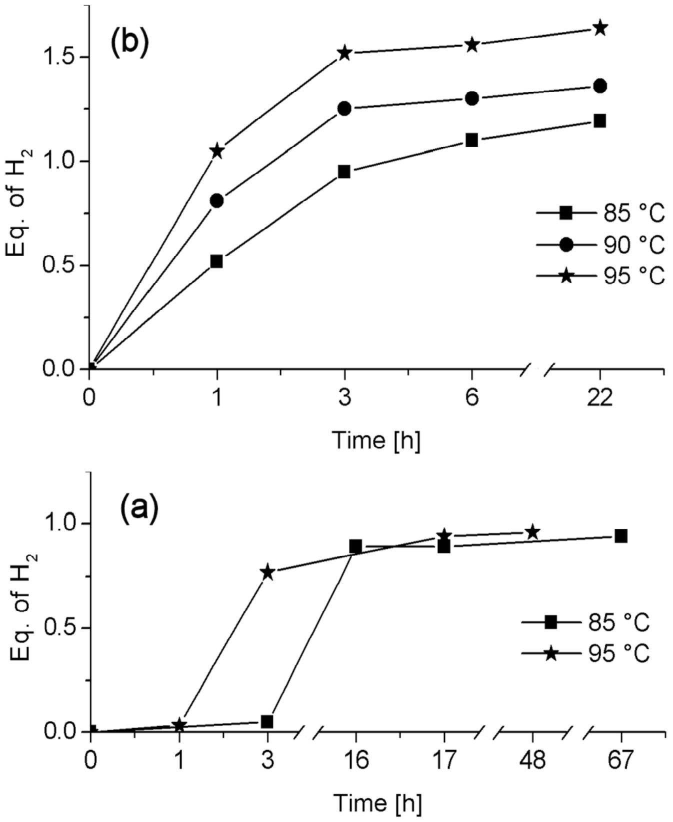

Figure 1. Summary of H_2 release at different temperatures from: (a) solid ammonia borane, and (b) from equal weight mixtures of bmimCl and ammonia borane.

The ^{11}B NMR spectra obtained from pyridine (dried) extracts of the residues of the 85 °C solid-state and IL reactions are compared in Fig. 2. Consistent with the observed absence of H_2 loss, the spectrum (Fig. 2a) of the residue of the 1 h solid-state reaction showed only unreacted ammonia borane (–22.4 ppm) whereas the 1 h bmimCl sample clearly showed significant reaction. The spectra of the residues of the 19 h solid-state and 3 h bmimCl reactions (Figs. 2b and 2d) were quite similar showing multiple resonances.

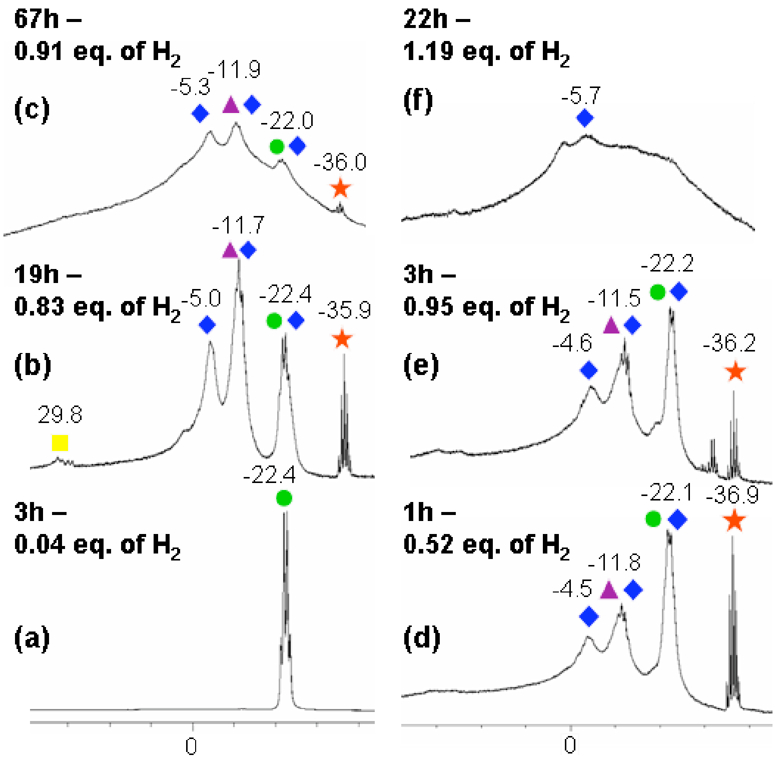

Figure 2. ^{11}B NMR spectra (128 MHz) of the residues (dissolved in pyridine) of ammonia borane dehydrogenation: (left) in the solid-state, and (right) in bmimCl. ● ammonia borane, ★ BH_4^-, ▲ BH_2^+, ◆ polyaminoborane, 🟨 B=N. (The signals near -11 ppm may also include a resonance from pyridine-BH_3).

The role of bmimCl in enhancing both the rate and extent of ammonia borane dehydrogenation has yet to be proven, but it is significant that the "diammonate of diborane"[6] $[(NH_3)_2BH_2^+]BH_4^-$ has also been reported[7] to form polyaminoborane upon heating. Because of their ionic compositions, ionic liquids are known[5] to favor the formation of polar intermediates and transition-states and the observation that there is substantial $[(NH_3)_2BH_2^+]BH_4^-$ produced in the ionic liquid reaction within the first hour suggests that the activating effect of the ionic liquid may be related to its ability to induce the formation of $[(NH_3)_2BH_2^+]BH_4^-$.

Future Plans

We are now further exploring the activating effect of ionic liquids in conjunction with their established ability to stabilize nanoparticle dehydrogenation catalysts to develop new more active chemical hydrogen storage systems.

Preliminary results at Los Alamos have now shown that base metal complexes containing N-heterocyclic carbene (NHC) ligands are uniquely stable under the reducing conditions required for catalyzed dehydrogenation of amine-boranes and related B-N compounds. As heterogeneous catalysts present advantages for this application, we will attempt to prepare metal nanoparticles that are capped with NHC ligands and test these nanoparticles as amine-borane dehydrogenation catalysts. We will assay a variety of ionic liquids as novel media for both synthesis of the nanoparticles and as solvents for the dehydrogenation reactions. Mechanistic details of promising systems will be probed using substrate isotopic labeling coupled with vibrational spectroscopies and high-field multinuclear NMR in the solid state and solution.

Recent DOE Sponsored Publications (September 1, 2005-present)

M. Bluhm, M. G. Bradley, R. Butterick III, U. Kusari, and L. G. Sneddon "Amineborane Based Chemical Hydrogen Storage: Enhanced Ammonia Borane Dehydrogenation in Ionic Liquids" submitted.

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Basic Research for the Hydrogen Fuel Initiative: Control of Hydrogen Release and Uptake in Condensed Phases

Nancy Hess, John Fulton, John Linehan, Wendy Shaw, Ashley Stowe, Luke Damean, Craig Brown, Eugene Mamnotov, Maciej Gutowski, Tom Autrey

Pacific Northwest National Laboratory
Los Alamos National Laboratory
National Institute of Standards & Technology

Program Scope

This research effort will result in knowledge that will provide the basis for development of new materials that release and absorb hydrogen at moderate temperatures and pressures. New theoretical and experimental tools to investigate hydrogen-rich materials will be developed. The proposed work specifically addresses the focus area “Novel Materials for Hydrogen Storage” and peripherally “Design of Catalysts at the Nanoscale” of the Hydrogen Fuel Initiative. These fundamental studies will provide a strong basis for support of DOE’s EERE Centers of Excellence in hydrogen storage.

The long-term objective of the proposed research is to develop knowledge about hydrogen-rich materials that will provide the basis for developing new hydrogen storage systems. We contend that: (i) hydrogen can be stored reversibly in materials with alternating electron-rich and electron-poor sites, (ii) thermally reversible hydrogen storage can be accomplished with chemical hydrides based on the B,N,C elements, and (iii) nanoscale effects and interfacial interactions can enhance kinetics and modify thermodynamics of hydrogen release and uptake.

Structure and bonding in the NBH materials

- How do the properties of the B—N, N—H, and B—H bonds change in the NH_xBH_x series (x=0-4)?
- How do the proton and hydride affinities of the N and B sites, respectively, evolve in this series?
- How do the properties of the di-H bonds; i.e., $N—H^{\delta+} \cdots {}^{\delta-}H—B$, evolve in this series?
- What is the directionality of di-H bonds?
- What is the interplay of perturbation components, such as electrostatics, induction, dispersion, and valence repulsion, in di-H bonds?
- How important are cooperative (non-additive) effects?
- Is a dihydrogen bond a precursor to molecular hydrogen formation?
- How do substitutions on the B and/or N atoms affect properties of the B—N, N—H, B—H, and di-H bonds?

Thermodynamics and kinetics of hydrogen release and uptake

- Can the stability of NBHs be analyzed in terms of proton and hydride affinity of electron-rich and electron-poor sites, respectively, and long-range intermolecular interactions?
- What is the mechanism for H_2 release and uptake from NBH materials?
- What are reaction pathways and barriers for the two distinct steps of hydrogen release, nucleation and growth?

- How do the substitutions on B and/or N atoms affect the mechanism, barriers, and thermodynamis of hydrogen release and uptake?
- What is the role of quantum effects in dynamics of molecular and atomic hydrogen?
- Will alloying of NBH materials with carbon or other, light, main-group elements lead to HRMs with desirable thermodynamics of hydrogen release and uptake?

Interfacial chemistry and catalysis

- How do interfaces with various supports affect the kinetics, thermodynamics, and selectivity of reversible hydrogenation?
- Are the nucleation and growth steps the same in neat NBH and NBH deposited in a nanoporous scaffold?
- How do nanocatalysts immobilized on the support and/or dispersed in bulk of the NBH materials affect kinetics of hydrogen release? Are the nucleation and growth steps the same as in neat NBH?
- Can we use neutron scattering, EXAFS, and NMR techniques to investigate catalytic activation of hydrogen in the solid state?

Recent Progress

Neutron vibrational studies of di-hydrogen bonding: The low frequency region of the inelastic neutron scattering (INS) spectrum collected at 15 K is shown in Figure 1 for $H_3N^{11}BH_3$, $D_3N^{11}BH_3$, and $H_3N^{11}BD_3$. Specific isotopic labeling of the hydridic and protic positions has allowed for study of the soft dihydrogen vibrational modes.

In an attempt to predict the change to these vibrational modes with deuteration, we have mapped the N-H…B-H unit involved in dihydrogen bonding to a traditional model of hydrogen bonding. A proton acceptor, proton donor and proton are required for conventional hydrogen bonding. In the case of ammonia borane which has both protic and hydridic hydrogens, we have made the assumption that the proton acceptor includes the entire (B-H) unit. The nitrogen atom is then the traditional proton donor. Under these constraints, deuteration of the hydridic hydrogen has a weaker effect on the vibrational frequency based solely on the reduced mass change (see Table 1). This model underestimates the softening which results from deuteration of the (B-H) unit, but does predict observed weaker vibrations. Deuteration of the protic positions again results in less energetic vibrations; however, the observed change is far less dramatic than predicted by this model. One explanation may be due to the molecular arrangement in the solid state. The protons are oriented between two hydridic positions of an adjacent molecule. Hydrogen bonding is therefore a cooperative

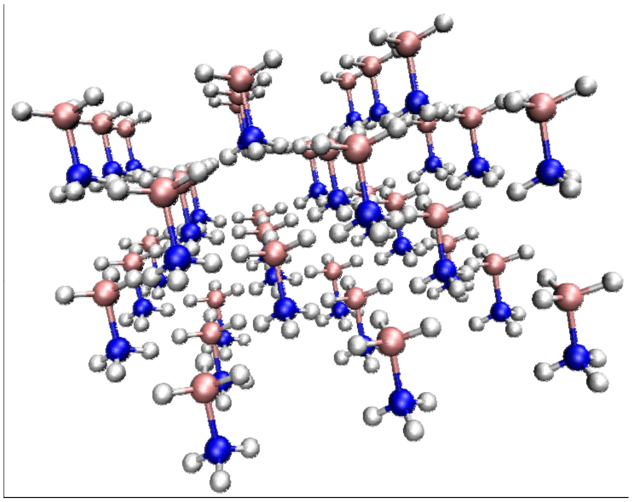
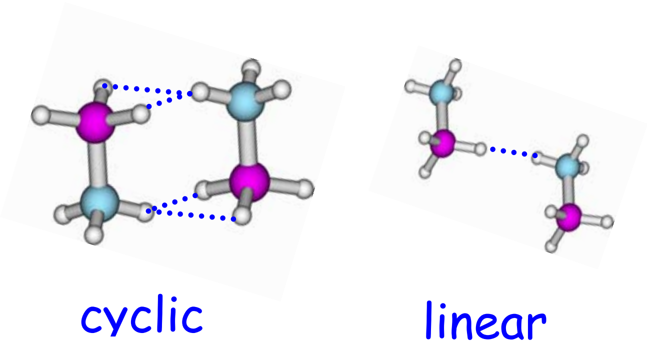
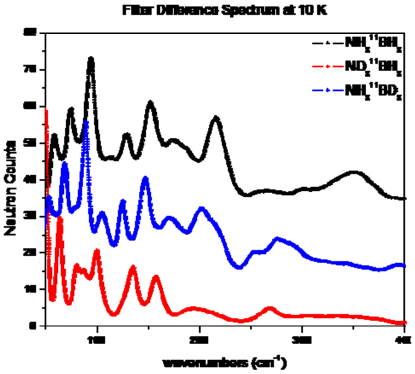


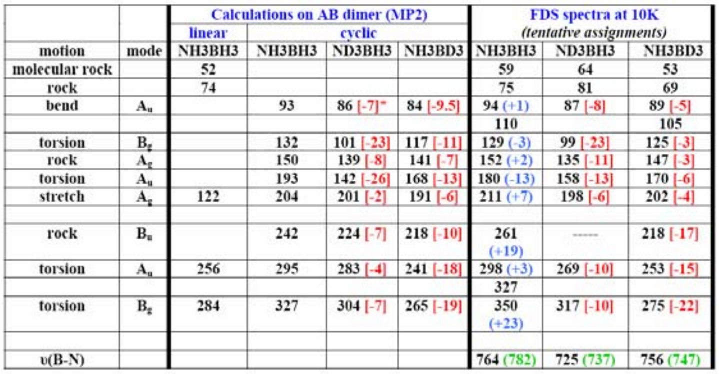
Figure 1. Orthorhombic phase of ammonia borane illustrating extended network of intermolecular dihydrogen bonding between adjacent BH—HN.

process which involves more than one proton, proton donor, and proton acceptor. This model does predict a weakening on the dihydrogen vibrational energy upon deuteration as observed in the INS spectra.

Our experimental results are compared with various levels of theory for the perprotonated ammonia borane as well as with expected shifts in the vibrational frequency due to isotopic labeling. Experimental and calculated vibrational positions are tabulated in Table 1. Semi-empirical MP2/aug-cc-VDZ results of the ammonia borane dimer are for each isotopomer reveals the relative changes in the soft modes. Clearly the vibrational frequencies for the dimer are not equivalent to those in the bulk; however, trends in the soft mode frequency changes due to isotopic substitution are consistent with observed INS results. The dihydrogen symmetric stretching mode (A_g) at 204 cm^{-1} for $H_3N^{11}BH_3$ is relatively stable upon H/D substitution. Further, the bend (A_u) at 93 cm^{-1} and the rocking modes at 150 (A_g) and 242 (B_u) cm^{-1} for $H_3N^{11}BH_3$ are relatively stable. The other low energy vibrations are assigned to rotational and lattice modes.







		Calculations on AB dimer (MP2)				FDS spectra at 10K *(tentative assignments)*		
		linear	cyclic					
motion	mode	NH3BH3	NH3BH3	ND3BH3	NH3BD3	NH3BH3	ND3BH3	NH3BD3
molecular rock		52				59	64	53
rock		74				75	81	69
bend	A_u		93	86 [-7]*	84 [-9.5]	94 (+1)	87 [-8]	89 [-5]
						110		105
torsion	B_g		132	101 [-23]	117 [-11]	129 (-3)	99 [-23]	125 [-3]
rock	A_g		150	139 [-8]	141 [-7]	152 (+2)	135 [-11]	147 [-3]
torsion	A_u		193	142 [-26]	168 [-13]	180 (-13)	158 [-13]	170 [-6]
stretch	A_g	122	204	201 [-2]	191 [-6]	211 (+7)	198 [-6]	202 [-4]
rock	B_u		242	224 [-7]	218 [-10]	261 (+19)	-----	218 [-17]
torsion	A_u	256	295	283 [-4]	241 [-18]	298 (+3)	269 [-10]	253 [-15]
						327		
torsion	B_g	284	327	304 [-7]	265 [-19]	350 (+23)	317 [-10]	275 [-22]
υ(B-N)						764 (782)	725 (737)	756 (747)

Figure 2. Neutron vibrational spectrum was obtained for there isotopomers of ammonia borane at 15 K to gain insight into the nature of dihydrogen bonding in the solid state. Linear dimer is solid state structure, cyclic dimer is gas phase structure.

Publications.

In-situ XAFS and NMR Study of Rhodium Catalyzed Dehydrogenation of Dimethylamine Borane. Y Chen, JL Fulton, JC Linehan, T Autrey, J. Am. Chem. Soc. *127*, 3254, **2005**.

Dynamics of Ammonia Borane Using Neutron Scattering. CM Brown, TL Jacques, NJ Hess, LL Daemen, E. Mamontov, JC Linehan, AC Stowe, and T Autrey, accepted Physica B, **2006**.

and/or Infrared and/or Neutron INS measurements and comparing the results with our calculations. Among many unique modes of C_{60}TiHx, we found that the first three lowest energy modes all involve the TiHx group vibrating as a whole as shonwn in the left panel to Figure 1. The lowest energy mode is the one where the TiHx group oscillates towards the nearest neighbor hexagon centers (shown as red arrow). The second lowest energy mode is the similar one but this time the TiHx group vibrates along the bridge bond (rather than towards hexagons – see blue arrow in Fig. 1). And finally, the third lowest energy mode is the radial oscillation of the TiHx group (black arrow in Fig. 1). We note that these modes have low energies not due to the weak interaction of the C_{60} and TiHx group but rather due to large mass of the TiHx group. The fact that these modes are positive suggests that proposed structures form stable local energy minima. In order to test the stability and metal-segregation in these systems further, we are currently performing high-temperature first-principles dynamics simulations. Within the MD simulation time, we have found that the diffusion of metal is very small (to be more pricise, we have not observed any diffusion within the MD simulation time of 1 ps and temperatures up to 800 K). Hence, it is very likely that if Ti-decorated C_{60} and SWNT systems can be synthesized, they will preserve their intial structures during the hydrogen charging and decharging cycles. The right panel in Figure 1 shows the Ti-Ti distance during the MD simulation at 800 K for a pair of two TiH_2 group bonded to two nearest neighbor bridge sites on a C_{60} molecule. From this simulation, no the evidence for clustering has been observed.

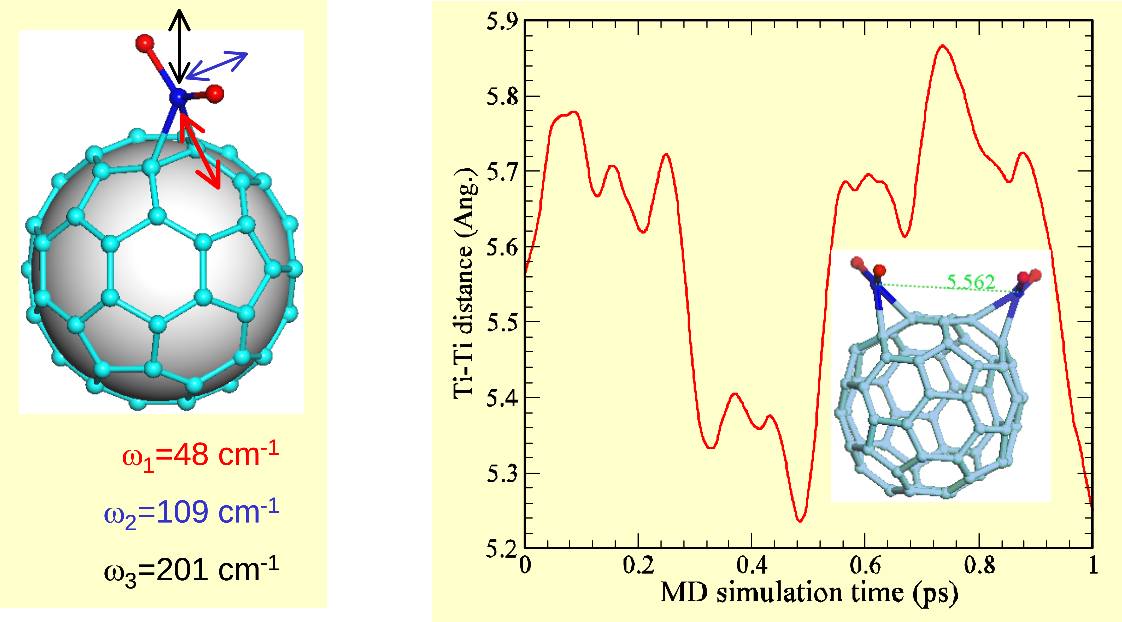


Figure 1. *LEFT: The three lowest energy modes of a $C_{60}TiH_2$ cluster. The mode energies given at the bottom are all positive, indicating that the system is in a local minima structure. RIGHT: The Ti-Ti distance as a function of MD simulations at 800 K for a $C_{60}(TiH_2)_2$ cluster as shown in the inset. No evidence for clustering is observed within the MD simulation time length.*

From fundamental understanding to predicting new nanomaterials for high capacity hydrogen storage and fuel cell technologies

DE-FG02-98ER45701 (Duration: 03/01-2006 – 06/30/2007)

T. Yildirim[1,2] and J. E. Fischer[1]
[1]Department of Materials Science and Eng., University of Pennsylvania,
Philadelphia, PA 19104
[2]National Institute of Standards and Technology, NCNR, Gaithersburg, MD 20899

Program Scope:

This is an add-on BES proposal to Jack Fischer's existing grant on "Carbon Nanotubes: Properties and Applications", which will focus on achieving fundamental understanding of the chemical and structural interactions governing the storage and release of hydrogen in a wide spectrum of candidate materials. Even though we have just started our theory and modeling efforts coupled closely to neutron experiments at NIST, we have already obtained significant results that will be briefly discussed in this abstract. The main purpose of our proposal is to launch a broad modeling effort, in the framework of this BES grant. The goals are

- To provide fundamental underatanding of how the most of the candidate materials (MOF's, alanates, destabilized chemical hydrides, etc) interact with H_2 chemically, structurally and energetically; and
- To provide timely feedback and guidance from theory to *de novo* materials design and targeted syntheses throughout the DOE programs.

We expect that this new modeling initiative will have a major impact on the extensive experimental work at NIST, where senior staffs are coupled to essentially all of the EERE Centers of Excellence.

Recent Progress:

(a) High-Temperature Molecular Dynamics Study and Normal Mode Analysis of Ti-decorated C_{60} and SWNT for Room-Temperature Hydrogen Storage Media

There is accumulating experimental and computational evidence that Ti additions to low-capacity storage materials can have dramatic beneficial effects on H_2 capacity. We recently showed that a single Ti could adsorb four H_2 molecules with interaction strength intermediate between chemi- and physorption, precisely what is needed for reversible room temperature storage. This recent discovery opens a totally new way of engineering nanostructured materials by tuning the interaction centers in high-surface area materials and will be one of the main focuses of this project. We are currently studying several important questions such as "metal clustering" or "segregation" in Ti-decorated nanostructures using high-temperature molecular dynamics simulations and normal-mode analysis.

We have calculated normal modes (i.e. phonons) of several C_{60}TiyHx (y=0,1,6, x=0,2,4, and 8) clusters and the corresponding Neutron and Raman intensities. We found that all modes are positive suggesting that the predicted Ti-decorated C60 stuctures are at least metastable phases. Hence if one could synthesize them, they will stay in that way below some critical temperature. The calculated phonon-spectrums will be also in valuable in confirming that any attempted synthesis was successful or not via Raman

(b) Ti-enhanced kinetics of hydrogen adsorption and desorption in $NaAlH_4$ surfaces (submitted Phys. Rev. B see cond-mat/0604472)

In this work, we report a first-principles study of the energetics of hydrogen absorption and desorption (i.e. H-vacancy formation) on pure and Ti-doped sodium alanate ($NaAlH_4$) surfaces. We find that the Ti atom facilitates the dissociation of H_2 molecules as well as the adsorption of H atoms. In addition, the dopant makes it energetically more favorable to creat H vacancies by saturating Al dangling bonds. Interestingly, our results show that the Ti dopant brings close in energy all the steps presumably involved in the absorption and desorption of hydrogen, thus facilitating both and enhancing the reaction kinetics of the alanates. We also discuss the possibility of using other light transition metals (Sc, V, and Cr) as dopants.

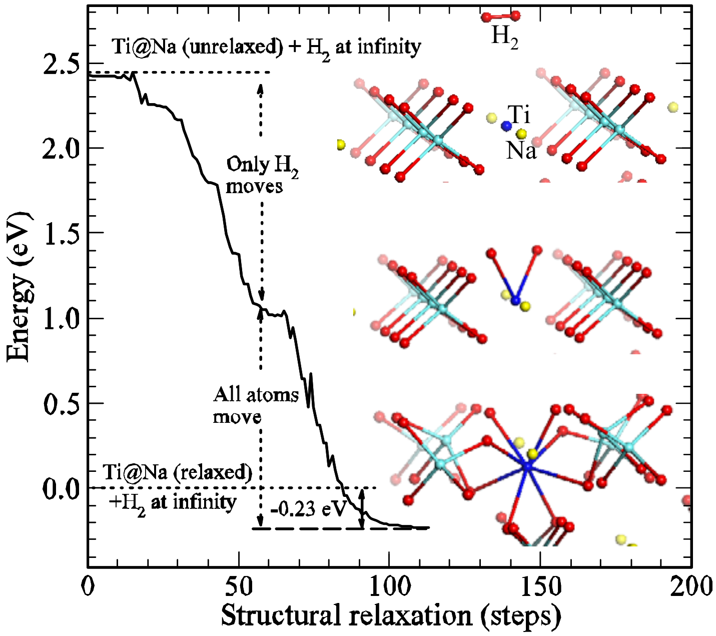


Figure 2: *Energy versus structural relaxation step for the H_2 dissociation and absorption by the Ti@Na surface. The starting point is the unrelaxed Ti@Na surface with an H_2 molecule close to it, which is taken as the zero of energy. In the first part of the relaxation, only the H_2 molecule is allowed to move; then, all the atomic positions are relaxed. Given for reference is the result for the relaxed Ti@Na plus an H_2 located at infinity. The insets show the various steps of the absorption process.*

(c) H_2 and CH_4 adsorption in MOF5: A High-Pressure Volumetric and INS Study

We measured the H_2 and CH_4 adsorption isotherms in MOF5 over a large temperature range (30-300 K) and pressure range (up to 65 bar) using a home-built, fully computer-controlled Sieverts apparatus. We found that in a volumetric method, properly choosing the real gas equation of state is of critical importance for obtaining reliable isotherm data. For H_2 and CH_4, the widely used van der Waals equation of state (EOS) is not adequate and the modified Benedict-Webb-Rubin (MBWR) EOS should be used in the data reduction. With the sample mass and bulk density known, the skeleton density and the specific pore volume of MOF5 were also measured and found to be ~1.78 g/cc and 66.2 % respectively. The absolute adsorption, excess adsorption and effective adsorption were then all experimentally determined. At low temperature, the maximal excess adsorption capacities of H_2 and CH_4 in MOF5 are found to be 10.3 wt% and 51.7 wt% respectively. From the isotherm data, the isosteric heat of adsorption (Qst) was estimated. The excess Qst's for the initial H_2 and CH_4 adsorption in MOF5 are ~4.8 KJ/mol and ~12.2 KJ/mol, respectively. When the amount adsorbed is large, Qst increases with increasing amount adsorbed, a result of cooperative interactions between adsorbed molecules.

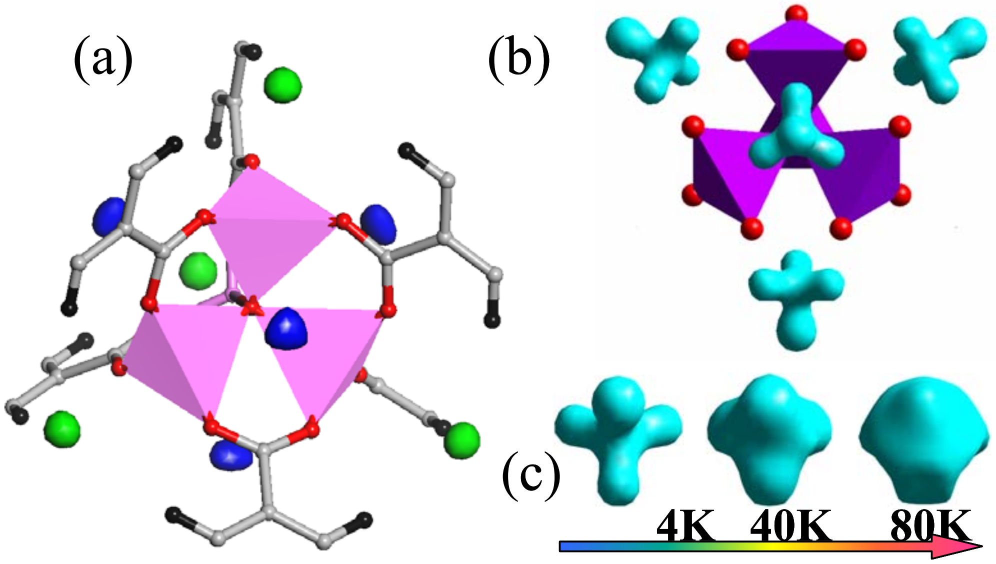


Figure 3. (*a) First two hydrogen absorption sites in MOF5 as directly measured by neutron scattering. (b) The methane absorption sites in MOF5. Light-blue are actual experimental scattering density of CH_4 absorbed in MOF5. (c) Temperature evaluation of the CH_4 orientation as T increases from 4K to 80 K.*

Finally, we also performed several neutron scattering measurements to study the H2/CH_4 interactions in MOF-host lattice as shown in Fig. 3. We successfully identified the absorption sites as a function of gas-loading concentration. We also measured and calculated the elementary excitions such as ortho-para transition of H_2 and "rotational tunnel splitting of methane" in MOF, which gives very detailed information about the H_2-MOF interactions.

(d) Unusually Short Hydrogen-Hydrogen Pairing in LaNiInH$_x$

A recent neutron powder diffraction study of the *R*NiIn-D_2 systems (*R* = La, Ce, Nd) [J. Alloys Comp. 330-332 (2002) 132] showed an unusual double H occupancy in the trigonal bipyramidal R_3Ni_2 sites (see Fig. 4), leading to the formation of hydrogen pairs with the shortest documented interatomic H···H separation (1.56-1.63 Å) for intermetallic hydrides, *raising several important fundamental questions and possible practical applications related to hydrogen storage.*

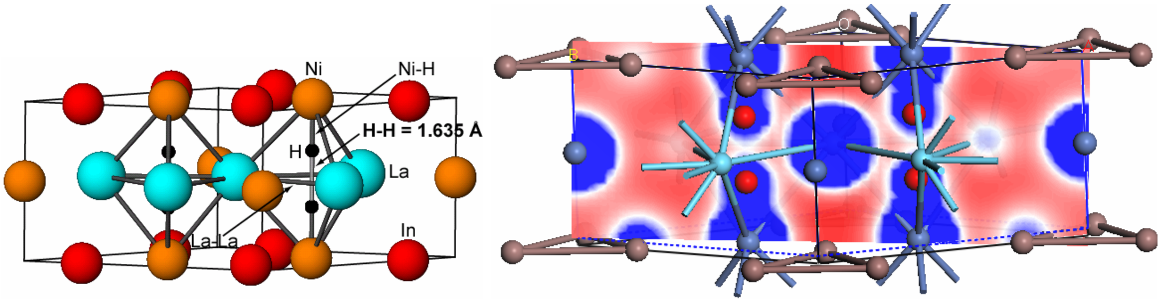


Figure 4. *(LEFT) Crystal structure of* $LaNiInH_{1.333}$ *(RIGHT) Calculated charge density contour indicating that H atoms are strongly hybridized with Ni (blue color) and there is nobonding between two hydrogen atoms (white region).*

In order to understand the nature of bonding, structure and dynamics in these interesting intermatallic hydrides, $RNiIn\text{-}H_X$, we have performed (a) inelastic neutron scattering measurement for x=1.333 and 0.666 and (b) first-principles structure and dynamics calculations for three different values of hydrogen concentration. Both INS spectrum and calculations suggest that in $LaNiInH_{0.666}$, H atoms are on different sites. Charge and bond-population analysis indicate that the bonding in these interesting system is a combination of ionic and covalent. There is a little H—H chemical bonding (if any) as shown in Figure 4. The neutron vibrational spectrum shows only the modes where H vibrates in the ab-plane. Somehow the high-energy vibrations along the c-axis are missing (probably due to anharmonic behavior which results in large rms displacement, and therefore large temperature-factor)! Comparison between experiement and calculations indicate that the force constant between H—H is about 10% of the Ni-H force constant, consistent with the charge density plot shown in Fig. 4.

Future Plans:

Based on the current results discussed above, we will contiune to use the following unique approaches to solve the outstanding problems in hydrogen storage field:

- Major emphasis will be placed on fundamental issues, such as understanding the mechanism of hydrogen interaction in different candidate materials, by employing a powerful combination of first-principles modeling and closely coordinated neutron scattering experiments to develop and test intermolecular potential surfaces, etc.
- A major focus will be on nanoscale materials and the practicality of exploiting metastable states, in contrast to traditional theory which goes to great lengths to avoid local minima in atomic configuration energies. This approach is much more consistent with the manner in which many of these materials are synthesized, e.g. ball-milling to realize Ti-doped alanates, in which high energy nonequilibrium methods are a prerequisite to obtain the targeted phase.
- Theory and experiment will be done under the same roof at NIST. Frequent interactions *via* group meetings, web-conference and email will be programmed.

In particular, in the rest of the project, we will try to accomplish the following objectives:

- Study hydrogen sorption properties of Ti and other transition metal coated carbon, boron-nitride and TiS_2 nanotubes. Determine trends in binding energies, geometries and hydrogen sorption capacity as a function of tube type, radius, transition metal and coverage.
- Apply Ti doping/activation to other promising materials, e.g sodium alanates and borates and novel clusters such as metcarb (i.e. $Ti_{12}C_8$).
- Establish the stability and energetics of MOF materials doped with alkali and transition metals (Li being particularly attractive). Identify metal absorption sites and their interactions with high-energy molecules such as hydrogen and methane.
- In parallel with the theory effort, synthesize and characterize the most promising doped nanostructured materials predicted by the modeling. Perform high-pressure hydrogen adsorption isotherms to determine capacity and kinetics. Use neturon scattering to determine the location of interaction centers, hdyrogen dynamics and the nature of bonding.

Publications in 2006 (related to this project)

1. *Ti-enhanced kinetics of hydrogen absorption and desorption in NaAlH4 surfaces*, J. Iniguez and T. Yildirim (PRB, submitted 2006,cond-mat/0604472).

2. *Structure, Dynamics and Rotational Tunneling of Methane in MOF,* W. Zhou and T. Yildirim (in preparation, 2006.)

3. *Unusually Short Hydrogen-hydrogen distance in LaNiInH$_X$*,T.Yildirim, J. Iniguez, T. J. Udovic, V. A. Yartys, PRB rapid comm. (in preparation, 2006).

4. *Lattice Dynamics of MOF5; A combined neutron scattering and first-principles study,* W. Zhou and T. Yildirim (in preparation, 2006.)

5. H_2 and CH_4 adsorption in MOF5: A High-Pressure Volumetric Study, W. Zhou, M. R. Hartman and T. Yildirim (in preparation, 2006).

6. *Normal Mode Analysis and First-Principles Molecular Dynamics Study of C60TiyHx Clusters for Room Temperature Reversible Hydrogen Storage*, J. Iniguez, W. Zhou and T. Yildirim (in preparation, 2006.)

Invited Talks in 2006 (related to this project)

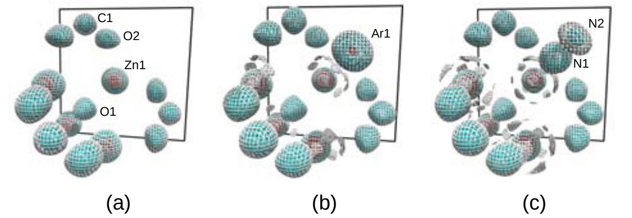
1. *From fundamental understanding to predicting new nanomaterials for high capacity hydrogen storage technologies***,** T. Yildirim, APS March Meeting, Baltimore 2006.

2. *Combined Neutron Scatterig and First-Principles Study of Novel Hydrogen Storage Materials,* T. Yildirim, MRS Spring Meeting, San Francisco 2006.

3. *Magic Role of Ti in Novel Hydrogen Storage Materials,* T. Yildirim, the XV International Materials Research Congress (IMRC), Cancún, Aug. 20 -24, 2006.

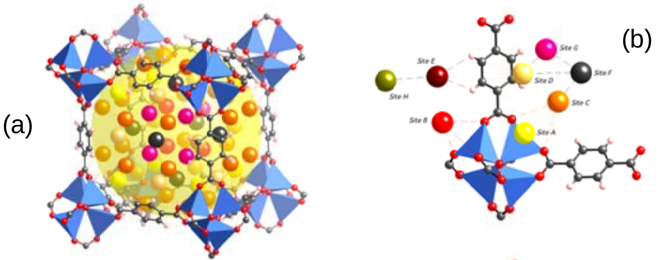
4. *Neutron Scatterig and First-Principles Characterization of Novel Hydrogen Storage Materials,* T. Yildirim, American Conference on Neutron Scattering St. Charles, IL, June 18-22, 2006.

1. Adsorption sites in MOFs. The primary adsorption sites for Ar and N_2 within metal-organic framework-5 (MOF-5), a cubic structure composed of $Zn_4O(CO_2)_6$ units and phenylene links defining large pores 12 and 15 Å in diameter, have been identified by single crystal X-ray diffraction. Refinement of data collected between 293 and 30 K revealed a total of eight symmetry-independent adsorption sites. Five of these are sites on the zinc oxide unit and the organic link; the remaining three sites form a second layer in the pores. The structural integrity and high symmetry of the framework is retained throughout, with negligible changes resulting from gas adsorption. This has facilitated the design of specific frameworks for storage and separation of gases as well as the separation of polar and nonpolar, and aromatic organics.



(a) (b) (c)

Figure 1. Three-dimensional electron density maps (F_{obs}) of the primary adsorption site in MOF-5, calculated from X-ray diffraction data collected from single crystals loaded under gases. At 293 K, only regions of electron density assigned to the framework are observed, including the Zn_4O cluster and three carboxylates (a), while at 30 K, regions of electron density ascribed to adsorbed argon (b) or dinitrogen (c) are also prominent. At 30 K, Fourier ripples around the Zn atoms are observed. Contours (e-/Å^3): silver > 3, blue > 5, red > 25.



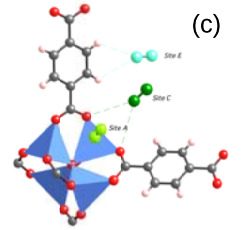
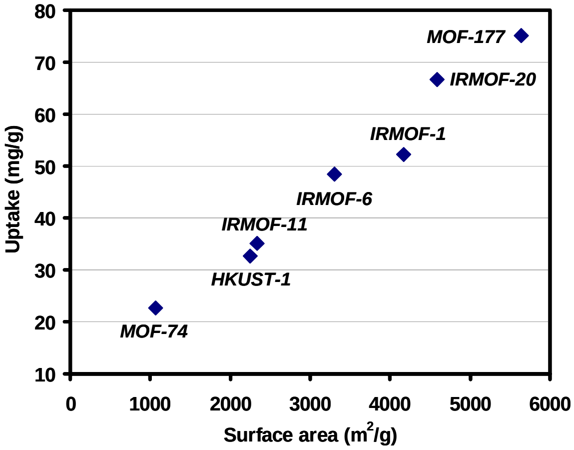


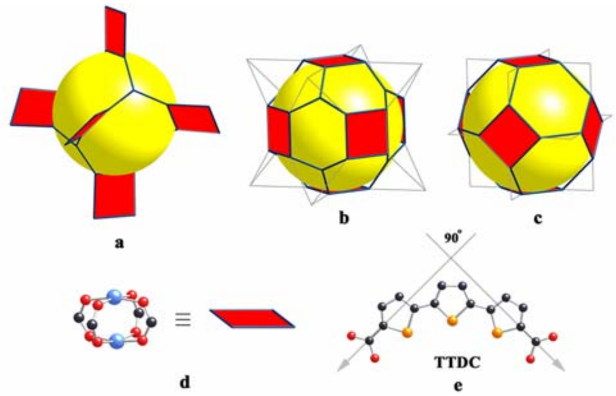
Figure 2. At 30 K, eight symmetry-independent sites are identified as partially occupied by argon atoms, one highly-packed pore is illustrated (a), with some framework and inter-site contacts highlighted (b). Relevant interatomic distances (Å): Site **A**, 3 C at 3.572, 9 O at 3.601, 3 Zn at 3.926; **B**, 3 O at 3.492, 3 H at 3.281, 1 Zn at 3.686; **C**, 2 O at 3.792, 2 H at 3.306; **D**, 6 C at 3.64; **E**, 2 H at 3.288. Sites **F-H** form a second layer, with only contacts to other argon atoms. Inter-site distances include (Å): **B-E** 3.270, **B-C** 3.471, **D-G** 3.652, **A-C** 3.677, **F-G** 3.716, **C-F** 3.729, **G-G'** 3.763, **E-E'** 3.770, **C-D** 3.820, **A-G** 3.828, **C-E** 3.968, **E-H** 4.073, **D-F** 4.112 (primes indicate symmetry equivalents). Surface sites well-separated from each other are occupied by dinitrogen at 30 K (c). Relevant interatomic distances (Å), from closest nitrogen atom to framework: Site **A**, 3 C at 3.379, 6 O at 3.372, 3 Zn at 3.606; **C**, 2 O at 3.668, 2 H at 3.244, **E**, 2 H at 3.097 and inter-site distances (measured between molecular centers of mass): **A-C** 4.104, **C-E** 4.026, **E-E'** 3.708.

2. Hydrogen storage. Understanding the relationship of surface area to hydrogen uptake is a very important aspect of achieving the DOE goals for hydrogen storage. Under this grant, we find a clear relationship between hydrogen storage capacity and surface area (reported in JACS 2006). We reported adsorption data collected for seven MOF materials at 77 K which leads to saturation at pressures between 25 and 80 bar with uptakes from 2% to 7.5%. In this study we show that the saturation uptake of H_2 in MOFs correlates well with surface area and that viable volumetric densities in highly porous structures can indeed be achieved.

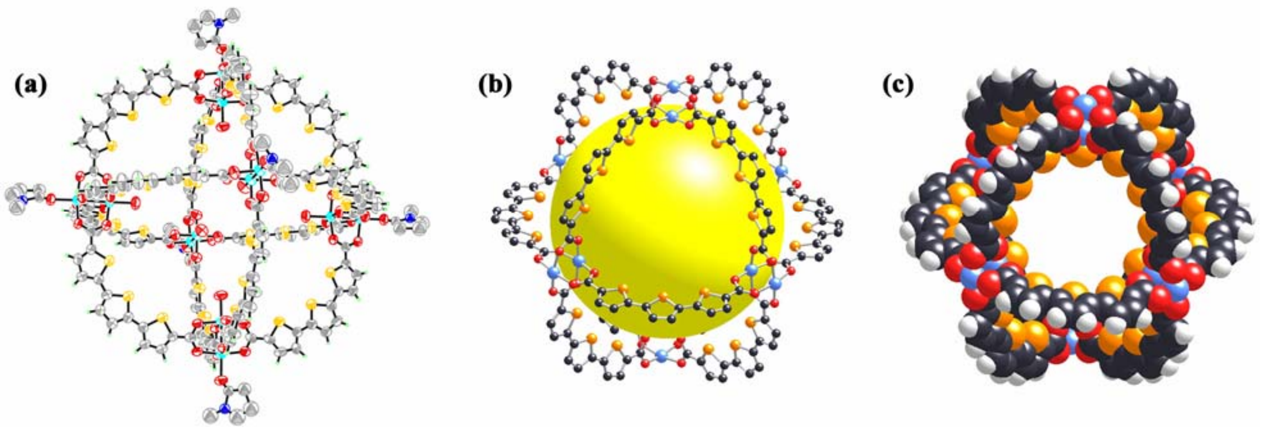


3. Porous polyhedra. A more recent development focused on designing and using small porous molecules that can be employed in solution to trap and separate organics and small gas molecules. The remainder of the report will discuss this aspect; although the publications listed below are indicative of the tremendous success we have achieved in the last year on this project.

A number of designed 3-D discrete molecular shapes have been assembled by joining metal ions with organic linkers. Success of such syntheses is critically dependent on identifying chemical units with specific geometry that would assemble into a target structure. In this context, for a square unit, there are *only* three truncated 3-D discrete shapes that can be assembled in which all squares and all links are equivalent: octahedron, cuboctahedron, and icosidodecahedron. Our studies concerns the truncated octahedron for which two construction strategies have been previously implemented wherein either alternative faces, **a**, or all faces, **b**, of the octahedron are built from triangular organic linkers, and vertices from protected squares (Pd^{2+}, Pt^{2+}, Mo_2^{4+}), **a**, or unprotected squares, **b**. Here, we report the construction of a truncated octahedron of the third type, **c**, from $Cu_2(CO_2)_4$ building blocks, in which the carboxylate carbon atoms define a *rigid* square, **d**, and 2,2':5',2"-terthiophene-5,5"-dicarboxylate (TTDC) having a linking angle very close to *90°* when in the *cis*,*cis* conformation, **e**. We further show that molecular structures of this kind can be designed to have truly porous architectures and remarkable capacity for adsorption of gases, as evidenced by this compound's Type I gas sorption isotherm.



To prepare truncated octahedron, **c**, we used reactions known to produce the $Cu_2(CO_2)_4$ paddle-wheel unit. These were uncovered in an earlier study involving the use of such units with 1,3-benzenedicarboxylate to produce a 25 Å-sized truncated cuboctahedron, metal-organic polyhedron-1 (MOP-1). Reaction of equimolar amounts of $Cu(NO_3)_2\cdot2.5H_2O$ and H_2TTDC at 85 °C for 24 hours in a mixture of NMP (2-methyl-1-pyrrolidinone) and DMA (*N*,*N*-dimethylacetamide) gives green crystals of $[Cu_{12}(TTDC)_{12}(NMP)_6(H_2O)_6]\cdot 13NMP\cdot DMA\cdot H_2O$ (termed MOP-28). The structure of MOP-28 was determined by single crystal X-ray diffraction studies. Each MOP-28 molecule is composed of 6 $Cu_2(CO_2)_4$ paddle-wheel building blocks and 12 *cis*,*cis*-terthiophene linking units (Fig. 1a-c).



The reproducibility of the isotherm was confirmed by repeating adsorption-desorption cycle three times. Significantly, all gas molecules can be removed as observed from the desorption branch of the plot. A small H4 type hysteresis loop is also observed in the isotherm. Given the location of the lower closure point of the loop ($P/P_0 = 0.21$), the hysteresis must be attributed to causes other than capillary condensation of N_2 in large pores. From the adsorption branch of the isotherm, Langmuir surface area of 1,100 m^2/g and pore volume of 0.39 cm^3/g (Dubinin-Radushkevitch model) have been obtained. The amount of N_2 adsorbed in the pores (337 mg/g) corresponds to 57 N_2 molecules per truncated octahedron. It is remarkable that MOP-28 being a solid composed of discrete molecules, exhibits porosity similar to that of extended metal-organic frameworks. To our knowledge, MOP-28 is the most porous *molecular* structure and stands among the first metal-organic polyhedra to be characterized by gas sorption.

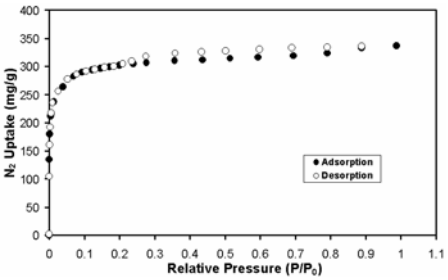


Figure 2. Nitrogen sorption isotherm (77K) for MOP-28.

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- Porous, crystalline, covalent organic frameworks, A. P. Cote, A. Benin, N. Ockwig, A. Matzger, M. O'Keeffe, O. M. Yaghi *Science*, **2005**, *310*, 1166.

- Porous Metal-Organic Truncated Octahedron Constructed from Paddle-Wheel Squares and Terthiophene Links, Z. Ni, A. Yasser, T. Antoun, O. M. Yaghi *J. Am. Chem. Soc.* **2005**, *127*, 12752.

- Gas Adsorption Sites in a Large-Pore Metal-Organic Framework, J.Rowsell, E. Spenser, J. Eckert, J.A. K. Howard, O. M. Yaghi, *Science*, **2005**, *309*, 1350.

- Design, Synthesis, Structure, and Gas (N_2, Ar, CO_2, CH_4 and H_2) Sorption Properties of Porous Metal-Organic Tetrahedral and Heterocuboidal Polyhedra, A. Sudik, N. Ockwig, A. Millward, A. Cote, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 7110.

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  Angew. Chem. Int. Ed. **2005**, *44*, 4670.

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- A Route to High Surface Area, Porosity and Inclusion of Large Molecules in Crystals, H. Chae, D. Y. Siberio-Perez, J. Kim, Y. Go, M. Eddaoudi, A. Matzger, M. O'Keeffe, O. M. Yaghi, *Nature*, **2004**, *427*, p. 523.

Addressing Grand Challenges Through Advanced Materials

M.S. Dresselhaus
Department of Electrical Engineering and Computer Science
and Department of Physics
Massachusetts Institute of Technology
Cambridge, MA 02139, USA
email: millie mgm.mit.edu

In this overview talk, the grand energy challenges are reviewed succinctly and the elements of the hydrogen initiative are reviewed with particular emphasis given to hydrogen storage, the most vexing challenge of the hydrogen initiative. This is followed by a discussion of promising approaches that have been opened up through nanoscience and recent progress that has been made.

Because of the worldwide population expansion that has been occurring in the last 50 years and the projected population increases for the next 50 years, when coupled with increasing per capita energy demands of developing countries (such as China, India, Brazil, and Malaysia), we can expect a superlinear increase in world energy demands for the 21st century (Fig.1). The world energy supply from fossil fuels cannot meet this demand because resources are not being discovered fast enough to meet the growing demand and therefore the conversion to renewable energy sources will have to occur by the middle of this century. An equally important driver to the conversion to renewable energy sources are environmental concerns about our planet, including the increase in greenhouse gases (CO_2 and CH_4) in the earth's atmosphere, global warming effects, the melting of the polar ice caps, and the increase in the acidity of the oceans.

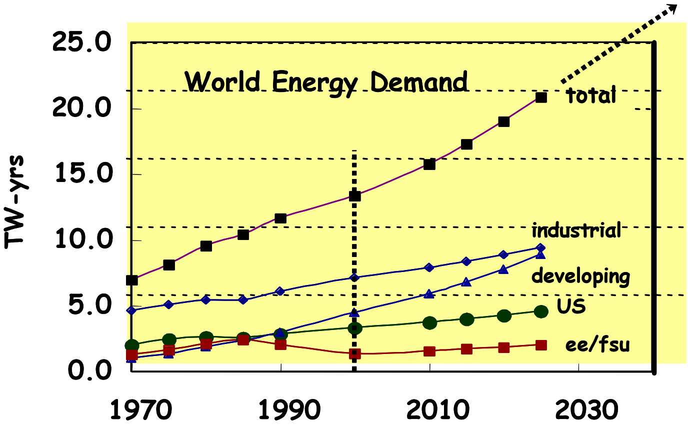


Fig.1 Growing world energy needs

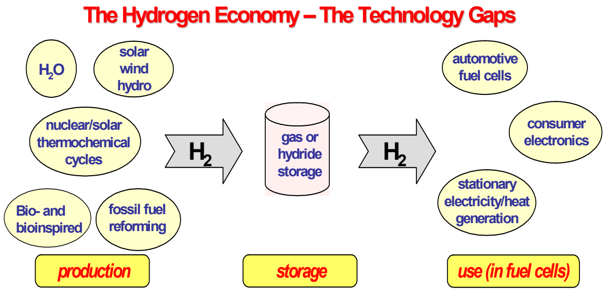


Fig. 2 The hydrogen economy consists of production, storage and use. Large technology gaps are present in each of the three sectors.

These factors have led the Bush administration to launch the hydrogen initiative in January 2003. The hydrogen initiative (Fig.2) firstly involves an effort to greatly increase our capability to produce hydrogen using renewable energy sources and water, since hydrogen is an energy carrier and not a fuel found on our planet. The hydrogen storage problem has been identified as the most challenging, because neither liquid hydrogen nor solid hydrogen can meet the 2015 DOE goals for hydrogen storage (Fig.3). Thus, it is not surprising that the largest number of papers at the BES workshop are devoted to hydrogen storage. Finally we come to the third element of the hydrogen initiative and this involves the development of fuel cells with much enhanced performance available at a much reduced cost. Fuel cells are attractive because of their higher efficiency, but improvement in their performance and lowering their cost remain a major challenge. The conclusions of several studies concluded that expanding our knowledge base will be necessary to have a chance at achieving success with the hydrogen initiative.

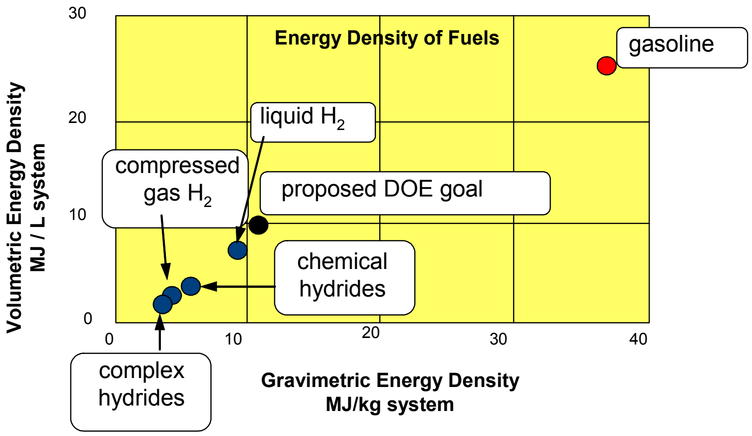


Fig.3 Hydrogen storage is the most critical challenge.

Reaching the DOE requirements for hydrogen storage involves two factors: sufficiently large storage capacity and rapid hydrogen release with small energy expenditure. The former factor requires strong bonding of hydrogen to a chemical species, much stronger than that between two hydrogen atoms.

The second factor suggests weak binding and seems incompatible with the first, and hence the grand challenge.

In the realm of metal hydrides, we see in Fig.4 a phase space of hydrogen volume density vs. mass density where the upper right hand sector shows a region of sufficiently large storage capacity. By clever approaches, various groups worldwide have succeeded in obtaining hydrogen release rates that are promising. These approaches are based on the use of nanostructures to increase molecular diffusion, to increase the sorption rate and to simultaneously decrease the desorption temperature (Fig.5).

For bulk hydrides, the sorption rate is prohibitively small and the release temperature is too high. Poor heat transfer in the bulk leads to process interruption in the adsorption of hydrogen. By reducing the grain or particle size, the kinetics and hydrogen uptake can both increase. For porous nanostructures, the increased porosity and smaller size increases the discussion rates. Furthermore, surface energies and materials properties at the nanoscale offer ways to tune the absorption and desorption to reduce the release temperature and speed up the release process.

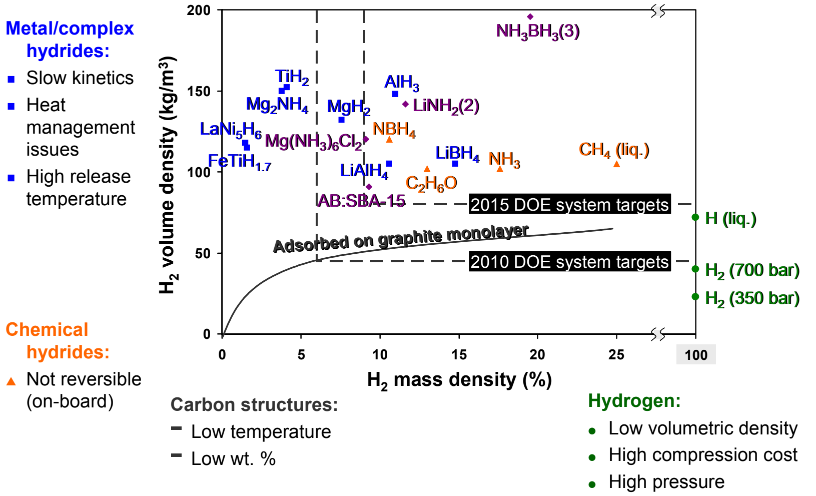
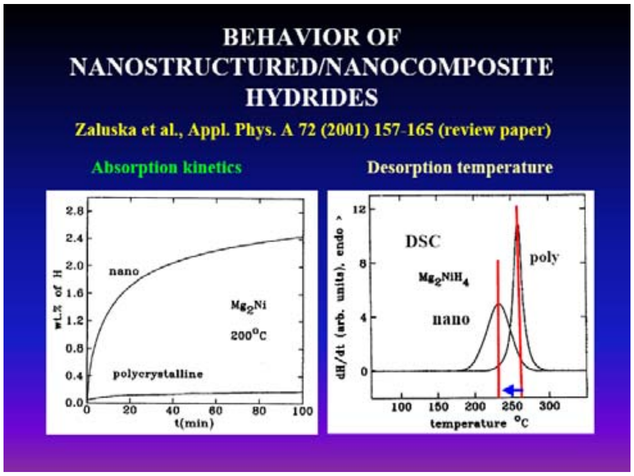


Fig.4 Storage options exist within the range of DOE requirements but release rates and pressures require improvements.

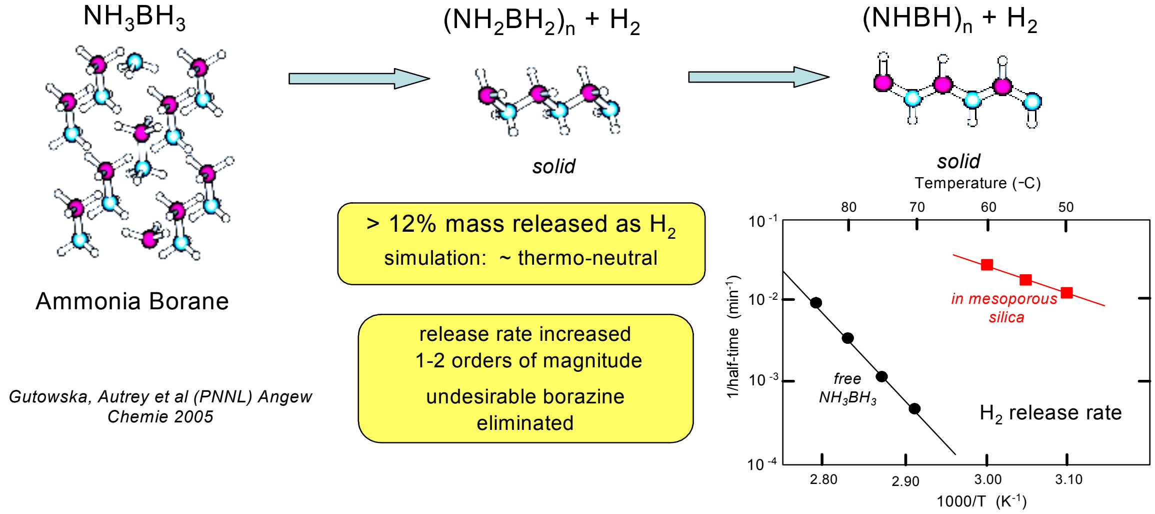
Some examples of actual systems where these concepts have been applied are given below. The Autrey group at the Pacific Northwest Laboratory have used special mesoporous silica templates to increase the hydrogen release rate, decrease the release temperature and remove the undesirable borazine species from the hydrogen emission for borane (NH_3BH_3) as shown in Fig.6. The Christensen group at the Technical University in Copenhagen have developed a process for storing and releasing hydrogen in the metal amine complex $Mg(NH_3)_6Cl_2$. This complex can store large amounts of hydrogen in porous tablets with a capability for recharging (Fig.7). This technology is being considered presently for solid oxide fuel cell and battery applications because the release temperature presently is too high for use for automotive applications.


BEHAVIOR OF NANOSTRUCTURED/NANOCOMPOSITE HYDRIDES

Zaluska et al., Appl. Phys. A 72 (2001) 157-165 (review paper)

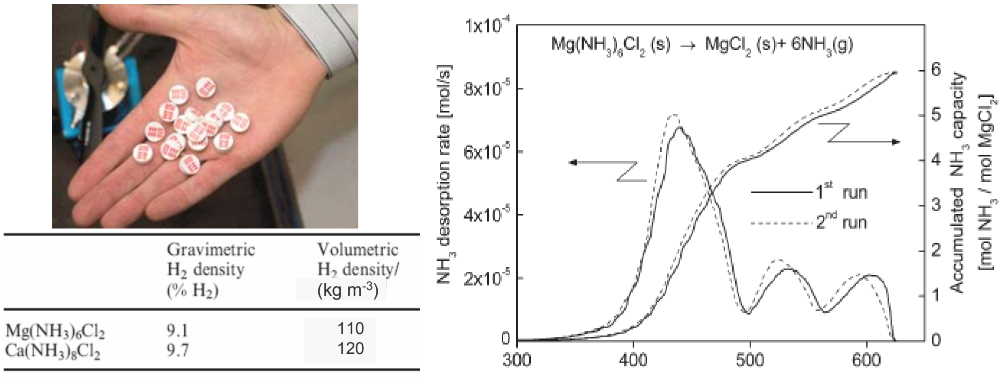
Fig.5 Nanoscience shows a direction toward enhancing hydrogen release pressures and lowering release temperature.

An example in the use of alloying to lower the release temperature and to increase the release pressure in the $LiNH_2$ compound is



Gutowska, Autrey et al (PNNL) Angew Chemie 2005

Fig.6 Progress made with the ammonia borane system.



	Gravimetric H_2 density (% H_2)	Volumetric H_2 density/ (kg m^{-3})
$Mg(NH_3)_6Cl_2$	9.1	110
$Ca(NH_3)_8Cl_2$	9.7	120

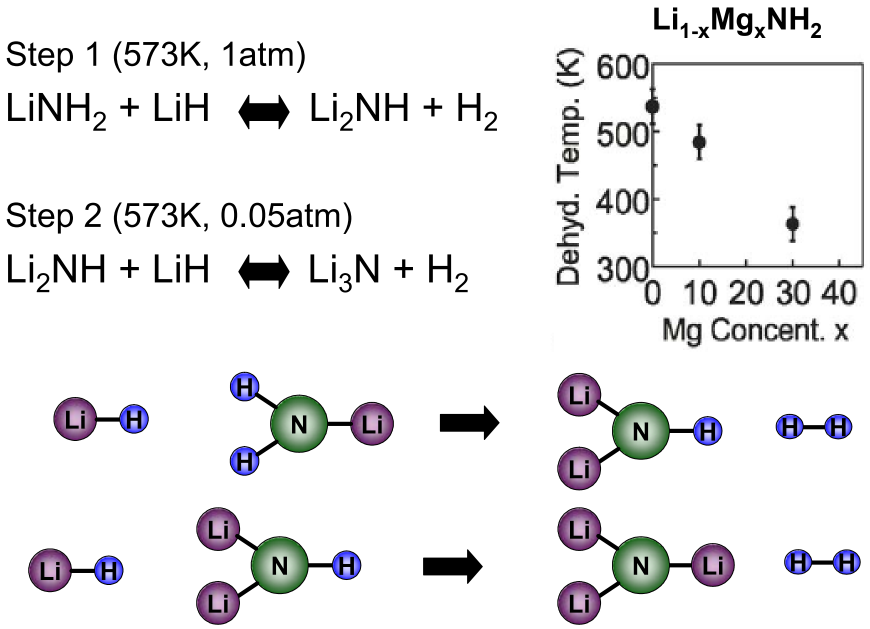
Fig.7 Progress made with the $Mg(NH_3)_6Cl_2$ system.

$Mg(NH_3)_6Cl_2$ ➡ $MgCl_2 + 6NH_3$ (9.1%) @ T <620K

$2NH_3$ ➡ $3H_2 + N_2$ @ ~600K

Christensen et al., J. Mater. Chem., 2005, 15, 4106–4108 shown in Fig.8. Here Mg is added to lower the release temperature by 200C to a promising range for applications. Thus by the use of scaffolding, metal alloying, the doping of catalysts, strategies have been found to control the sorption of hydrogen gas and its release at more controlled ranges with some potential for applications. Success has been achieved through small teams with multiple skills, and by combining modeling with optimization strategies.

Thermal management remains a challenge since temperature rise suppresses reactions that evolve hydrogen. Thus thermal management requires composites with relatively good heat transfer capability, but with adequate porosity and nanostructural integrity. Thermal management, like the storage/release challenge, requires an optimization of materials properties that are not normally found in 3D materials.



S. Orimo et al., Appl. Phys. A:Materials Science & Processing, Vol 79, No 7, p. 1765 - 1767.

Fig.8 Progress made with the $LiNH_2$ system. Alloying with increasing fraction of magnesium is shown to reduce the release temperature.

Though many challenges remain, the short period of effort of the present hydrogen initiative has demonstrated that there are solid hydrides that can reach DOE goals for volumetric and gravimetric densities for automotive applications. Though high release temperature and slow hydrogen absorption and desorption rates remain a challenge, much progress has been achieved by a number of strategies, including scaffolding, metal alloying, catalyst doping, etc. Most of the solutions that have been found thus far are based on the use of nanoscience to allow the possible confluence of desired materials properties that do not occur in 3D materials. The use of simulations also has been a key factor in accelerating the optimization of disparate materials properties that do not occur in 3D materials. Lifetime studies to maintain these disparate metastable properties over many cycles in a reversible way is yet another technical challenge for the future of this field.

Atomistic Transport Mechanisms in Revisible Complex Metal Hydrides

PIs: Peter Sutter[1] (psutter@bnl.gov), James Muckerman[2], Y. Chabal[4]
Collaborators: Jason Graetz[3], James Reilly[3], James Wegrzyn[3], Eli Sutter[1]
[1]Center for Functional Nanomaterials, [2]Chemistry Department, [3]Energy Science & Technology
Department, Brookhaven National Laboratory, Upton, NY 11978,
[4]Laboratory for Surface Modification, Rutgers University, Piscataway, NJ 08854

Program Scope

This fundamental research program has two major objectives: **i)** the development of a comprehensive, quantitative understanding of the atomic-scale mechanisms underlying the facile reversible hydrogen storage in titanium-doped sodium aluminum hydride ($NaAlH_4$), the only complex hydride allowing fully reversible hydrogen storage under near-ambient conditions; and **ii)** the utilization of this basic knowledge for a rational search for novel complex hydride storage materials with properties – hydrogen storage capacity, reaction thermodynamics and kinetics during hydrogen uptake and release, etc. – superior to those of $NaAlH_4$.

Surface processes in the hydrogen storage reaction in $NaAlH_4$, starting from a depleted phase consisting of NaH and metallic Al, and proceeding via cryolite Na_3AlH_6 to the hydrogen-rich $NaAlH_4$, are considered as the basis for understanding reversible hydrogen storage in the chosen prototype system. Key questions to be addressed via experiments on carefully designed model systems coupled strongly to theory include:

- The mechanism of hydrogen dissociation on Al surfaces doped with Ti.
- The identification of the predominant carrier of mass transport, and quantitative measurements of its diffusion kinetics
- The detailed reaction mechanisms and their rate-limiting step as NaH and Al react to Na_3AlH_6 and ultimately $NaAlH_4$ in the presence of hydrogen and of dopants such as Ti.

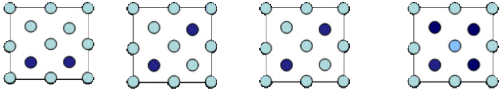
The long-term goal of this project is to develop an atomistic understanding of the interaction of hydrogen with metal and alkali metal surfaces and nanostructures, hence providing a scientific basis for solid-state hydrogen storage in support of the DOE BES hydrogen fuel initiative.

Recent Progress

(a) Interaction of Hydrogen with Al and Ti-doped Al Surfaces

A major initial focus has been to investigate the role of Ti dopants in enabling the facile rehydrogenation of depleted sodium alanate. The depleted material consists of nanoscale particles of NaH and Al metal. As Al poorly activates molecular hydrogen, our working hypothesis is that Ti, localized near the surface of the metallic Al phase, could form active complexes that dissociate H_2 and generate the supply of atomic H or of Al-H molecular species (alanes) necessary to crystallize large grains of the hydrogen-rich $NaAlH_4$. Predictive theoretical studies are combined with scanning tunneling microscopy (STM) and infrared (IR) spectroscopy experiments on Al single crystal model surfaces, and with x-ray diffraction and fluorescence measurements on the actual storage materials.

In our initial theoretical work, a series of model active sites was constructed by substituting Ti for Al near a Al(001) surface (in the surface and the first two sub-surface layers), at Ti coverages of 0.125 - 0.5 monolayers (ML). Each of these model sites was characterized by its activation energy for dissociatively chemisorbing H_2, and by its chemical potential with respect to a convenient reference state, taken to be the most stable surface termination of the $TiAl_3$ alloy. The most effective sites, shown in table 1, are third-nearest neighbor Ti configurations in the surface (Model 4) and in the first



Property	Model 3	Model 4	Model 4s	Model 8
Site ΔG_f	3.13	2.08	1.65	1.04
E_a	0.89	0.00	0.26	1.62
Site ΔG_f+E_a	4.02	2.08	1.91	2.66

Table 1: Free energy of formation relative to $TiAl_3$ reference (ΔG_f) and activation energy for H_2 dissociation (E_a) of Ti:Al model complexes with 0.25 ML – 0.5 ML Ti coverage.

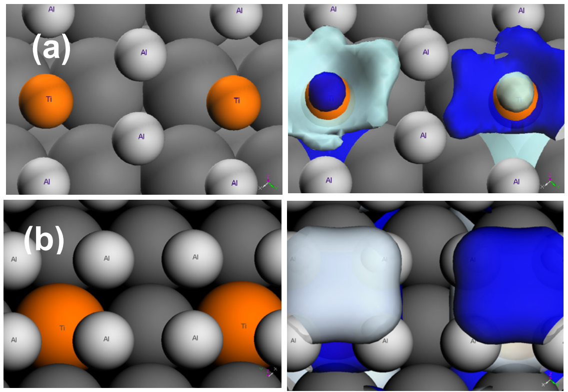


Figure 1: Arrangement of Ti-atoms of Model 4 active sites (left frames): **(a)** surface and **(b)** sub-surface. Right frames show the surface LUMO forming an adduct with the incoming H_2 molecule. Light/dark blue indicates different phases of the molecular orbitals.

sub-surface layer (Model 4s). Hydrogen dissociation is predicted to be spontaneous on the former, and exhibits no barrier in excess of the intrinsic endothemicity in the latter.

All sites with low computed barriers to H_2 dissociation have a common orbital symmetry property that is responsible for their effectiveness: the highest occupied molecular orbital (HOMO) of the incipient doped-surface/H_2 adduct has a nodal plane perpendicular to the Ti-Ti axis and midway between the two Ti atoms (fig.1). This nodal symmetry arises from the out-of-surface d_{z^2} Ti orbitals having opposite phases such that they overlap with the H_2 σ^* orbital so that electron density can be transferred from the surface to the antibonding H_2 orbital to weaken the H-H bond. Complexes without this nodal symmetry (e.g., Model 8) have large barriers for dissociative H_2 chemisorption. Additional computational studies addressed the question of how the hydrogen and aluminum are transported into NaH to ultimately reform hydrogen-rich $NaAlH_4$. First-principles molecular dynamics (MD) studies show that dissociated H does not readily recombine at Ti:Al active sites, is mobile but cannot migrate to all-Al sites because such a process is both endothermic and activated. The likelihood of H being picked up by Al adatoms breaking off from steps and other mechanisms for alane formation is being explored, as is the chemical behavior and mobility of alanes on Al surfaces.

First experiments on measuring H_2 dissociation on Al:Ti complexes have used STM imaging on extended Al surfaces, progressively complemented by IR spectroscopy. Below the desorption threshold of ~ 280K, atomic H (but not H_2) interacts strongly with Al by extracting surface atoms to form alane (AlH_3) and its oligomers. Alane evolution can thus be used as a fingerprint for the presence of H on Al, e.g., caused by H_2 dissociation at active Al:Ti complexes. To establish conditions under which H_2 dissociation can be probed in this way, Al(111) and 0.25 ML Ti/Al(111) surfaces were exposed to different amounts of atomic and molecular hydrogen. Dosing of atomic H on clean Al(111) clearly produces a characteristic population of surface alanes (fig. 2 a,b,c,). This is confirmed by IR experiments (fig. 2d) that show H

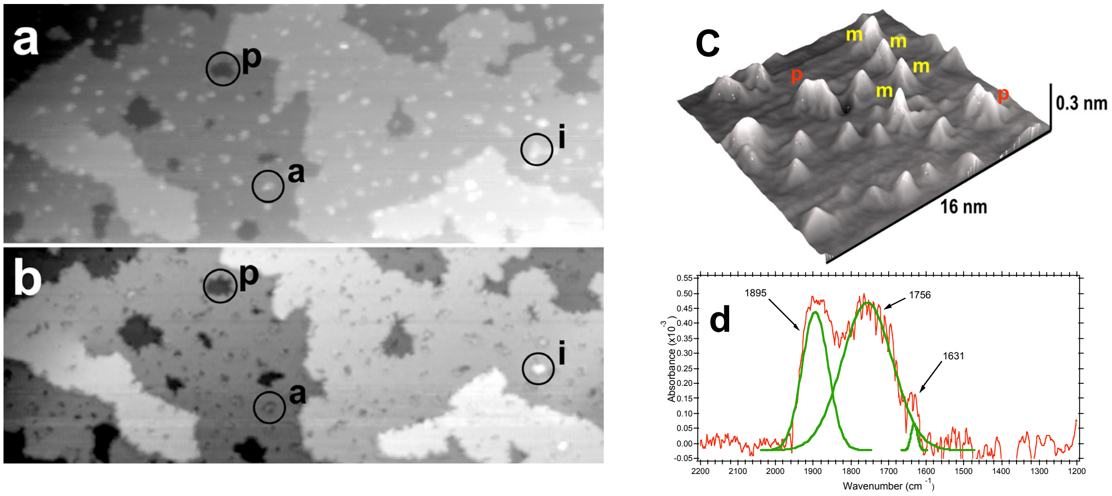


Figure 2: **(a), (b)** STM images (150x60 nm^2) of Al(111) after H-dosing at 200 K, with W-tip (a), and alane 'functionalized' W-tip (b). Alane decorated probes can be used to distinguish surface alanes ('a') from topographic features ('i': islands; 'p': surface pits). **(c)** STM image of an alane population obtained by H-dosing of Al(111) at 200 K, with tentative species assignments ('m': monomer; 'p': monomer pair). **(d)** IR spectrum obtained under the same conditions. The vibrational envelope at 1895 cm^{-1} corresponds to Al-H stretch of terminal H, the broad band centered at 1756 cm^{-1} to Al-H-Al stretch of bridging H of alane oligomers.

chemisorbed in several configurations (terminal and bridging H) consistent with alane formation. In contrast to pure Al(111), exposure of 0.25 ML Ti/Al(111) to H does not induce any detectable alane. Our STM observations suggest that the Ti atoms are randomly dispersed near the Al surface, which may stabilize the surface layer against H-etching and hydride formation. Thus, samples with high Ti coverage may not be suitable to study H_2 dissociation. A third class of samples, consisting of 0.25 ML Ti/Al(111) capped with 1 ML Al, has shown promise as a model system to detect H_2 dissociation at Ti active sites. Atomic-H dosing onto these samples causes surface etching and alane evolution. First STM experiments, in which such surfaces were exposed to H_2 have shown features similar to surface alanes, i.e., showing the characteristic dual contrast (fig. 2 a,b) found on alane decorated surfaces. These observations suggest that H_2 may indeed have been dissociated on these samples, providing a starting point for a systematic characterization of active Ti:Al complexes. Thorough quantification and comparison with IR spectroscopy and theory are now needed to corroborate this tentative conclusion.

X-ray absorption spectroscopy (XAS) on bulk materials was used to measure the local atomic structure of Ti in doped sodium alanate. Our results clearly show that Ti is in a zero-valent state and coordinated by 10 Al atoms at ~2.8 Å. The reduced coordination (10 Al atoms, vs. expected 12) and the lack of order beyond the Al first shell suggests that the Ti exists in well dispersed clusters of Ti-Al possibly located on/near the surface, which further justifies the hypotheses underlying our experiments in UHV.

In a key solid-state chemistry experiment guided by theory, finally, we have demonstrated that once alane (AlH_3) is formed, the solid-state reaction of AlH_3 with NaH leads to the formation of $NaAlH_4$ through the intermediate Na_3AlH_6 phase in the absence of any Ti. Although not excluding other (beneficial) effects of the Ti dopants, this finding suggests that Ti-induced H_2 dissociation and the concomitant formation of surface alanes would be sufficient to enable reversible hydrogen storage in $NaAlH_4$.

(b) Rational Search for Novel Metal Hydride Hydrogen Storage Materials

Our initial solid-state chemistry effort accompanying the work on model systems has concentrated on the synthesis of novel mixed alkali alanates of the form $M_xM'_{1-x}AlH_y$ (M, M' = Li, Na, K,…), and investigation of the possibility of tuning the hydrogenation thermodynamics by cation substitution. These studies were complemented by the synthesis and characterization of aluminum hydride (AlH_3) polymorphs, a potential storage material with very high gravimetric hydrogen content. In particular, we have investigated reaction products formed from aluminum hydride and alkali hydrides.

The thermodynamics and structural properties of the hexahydride alanates ($M_2M'AlH_6$) with elpasolite structure were investigated. Two new alanates were synthesized: K_2LiAlH_6 and K_2NaAlH_6. Both compounds reversibly absorb/desorb hydrogen without a catalyst. Structural analyses using synchrotron x-ray diffraction show that these compounds favor the *Fm*-3*m* space group with the smaller

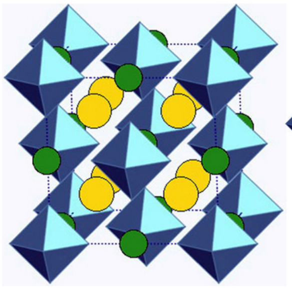


Figure 3: General structural diagram for the mixed alkali alanates (elpasolites) of the form $M_2M'AlH_6$ showing AlH_6 octahedra, M cations (large) and M' cations (small). Structures of Na_2LiAlH_6, K_2LiAlH_6 and K_2NaAlH_6 were determined by high resolution synchrotron x-ray diffraction.

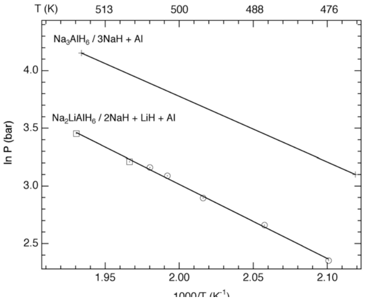


Figure 4: Van't Hoff plot for the reversible dissociation of Ti-doped Na_3AlH_6 (+) and Na_2LiAlH_6 (○-4 mol% $TiCl_3$ and □-undoped), demonstrating that Li for Na cation substitution results in a significant decrease in equilibrium pressure. In addition, the pressure-temperature data for doped (○) and undoped (□) Na_2LiAlH_6 have identical behavior and therefore no there is no discernable change in thermodynamics with the addition of 4 mol% Ti.

ion (M') occupying an octahedral site and the larger ion (M) in a 12-fold coordinated site (fig. 3). Thermodynamic measurements demonstrated that appropriate cation substitutions could be used to alter the alanate stability (fig. 4).

Future Plans

The next phase of work on well-defined model samples will closely link surface microscopy, IR spectroscopy, and theory to address the following key aspects of reversible hydrogen storage in $NaAlH_4$: i) Atomic pathway and efficiency of Ti-induced H_2 dissociation on Al (STM & IR); ii) Evolution of surface alanes and their role in mass transport (STM, IR, LEEM); iii) Main factors affecting the hydrogenation kinetics, and role of Ti (STM, LEEM). In addition to STM and IR spectroscopy, low-energy electron microscopy (LEEM) will be used to map surface mass transport in real time, and quantify differences in alane and Al diffusion. Building on our initial experiments on the interaction of H/H_2 with Al surfaces, we will begin to analyze complete steps of the hydrogenation reaction, e.g., use NaH/Al(111) as a model system to study the reaction $6\ NaH + 2\ Al + 3\ H_2 \leftrightarrow 2\ Na_3AlH_6$. Theory will be strongly coupled to the STM and IR studies now underway. The objective will be to suggest experimental models to isolate individual steps in the rehydrogenation reaction, and to interpret observed surface structures, dynamic phenomena, and IR signatures. The transfer of what is being learned about the sodium alanate system to other promising hydrogen storage materials to make them reversible will be another focus of the theoretical effort.

Our solid-state chemistry effort will expand the studies on transition metal catalysts to include other catalyzed complex metal hydrides, such as metal-doped $LiBH_4/MgH_2$. XAS will be used to determine the location and valence of the catalyst immediately after ball milling and at different stages of hydrogen cycling. Doped borohydrides have a number of similarities with the alanates. Studies of doping in these materials will lead to a better understanding of kinetic enhancements and long-range mass transport. In complementary studies, we will synthesize various AlH_3 polymorphs for vibrational spectroscopy. Pure phases of α-AlH_3 and γ-AlH_3 and solvated AlH_3 will be prepared. We will determine AlH_3structures, and attempt to gain a better understanding of how bulk AlH_3 can be stable at room temperature despite its high equilibrium hydrogen pressure.

Publications to Date

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3. J. Graetz, A.Y. Ignatov, T.A. Tyson, J.J. Reilly and J. Johnson, "Characterization of the local titanium environment in doped sodium aluminum hydride using X-ray absorption spectroscopy", *Mat. Res. Soc. Conf. Proc.* ***837*** (2005).
4. S. Chaudhuri and J.T. Muckerman, "First-principles study of Ti-catalyzed hydrogen chemisorption on an Al surface: A critical first step for reversible hydrogen storage in $NaAlH_4$", *J. Phys. Chem. B* **109**, 6952 (2005).
5. S. Chaudhuri and J.T. Muckerman, "A Density Functional Theory Study of the Catalytic Role of Ti Atoms in Reversible Hydrogen Storage in the Complex Metal Hydride, $NaAlH_4$", *Materials and Technology for Hydrogen Storage and Generation,* ed. G-A. Nazri, C. Ping, R.C. Young, M. Nazri, and J. Wang, *Mat. Res. Soc. Symp. Proc.* **884E**, Warrendale, PA, 2005; GG2.1.
6. S. Chaudhuri, J. Graetz, A. Ignatov, J.T. Reilly and J.T. Muckerman, "Understanding the role of Ti in reversible hydrogen storage as sodium alanate: A combined experimental and first-principles theoretical approach", *J. Am. Chem. Soc.*, submitted.
7. S. Chaudhuri and J.T. Muckerman, "Catalytic activity of Ti-doped NaH nanoclusters towards hydrogenation of terminal alkenes", manuscript in preparation for Communication in *Phys. Chem. Chem. Phys.*
8. E. Muller, P. Zahl, E. Sutter, and P. Sutter, "Ripening and Texture Evolution in Al Epitaxy on Si(111)-(7x7)", manuscript in preparation.
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In-situ Neutron Diffraction Studies of Novel Hydrogen Storage Materials

William B. Yelon, William J. James
Department of Chemistry and Materials Research Center
Jinbo Yang
Department of Physics and Materials Research Center
University of Missouri-Rolla yelonw@umr.edu

Program Scope

Our work couples the unique capabilities of the University of Missouri Research Reactor (MURR) to conduct *in-situ* neutron diffraction experiments as a function of temperature and gas environment, with the wide range of capabilities of the Materials Research Center at the University of Missouri-Rolla (MRC) in the area of materials synthesis and characterization. In the first year of this project we intend to study the decomposition reactions of systems of the type AMH_4 where A is an alkali metal (Li, Na, K) and M is either Al or B, as well as to begin research on other chemical hydrides with potentially high reversible H capacity, such as $LiNH_2$ and $Mg(BH_4)_2$. Experiments will reveal the phases that form during these reactions and experiments will be conducted with and without catalysts, to determine if the catalysts participate in intermediate phase formation or are merely donating or accepting electrons in the reactions. Materials for study are being acquired both commercially and through synthesis at the MRC. In later years studies will be extended to the re-absorption of hydrogen and the reformation of the starting compounds to better understand the questions of reversibility.

Recent Progress

(a) In-situ neutron diffraction measurements

Prior to the start of this project we had constructed a furnace for *in-situ* studies, which had been used to examine phenomena such as oxygen loss in perovskites, and hydrogen absorption/desorption in LiAl alloys. This furnace is less than optimum because its original (fragile) heater was replaced by a potted heater that attenuates roughly 40% of the incident neutrons, but we have continued to make use of it while constructing a new furnace with heaters above and below the sample region. This new design has the further advantage of having independent control of the two heaters, thereby allowing differences in heat loss above and below the sample to be compensated by different power levels. The thermal gradient across the sample thus can be minimized and in bench tests has been found to be of order 1° C at 200° C. Unfortunately, unexpected delays occurred because of late deliveries of some critical components and the necessity of making some design modifications. However the new furnace will probably be commissioned about the last week in April. Thus, measurements to date have been performed in the old furnace, and later work should be of still higher quality.

Subsequent to the submission of our proposal to the DOE, we discovered that researchers at the Norwegian research reactor JEEP-II had carried out a number of the studies we had proposed [1], especially on the alanates, where the neutron absorption by B is not a problem. We found this particularly ironic since the Norwegian reactor uses the same neutron detector technology we employ at MURR, and, in fact, they had purchased the system (developed by our former colleague Ron Berliner) from MURR several years ago. Despite their head start, the higher power of MURR and its longer operating schedule than JEEP-II should allow us to catch up and surpass them in the near future. In the meantime, comparison of our data on $LiAlD_4$ (Fig. 1) has allowed us to confirm the reliability of our measurements. The two data sets (not shown) are virtually indistinguishable except for differences in wavelength, but the resolution of the MURR instrument at the highest q vectors is slightly superior to the JEEP-II data.

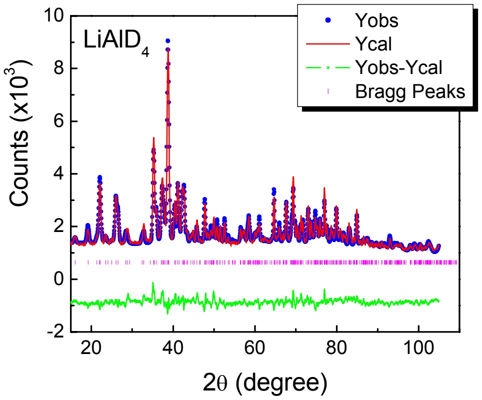

Fig. 1: Neutron diffraction pattern of $LiAlD_4$

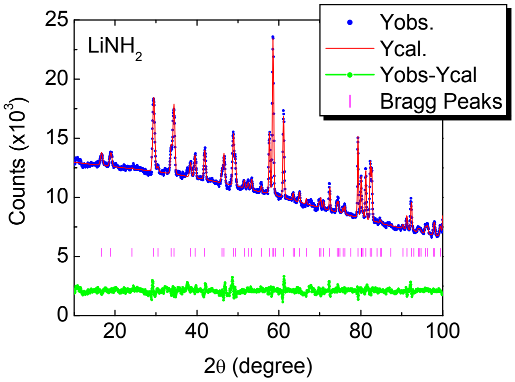

Fig. 2: Neutron diffraction pattern of $LiNH_2$

In addition to the room temperature work on $LiAlD_4$, we have studied $LiNH_2$ at RT [2]. In mixtures with 2LiH, it can reversibly yield 5.5% H under practical conditions. Early x-ray and neutron diffraction studies of the material gave anomalously short N-H bonds (0.70Å). Our study was carried out with H (and not D) and we found (Fig. 2) that despite the large incoherent scattering cross section of H, excellent data could be collected and refined. This is possible because the MURR samples are small, and coherently scattered neutrons have only a small chance of being rescattered (and their information lost). Thus, the information content is maximized. Rietveld refinement shows that the N-H bonds are actually 0.986Å and 0.942Å long, in much better agreement with other results, and indicative of normal bond strength, as expected from the decomposition. We have also carried out a theoretical study of the electronic density of states and charge density distribution in this material [2].

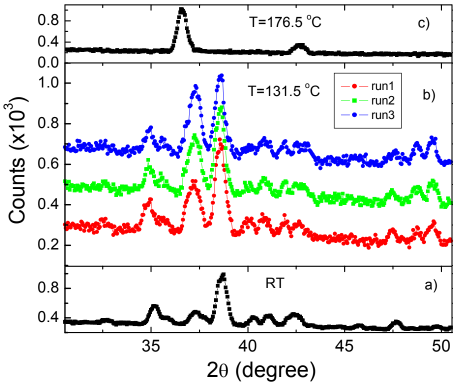

Fig. 3: Data for $LiAlD_4$ as a function of temperature and time. Each spectrum is measured in 30 minutes and spans 20º (2Θ). The lower panel show the data at room temperature; the middle panel shows 3 successive scans at 131.5 °C and shows the coexistence of $LiAlD_4$ Li_3AlD_6 and Al. The upper panel shows data at 176.5 °C, and consists of diffraction from LiD and Al.

Preliminary work at elevated temperature has been carried out on $LiAlD_4$. It shows the expected decomposition steps, resulting finally in Al + LiH (Fig.3). The detector geometry allows for data collection over a 20° (2θ) range simultaneously, and good quality data was obtained in only a few minutes. The intensity gains associated with the new furnace will improve this further. Unfortunately, these first data sets (which also confirm the Norwegian results), were compromised by a large (10°C) gradient across the sample. The furnace has been since improved and can be better used, but, as mentioned above, the new design will reduce the gradient to less than 1°C.

As this report is being written we are collecting data on $NaBD_4$ as a function of temperature. Once again, the instrument geometry is very helpful; a conventional diffractometer would show negligible intensity due to the B absorption, unless the separated ^{11}B isotope was employed. We will know in the next few days whether the quality of these data is sufficient for detailed analysis, but preliminary data indicate that the first decomposition is at a higher temperature than previously reported.

(b) Sample synthesis

Although many of the materials of interest to this project can be obtained commercially, the special needs of neutron diffraction in (sometimes) demanding deuterium or isotopically separated B, and the desire to study the effects of various catalysts makes synthesis an essential component of the work. While the scientists at the MRC have extensive experience in solid state synthesis methods, the special environmental requirements (dry, preferably inert, atmosphere) have led us to procure new tools for this program. These include a high quality dry box with airlock and high energy mills with controlled environment and temperature. Efforts have begun to synthesize some novel compounds through high energy milling of metal hydrides with B metal, followed by high temperature-high pressure treatment in hydrogen (deuterium) gas to complete the reaction.

1) Borohydrides

Attempts to synthesize the borohydrides of Li and Mg have been made using the high energy mill and either the pure metal precursors or hydrides (LiH, MgH_2) followed by heat treatment under hydrogen (deuterium) atmosphere at pressures up to 500 psi and temperatures up to 310° C (the limit of our current “bomb”). Since MgB_2 is commercially available, it was also used as a precursor for potential hydrogenation. After six hours of milling, x-ray diffraction showed that all samples became amorphous. However, the subsequent attempts at hydrogenation did not lead to the formation of the borohydrides. We believe that the heat treatment conditions are too mild to allow this reaction to proceed. Thus were are procuring a new PARR pressure cell that will allow the application of 1800 psi at temperatures up to 700°C.

In addition to these solid state reaction pathways, we will attempt to prepare these borohydrides by means of a liquid state reaction using LiH (MgH_2) and B_2H_6 liquid and ether under D_2 atmosphere. One important question we will attempt to answer is the rate of exchange of H and D under these conditions and whether treatment in the appropriate deuterated solvent can result in highly deuterated products.

2) $LiNH_2$ –$LiBH_4$ mixtures[3]

Mixtures of $LiNH_2$ –$LiBH_4$ in ratios of 3:1, 2:1 and 1:1 were prepared by ball milling of the precursors. The results of the milling appear to be nearly single phase materials with stoichiometry $Li_4N_3BH_{10}$, $Li_3N_2BH_8$ and Li_2NBH_6, respectively. In each case a small impurity phase was observed and will be characterized. We plan to run high resolution neutron diffraction at room temperature on these samples to determine their crystal structures as well as to perform *in-situ* temperature dependent studies. Based on our results on the

$LiNH_2$ system, which yielded perfectly useful data with 50% hydrogen, and examination of the $NaAlH_4$ system which was unsatisfactory with 67% hydrogen, we hope that the first two of these compounds will be accessible for study without deuteration, while the last may well exceed the limits of our method. Based on research by other groups, it seems likely that these compounds can be made to yield a large quantity of hydrogen, but that reformation of the compounds after hydrogen desorption may be quite difficult.

3) $LiNH_2$ –$LiAlH_4$ mixtures

Mixtures of $LiNH_2$ –$LiAlH_4$ in the same ratios as was examined in 2) above, i.e. 3:1, 2:1 and 1:1, were processed by ball milling. Unlike the previous case, amorphous products were formed (based on x-ray diffraction). These samples will be heat treated in the new PARR apparatus, with the same products expected as above with Al substituted for B. Assuming success in the synthesis, the same studies will be carried out using room temperature and high temperature neutron diffraction.

4) Catalyzed $LiAlD_4$

Attempts to prepare $LiAlD_4$ mixed with catalysts such as $TiCl_3$ or $TiCl_4$, using high energy ball milling have thus far been unsuccessful due to decomposition induced by the high energy process. These samples will be remade using low energy milling (or perhaps very brief high energy milling), and the resulting products characterized by neutron diffraction.

5) Other studies

We will be studying the low temperature exchange of H and D in both the alanates and borohydrides by soaking the hydrogenated systems in D_2 gas at temperatures below the first decomposition reactions. Because the neutron diffraction measurements are very sensitive to the H-D ratio it will be easy to determine the degree of exchange. Samples prepared in this way may be a lower cost alternative to acquisition of deuterated materials, and could be used in the preparation of catalyzed samples for further studies.

Future Plans

Our early results have given us confidence that the program we originally outlined in our proposal is feasible and can be accomplished in the time period outlined (more or less). While the first year's studies are focused on the decomposition reactions, work in later years will also focus on reformation reactions *in-situ*. These will require the construction of a small volume pressure cell that can be inserted into the neutron diffraction furnace and operated at the same temperatures and pressures as the PARR cell. Studies will be conducted as a function of both parameters; temperature and pressure to establish the smallest energy input needed to achieve the desired result. Still later work will build on all of the earlier results to characterize material that is undergoing multiple cycles of decomposition and reformation. In these we hope to uncover any undesirable side reactions and search for methods to ameliorate them.

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In Situ NMR Studies of Hydrogen Storage Systems

Mark S.Conradi[1], Robert C. Bowman, Jr.[2], Timothy Ivancic[1], and Michael P. Mendenhall[1]
[1]Washington University, Department of Physics, St.Louis, MO
[2]Caltech and Jet Propulsion Lab, Pasadena, CA

Program Scope

Our research program focuses on *in situ* NMR studies of solid-state hydrogen storage systems. In particular, NMR measurements at the high temperatures and/or high pressures of the dehydriding and rehydriding reactions offer the best opportunity of detecting and identifying the mobile species that must be present, as well as the chemical intermediate species that are crucial to the reactions. For example, we expect to identify mobile H atoms in partially dehydrided $NaAlH_4$. From high-field measurements on the nuclear spins of catalytically active species like Ti and Sc, we will determine the local environment of the catalyst atoms in terms of the neighboring nuclear spins, using spin-echo double resonance.

Recent Progress

(b) *In Situ NMR Studies*

Background: The new classes of hydrogen-storing solids, such as sodium alanate, lithium borohydride, and the imides and amides, represent fundamental departures from the interstitial metallic hydrides that were formerly the focus of hydrogen storage interest. As light interstitials, the H atoms in metals typically display high diffusivity[1]. In the new materials, the H diffusivity is quite low, at least in the pure, unreacted materials. Furthermore, recharging of the spent material (e.g., by addition of H_2 gas to the Al and NaH from dehydriding of $NaAlH_4$) must involve mobility of the metallic species (Na, Al) as well. Despite intensive study, the mechanistic details of the dehydriding and rehydriding reactions are not known. For $NaAlH_4$, the role of catalyst species is not understood.

Our project addresses these open questions by NMR studies at the conditions of the reactions, as distinct from NMR at ambient conditions on materials recovered from reaction in a separate vessel. *In situ* measurements will identify the mobile species present, which clearly have an important role in the chemistry, as well as reactive chemical intermediates. These *in situ* measurements involve temperatures to 300 C and pressures to 100 atm, depending on the system under study.

Results: The overall design approach of such an NMR apparatus has been reported[2] and a version for pressures to 55 atm constructed and tested. While it seems unlikely that anyone would want to construct an exact copy of the device, the ideas and strategies should be relevant to other *in situ* NMR and neutron scattering efforts. Thus, we present here the basic components of our design. The complete design appears as Figure 1.

The powdered NMR sample is held in a ceramic (or glass) tube, with an rf coil on its outside. The ceramic tube is 30 cm long with a closed bottom; it is heated near its bottom 8 cm by a resistive, non-inductive heater assembly. Thus, the top (open) end of the ceramic sample tube remains cold, so that an O-ring fitting can connect it to external gas plumbing. This plumbing allows H_2 gas to be removed or added during the NMR measurements, yielding true *in situ* capability.

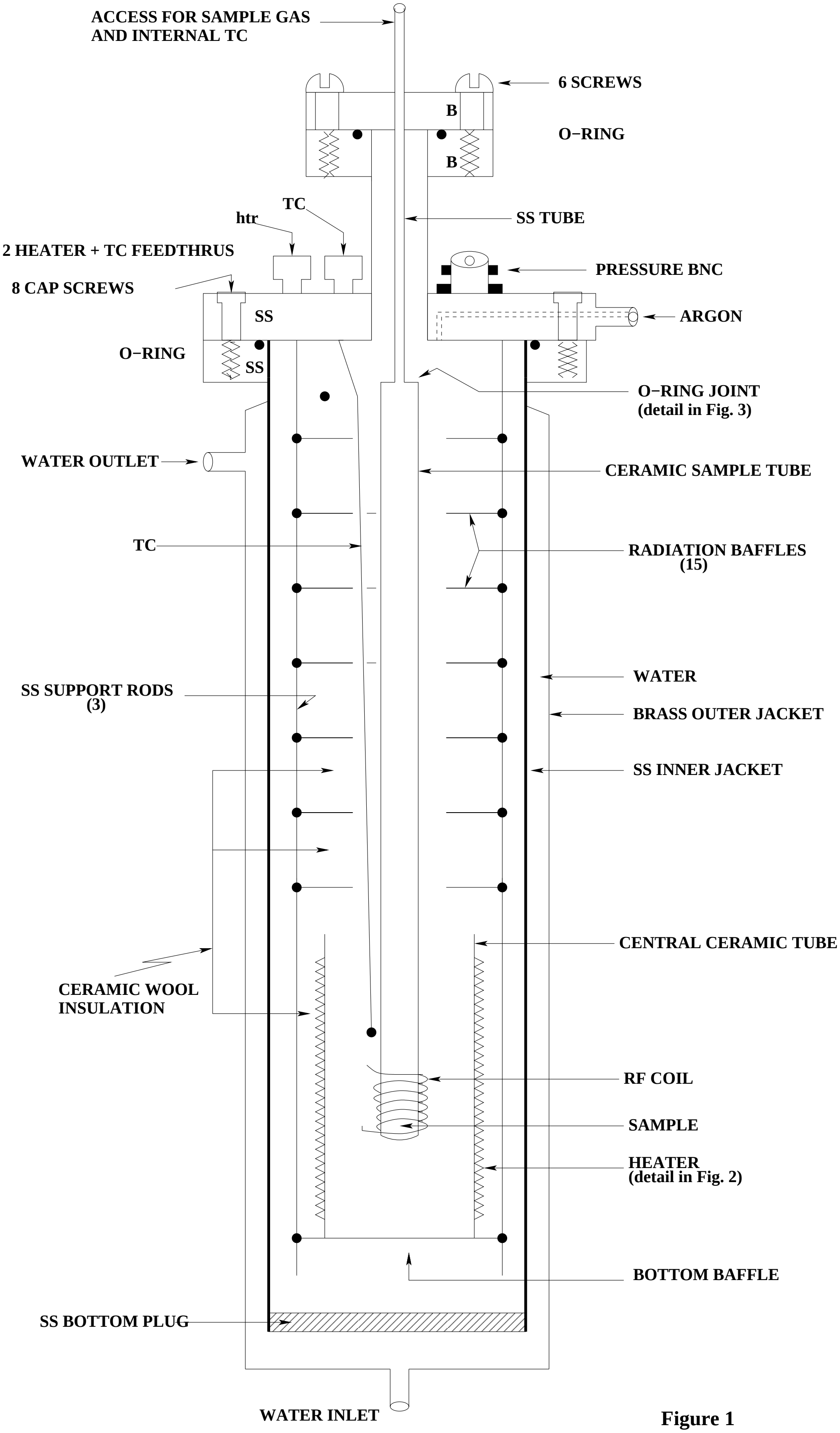
ACCESS FOR SAMPLE GAS
AND INTERNAL TC
6 SCREWS
B
O−RING
B
TC
htr
SS TUBE
2 HEATER + TC FEEDTHRUS
PRESSURE BNC
8 CAP SCREWS
SS
ARGON
O−RING
SS
O−RING JOINT
(detail in Fig. 3)
WATER OUTLET
CERAMIC SAMPLE TUBE
TC
RADIATION BAFFLES
(15)
WATER
SS SUPPORT RODS
(3)
BRASS OUTER JACKET
SS INNER JACKET
CENTRAL CERAMIC TUBE
CERAMIC WOOL
INSULATION
RF COIL
SAMPLE
HEATER
(detail in Fig. 2)
BOTTOM BAFFLE
SS BOTTOM PLUG
WATER INLET

Figure 1

The ceramic tube has no particular strength and would rupture at the high pressures. Thus, argon gas surrounding the sample vessel is always maintained at a higher pressure than that inside the vessel, making use of the tube's strength under compressive forces.

The inner wall of the water cooling jacket is stainless steel and holds the argon gas pressure. The larger diameter of this tube and the larger volume of compressed gas (compared to pressurizing only the sample vessel) make this tube a crucial element of the design in terms of safety against rupture. Since this tube remains cold, its strength does not decrease as the sample temperature is increased.

The rf coil is tuned and coupled to appear as 50 ohms resistive with tuning capacitors in a shielded box on top of the apparatus. The design has been used at 21 and 53 MHz in a Varian iron-core electromagnet. Modifications for use in a superconducting solenoid have been thoroughly discussed.[2]

To eliminate the effects of the residual magnetic field from the nominally non-inductive heater winding, the current to the heater is disabled by a relay during NMR data acquisition. The effect upon temperature regulation (Omega temperature controller with thermocouple input and on-off output) is negligible.

Future Plans

The first system to be studied will be $NaAlH_4$, because of its central role in the development of non-metallic hydrides. We will look for mobile H species; their signals should stand-out from the signals of $NaAlH_4$, Na_3AlH_6, and NaH because the mobile species will have long T_2 (and thus be the only signal remaining at long times). A sample of Sc-catalyzed $NaAlH_4$ will be studied by MAS-NMR to identify the chemical species of Sc present (e.g., Sc metal, Sc-Al alloy or compound, or ionic Sc as in $ScCl_3$). While catalysis by Sc is relatively new, the properties of its nucleus are much more favorable for NMR than is Ti (e.g., ^{45}Sc is 100% abundant while ^{47}Ti and ^{49}Ti have 8 and 5% abundances each, very large electric quadrupole moments, and small magnetogyric ratios).

In parallel with the hydrogen studies in the existing high-T, high-P apparatus, a student will build a second version for the high-field magnet (8.4 T). This device will be useful for examining metal nuclear spins, such as ^{29}Al, ^{23}Na, and ^{7}Li. Its first use will be to detect and identify mobile Al and Na species in the recharging of $NaAlH_4$ from the fully or partially dehydrided state.

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High Throughput Screening of Nanostructured Hydrogen Storage Materials

Gang Chen[a], Mildred S. Dresselhaus[a], Costas P. Grigoropoulos[b],
Samuel S. Mao[b], Xiaodong Xiang[c], Taofang Zeng[d]

[a]Massachusetts Institute of Technology
[b]University of California, Berkeley
[c]Intematix Corporation
[d]North Carolina State University

Program Scope

Our project combines high throughput combinatorial materials synthesis, high throughput screening along with fundamental studies to identify high capacity hydrogen storage materials with fast sorption and desorption kinetics. The project was initiated in September 2005. This extended abstract reports our research targets, the progress achieved and future plans.

Our program aims at the development of nanostructured metastable hydride materials that are capable of storing hydrogen based on both chemisorption and physisorption mechanisms, and with fast sorption and desorption kinetics, enabled by the small size and good heat transfer characteristics. In the early phases of this program the following targets have been identified:

- Development of combined synthesis and high throughput screening methods for discovery of nanostructured metastable metal and complex hydrides.
- Development of nanoporous hydride materials with integrated chemisorption and physisorption characteristics through the synthesis of nanocomposite materials with fine-tuning of the process conditions.
- Development of materials characterization techniques that are compatible with the combinatorial synthesis approach.
- Development of models and simulations for increasing our fundamental understanding of size effects on the thermodynamics, kinetics of hydrogen sorption and desorption, and heat transfer processes in nanostructured hydrogen storage materials.

Recent Progress

(a) Synthesis of metastable hydride materials

Metal hydrides are solid alloys, some of which are capable of storing larger amounts of hydrogen at ambient temperatures and at much lower pressures than can be achieved with gaseous or liquid hydrogen. Hydrogen is a highly reactive element and is known to form hydrides with thousands of metals and alloys. However, there are some metals that do not form stable hydrides, such as iron and nickel. Metal hydrides are typically composed of metal atoms with a host lattice and hydrogen atoms that are trapped in the interstitial sites. Many of these compounds, MH_n, show large deviations from ideal stoichiometry and they can exist as multiphase systems, for example, α-phase where only some hydrogen atoms are adsorbed, and β-phase where the hydride is fully formed (e.g., Mg_2Ni forms hydrides of $Mg_2NiH_{0.3}$ and Mg_2NiH_4).

Most metals and complex hydrides, however, suffer from high thermal stability (hydrogen desorption temperatures > 250ºC) and/or slow kinetics, which prevent these materials from being used in practice, as for example for automotive applications. The challenge with stable high capacity hydride materials is therefore to develop destabilization approaches that lower the enthalpy for hydride formation and to increase the kinetics. We aim to search for nanostructured metastable hydrides that consist of atoms or molecules arranged in a higher energy state than expected for the most stable configuration. Kinetics will be increased by nanostructures, as discussed further in the next section. The metastable nature is a result of an energy barrier between the higher energy state and the stable lowest energy state of the material, and this barrier can also be tuned by nanostructures. The fundamental mechanism behind destabilizing hydride materials is to modify a material's atomic configuration, and thus the hydrogen-binding environment, by introducing structural and/or compositional disorder. This can be achieved by applying non-equilibrium materials synthesis methods, incorporating substitution and doping elements, adding catalysts, as well as using nanostructures such as nanoparticles. The purpose of substitution/doping using elements that do not form stable hydrides is for structural and compositional destabilization in the bulk of the material, while catalyst addition is to promote surface modification that can be done during the last stage of the hydride synthesis process.

In the past six months, we have completed calibration of a new laser pyrolysis system and successfully synthesized Mg and binary MgNi nanoparticles using the combinatorial laser pyrolysis method. Figure 1 shows a library of Mg-Ni nano-powders obtained under two laser pyrolysis conditions and four elemental ratios of Mg to Ni. The ability to synthesize Mg and Mg-Ni nanoparticles and to incorporate them into nanoporous structures is an important first step in our quest to use nanostructured metastable hydrides to enhance hydrogen storage.

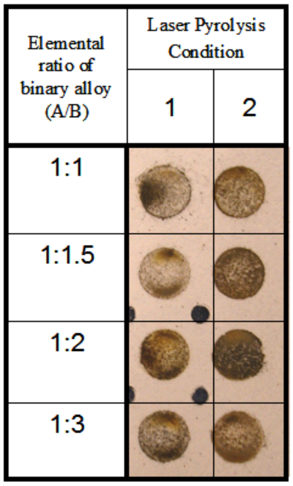

Figure 1 Pictures of synthesized Mg-Ni nanoparticles.

(b) Mesoporous silica scaffolds for enhancing the MgH_2 release kinetics

The use of nanostructures serves multiple functions. Nanoporous structures tune the thermodynamics by incorporating destabilizing metals or catalysts onto a composite material, enhance the kinetics by increasing the diffusivity and reducing the diffusion distance, and increasing the reaction surface area. In addition, nanoporous structures offer mechanical durability, a property that ensembles of nanoparticles do not have. Nanoporous materials with high internal surface densities can also be exploited for physisorption. At Berkeley, experiments have been carried out on hydrogen storage in aerogels and preliminary results showing up to approximately 2% hydrogen storage at 20 Bar (Figure 2) have been achieved.

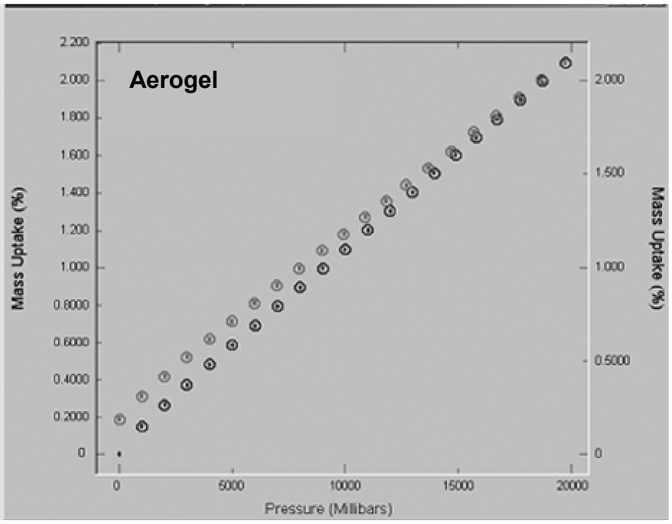

Figure 2 Hydrogen sorption results in pure aerogel.

At North Caroline State University (NCSU), Magnesium hydride (MgH_2) powders and two other types of metal nanoparticles (100 nm) have been successfully incorporated into nanoporous silica aerogels. During alcogel synthesis, water is required for the hydrolysis of silicon alkoxide (TEOS) and water is also produced in the condensation or gelation step. We have modified a well established aerogel synthesis route to eliminate the residual water after hydrolysis and we have greatly minimized MgH_2 dehydrogenation by rapid condensation and solvent exchanges.

A selected type of nanoparticle that can be used to catalyze the MgH_2 decomposition has also been incorporated into the gels. We have developed a new synthesis procedure for the preparation of the selected metal nanoparticles which employs metal displacement reduction. The resulting aerogels are heavily loaded with nanoscale metal particles (1-50 nm). This "in-situ" technique provides much greater loading of metal nanoparticles than the conventional "wet impregnation" techniques and allows all metal precursors to be removed through solvent exchanges. Figure 3 shows three synthesized samples and preliminary results for their kinetics. The results of Figure 3 clearly show that MgH_2 embedded in an aerogel with metal catalysts has a faster kinetics. We anticipate that the use of a silica nanoporous scaffold and nanostructured MgH_2 will facilitate MgH_2 decomposition at a significantly lower temperature than MgH_2 alone and that the addition of selected catalytic metal nanoparticles to the scaffold will further reduce the H_2 release temperature and enhance the kinetics of the hydrogen release.

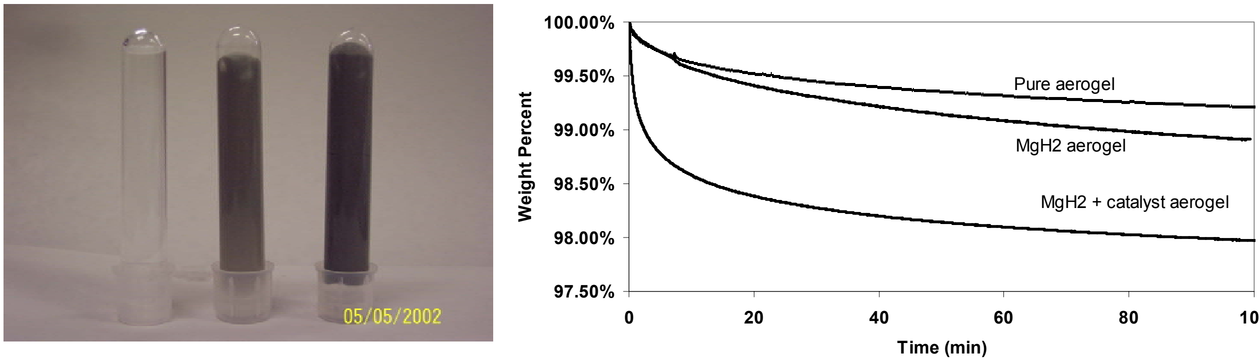

Figure 3 Nanocomposite MgH_2 and preliminary results of the kinetics. Left Vial - pure aerogel (no additives); Middle Vial - aerogel with embedded MgH_2 powder (~50 wt%); Right Vial - aerogel with MgH_2 (~50 wt%) and a catalyst with the size of 100nm (~2 wt%). Data in the right figure show an improvement in the kinetics of nanocomposite MgH_2 material with regard to the control of the amount of hydrogen released and the time constant for the release.

(c) Modeling

The MIT team has been engaged in modeling the effects of size on the thermodynamics and kinetics for physisorption and chemisorption. Efficient hydrogen storage materials should have a small enthalpy of formation. Our preliminary study shows that the enthalpy of reaction can be tuned by exploiting the size effect, potentially leading to a smaller enthalpy of formation and thus less heat released during the sorption processes, and conversely, less heat addition required in the dehydration process. We are also studying the kinetics of hydrogen diffusion through nanopores using Monte Carlo simulation and diffusion through the solid, aiming at identifying conditions under which the kinetics for both the gas phase and solid phase transport can be balanced.

(d) Characterization

The Berkeley team has completed a setup including an infrared camera integrated with a new hydride testing chamber for high throughput characterization of combinatorial metal hydride samples based on infrared reflectivity measurements. Fabrication of microcantilever array for qualitative weight measurements is in progress at the Berkeley microfabrication laboratory. The MIT team is also developing laser pump-and-probe techniques for fast screening of the thermal conductivity of combinatorial synthesized materials. The technique could also probe the ultra-fast non-equilibrium hot electrons, electron phonon interaction and phonon transport to gain fundamental understanding of the electronic and thermal properties at the material interface. Better understanding of the structure of the hydrogen binding at the interface will in turn help in synthesizing better hydrides. Figure 4 shows some preliminary signals we obtained from the system.

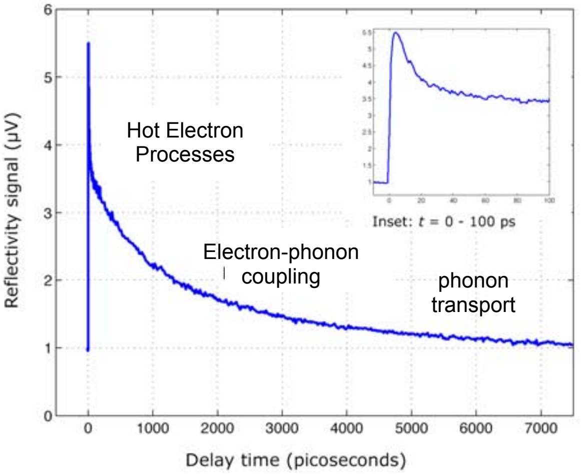

Figure 4 Pump-and-probe techniques for characterization of thermal and electronic properties.

Upper right: Zoom on the first 100ps of the decay.

Future Plans

For better understanding of the effects of particle or grain size on the thermodynamic properties of potential hydrogen storage materials, an accurate determination of the surface energy and reaction enthalpy at the nanoscale is essential. In the future we plan to carry out modeling studies, followed by first principles calculations to determine such quantities. We will continue the development of Monte Carlo simulation schemes for gas phase transport, and eventually combine these with first principle simulation studies of adsorption processes at interfaces. Thermal properties of nanoporous structures will also be modeled, aiming at a balanced development of materials with good kinetics and good heat transfer.

For combinatorial metal hydride material synthesis, by replacing Ni with other element(s), we will move from fabricating nanoscale Mg-Ni alloy system to screening Mg-X and Mg-X-Y alloys in the second half of this fiscal year. We will continue with the development of high throughput characterization approaches, including the laser pump-and-probe technique for fast screening the thermal and electronic properties of candidate materials, the infrared reflectivity measurements, and the microcantilever technique. Our current focus is on improving the sensitivity of the three different characterization systems.

For the development of nanostructured porous hydride materials, we will synthesize a series composition-controlled nanocomposite metal hydrides by integrating aerogels or other nanoporous matrix scaffolds with different destabilized hydride materials, starting from nanoscale MgH_2 embedded with selected metal catalysts to achieve the desired chemisorption properties. We will also tune the pore size to optimize the joint physisorption and fast kinetics requirements.

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Complex Hydrides – A New Frontier for Future Energy Applications

Vitalij K. Pecharsky (vitkp@ameslab.gov), Oleksandr Dolotko, Haiqiao Zhang, L.Scott Chumbley, and Ozan Ugurlu, Materials and Engineering Physics Program, Ames Laboratory, Iowa State University, Ames, IA, 50011-3020

Marek Pruski and Victor S.-Y. Lin, Chemical and Biological Sciences Program, Ames Laboratory, Iowa State University, Ames, IA, 50011-3020

Purusottam Jena and Sa Li, Department of Physics, Virginia Commonwealth University, Richmond, VA 23284-2000

Program Scope

Hydrogen storage is one of the enabling materials technologies required to assure a successful future transition from fossil to hydrogen-based fuel. The scope of the multidisciplinary effort, which draws on considerable experimental and modeling experience and expertise at the Ames Laboratory and Virginia Commonwealth University, is to achieve a fundamental understanding of the relationships between the chemical composition, bonding, structure, microstructure, properties and performance of hydrogen-rich solids. The specific objectives of this program are to address relevant issues, which have the potential to advance basic materials science of novel hydrides and open up possibilities for their future practical use.

- Synthesize an array of novel non-transition metal-based complex hydrides where the metal, metalloid or nonmetal atom is coordinated by two to six hydrogen atoms by means of solvent-free, mechanochemical technique starting from several parent light-element hydrides.
- Fully characterize the products using state-of-the-art experimental techniques.
- Create a knowledge base relating composition, structure and properties of various classes of complex hydrides by investigating the effects of varying stoichiometry and processing history on their crystal and microscopic structure, chemical, thermodynamic and physical properties.
- Extend and refine the current understanding of the mechanisms of the solid-state transformations occurring in a few model hydrides, which is in a rudimentary state, by examining the effects of various chemical and structural modifications and processing strategies on the structure-property relationships, and dehydrogenation and hydrogenation behavior of novel non-transition metal-based complex hydrides. Special emphasis is placed on bridging lengths scales ranging from a few tenths of a nanometer (a single interatomic distance) to microns (a single grain) and centimeters (assemblies of multiple particles varying in size, shape and structure) in order to fully explore the potential of novel solids.
- Integrate experiment with modeling and first principles theory to provide a fundamental understanding of the nature of hydrogen bonding, the structure and stability of the complex hydride phases, the effect of dopants and catalysts, temperature, and pressure in altering the nature of hydrogen-metal bond, and the role of nanostructuring on the absorption and desorption properties of hydrogen.

In addition to explaining the experimental data, the theory will be used to guide experiments in search of desirable chemical composition, preparation and processing strategy, atomic scale structure and microstructure, and the nature of the substituting element(s) – all related to resultant cyclic hydrogenation and dehydrogenation properties of complex hydrides.

Recent Progress

Mechanochemically-induced transformations have been studied in various systems containing complex metal hydrides such as $NaAlH_4$ (total hydrogen content 7.4 wt. %) and $LiAlH_4$ (10.5%), amides $NaNH_2$ (5.1%) and $LiNH_2$ (8.7%), binary metal hydrides ZrH_2 (2.2%), CaH_2 (4.8%), MgH_2 (7.7%), and LiH (12.5%), and different allotropic forms of carbon (graphite and carbon black). Several previously unknown mechanochemical reactions have been discovered. One of these is a rapidly occurring transformation in the $LiAlH_4 + LiNH_2$ system. The reaction products have been characterized by X-ray powder diffraction and ^{27}Al and ^{7}Li solid state NMR spectroscopy, see Table 1 and Fig. 1.

Table 1. Results of the solid state NMR spectroscopic analysis of an equimolar mixture of $LiAlH_4$ and $LiNH_2$ and of the same ball milled in a Spex-8000 mill for 4, 12 and 30 min. Total mass of the hydrides was ~1g, total mass of balls was ~21 g.

Compound Milling time	$LiAH_4$	$LiNH_2$	Li_3AlH_6	AlN	LiH	Al
0 min	+	+	-	-	-	trace
4 min	+	+	+	+	+	-
12 min	↓	-	↑	↑	+	-
30 min	-	-	-	↑	↑	-

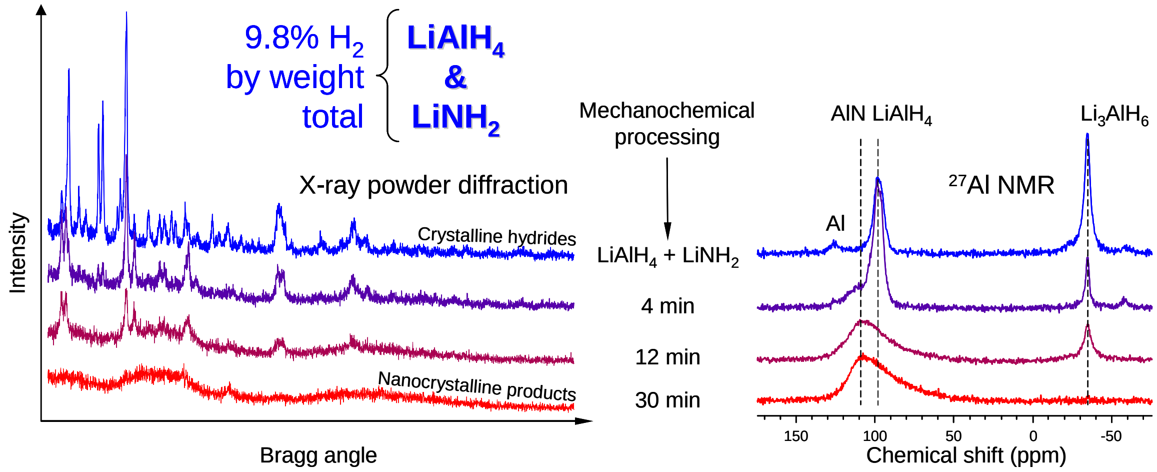

Fig. 1. X-ray powder diffraction (left) and ^{27}Al solid state NMR (right) traces of an equimolar mixture of $LiAlH_4$ and $LiNH_2$ and of the same ball milled in a Spex-8000 mill for 4, 12, and 30 min. Total mass of the hydrides was ~1g, total mass of steel balls was ~21 g.

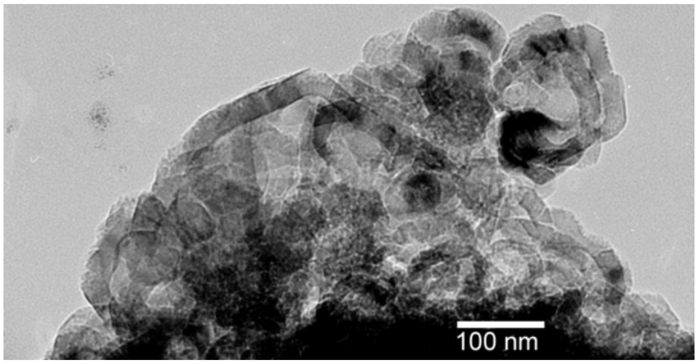

Fig. 2. TEM micrograph of the products of the mechanochemical reaction between $LiAlH_4$ and $LiNH_2$ taken in a 1:1 (molar) ratio after ball milling for 30 min.

Identification of the reaction products from the X-ray powder diffraction data is impossible because they are formed as a few micron size conglomerates of much smaller, nanometer-scale particles, see Fig. 2. Solid state NMR analysis, however, provides the much needed information in order to establish the nature of the final reaction products (Eq. 1) leading to a conclusion that several competing solid state reactions are likely (some possible examples are shown in Eqs. 2 through 4). Although the exact mechanism remains unclear, we show that a total of 6.6 wt.% hydrogen can be easily obtained from the $LiAlH_4 + LiNH_2$ system. The reversibility of reaction (1) has not been yet demonstrated but the process is fundamentally reversible (this effort will commence as soon as the construction of a high hydrogen pressure milling vial is completed).

$LiAlH_4 + LiNH_2 \rightarrow AlN + 2LiH + 2H_2\uparrow$ [6.6 wt.% H_2] (1)

Al (trace) $+ LiNH_2 \rightarrow AlN + 2LiH + \frac{1}{2}H_2\uparrow$ (2)

$LiAlH_4 + 2LiH \rightarrow Li_3AlH_6$ (3)

$Li_3AlH_6 + LiNH_2 \rightarrow AlN + 4LiH + 2H_2\uparrow$ (4)

Synergistic effect of these two individual compounds ($LiAlH_4$ and $LiNH_2$) enables one to destabilize both the complex hydride and the amide without adding halides of Ti. The latter renders as much as 9 mol.% of an alanate irreversible (assuming a ~3 mol.% doping level by any Ti^{3+} halide), contaminates the hydride with an alkali metal halide, and reduces both the reversible and total hydrogen contents of the hydride. For example, 0.03 mol.% $TiCl_3$ doped $LiAlH_4$ has a total hydrogen content of 8.5 wt.% H_2 instead of 10.5%, and its theoretical reversible capacity becomes 6.4 wt.% H_2 instead of 7.9%. Examination of equimolar systems containing alanates and amides of both lithium and sodium indicates that following mechanochemical transformations also proceed quite rapidly.

$NaAlH_4 + NaNH_2 \rightarrow AlN + 2NaH + 2H_2\uparrow$ [4.3 wt.% H_2] (5)

$NaAlH_4 + LiNH_2 \rightarrow AlN + NaH + +LiH + 2H_2\uparrow$ [5.2 wt.% H_2] (6)

$LiAlH_4 + NaNH_2 \rightarrow AlN + NaH + LiH + 2H_2\uparrow$ [5.2 wt.% H_2] (7)

Other mechanochemical reactions that have been studied are as follows:

$LiAlH_4 + MgH_2 \rightarrow LiMgAlH_6 \rightarrow LiH + Al + MgH_2 + 1\frac{1}{2}H_2\uparrow$ [4.7 wt.% H_2] (8)

$3LiAlH_4 + C(graphite) \rightarrow Li_3AlH_6 + 2Al + C(graphite) + 3H_2\uparrow$ [5.3 wt.% H_2] (9)

$3CaH_2 + NaNH_2 \rightarrow CaNH + NaH + H_2\uparrow$ [2.5 wt.% H_2] (10)

$$3CaH_2 + LiNH_2 \rightarrow CaNH + LiH + H_2\uparrow \qquad [3.1\ \text{wt.\%}\ H_2] \tag{10}$$

Controlled nanostructuring experiments exploring micellar self-assembly of alanates in Et_2O in order to prepare mesoporous hydrides encountered some difficulties in synthesis of desired hydrocarbon-fluorocarbon compounds. While synthesis work continues, we attempted self assembly using simpler, commercially available surfactants in a system $2LiAlH_4 + MgCl_2$ in Et_2O expecting to prepare mesoporous $Mg(AlH_4)_2$. To date we established that surfactants have a considerable effect on both the size and topology of sub-micrometer scale hydride particles.

Theoretical effort included two model systems studied from first principles: $NaAlH_4$ and MgH_2, both extensively studied experimentally in the past. In the alanate system, Na vacancies and stabilization of the AlH_3 clusters, rather than substitutions by Ti have been found to have the greatest effect on lowering the energy required to dehydrogenate the alanate. In the MgH_2, on the other hand, small substitutions of Nb in Mg sublattice during mechanochemical reactions with Nb_2O_5 catalyst appear to play a major role.

Future Plans

Considering preliminary transformation mechanisms (see Eqs. 2-4), understanding their details and identifying all possible solid state reactions is a critical enabling step in discovering the most suitable pathways toward rehydrogenation of the respective decomposition products. The most promising mixed light metal hydride systems exhibiting synergistic effects will be modeled from first principles and these theoretical results will guide our experimental efforts. Simultaneously, experiments will be designed to verify our models (e.g. reaction of Eq. 2) and refine theoretical predictions. We will also focus on the preparation and characterization of $LiAlH_4$, $NaAlH_4$, $LiNH_2$ and $NaNH_2$ nanocomposites with various volume fractions of AB_5-, AB_2-, and AB-type conventional hydrides to establish the most active combinations of the two.

In order to provide a better control over nano-structured metal hydrides, understand the role of surface effects, and exploit the potential of the nano-scale, we will continue our effort on self-assembled micelles of known alanates and other complex hydrides. The rates of absorption and desorption of hydrogen as well as the cycling properties of these materials at various temperatures and pressures will be studied.

When our PCT system arrives (HyEnergy LLC, planned shipment on May 15, 2006) and becomes operational we will begin experiments to establish whether the transformations shown in Eqs. 1, 5-10 can be induced thermally. Ball milling experiments on mechanochemically induced hydrogenation of the decomposition products shown in Eqs. 1-10 will be initiated upon completion of the construction of a high pressure vial (up to 300 bar H_2).

Publications in 2005

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3. S. Li, P. Jena and R. Ahuja, Dehydrogenation mechanism in catalyst activated MgH_2, Phys. Rev. Lett., submitted.

Molecular Hydrogen Storage in Novel Binary Clathrate Hydrates at Near-Ambient Temperatures and Pressures

L.J. Rovetto, T.A. Strobel, K.C. Hester, S.F. Dec, C.A. Koh, K.T. Miller, E.D. Sloan
Colorado School of Mines, Center for Hydrate Research
Golden, CO (80401) esloan@mines.edu

Program Scope

Clathrate hydrates are inclusion compounds in which guest molecules occupy the cages formed by a hydrogen-bonded water network [1]. Solid gas clathrate hydrates generally form at high pressures and temperatures near or even above the ice point. Pure hydrogen hydrates have been reported to form cubic structure II hydrates under extreme conditions (200 MPa at 280 K) [2].

We have recently demonstrated that hydrogen molecules can be stored in binary H_2/THF (tetrahydrofuran) clathrate hydrates at pressures nearly two orders of magnitude lower than that in pure hydrogen hydrates [3]. This decreased pressure (Figure 1) makes binary clathrate hydrates a more feasible hydrogen storage material, with a unique combination of advantages not found in any other class of materials. Hydrogen storage is completely reversible is this material, since the gas molecules are free within the clathrate hydrate framework.

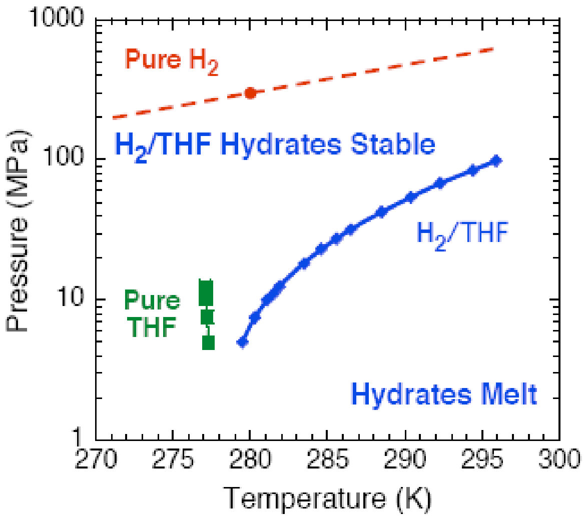

Figure 1. Phase diagram and stability regions of pure H_2 hydrate, pure THF hydrate, and binary H_2/THF hydrate.

Determination of a fundamental understanding of the structure, molecular-level dynamics, and H_2 formation/release rates and mechanisms in these novel crystalline compounds is the main objective of our research.

The final goal of this project is develop binary clathrate hydrates that will efficiently store and release molecular hydrogen at near-ambient temperatures and pressures, achieving targets for energy density, energy uptake, and release kinetics.

Recent Progress

a) Hydrogen Storage Capacity

Several techniques have been employed to determine the hydrogen storage capacity of the stoichiometric THF/H_2 binary hydrate (5.6 mol% THF), which corresponds to all of the large cages of sII hydrate being occupied by THF. The primary technique used was direct gas release measurements from samples prepared from preformed crushed THF hydrate (particle sizes of 45 and 250 μm), and by formation from the liquid phase. Integration of $_1$H MAS NMR spectra, as well as high resolution neutron scattering of the binary THF/H_2 hydrate was also used to determine the storage capacity.

Our experimental results have shown that stoichiometric tetrahydrofuran (THF) hydrate can store up to about 1.0 wt% hydrogen, which is in agreement with our previous work [3]. The storage capacity of hydrogen increases with increasing pressure. The storage capacity of hydrogen in the binary hydrate shows little dependence on the amount of sub-cooling applied during formation.

Using high resolution neutron diffraction (at Argonne National Laboratory), we have determined the time-space average filling of hydrogen molecules in a binary tetrahydrofuran (THF)-d_8 + D_2 sII clathrate hydrate. The diffusional filling of hydrogen in the lattice of a THF-d_8 clathrate hydrate occurred upon pressurization. The hydrogen molecules were localized in the small dodecahedral cavities at 20 K, with nuclear density from the hydrogen approximately spherically distributed and centered in the small cavity. With a formation pressure of 70 MPa, molecular hydrogen was found to only singly occupy the sII small cavity. The occupancy in the small dodecahedral (5^{12}) cavity is a very important parameter to assess whether these materials will be a viable hydrogen storage medium. Hydrate structures which enable multiple occupancy of hydrogen will likely be required for the increase in stored hydrogen density. An understanding of the occupancy and orientation of hydrogen in the host water lattice will be key in future development and studies of these binary hydrate materials.

It has been suggested [4] that at low concentrations of THF, some of the large cages could become quadruply occupied by hydrogen (forming a non-stoichiometric hydrate), with hydrogen storage slightly greater than 4 wt%. Non stoichiometric hydrates (below 5.6 mol% to 0.5 mol%), were formed and gas release experiments were performed in order to investigate the possible manipulation of the large cage occupancy. As the THF concentration was decreased from 5.56 mol% to 0.5 mol%, there was no detectable change in storage capacity with a constant formation pressure of 13.8 MPa. This indicates that, contrary to previous reports [4], THF remains the favorable guest for the large cage, and that multiple hydrogen occupancies cannot be achieved at moderate pressures.

Over the range of experimental conditions tested, the maximum hydrogen storage capacity of the binary sII THF-H_2 hydrate was found to be approximately 1.0 wt%.

b) Hydrogen Stabilization Effect

Cyclohexanone is a known sII hydrate former. However, like other large sII formers (e.g. cyclohexane or benzene), a second guest molecule is required to stabilize the structure, and no pure cyclohexanone hydrate is currently known. Through neutron powder diffraction at the Argonne National Laboratory, we have

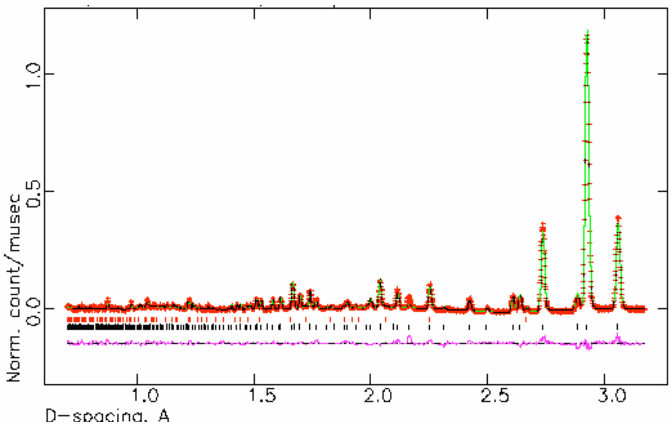

Figure 2. Diffraction pattern for the CHone/D_2 system. Rietveld profile refinement indicates that D_2 had entered the lattice. The large cavity is fully occupied by CHone molecules whereas occupancy of ~ 0.54 of the small 5^{12} cage was determined for D_2.

determined that hydrogen acts like a well behaved hydrate former, in the sense that it can stabilize the larger lattice in cooperation with cyclohexanone (CHone) at -253ºC/20 K and 1 atm. (Figure 2).

The ability of hydrogen to stabilize the larger hydrate lattice may have some implication for formation of other hydrate structures with hydrogen, where a second guest molecule is needed for stability, for example sH.

c) First Semi-clathrate formed with H_2

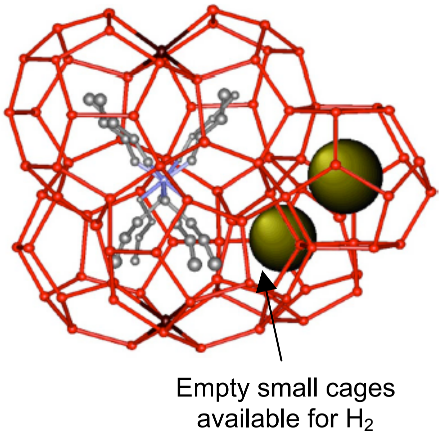

Figure 3. TBAB semi-clathrate molecular structure. (Picture from: Shimada et al., Acta Cryst. (2005), C61, 65-66

Semi-clathrates, unlike clathrate hydrates, gain their stability from the participation of the guest molecule inside the hydrate cavities. Tetra-n-butylammonium bromide, forms a semi-clathrate with water at atmospheric pressure.

Recently, we have shown for the first time that hydrogen molecules can be encapsulated inside the small cavities of this structure. This gives indication that hydrogen storage inside clathrate compounds is not limited to the classical clathrate hydrate structures, but rather open to a wider variety of water-based host complexes.

d) Hydrotrope effect on Gas Hydrates

It has been reported that the use of hydrotropes molecules promotes gas hydrate thermodynamics [5], by shifting the three phase (H-L_w-V) equilibrium curve to more stabilizing conditions; this would provide reduced pressure requirements for gas hydrate formation, and gas storage/transportation applications.

Motivated by this intriguing phenomena and its potential applicability to pure hydrogen hydrates, the effect of p-TSA on the three phase (H-L_w-V) equilibria of three different gas hydrate forming systems (CH_4-water-p-TSA, CH_4+C_2H_6-water-p-TSA and a natural gas mixture-water-p-TSA) has been investigated and quantified in the present work. The equilibrium conditions (H-L_w-V) of these gas hydrate systems were obtained using the isochoric temperature cycle method at different p-TSA concentrations. However, no effect was observed on the hydrate phase equilibria with hydrotrope concentrations in the range of 2000-5000 ppm. Furthermore, at higher concentrations (up to 138 000 ppm), an inhibitor effect on CH_4 hydrate stability was measured. The accuracy of the hydrate equilibrium points, using the temperature cycling procedure, was found to be highly dependent on the heating rate during hydrate dissociation.

Future Plans

Based on our results, with single occupancy of H_2 molecules in the small cavity of sII binary THF/H_2 clathrate, a maximum storage of 1 wt% can be achieved. In order for clathrate hydrates to be practical hydrogen storage medium, hydrate structures which enable multiple occupancy of hydrogen will likely be required.

Understanding the pressure dependence of the hydrate cavity occupancy is a prerequisite for possible manipulation of the storage capacity in clathrates hydrates. Raman studies of pure H_2 hydrate will be preformed in a new high pressure device (up to 60,000 psi). These studies will also provide valuable information on the formation and dissociation mechanism of hydrogen hydrates, necessary for practical applications.

Further search of different sH hydrate formers with the possibility of multiple occupancy of the large cavities, as well as other possible structures are the primary objectives of this project, to achieve the H_2 storage target values.

NMR studies will be carried out in order to investigate the hydrogen diffusion mechanism in ice and different hydrate structures. These studies, in conjunction with determination of dissociation rates of binary H_2 hydrates at different storage conditions, will establish if hydrogen hydrates show self preservation behavior [6], in which case the dissociation rate of the hydrate outside the stability region (i.e. higher temperatures or lower pressures) is extremely low (i.e. weeks or months), offering the possibility of storage of the hydrogen at middle conditions, in a reversible and environmentally friendly storage material.

Publications

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3) L.J. Rovetto, T.A. Strobel, C.A. Koh, E.D. Sloan Jr. Is gas hydrate formation thermodynamically promoted by hydrotrope molecules? Fluid Phase Equilibria. *Submitted*

4) Neutron diffraction studies of binary hydrates with H_2 and cyclohexanone. *In preparation*

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Atomistic Mechanisms of Metal-Assisted Hydrogen Storage in Nanostructured Carbon

Nidia C. Gallego[1], Cristian I. Contescu[1], Frederick S. Baker[1], Xianxian Wu[1],
Chong L. Fu[1], James R. Morris[1], Rachel S. Aga[1],
Stephen J. Pennycook[1], Klaus van Benthem[1],
Dan D. Edie[2], Halil Tekinalp[2]
[1] Materials Science and Technology Division, Oak Ridge National Laboratory
Oak Ridge, TN 37831-6087 gallegonc@ornl.gov
[2] Center for Advanced Engineering Fibers and Films, Clemson University
Clemson, SC, 29630

Program Scope

This program received initial funding from the Office of Basic Energy Science in August 2005. The research program was built upon initial results from a Laboratory-Directed Research and Development (LDRD) grant at Oak Ridge National Laboratory (ORNL).

The project is directed towards the development of a broad science foundation to identify and understand the atomistic mechanisms of metal-assisted hydrogen storage in nanostructured carbons. It capitalizes on strengths in synthesis and behavior of nanostructured carbons, sub-angstrom resolution electron microscopy, neutron scattering, and theoretical modeling. ORNL, in partnership with Clemson University, is investigating the mechanisms of metal-assisted hydrogen storage in nanostructured carbon in terms of catalytic activation of molecular H_2, surface diffusion of H atoms, and subsequent incorporation on carbon structural defects through either chemical bonding or intercalation. The work plan is organized on three interactive levels: (1) First principles computations for simulation of hydrogen interactions with graphite-like structures and prediction of optimal material properties; (2) Synthesis of metal-doped activated carbon fibers and identification of the microstructures of the fibers and catalyst; and (3) In-depth examination of the nanostructures of the carbon substrate and metal catalyst particles, and correlation of these structures with the hydrogen storage characteristics of the fibers. This project addresses the long-term program targets of BES in the area of design, modeling, fabrication, and characterization, at the nanoscale level and with atomic precision, of novel materials for energy-related applications. The research will provide a sound understanding of the fundamental factors that influence hydrogen sorption on carbon materials and how they can be manipulated to attain the on-board storage targets for the FreedomCAR Program.

Recent Progress

(a) *Initial synthesis activities and building of inventory of Pd-doped activated carbon fibers.*

A series of Pd-containing activated carbon fibers (ACF) were prepared at Clemson University by melt-spinning an isotropic pitch precursor mixed with a Pd salt (Pd content in pitch precursor: 1 wt%). Additionally, a series of ACF without metal doping were prepared under equivalent processing conditions. After melt-spinning, all samples were stabilized and carbonized in a nitrogen atmosphere. After heat treatment, samples were activated in CO_2 to develop the micropore structure and large surface area. The level of activation (or percent burn-off) was varied systematically from 0% to 80%. Characterization of these samples (surface area, pore size and distribution, electron microscopy, X-ray analysis, etc) is under way.

Work has also started on fractionation of isotropic pitch by solvent extraction with high density supercritical gas. This work will lead to separation of pitch into components of various molecular weights, which will be used for the production of ACF. The effect of several of these components on metal particle dispersion within the ACF will be studied.

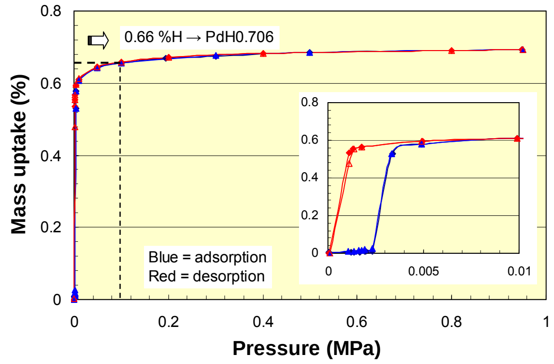


Figure 1. Hydrogen isotherm (at 30°C) of Pd sponge showing hydride formation and hysterisis at low pressure.

(b) High pressure adsorption

Hydrogen sorption measurements are made using an Intelligent Gravimetric Analyzer (IGA) from Hiden Analytical, coupled with an on-line mass spectrometer. The system accounts for buoyancy effects and temperatures variations. To verify the accuracy of our measurements, a calibration run using a Pd sponge was performed. Figure 1 shows the hydrogen isotherm at 30^{o}C for the Pd sponge. It is seen that at 0.1 MPa, the hydrogen uptake of 0.66% corresponds to the formation of Pd hydride ($PdH_{0.706}$). The inset in Figure 1 shows the low-pressure hysterisis typical of this phase.

(c) *Structural changes in Pd-doped carbon fibers during carbonization and exposure to hydrogen*

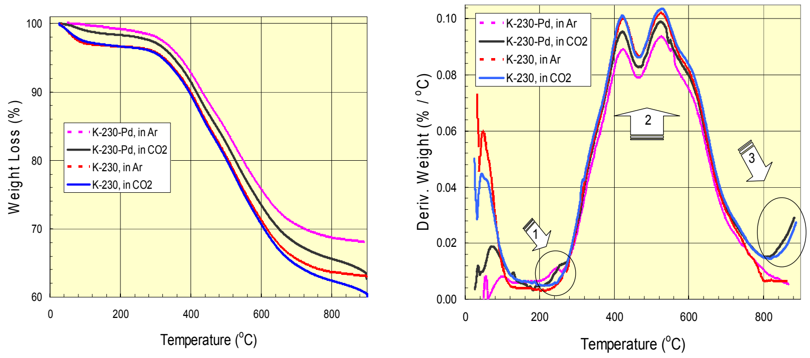


Figure 2. TGA analysis of stabilized pitch fibers, with and without Pd, under different atmospheres. The following processes were identified: 1 – decomposition of Pd salt to Pd metal (only in Pd-containing fibers); 2 – pitch carbonization; 3 – initiation of fiber activation (only in CO_2).

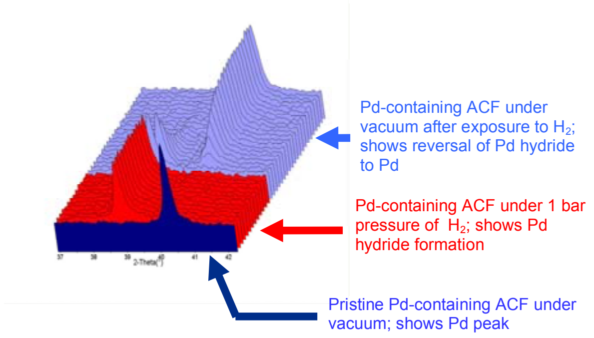


Figure 3. In-situ XRD patterns of Pd-containing ACF showing reversible Pd hydride formation upon exposure to hydrogen at 0.1 MPa and room temperature.

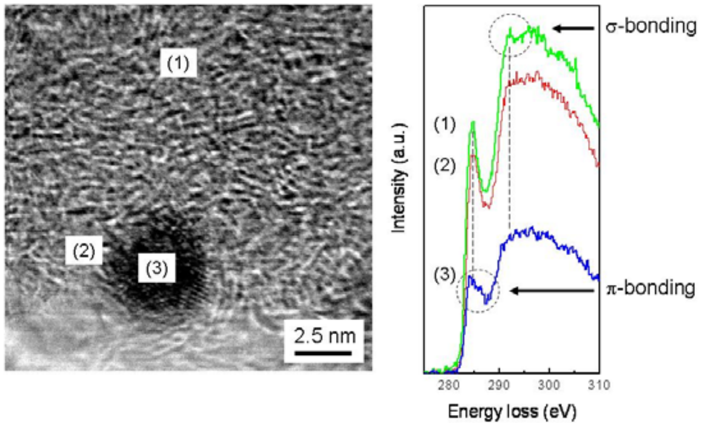
A distinctive feature of the systems investigated in this project is that the carbon structure develops around pre-existing metal particles (Pd), unlike traditional carbon-supported catalysts in which the metal component is dispersed upon a pre-existing carbon support. This process causes specific ordering of the carbon atoms around Pd nanoparticles.

A major task of this project is to develop a basic understanding of the chemical interactions occurring between pitch components and metal precursors in the early stages of fiber formation, and to tailor the metal-doped carbon structures through the carbonization and activation stages. Accordingly, a detailed understanding of particle growth (or sintering) during thermal treatments is needed. To this end, a combination of thermo-gravimetric analysis (TGA), electron microscopy and X-ray diffraction (XRD) was used to determined the temperatures at which: (1) the Pd salt decomposes to Pd metal, (2) pitch carbonization is accomplished, and (3) activation (burn-off) starts (Figure 2).

In-situ XRD analysis of Pd-doped ACF showed that after exposure to hydrogen at 0.1 MPa and room temperature, Pd is quickly transformed into Pd hydride. This transformation is completely reversible if vacuum is applied to the system. Figure 3 shows the XRD patterns for these series of events.

(d) *Characterization of carbon nanostructures in Pd-containing ACF using aberration-corrected STEM (poster presentation by K. van Benthem, X. Wu, S. J. Pennycook, C. I. Contescu, and N. C. Gallego)*

Aberration-corrected scanning transmission electron microscopy (STEM) is being used to characterize the atomic and electronic structure of activated and non-activated carbon fibers in the vicinity of embedded Pd particles. STEM analysis coupled with electron energy-loss spectroscopy (EELS) measurements will allow for the determination of the local electronic structures and bonding character at about 0.1 nm spatial resolution. The C K absorption edge is used to quantitatively determine sp^2/sp^3 hybridization ratios of the local carbon nanostructure.



(a) **(b)**

Figure 4. Coherent bright-field STEM image of a Pd particle embedded in ACF after 20% burn-off. EELS spectra of the C K absorption edge taken at positions (1), (2) and (3).

Preliminary results show that development of carbon structure during carbonization is influenced by presence of Pd particles. Figure 4a shows the coherent bright-field STEM image of a Pd particle embedded in ACF after 20% burn-off. EELS spectra of the C K absorption edge (Figure 4b) were taken at three different positions. It is observed that in the vicinity of the Pd particle (positions 1 and 2) the C K-edge reveals a more dominant σ*-type bonding behavior, while underneath the Pd particle (position 3), the C K-edge spectra show slightly modified π* states.

(e) *Theoretical investigation of the energetics of hydrogen interaction with grapheme layers: the effect of interlayer spacing on hydrogen storage (Poster presentation by Rachel Aga. Maja Krcmar, J.R. Morris and C-L. Fu)*

Carbon layers are stacked too close to each other in graphite for H_2 molecules to fit between graphene sheets. Theoretical models show that it would be difficult to dissociate H_2 between rigid graphene layers because of the high activation energy required, but relaxation of carbon atoms from their rigid positions is energetically feasible upon interaction with hydrogen. First-principle calculations show that high concentrations of H_2 molecules can be stabilized energetically in an intercalated state between graphene layers. Figure 5a shows the dependence of H_2 sorption energy on graphite interlayer spacing upon intercalation of molecular H_2 between two adjacent graphene sheets. Although, in the dilute limit, the existence of intercalated H_2 molecules is energetically unfavorable, at high concentrations a large number of H_2 molecules can be stabilized in the graphite lattice through a dramatic expansion of the lattice (Figure 5b).

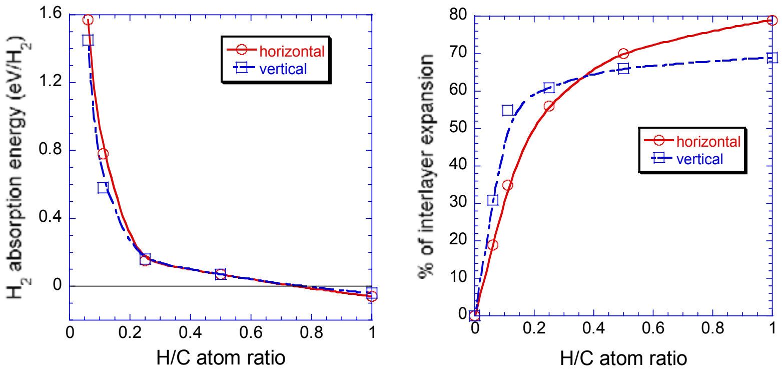


Figure 5. Hydrogen sorption energy between two graphene sheets (left panel) and the percentage of induced interlayer expansion (right panel) as afunction of H/C atom ratio per layer. Both horizontally and vertically oriented H_2 molecule axes are considered.

These results show that it is possible to achieve high hydrogen storage capacity if the high potential energy associated with the initial stage of intercalation can be overcome. In this context, catalytic metal particles should help reduce the activation energy for H_2 dissociation and provide an electronic interaction that lowers the energy for sorption of H_2 molecules on carbon sites adjacent to the metal particles. Once the first H_2 is sorbed, additional lattice expansion is induced and further hydrogen sorption is facilitated.

Future Plans

- In-situ X-ray diffraction studies at high pressures (up to 10 bars) will be performed. The results will reveal the type of structural changes occurring in the metal and carbon phases of the activated carbon fiber under exposure to hydrogen at high pressures.
- In-situ X-ray diffraction studies at high temperatures will be performed. The results will show the phase transformations occurring during the heat treating processes required for the production of activated carbon fibers.
- Characterization of hydrogen storage capacity by measurements of hydrogen uptake at pressures of up to 20 bar on selected Pd-doped ACF will continue.
- 3-D imaging will be used to study the structure of carbon-supported Pd particles and metal-carbon interface; as well as the 3-D sp^2/sp^3 ratios in carbon structures surrounding embedded Pd particles.
- Grand canonical Monte Carlo simulation will be performed to study the adsorption/desorption of hydrogen in graphene sheets

Publications and Presentations

1. N.C. Gallego. "Materials and Solutions for Hydrogen Storage". Invited talk at the *AutoPolymers* 2005 Workshop, Charleston, SC, October 28-31, 2005.
2. N.C. Gallego, F. S. Baker, C.I. Contescu, X. Wu, C.L. Fu, D.D. Edie, and T. Burchell, Metal-Assisted Hydrogen Storage in Nanostructured Carbons", invited keynote presentation at Symposium on "Advanced Materials for Energy Conversion", The Minerals, Metals, and Materials Society (TMS) Annual Meeting and Exhibition, San Antonio, TX, March 12-16, 2006.
3. N.C. Gallego, X. Wu, C.I. Contescu, F.S. Baker, H. Tekinalp, D.D. Edie. "Effect of Pd on the hydrogen adsorption capacity of activated carbon fibers". Materials Research Society – Spring Meeting. San Francisco, CA, April 17-21, 2006.
4. N.C. Gallego, F.S. Baker, C.I. Contescu, X. Wu, S.A. Speakman, H. Tekinalp, and D.D. Edie, "Effect of Pd on the Hydrogen Adsorption Capacity of Activated Carbon Fibers", Carbon 2006, International Carbon Conference, Aberdeen, U.K., July 16-21, 2006.

A Synergistic Approach to the Development of New Classes of Hydrogen Storage Materials

A. Paul Alivisatos, Marvin L. Cohen, Jean M. J. Fréchet, Martin Head-Gordon,
Jeffrey R. Long, Steven G. Louie, Samuel S. Mao, Thomas J. Richardson, and Alex Zettl
Departments of Chemistry and Physics, University of California, Berkeley and
Divisions of Materials Science and Environmental Energy Technologies,
Lawrence Berkeley National Laboratory, Berkeley, CA 94720; jrlong@berkeley.edu

Program Scope

Our program brings together an eclectic group of scientists with experience in materials discovery and theoretical prediction of properties to work together in developing new types of hydrogen storage materials. Particular emphasis is on exploring the possibilities for nanoporous polymers, nanoporous coordination solids, destabilized high-density hydrides, nanostructured boron nitride, and magnesium and light alloy nanocrystals to meet the 2010 DOE hydrogen storage system targets, especially specific energy, energy density, durability, and uptake and discharge kinetics. This project is funded jointly by BES (Alivisatos, Cohen, Louie, Mao, and Zettl) and EERE (Fréchet, Head-Gordon, Long, and Richardson), but represents a cohesive effort with close collaborations and regular meetings involving all investigators.

Recent Progress and Future Plans

Nanocrystals (Alivisatos). To investigate the potential benefits of nanosized materials and understand their interactions with hydrogen, we are synthesizing nanoparticles with different sizes, shapes, crystallinity, and composition. Our goal is to observe shape and volume changes in each nanocrystal, and further study the size-dependent kinetics of uptake and release of hydrogen. We intend to measure hydrogen cycling with *in situ* X-ray diffraction, as well as with pressure-composition isotherms. First, we will focus on the palladium-hydrogen system, which is well-understood in bulk. This work will then be extended to palladium alloys with lighter elements incorporated and other lighter nanocrystal systems.

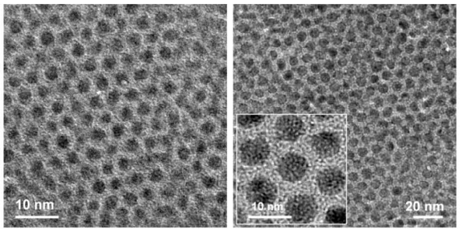


Figure 1. Transmission electron micrographs of three-dimensional superlattices formed by 3.0 nm (left) and 6.9 nm (right) Pd nanoparticles, respectively.

Differently-sized Pd nanoparticles with narrow particle size distributions have been prepared (see Figure 1) for investigating hydrogen uptake and release as a function of particle size and surface-ligand composition. Being monodisperse, these nanoparticles have a strong tendency to form periodic arrays or superlattices. The arrays usually have highest packing density and provide the optimal filling of the system. On the other hand nanoparticles adsorbing hydrogen could be a part of binary periodic superlattices. Ultimately, we plan to investigate the behavior of both single-component superlattices and binary superlattices in which at least one constituent can undergo shape transformation upon hydrogen adsorption.

Nanostructured Boron Nitride (Cohen, Louie, and Zettl). Our efforts have focused on materials composed of atoms in the first two rows of the periodic table. In particular, we have been investigating the adsorption of molecular hydrogen on various nanostructured materials to find better hydrogen storage materials using *ab initio* density functional theory within GGA. Our investigation has been performed in two ways. One is to identify new materials that may store and release hydrogen more than 6% by weight at ambient condition, and the other is to find structural modification of known materials, such as carbon, that may increase hydrogen adsorption. We have already identified several new potential candidate materials in addition to carbon-based materials. Among those are boron nitrides and boron oxides. We also found that structural modifications, such as introducing 5-7 defects, or substitutional doping, may increase hydrogen binding energy.

We are also currently working on various polymers and their modification. Some of them show promising results. For example, when some hydrogen atoms, which have originally formed C-H bonds in polymers, are substituted by metal atoms with *d* electrons, such as Sc or Ti, the calculated molecular hydrogen binding energies fall into the right temperature range. Moreover, our study shows that each of these metal atoms can attract 5-6 hydrogen molecules with the right binding energy. This implies that such polymers would store hydrogen much more than 6% by weight. We are performing further calculations to check stability of polymers containing those metal atom and to verify our current results.

The experimental approach is to use the theoretical calculations to suggest the best candidate materials. We are developing synthesis and characterization techniques involving nanostructured or activated systems. For example, layered materials such as BN and $B_xC_yN_z$, are being synthesized using arc-plasma methods, CVD, and laser ablation. Often the materials undergo post-synthesis processing to increase defect concentration and effective surface area. Oxides are also being investigated in nanocrystal, layer, tube, and nanowire form. Of particular interest are systems analogous to activated carbon. Characterization is via TEM, binding energy, and surface area isotherm methods.

Nanoporous Polymers (Fréchet). Porous polymers could potentially provide an excellent support for hydrogen storage since they can be easily prepared from most often readily accessible monomers and afford very high surface area. These porous materials can be manufactured reproducibly and inexpensively on a large scale in a single reaction step from polymerization mixtures comprising suitable monomers and porogens. Although polymers represent a class of materials that may match most of the requirements set for hydrogen storage, almost no research concerning this application has been reported. Assuming just formation of a monolayer on the available surface, enhancement in the hydrogen adsorption capacity can then be achieved via an increase in surface. A simple calculation reveals that a nanoporous polymer with a surface area of 2000 m^2/g should be able to accommodate up to 5.4 wt % hydrogen. While porous polymers with surface areas of up to 800 m^2/g have already been reported, redesigning the polymerization systems can further increase this value.

Our first hydrogen adsorption/desorption screening experiments were carried out using various porous beads exhibiting high surface areas, but differing in their internal structure and chemistry. The surface areas varied in a broad range of 300-800 m^2/g depending on the preparative method. Most of these beads were prepared by direct polymerization of divinylbenzene or via Friedel-Crafts crosslinking reaction of slightly crosslinked polystyrene. Despite the modest surface area of these sorbents, we found materials exhibiting a promising hydrogen adsorption of 1.4 wt % at 77 K and 1 bar. We are now preparing series of polymers with surface areas exceeding 1500 m^2/g using a variety of functional monomers. These experiments should reveal the effects of chemistry on hydrogen adsorption. In addition, we are testing adsorption ability after carbonization of porous polymers at high temperature in an inert atmosphere. Although a good subject for screening, beads cannot completely fill the available space. Consequently, we are simultaneously studying nanoporous monoliths, which, in contrast to beds packed with particles, do not include any interstitial voids. This better utilization of space will increase the volumetric storage capacity. Initially, porous polymer monoliths were prepared using direct polymerization in a mold with a surface area of 380 m^2/g. Although the surface area of these polymers does not yet reach that of particulate adsorbents, the results of adsorption experiments are promising. New techniques are now being tested for preparing monoliths with significantly higher surface areas.

Nanoporous Coordination Solids (Long). Porous materials containing coordinatively unsaturated metal centers are being explored for use as hydrogen storage materials. In metal-cyanide frameworks with lattice vacancies, such as $Fe_4[Fe(CN)_6]_3$, as well as in anionic metal-cyanide frameworks with interstitial cations, water occupies some of the coordination sites on the metal cation. This bound water can typically be removed by heating the framework under vacuum, leaving open coordination sites on the metal that can potentially bind hydrogen. We first examined hydrogen adsorption in a series of Prussian blue analogs of the type $M_3[Co(CN)_6]_2$ ($M = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}). Of these, the most promising material is $Cu_3[Co(CN)_6]_2$, which stores 1.7 wt% hydrogen and 0.024 kg H_2/L at 77 K and 1 atm. Hydrogen uptake measurements at lower temperatures for $Cu_3[Co(CN)_6]_2$ showed a saturation capacity of 2.7 wt% H_2. In order to better understand the effect of varying the metal ion on hydrogen uptake, the strength of the hydrogen-framework interaction was probed by measuring the enthalpy of adsorption of hydrogen, which ranged from 7.5 kJ/mol for $Ni_3[Co(CN)_6]_2$ to 5.9 kJ/mol for $Mn_3[Co(CN)_6]_2$, compared to 5.5 kJ/mol for $Zn_4O(BDC)_3$. Powder neutron diffraction studies of $Cu_3[Co(CN)_6]_2$ in the presence of hydrogen showed that at a loading of 1 H_2/Cu^{2+}, 25% of the hydrogen molecules were interacting with the open coordination sites on Cu^{2+}, with the remainder interacting with the pore walls.

We have also examined H_2 adsorption in $A_2Zn_3[Fe(CN)_6]_2$ compounds, wherein it may interact with the monovalent cations residing in the pores of the $Zn_3[Fe(CN)_6]_2$ framework. We have synthesized and measured the H_2 sorption properties of the alkali metal series ($A = Li(H_2O)^+$, Na^+, K^+, Rb^+, H_3O^+). All five materials have similar surface areas and H_2 sorption capacities and showed enthalpies of adsorption in the range 7.5-9.0 kJ/mol at low surface coverage, with the trend $K^+ > H_3O^+ \approx Li(H_2O)^+ > Rb^+ > Na^+$.

Most recently, we have been investigating porous coordination solids that can bind low-valent transition metal complexes. These relatively electron-rich metals are expected to have a strong π back-bonding interaction with dihydrogen, resulting in a stronger metal-H_2 interaction than the electron-poor cations in the metal-cyanide compounds discussed above. Towards this end, we have synthesized analogs of Zn_4O(1,4-benzenedicarboxylate)$_3$ with bound metal-carbonyl complexes, $Zn_4O[Cr(CO)_3$(1,4-benzenedicarboxylate)$]_3$, $Zn_4O[Mo(CO)_3$(1,4-benzenedicarboxylate)$]_3$, and $Zn_4O[Co_2(CO)_6$(2-propynyloxy-1,4-benzenedicarboxylate)$]_3$. Future work will focus on finding methods to remove the carbonyl ligands from these compounds and then measuring the H_2 sorption properties of the resulting materials.

Predictive Theory for H_2 Binding in Nanoporous Materials (Head-Gordon). In close support of the foregoing experimental efforts, we have completed a computational study of model complexes between H_2 and derivatized benzene dicarboxylate linkers in metal-organic frameworks, as well as simple charged ligands such as CN^-, CO, NO^+, Cp^-, F^-, and SO_4^{2-}, free lightweight metal ions such as Li^+, Na^+, Mg^{2+}, Al^{3+}, and the corresponding ions complexed with simple ligands. The purpose of this study was to systematically explore H_2 binding affinities across the full scale of interaction strengths from just a few kJ/mol to hundreds of kJ/mol that may be accessible in novel hydrogen storage materials. Such a survey and associated physical insight can potentially provide ideas and perhaps principles to assist in the design of next generation synthetic targets.

There is a close link between the interaction strength and the mode of binding, and so we have placed emphasis on characterizing the physical and chemical interactions responsible for the binding affinities. These interactions range from long-range dispersion forces, which are weakest, through to stronger electrostatic and induction effects that include the coupling of the H_2 quadrupole moment to localized charges (as associated with metal centers or charged ligands) and the induction of a dipole moment on H_2 by such charges. These interactions are each in turn smaller again than the donor-acceptor interactions between orbitals of H_2 and orbitals of the hydrogen storage material itself. However H_2 has a very deep filled level and a very high corresponding antibonding level and is therefore reluctant to participate in strong donor acceptor interactions, relative to more standard ligands.

A first message of our study is that given some level of donor-acceptor participation, or exceptionally strong electrostatic/inductive interactions, one can achieve H_2 binding affinities in the target regime of 15-40 kJ/mol considered optimal for hydrogen storage. Lightweight positively charged metal centers without d electrons are quite capable of yielding such binding affinities, as indeed are corresponding negatively charged centers such as F^-. A second message is that because all interactions (orbital, electrostatic, dispersion) are present at once, the opportunity exists to significantly tune the binding affinity by control over the coordinating environment. Indeed we find the presence of ligands exerts a substantial perturbation on the binding affinity. Ongoing efforts are now focused upon applying these ideas in delivering specific improvements upon the new metal-organic and polymer systems described above.

Destabilized High-Density Hydrides (Richardson). In our previous work on thin film metal hydrides, we studied hydride formation in Mg-alloy films by absorption of H_2 from the gas phase and by means of electrochemical reactions. At ambient temperature, complete conversion of metallic films to the corresponding hydrides is achieved in minutes or even seconds. By varying alloy compositions and ratios, we optimized the amount of hydrogen absorbed by the films. In this program, we are now working with bulk materials. In particular, we are developing metal hydride alloy systems based on magnesium and lithium in which the thermodynamic barrier for desorption of hydrogen is reduced by alloy stabilization of the metal phase. Candidate alloys and mixtures are being prepared in powder and bulk form using standard metallurgical techniques. The phase purity is then assessed by X-ray diffraction, and storage properties are measured using the gravimetric analyzer described above. Phase analysis is carried out at different points in the hydrogen absorption-desorption cycle to determine the mechanism and sequence of reactions. Our goal is to optimize compositions through systematic variation of stoichiometries. The formulations discovered here may then be utilized in the preparation of nanocrystalline samples by the Alivisatos group, in order to study the size- and shape-dependence of their hydrogen storage properties.

Publications

1. "Hydrogen Storage in the Dehydrated Prussian Blue Analogues $M_3[Co(CN)_6]_2$ (M = Mn, Fe, Co, Ni, Cu, Zn)" Kaye, S. S.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 6506-6507.
2. "Strong H_2 Binding and Selective Gas Adsorption within the Microporous Coordination Solid $Mg_3(O_2C\text{-}C_{10}H_6\text{-}CO_2)_3$" Dinca, M.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 9376-9377.
3. "Computational Studies of Molecular Hydrogen Binding Affinities: The Role of Dispersion Forces, Electrostatics, and Orbital Interactions" Lochan, R. C.; Head-Gordon, M. *Chem. Phys. Phys. Chem.* **2006**, *8*, 1357-1370.
4. "The Role of Vacancies in the Hydrogen Storage Properties of Prussian Blue Analogues" Kaye, S. S.; Long, J. R., submitted for publication.
5. "Neutron Diffraction and Neutron Vibrational Spectroscopy Studies of Hydrogen Adsorption in the Prussian Blue Analogue $Cu_3[Co(CN)_6]_2$" Hartman, M. R.; Peterson, V. K.; Liu, Y.; Kaye, S. S.; Long, J. R., submitted for publication.

Poster Sessions

Elucidation of Hydrogen Interaction Mechanisms With Metal-Doped Carbon Nanostructures

Ragaiy Zidan, Steven Serkiz, Scott McWhorter, Polly Berseth, Jennifer Pittman,
Savannah River National Laboratory Aiken SC 29808
ragaiy.zidan@srnl.doe.gov

Puru Jena
Physics Department, Virginia Commonwealth University, Richmond, VA 23284, USA

Apparao Rao
Physics Department, Clemson University
Clemson, SC 29634-0978

Program Scope

This research work is aimed at obtaining a better understanding of the nanoscale level of hydrogen sorption behavior of Metal-Doped Carbon Nanostructures. The experimental work is closely linked to relevant modeling studies of these materials. Advances hydrogen storage technology based on carbon nano-structures and particularly metal-doped carbon nanotube (MD-CNT) require the development of a basic understanding of their physicochemical properties and the manner in which these properties influence the hydrogen bonding. Our effort is focused on understanding of the hydrogen interaction mechanisms such as physisorption, weak covalent bonding, and chemisorption in these nano-carbon systems.

We hypothesize that hydrogen bonding in MD-CNTs is controlled by:

1. modification of the electronic structure in the MD-CNT from the back-donation of electrons from the metal to the carbon;
2. quantized electron energy states that are controlled by the size of the metal particle and its composition/speciation; and
3. the presence of defects in the CNT and lattice deformation resulting from coherency strain at metal-CNT interface.

Our effort is conducted along the following integrated and parallel activities:

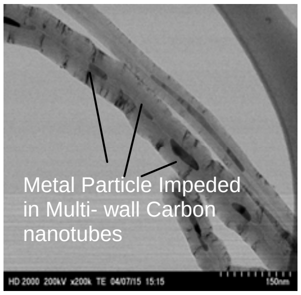
- Production, purification, and separation to develop MD-CNTs of highly controlled size and composition.
- Characterization of these materials and determination of hydrogen bonding pathway and equilibrium distribution of hydrogen bond types by analytical techniques (e.g., Raman spectroscopy, NMR, and neutron scattering and thermo-gravimetric and volumetric analyzers).
- Theoretical modeling is an essential part of our effort in order to confirm and guide the experimental work. The theory will guide the experiments toward

investigating stable and high hydrogen capacity structures. Theory will use experimental results to modify assumptions and reach realistic understanding of carbon nano-structures and MD-CNT systems.

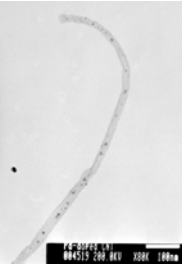
Recent Progress

(a)Production of controlled Size carbon nanotubes doped with different metals

Carbon nanotubes doped with different metals have been produced and the process is being optimized. The ultimate goal is to control the size and type as needed. Different diameter patches of carbon nano tubes were produced in order to investigate the effect of curvature on the hydrogen bond.



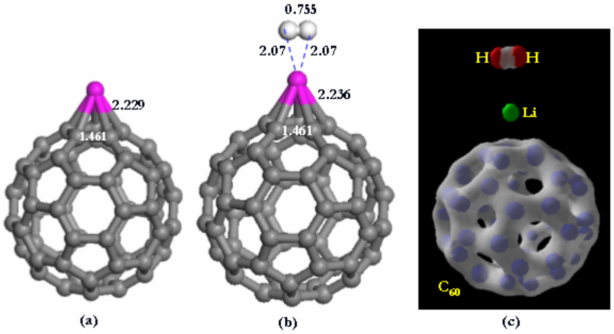
Synthesized Carbon Nanotubes doped with metals



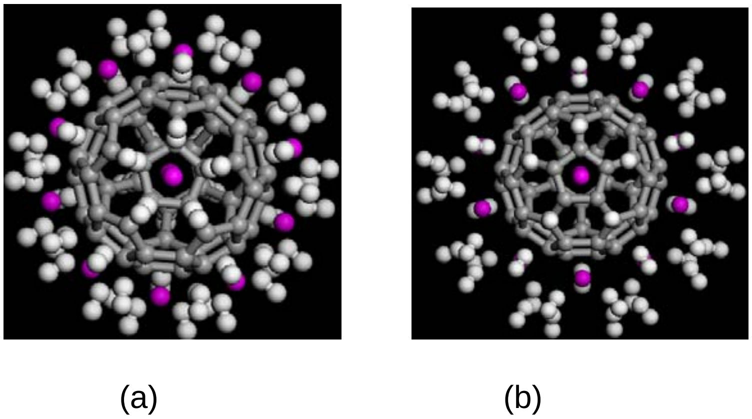
Comparable particles size of impeded metal

b) Density functional theory calculation identifies dihydrogen bond with carbon nanostructure

Recent studies illustrate that metallization of carbon nanotubes and fullerenes may enhance the strength of hydrogen bonding and lead to high gravimetric density. However, choosing the correct metal dopant is essential as they may cluster on the carbon frame and adversely affect the hydrogen gravimetric density. Using density functional theory we show that Li coated C_{60} fullerene may be a potential candidate for hydrogen storage. In particular, $Li_{12}C_{60}$ with the Li atoms located on the 12 pentagonal faces of the fullerene is able to store 120 hydrogen atoms in molecular form yielding a gravimetric density of 13 wt % and a volumetric density of 128 g/L.



DFT Calculation showing:
(a) Geometries of LiC_{60} and (b) $LiC_{60}H_2$. The valence charge density distribution (in white) in $LiC_{60}H_2$ is given in (c)



(a) (b)

(a) Initial and (b) optimized geometry of $Li_{12}C_{60}(H_2)_{60}$
Qiang Sun et al. *Alloys and Compounds,* submitted

Future Plans:

We plan to continue the production and characterization of different carbon nano structures and investigate their interaction with hydrogen. Experimental methods have been developed to try making the dihydrogen nanostructures predicated by theory in our program. For example, electrochemical cell has been constructed in order to electrochemically intercalate Li ions into graphite, fullerenes and carbon nanotubes. The preliminary results of intercalation technique were found to promising. Other techniques are being developed such as electro-crystallization of fullerene in chlorobenzene solution and lithium tetraphenylborate in THF. The electrolytic process will be tuned to control the amount of Li intercalated into the carbon structures. The goal is to achieve controlled nanostructures within a narrow distribution of possibilities.

Characterization of Carbon Nanostructures in Pd Containing Activated Carbon Fibers Using Aberration-Corrected STEM

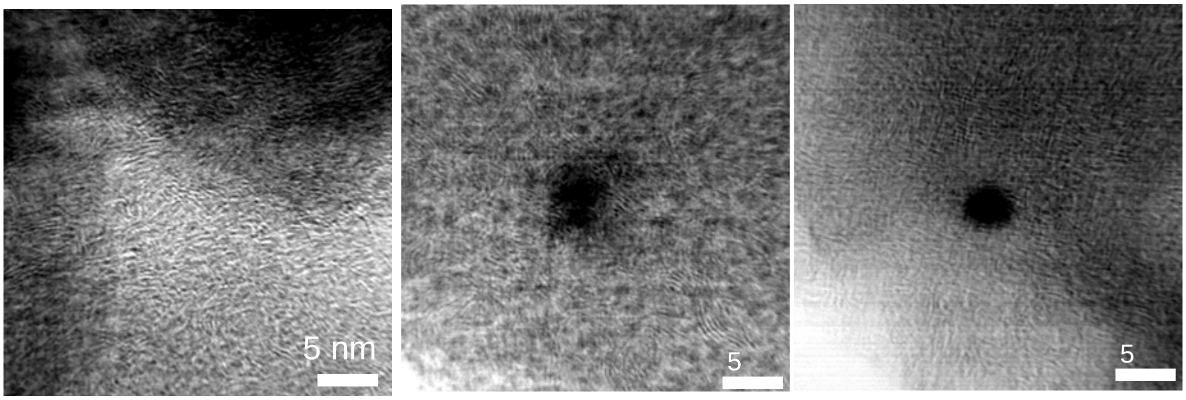
Klaus van Benthem, Xianxian Wu, Stephen J. Pennycook,
Cristian I. Contescu, Nidia C. Gallego
Materials Science and Technology Division, Oak Ridge National Laboratory
Oak Ridge, TN 37831-6114 pennycooksj@ornl.gov

This effort is part of the project on "Atomistic Mechanisms of Metal-Assisted Hydrogen Storage on Nanostructured Carbons". The objective is to obtain an in-depth characterization of atomic structures in Pd-doped activated carbon fibers (ACF) using sub-angstrom resolution electron microscopy, and to correlate these structures with their hydrogen storage properties.

The aberration corrected scanning transmission electron microscope (STEM) at ORNL currently provides a lateral spatial resolution of 0.67 Å, given by the electron beam diameter. The small diameter beam also brings greatly improved sensitivity and allows for single metal atom detection on light supports, such as carbon. Particle size and shape can also be extracted directly from Z-contrast images formed by monitoring transmitted electrons scattered to high angles using an annular detector. A significant advantage of the aberration corrected STEM is that it enables a high quality conventional phase contrast image to be obtained simultaneously with the Z-contrast image; this allows direct imaging of lattice structures in carbon and carbon-supported materials. In addition, measurements of electron energy-loss spectroscopy (EELS) enable the determination of the local electronic structures at about 0.1 nm spatial resolution, and of the local bonding character on carbon atoms. In particular, the K-ionization edge of carbon atoms provides information about the unoccupied local density of states, which is used to quantify the sp^2/sp^3 hybridization ratios.

A series of carbon fiber materials both with and without Pd (in the 1-2 wt% range) were prepared from an isotropic pitch precursor. The fibers were carbonized and activated in CO_2 to various degrees of burn-off. For the Pd-containing ACF, a Pd salt was mixed with the pitch precursor prior to spinning and heat treating. This process differs from the synthesis method of most carbon-supported Pd catalysts where the metal is added to a pre-existing carbon support.

The aberration-corrected STEM was used to characterize the atomic and electronic structure of carbon atoms in the vicinity of embedded Pd particles. Preliminary results show that



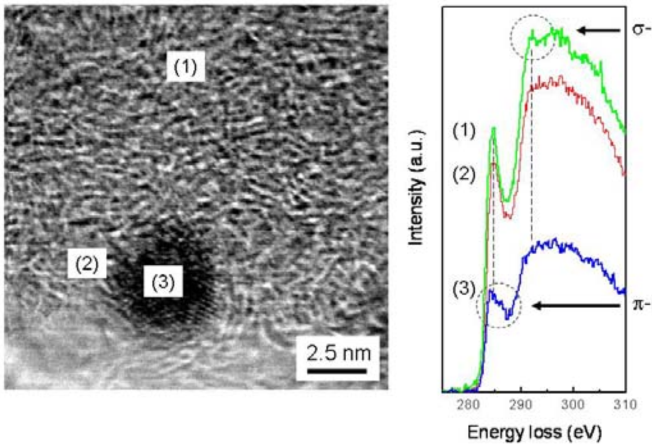
(a) (b) (c)

Figure 1: Coherent bright field STEM images of: (a) carbon structure in ACF without Pd; carbon structure around a Pd particle in (b) Pd-containing ACF before CO_2 activation, and (c) Pd- containing ACF after CO_2 activation (20% burn-off)

the development of atomic structures in Pd-doped carbons is influenced by the presence of Pd particles. The bulk of most materials is amorphous (turbostratic carbon). Small domains of organized carbon nanostructures consisting of quasi-parallel, although undulated, graphene layers were also identified. It seems that most Pd-containing carbons showed the presence of onion-like superstructures, which have not been observed in ACF without Pd (Figure 1).

High resolution images of the Pd-carbon interface in carbonized samples prior to CO_2 activation revealed a significant degree of order in the carbon atoms around the Pd nanoparticles (Figure 1b), although no Pd atoms were seen in the Z-contrast image. These "graphitic" regions were much less visible on materials activated to a 20 % burn-off (Figure 1c) which showed a typical amorphous speckle pattern. It seems that activation in CO_2 not only contributes to development of micro-porosity in carbon, but also frees the Pd particles from surface carbon deposits; this is probably an effect of the catalytic action of Pd during carbon gasification (activation) with CO_2.

The EELS spectra collected at various positions around Pd particles revealed spatial differences between the dominant types of bonding characteristic for carbon atoms. In the vicinity of Pd particles, the bonding character was more of σ*-type, while underneath the Pd particles, the EELS spectra showed slightly modified π* states (Figure 2).



(a) (b)

Figure 2: **(a)** Coherent bright-field STEM image of a Pd particle embedded in activated carbon fibers after 20% burn-off. (b) EELS spectra of the C K absorption edge taken at positions 1, 2 and 3. In the vicinity of Pd particle (positions 1 and 2) the C K-edge reveals a more dominant σ*-type bonding behavior; while underneath the Pd particle (position 3) the C K-edge shows slightly modified π* states.

Future Aspects:

Aberration corrected STEM not only enables the formation of sub-Angstrom electron probe sizes but also greatly decreases the depth of focus due to the use of larger illumination angles. By recording images through the acquisition of through-focal series, STEM imaging becomes a three-dimensional imaging technique comparable to confocal microscopy. In the future, three-dimensionally imaging of the embedded Pd particles will be used to study the three-dimensional shape and distribution of the catalyst particles and the true 3D structure of the surrounding carbon material. Furthermore, this technique will also be combined with electron energy-loss spectroscopy to record three-dimensional sp^2/sp^3 ratio volumes.

Theoretical Investigation of the Energetics of Hydrogen Interaction with Graphene Layers: the Effect of Interlayer Spacing on Hydrogen Storage

Rachel S. Aga, Maja Krcmar, James R. Morris, Chong-Long Fu
Materials Sciences and Technology Division, Oak Ridge National Laboratory
Oak Ridge, TN 37831-6114 fucl@ornl.gov

This theoretical effort is part of the project entitled “Atomistic Mechanisms of Metal-Assisted Hydrogen Storage in Nanostructured Carbon”. The objective is to understand the interactions of hydrogen with graphite-like structures and the role of metal particles on the intercalation of hydrogen on graphene surface.

Although the carbon layers are normally stacked too closely together for hydrogen molecules to fit between graphene sheets, it is believed that high concentration of H_2 molecules can still be sorbed in the graphite lattice. This is based upon first-principles calculations for the dependence of H_2 sorption energy and graphite interlayer spacing on H_2 molecular sorption between two graphene sheets (Figure 1). Although it is highly energetically unfavorable to exist between the graphene sheets, a large number of H_2 molecules can have low sorption energy due to their ability to induce a dramatic expansion of the graphite interlayer spacing. It is also observed that both H_2 sorption energy and graphite interlayer spacing show a non-linear dependence on hydrogen concentration; a substantial decrease in the H_2 sorption energy together with a significant expansion in the graphite interlayer spacing actually occurs within a very narrow H/C atom ratio.

The results suggest that the major barrier in limiting the amount of hydrogen storage in the graphite lattice comes during the initial uptake stage. Thus, it is possible to achieve high hydrogen storage if the difficulty associated with high H_2 sorption energy at the initial sorption stage can be overcome. It is thought that the initial sorption stage is where the presence of metal particles can be beneficial. A metal particle could play the role that not only expands graphite interlayer spacing but provides chemical interaction that lowers the sorption energy of H_2 molecules adjacent to the metal particles. Once these “initial” H_2 molecules are intercalated, further lattice expansion is induced (Figure 1). An expanded lattice would encourage further hydrogen intercalation. The intercalated H_2 molecules reach a lower energy state as the concentration of H_2 becomes saturated.

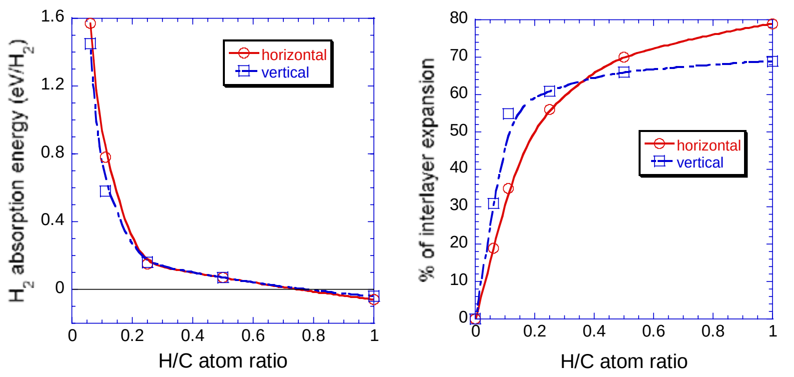


Figure 1 - H_2 sorption energy between two graphene sheets (far left) and the percentage of induced interlayer expansion as a function of H/C atom ratio per graphene layer (left). Both horizontally and vertically-oriented hydrogen molecule axes are considered.

Although preliminary results shown in Figure 1 already indicate the formation of a stable state for H_2 molecules between the graphene sheets, it is unclear if this level of H_2 sorption energy is too small for room temperature sorption/desorption. The sorbed H_2 molecules still have their rotational and stretching degrees of freedom between the graphene sheets. An effective approach to study the temperature and pressure effect on the sorption is to use the grand canonical Monte Carlo (GCMC) method. The technique allows for the determination of the distribution of intercalated particles at a given chemical potential, temperature and volume.

Shown in Figure 2 is the result of a preliminary calculation, using an ideal gas approximation. In the simulation, the interaction of hydrogen molecules with the carbon lattice is described by a Lennard-Jones potential [*J. Low Temp. Phys.* ***41*** *(1980) 611*] and the hydrogen-hydrogen molecular interaction is described by the Silvera-Goldman potential [*J. Chem. Phys.* ***69*** *(1978) 4209*]. The amount of hydrogen uptake shown in Figure 2 is lower than the amount observed in experiments. The discrepancy may be due to the fact that the initial model does not accurately describe the dependence of interlayer spacing on hydrogen concentration. One of the goals of the theory effort is to develop a set of potential energy parameters that can properly describe the interaction of hydrogen in nanostructured carbons such as these graphene layers, based on the results of first-principles calculations.

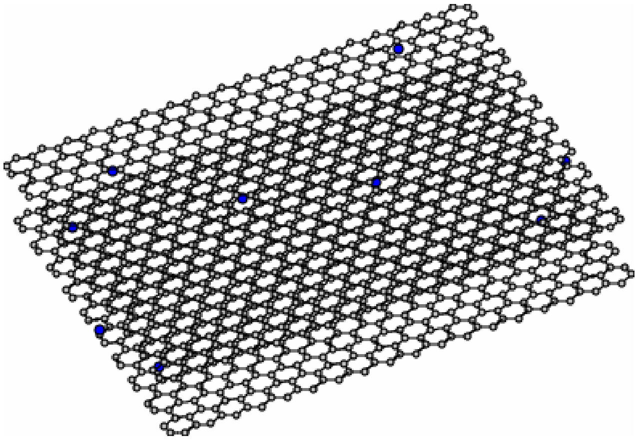


Figure 2 - Preliminary result for the configuration of hydrogen molecules (blue spheres) between two graphene layers, 6 Å apart, at 298 K and 1 MPa. The interaction is described by a Lennard-Jones potential and the hydrogen is assumed to behave as an ideal gas.

The model proposed in the study is fully atomistic, which allows for the study of local structural changes in the graphene lattice. First-principles calculations will be used to complement the simulation results and to obtain a detailed understanding of the change in behavior due to localized structural modifications. The GCMC approach will also be implemented to examine the effect of porosity on the hydrogen sorption. Existing models of activated carbon include “slit nanopores,” which are described by missing regions in the graphene sheets. Clearly, such regions provide pre-existing conditions for expanded interlayer distance that can favor hydrogen sorption. The structure, density, and size of such pores will clearly affect the uptake of hydrogen, and part of the experimental characterization will focus on determining these parameters, as well as the general description of the activated carbon with and without metal additions. The favorable formation of dense hydrogen between the graphene sheets, as shown in Figure 1, may cause hysteresis in the curves. Studying this process may help identify barriers to repeated charging/discharging cycles necessary for practical hydrogen storage.

Neutron scattering aided studies of the design, synthesis and thermodynamics of molecular hydrogen adsorption materials

J. Z. Larese[†*], Lillian Frazier*, Thomas Arnold[†], Michael Farinelli[*], Michael Hu[†], David Beach[†], A.J. Ramirez-Cuesta[+], and R.J. Hinde[*]
[†]Oak Ridge National Laboratory,
Oak Ridge, TN 37831
[*]Chemistry Dept., University of Tennessee, Knoxville, TN, 37996
[+]ISIS Spallation Neutron Facility, Rutherford-Appleton Laboratory, Chilton, England

Program Scope

Our basic research activities relevant to the DOE hydrogen program are part of our larger program in Materials Chemistry. This abstract concentrates on how our combined neutron scattering, thermodynamic, synthetic, and computational investigations of the structure and dynamics of molecular adsorption and liquid entrainment impact the development of new knowledge and materials relevant to the hydrogen initiative. Our program focuses on the development of accurate potential energy surfaces to describe the interaction of molecular hydrogen with solid surfaces and within porous media to ultimately achieve predictive powers to tailor-make new materials.

During the early phases of our investigations, several key milestones have been achieved:

- The application of novel synthetic methods to produce large quantities of morphology controlled pure and doped nm scale metal oxide (MgO, ZnO). In addition, we have produced size adjustable, nm scale, metal oxide and amorphous carbon materials with ordered, uniform arrays of cylindrical channels.
- The use of precise volumetric adsorption isotherm methods to effectively identify the wetting properties and heats of adsorption in gas surface reactions, and to identify thermodynamic regions of interest where neutron scattering studies can be performed on these new materials.
- Identification of the density-structure-dynamics relationship of molecular hydrogen adsorption on MgO(100) surfaces and entrainment within cylindrical channels introduced into porous carbon and aniodically anodized metal oxides materials.
- Development of computational methods to model the adsorption properties and potential energy surfaces.

Recent Progress

(a) *Investigations of the effect of confinement on the structure, dynamics and adsorption properties of molecular hydrogen and hydrogen bearing small molecules.*

Adsorption Isotherms

Volumetric adsorption isotherm techniques are a well-established, widely employed and accurate method to gauge the adsorption properties of porous and high surface-to-volume ratio materials. In addition to defining the gas capacity, isotherms are used to determine the heat of adsorption, the isothermal compressibility, and to delineate phase and wetting transitions. We developed a computer-automated instrument to perform adsorption isotherms volumetrically. This device is used at various neutron facilities for combined *in-situ* thermodynamic and neutron diffraction and inelastic scattering experiments. In Figure 1(a) we illustrate the layering behavior of H_2 on the MgO(100) surface. The step-wise increase in the amount adsorbed clearly shows the formation of at least seven discrete H_2 layers on the MgO(100) surface. By collecting adsorption data at different temperatures we can determine the heats of adsorption that are used to aid and constrain the theoretical models that are developed to describe the interaction of hydrogen with our materials. Naturally, not all materials show the layer-by-layer condensation of molecular hydrogen. In Figure 2 we show several adsorption isotherms performed using D_2 on aligned arrays of cylindrical channels in an amorphous carbon raft. As noted above, these measurements can be used to calculate a heat of adsorption.

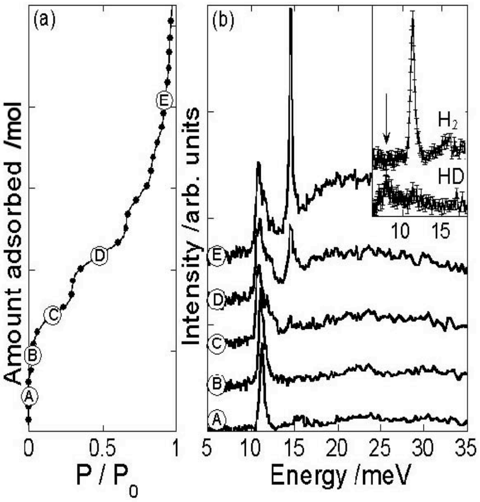


Figure 1. H_2 on MgO (a) 12K isotherm (b) INS spectra recorded at coverages noted in (a).

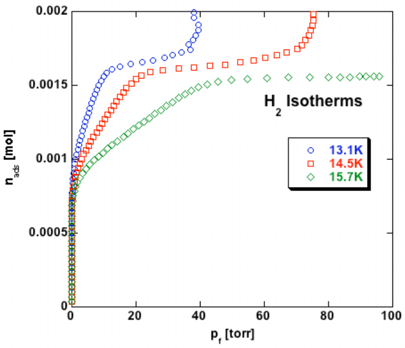


Fig. 2. Adsorption isotherms of H_2 on carbon pore materials.

Neutron Diffraction

Molecular systems confined to planar surfaces or entrained in well-defined channels or pores exhibit distinct diffraction lineshapes that can be used to identify details about the local structure and morphology of the adsorbed phase. Molecular films that grow on surfaces like an ideal 2D solid exhibit characteristic lineshapes that look like a kerf of a sawblade. Such behavior is recorded in our studies of D_2 adsorbed on MgO(100) surfaces in Fig. 3. Here we illustrate the variation of the structure of the solids formed in the layer closest to the surface both as a function of density and temperature. At low coverages the H_2 forms a c(2x2) solid, commensurate with the MgO(100). Our measurements show that by increasing the surface density results in a series of commensurate structures that are of the form (2x2n) where n=2,3,4 this formation of sequential commensurate solid structures is referred to as a devils staircase. Near monolayer completion a

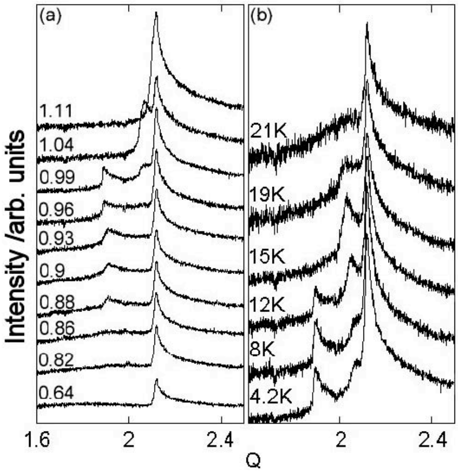


Fig. 3 Neutron diffraction difference scans as a function of (a) coverage (mnl) and (b) temperature (0.9 mnl)

close packed hexagonal phase forms. These diffraction data are being used to constrain and refine the hydrogen MgO interaction potential.

Inelastic Neutron Scattering (INS)

Inelastic neutron scattering is unrivalled in its sensitivity to the dynamical motion of hydrogen bearing molecules. Fig. 1 (b) illustrates coverage dependence of the INS spectra recorded using a time of flight spectrometer TOSCA at the ISIS spallation neutron facility at ~10K at film thicknesses indicated on the isotherm. The energy transfer range where the H_2 free rotor ($J = 0 \rightarrow 1$) transition is observed in the bulk solid (14.7 meV) is highlighted. For surface coverage, $\theta \leq 0.8$ (monolayers) this para-ortho transition occurs at 11.25 meV with an energy profile very close to the instrument resolution function. To our knowledge, such a clean shift in the position of this transition has not previously been observed on any material. To verify that this transition is related to the rotational motion of the molecule we performed an INS measurement at nearly the same coverage with an HD film (see inset to Fig. 1(b)). Although the scattering density of HD is significantly lower than for H_2 we are still able to obtain a small but statistically significant signal at ~ 7.9 meV. When H_2 molecules adsorb non-dissociatively on a surface, H_2–surface interactions mix together the roto-vibrational quantum states of gas-phase H_2 molecules, much like applying an external field to an atom leads to orbital hybridization by mixing together field-free atomic eigenstates. As a result, the energy levels of the adsorbed H2 molecule differ from those of gas-phase H_2 molecules. Using an empirical H_2–MgO adsorption potential energy function to compute the quantum mechanical rotational states of isolated H_2 molecules physisorbed on the MgO(100) surface we find that in the c(2x2) phase (i.e. $\theta \leq 0.8$) the molecules adsorb above Mg^{2+} ions on the MgO(100) surface and that rotational motion is hindered by the attractive influence of the substrate such that it is more planar that spherical in nature. The broadening of the high energy side of the spectrum signals the appearance of molecules not located above the Mg ions while at $\theta > \sim 3$ a signal appears from molecules that see a rotational potential similar to that in the bulk solid.

(b) *Development of synthetic methods to tune/control the composition, morphology and size distribution of novel metal oxides with unique physical and chemical properties.*

Metal oxides are widely used in catalysis, gas separation, sensor technology, micro and optoelectronics, cosmetics and medicine. The production of nanometer scale, well-characterized, pure and doped metal oxides with high surface to volume ratio and thus a large capacity for hydrogen storage and or rapid gas cycling

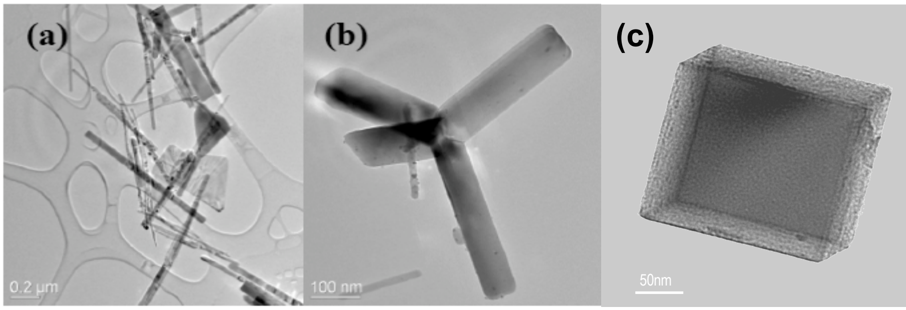


Fig. 4 Sample electron micrographs of ZnO (a) rods and plates and (b) tetrapod and (c) a Typical MgO nanocube.

remains a technological but realistic challenge. Larese and Kunnmann [US. Patent # 6,179,897] have recently developed a unique method for the production of size, morphology and compositionally controllable metal oxide (MO) materials with the formulation M $_{(1-x)}$R$_x$O, where M/R include Mg, Zn, Ni, Li, Cr, Cu, and Sn. To date, our efforts have focused on producing MgO and ZnO compounds (Figure 4). We have recently investigated the synthesis and study (see Figure 1 for adsorption isotherm) of amorphous carbon materials that have an aligned array of hexagonally ordered cylindrical channels. Figure 5 is a typical electron micrograph of the morphology of one of the of these porous carbon materials. The pore diameter is ~2.5nm and the typical thickness of the carbon wafer is about 1 μm.

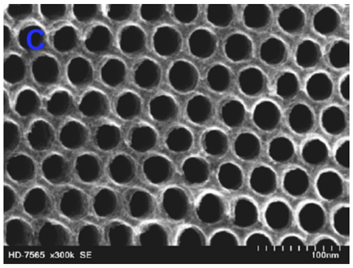


Fig. 5 Electron micrograph of amorphous carbon materials with a hexagonally ordered network of aligned cylindrical Channels.

Recent relevant publications

Arnold, T., S. Chanaa, S. M. Clarke, R. E. Cook, J. Z. Larese. *The structure of an n-butane monolayer adsorbed on Magnesium Oxide (100).* To be published Phys. Rev. B. 2006.

Drummond, M. L., B. G. Sumpter, W. A. Shelton, and J. Z. Larese. *Density functional investigation of the adsorption of a methane monolayer on an MgO(100) surfaces.* To be published Phys Rev B 2006.

Larese, J. Z., L. Frazier, M. A. Adams, T. Arnold, R. J. Hinde and A. Ramirez-Cuesta. *Direct observation of molecular hydrogen binding to Magnesium Oxide (100) surfaces.* To be published Physica B 2006.

Arnold, T., R. E. Cook, S. Chanaa, S. M. Clarke, M. Farinelli, P. Yaron, J. Z. Larese. *Neutron scattering and thermodynamic investigations of thin films of n-alkanes adsorbed on MgO(100) surfaces.* To be published Physica B 2006.

J. Z. Larese, R. Hinde, L. Frazier, T. Arnold, M. Adams, M. Telling and A. Ramirez-Cuesta, *Direct Observation of Molecular Hydrogen Binding to Metal Oxide Surfaces*, ISIS 2005 Scientific Highlights, ISIS Annual Report, Ruthrford Appleton Laboratory, www.isis.rl.ac.uk.

Arnold, T., R. E. Cook, J. Z. Larese. *Thermodynamic Investigation of Thin Films of Ethane Adsorbed on Magnesium Oxide.* J. Phys. Chem. B. 109 (2005) 8799.

Pearce J. V., S. O. Diallo, H. R. Glyde, R. T. Azuah, T. Arnold and J. Z. Larese. *Enhanced Bose-Einstein condensation and kinetic energy of liquid ^{4}He near a free surface.* J Phys.: Condens. Matter. 16 (2004) 4391.

First-Principles Studies of Phase Stability and Reaction Dynamics in Complex Metal Hydrides

Mei-Yin Chou
School of Physics, Georgia Institute of Technology
Atlanta, GA 30332-0430, meiyin.chou@physics.gatech.edu

Program Scope

Complex metal hydrides are believed to be among the most promising materials for developing hydrogen storage systems that are suitable for transportation applications. In order to create the much-needed breakthroughs in this field, we plan to perform extensive theoretical studies on various properties of hydrogen in these complex hydrides. The purposes are

- to understand the fundamental science associated with the intrinsic materials properties of these hydrides, the hydrogen absorption and desorption dynamics, and the mechanisms of catalytic reactions;
- to facilitate materials design and improvement; and
- to explore novel hydrides with various compositions.

We aim to identify and explore materials that have favorable and improved thermodynamic properties by modifications such as alloying and substitution, as well as investigate and understand the mechanisms that improve the kinetics of hydrogen desorption and absorption, such as doping and reduction of the particle size. With the simulations, we will explore and screen the possibilities of forming new complex hydrides with high hydrogen contents from various lightweight metals.

Recent Progress

Lattice dynamics and thermodynamic properties of $NaAlH_4$

We have performed detailed studies on the lattice dynamics and thermodynamic properties of $NaAlH_4$ within the density functional theory and pseudopotential methods. The optimal ground-state structure is investigated within the LDA and GGA approaches. The zero-point motion has a considerable effect on the calculated lattice parameters, giving rise to a volume expansion of $\sim 4.4\%$ for both LDA and GGA.

Born effective charges and dielectric permitivities are calculated within the linear response approach. $NaAlH_4$ exhibits complex vibrational properties at the Γ point. The normal modes are characterized with appropriate assignments within a point group of crystal (4/m). These assignments are related to the mode characters of the T_d point group of individual AlH_4^-. The four group of normal modes can be identified as: low-frequency translational modes, librational modes, hydrogen bending modes, and hydrogen stretching modes. The calculated frequencies are in reasonable agreement with the experiment. The phonon dispersion and phonon density of state also show four separate groups of normal modes. The projected phonon density of states indicates that Na and Al atoms are predominantly involved in the low-energy oscillations, while hydrogen motion dominates the three high-energy groups of modes. The total and projected phonon densities of states are shown in Fig. 1.

A number of thermodynamical properties have been calculated. We have used the quasi-harmonic approach estimate the changes of lattice parameters with temperature and the results indicate an expanding lattice on heating. The expansion is anisotropic, and the crystal expands more along axis c than in the perpendicular direction along axes a. The extent of expansion seems to be correlated with the amount of deviation of the c/a ratio from the ideal value of 2.

We have evaluated the mode Grüneisen parameters, an anharmonicity coefficient for individual normal modes, at a grid of $\mathbf{k}$ points in the Brillouin zone. The largest anharmonicity is detected among the low-energy vibrations, while very small values are found for

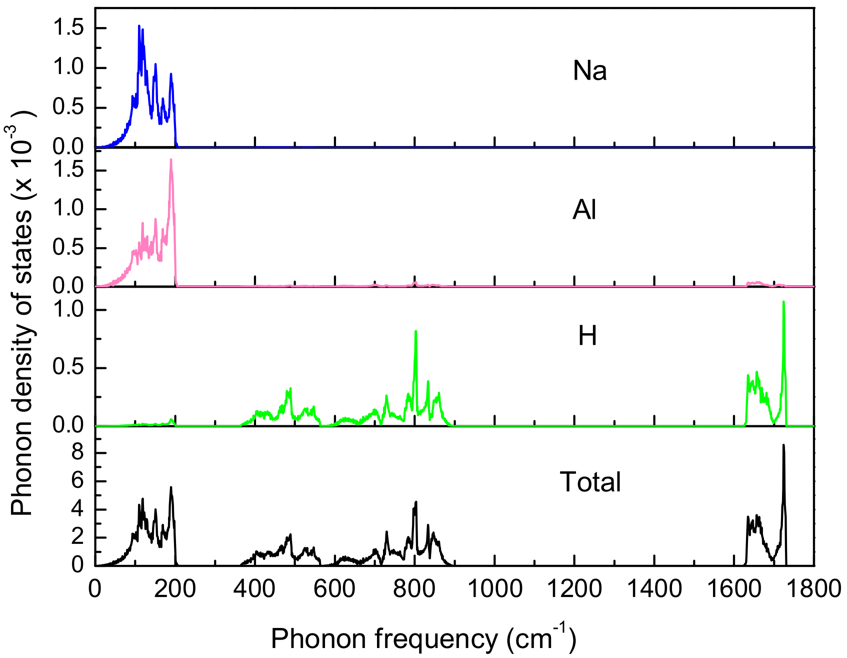


Figure 1: Total and projected phonon density of states calculated using GGA at the theoretical volume.

highest frequency modes. We have also calculated the anharmonic correction to the constant volume specific heat due to thermal expansion. The resulting C_P values for $NaAlH_4$ up to 300 K compare well with the experiment.

The "mobility" of the species in $NaAlH_4$ has been studied through the temperature dependence of the atomic mean-square displacements in the $NaAlH_4$ about their equilibrium position. The results are shown in Fig. 2. A good agreement of Deby-Waller factors with scattering experiments is found. The Lindemann empirical criterion is used to predict a melting temperature, which agrees very well with the observed value. Even at a temperature close to the melting temperature, the thermal energy ($k_B T_m$) is sufficient to excite only the low-energy vibrations involving the translational motion between Na^+ and the AlH_4^- complex. These vibrations are found to be the most anharmonic among all normal modes. This suggests that the melting of $NaAlH_4$ involves the breakup of lattice periodicity by large displacements of Na^+ and AlH_4^-, while Al remains in a tetrahedral coordination with hydrogen, and the Al-H bond is not broken.

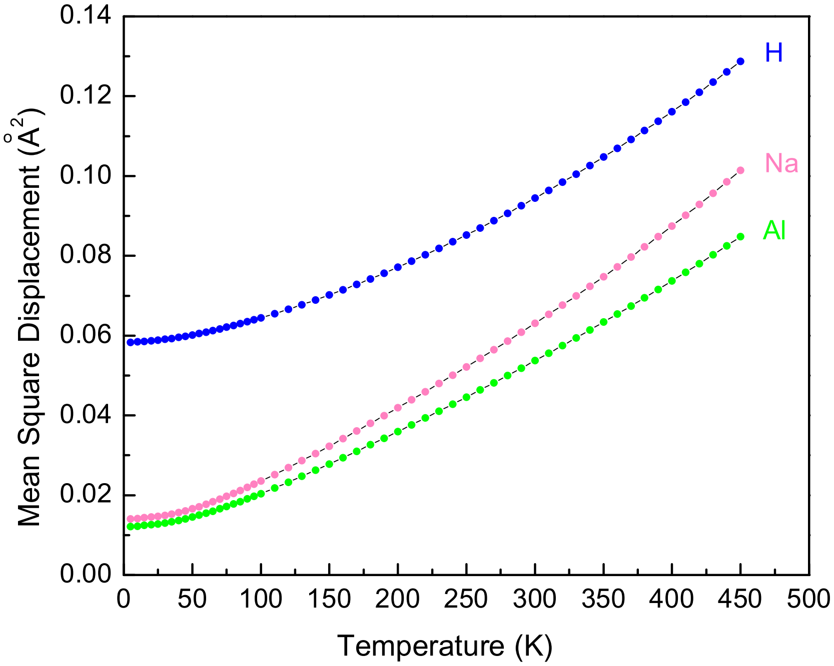


Figure 2: Temperature dependence of the mean square displacements of atoms about their equilibrium positions calculated using LDA.

Future Plans

Although possible mechanisms for the catalyst-assisted desorption process have been proposed in the literature, no definitive experimental conclusion has been drawn despite extensive efforts in the past few years. In general two possibilities exist. The first one is that the catalyst enters the bulk as a dopant and stimulates phase separation and crystal growth inside the material. The second one is that the catalyst does not enter the bulk, but acts as a hydrogen dissociation-recombination site near the surface, and at the same time helps the nucleation of the Al phase. The latter scenario involves a long-range diffusion of certain metal species (possibly in the form of AlH_3) through the alanate to the catalyst near the surface. Our unpublished results do not support the first scenario; therefore, our future plans focus on the surface effects.

Using first-principles simulations, we plan to answer the following questions that will shed light on the mechanism of the catalytic reaction:

1. *If Ti is deposited onto Al surfaces, what is the surface structure and composition ?*
2. *Does this surface facilitate the dissociation of a hydrogen molecule?*
3. *Is the formation of alane oligomers affected by the existence of Ti on the surface?*

Publications

Amra Peles and M. Y. Chou, "Lattice dynamics and thermodynamic properties of NaAlH4: Density-functional calculations using a linear response theory," Phys. Rev. B (in press).

Crystal and electronic structures of $LiNH_2$ and related compounds

J.B. Yang, X.D. Zhou, W.J. James and W.B. Yelon
Materials Research Center, University of Missouri-Rolla, Rolla, MO 65409
Q. Cai
Department of Physics, University of Missouri-Columbia, Columbia, MO 65211

Recently, Li-N-H has attracted much attention as a hydrogen storage material.[1] The crystal structure of $LiNH_2$ was first determined using x-ray diffraction by R. Juza and K. Opp in 1951,[2] and reinvestigated with neutron diffraction in 1972.[3] Its structure appears to be peculiar because the reported distance between the nearest nitrogen and hydrogen atoms, d_{N-H} is only 0.70 Å, which is much shorter than d_{N-H} =1.022 Å for monomeric, unsolvated $LiNH_2$[4] and d_{N-H} = 0.82 Å in Li_2NH.[5] The main problem in the x-ray structural analysis for compounds such as light metal hydrides, with low atomic numbers, is their poor scattering power of hydrogen for the incident x-rays. The intensity of coherently diffracted x-rays is proportional to the square of the atomic number and falls dramatically with the decrease of this value. In contrast, neutron scattering from the hydrogen proton (or alternatively, the deuteron) gives a reliable measurement of the hydrogen location and occupation. Hydrogen possesses a large incoherent cross section (related to processes in which the neutron and hydrogen atom spins flip during the interaction). These processes lead to a large, featureless background in the diffraction pattern, reducing the statistical accuracy of the final result. Thus, deuterium, with a much smaller incoherent scattering cross section, has been employed for many studies. The replacement of the hydrogen with deuterium will improve the statistical accuracy of the measurement, but might not be able to provide information relevant to hydrogen storage in the hydrides, such as chemical bonding and interactions, because the factor of two difference in mass between H and D may affect many properties. Knowledge of the fundamental properties of $LiNH_2$, especially the accurate location of the hydrogen atoms, is critical to an understanding of, and improvement in, the hydrogen absorption and desorption in the Li-N-H system. In addition, it may (or may not) be difficult to obtain deuterated samples of some of the interesting hydrides, but it is obviously easier and less costly to use protonated material for mixed hydrides and for cycling studies. Thus it is useful to determine the limits for which high quality neutron data can be obtained with protonated samples. In this presentation, we report the revised crystal structure for $LiNH_2$ and show data for $LiNH_2$-$LiBH_4$ compounds, using neutron powder diffraction with high sensitivity. We also report a calculation of the electronic structures of $LiNH_2$ based on the resulting structural parameters.

The crystal structures of $LiNH_2$ and $LiNH_2$-$LiBH_4$ system were reinvestigated using powder neutron diffraction with high sensitivity(Fig. 1 and Fig. 2) The $LiNH_2$ compound crystallizes in the tetragonal space group $I\bar{4}$ with lattice parameters a=b= 5.03442(24) Å, c=10.25558(52) Å. It is found that H atoms occupy 8g1(0.2429, 0.1285, 0.1910) and 8g2 (0.3840, 0.3512, 0.1278) sites. The bond lengths between the nearest nitrogen and hydrogen atoms are 0.986 and 0.942 Å, respectively. The bond angle between H-N-H is about 99.97°. These results are significantly different from those of previous experiments. The results confirm our ability to use such a sample with as much as 50% hydrogen (atomic concentration). The electronic structure was calculated according to the revised structural data using the Wien2k code. The full potential linearized augmented plane wave method was employed using the density function theory within the generalized-gradient approximation (GGA) with the exchange correction potential of Perdew-Burke-Ernzerhof-96. The calculated density of states and charge density distribution show strong ionic characteristics between the ionic Li^+ cation and the covalent bonded $[NH_2]^-$ anion (Fig. 3). Room temperature neutron diffraction data have also been collected on milled mixtures of $LiNH_2$ and $LiBH_4$ with different ratios. The samples appear to be nearly single phase[6,7], but the peaks appear to be broadened, probably due to the small crystallite size of the milled mixtures. It will be interesting to follow the peak shapes as a function of temperature. Nevertheless, we expect that detailed structures will be determined by refinement of neutron diffraction data. The structures and hydrogen desorption from $LiNH_2$ and $LiNH_2$-$LiBH_4$ system are being studied at elevated temperature with and without the addition of catalysts, in an effort to determine the role of the catalyst in forming intermediate phases.

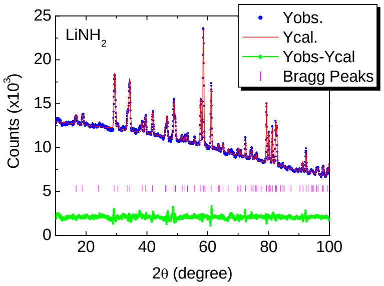


Fig. 1: Neutron diffraction pattern of $LiNH_2$ at RT.

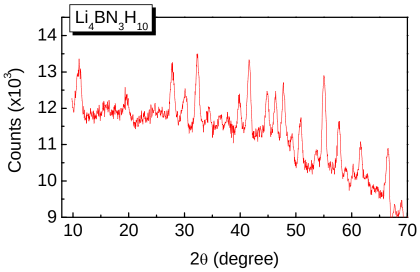


Fig. 2: Neutron diffraction pattern of $Li_4BN_3H_{10}$ at RT

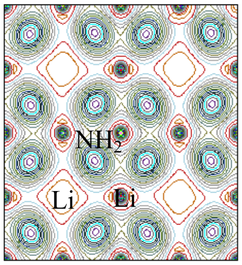


Fig. 3: Valence electron density contours of $LiNH_2$ in the a-b plane. The contour spacing is 0.01 e/Å^3.

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Acknowledgements

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Understanding the Role (and Controlling the Behavior) of Transition Metal Dopants in $NaAlH_4$ Systems

Tabbetha A. Dobbins (tdobbins@latech.edu), Daniela Mainardi, and Yuri Lvov
Institute for Micromanufacturing, Louisiana Tech University

Amitava Roy
Center for Advanced Microstructures and Devices, Louisiana State University

Program Scope

Our research program will develop the fundamental materials science and engineering surrounding the behavior of transition metal catalysts added to complex metal hydrides using synchrotron x-ray studies supported by density functional theory and molecular dynamics calculations. The three-year DOE Contract # DE-FG02-05ER46246 was initiated in September of 2005. The overall goals of the research program are to:

- Study correlations between dopant metal (and dopant oxidation state) with hydrogenation/dehydrogenation kinetics;
- Develop a novel doping scheme using polyelectrolyte layer-by-layer nanotechnology;

and

- Gain insight into hydride powder surface area variations with high energy milling and also with hydrogenation and dehydrogenation cycling.

Dopant effects and hydrogenation/dehydrogenation behavior of sodium alanate ($NaAlH_4$) have been studied extensively making this system well suited to a focused investigation. The work of Bogdanovic and Schwickardi[1] (in 1997) demonstrated reversible hydrogen desorption in the two-step reaction,

$$NaAlH_4 \overset{3.7wt\%}{\Leftrightarrow} 1/3Na_3AlH_6 + 2/3Al + H_2 \overset{1.9wt\%}{\Leftrightarrow} NaH + Al + 3/2H_2$$

after milling with titanium chloride.[1] In 2003, Anton reported the comparative kinetic enhancements results for various transition metals—and revealed that Ti^{2+}, Ti^{3+}, and Ti^{4+} provide the highest desorption reaction rates.[2] However, a study by Sandrock, et al. shows decrease in reversible hydrogen capacities associated with increasing Ti-dopant content—suggesting detrimental effects associated with excess dopant.[3] In studies which have explored the role of Ti dopants using x-ray absorption spectroscopy at the Ti K-edge[4-10], it has been realized that an amorphous $TiAl_3$ phase appears after dehydrogenation and that as-milled systems lead to the formation of nm-Ti or $TiAl_3$ metallic phases. Aluminum deficiency on the $NaAlH_4$ lattice (due to $TiAl_3$ intermetallic formation) is ultimately responsible for controlling hydrogen absorption capacity. The studies supported by this grant will further utilize synchrotron experiments—including small-angle x-ray scattering (SAXS) and x-ray absorption spectroscopy (XAS)—to guide materials engineering solutions related to doping in hydride systems.

Recent Progress

Effect of Mill Time on Dopant Oxidation State

We examined—by x-ray absorption spectroscopy (XAS)—the Ti K-edge for samples milled for various times (Blended– no milling, 1 minute, 5 minutes, 25 minutes, and 125 minutes). The XAS spectra were comprised of both x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectra and were collected at the DCM beamline (CAMD, Baton Rouge, LA). The samples contain 2 mol % $TiCl_3$ dopant. XANES spectra were collected in the fluorescence detection mode at energies between 4900eV and 5300eV (using 0.3eV stepsize near the absorption edge). XAS spectra were collected between 4770eV and 5970eV (using 1 eV stepsize near the absorption edge). The K-edge for pure Ti^0 occurs at 4966eV. The absorption energy may shift by (up to 9eV) depending upon the oxidation state of the absorber atom.

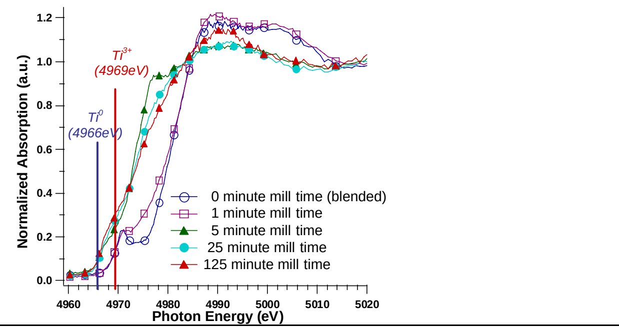

Figure 1. *XANES spectra reveal 5 minute window for transition from Ti^{3+} to Ti^0 oxidation state as indicated by shift in oxidation state from 4969eV to 4966eV. Samples were milled for 1 minute, 5 minutes, 25 minutes and 125 minutes.*

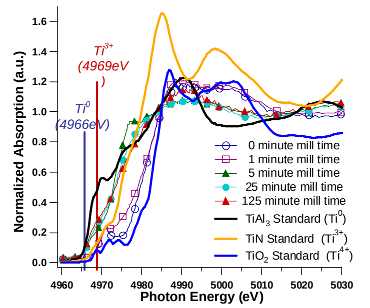

Figure 2. *XANES spectra of standards $TiAl_3$ (Ti^0), TiN (Ti^{3+}) and TiO_2 (Ti^{4+}) overlay spectra collected from samples.*

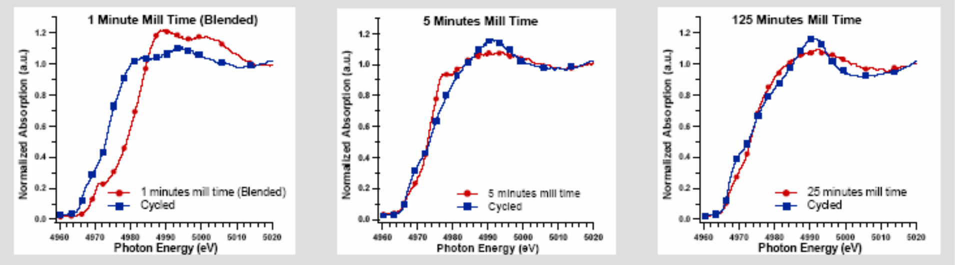

Figure 3. *XANES spectra before and after a single H_2 desorption/absorption cycle for samples milled for 1 minute, 5 minutes, and 25 minutes.*

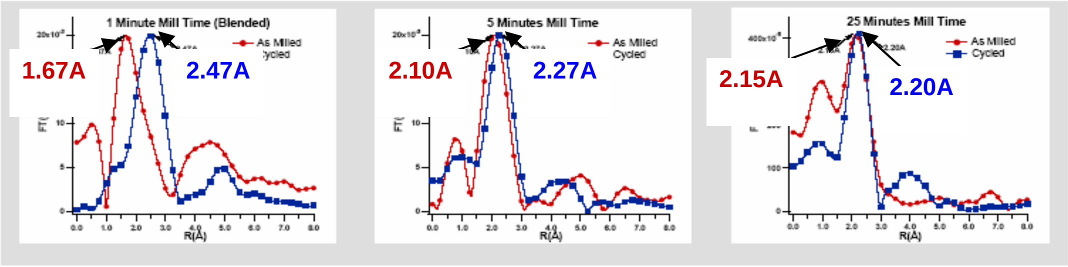

Figure 4. *Fourier Transform of $\chi(k)$ EXAFS signal for samples milled for 1 minute, 5 minutes, and 25 minutes.—shown here as indicator of distance to first coordination shell around the Ti^{3+} or Ti^0 species. Data or not phase shift ($\delta_j(k)$) corrected and only qualitative trends in these radial distribution functions may be found.*

M^{x+} Cation Loaded Polyelectrolyte assembly onto hydride surfaces.

One approach to mitigate aluminum deficiency would be to decrease catalyst content by directly introducing catalyst at the surface of $NaAlH_4$ particles using layer-by-layer self assembly. Because Sandrock, et al.[11] have already demonstrated a decrease in reversible capacities for organic-catalyzed materials in 100-g scaleup $NaAlH_4$ powder beds—care must be taken in the selection of polyelectrolytes. The polyelectrolytes selected for these film applications—polystyrene sulfonate (PSS) and polyallylaminehydrochloride (PAH)—are gas/liquid permeable and stable up to $140^{o}C$. These films, formed on planar silicon substrate test pieces, were studied by XAS—revealing that cations (added using precursor MCl_x) are immobilized in the films between sulfonate groups (of PSS). Figure 5 shows XAS spectra of M^{x+} (where $M^{x+} = Fe^{3+}$, Mn^{2+}, and Ca^{2+} loaded into polyelectrolyte films. The energy vs. normalized absorption data that MCl_x salts undergoes anion exchange from Cl^- to PSS^- anions—leaving M^{x+} immobilized in the PSS in film.

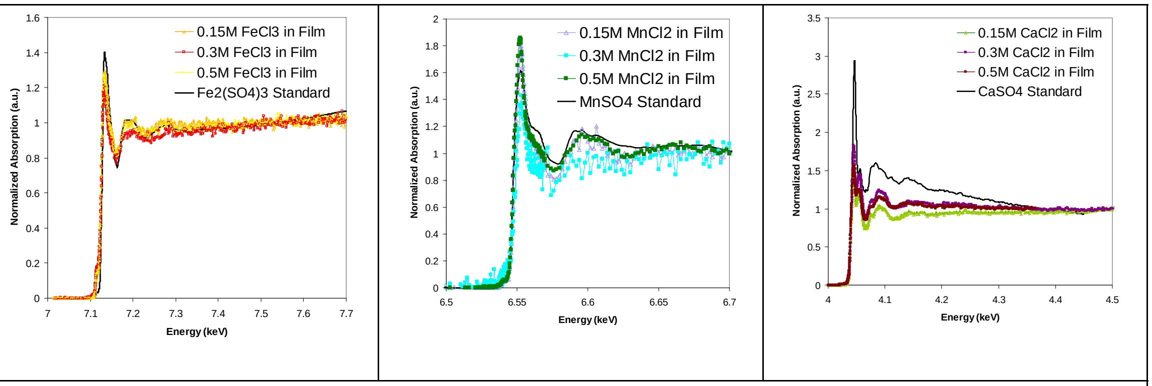

Figure 5. *EXAFS Spectra collected from cation loaded layer-by-layer polyelectrolyte films on planar silicon substrates. Films were assembled from 2mg/mL solutions of PAH and PSS containing dissolved (a)* ***$FeCl_3$; (b) $MnCl_2$ and (c) $CaCl_2$.***

Future Plans

We have used XAS to examine the effect of mill time and our study suggests a 5 minute window of opportunity to control the dopant behavior during milling. We plan to make attempts at tailoring behavior of Ti dopants via…

- Layer by Layer self assembly of films containing dopant cations at the surface of $NaAlH_4$ particles and testing of hydrogen desorption/absorption capacities.
- Co-doping (milling with 2 transition metal salts) of $NaAlH_4$ particles. Bogdanovic, et al. (2000) report synergistic effect while codoping with Fe and Ti (in 1:1 molar ratio).[12]

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1. Dobbins T.A., Tittsworth R., Speakman S.A., Schneibel J., “Synchrotron X-ray Absorption Spectroscopy (XAS) for Understanding Dopant Effects in Ti-doped NaAlH4”, *Advanced Materials for Energy Conversion III, A Symposium in Honor of Drs. Gary Sandrock, Louis Schlapbach, and Seijirau Suda* – ed. D. Chandra, J.J. Petrovic, R. Bautista, A. Imam, pg 263, 2006.
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Integrated Nanoscale Metal Hydride – Catalyst Architectures for Hydrogen Storage

***Yiping Zhao*[a]*, Jin Z. Zhang*[b] *and Matthew D. McCluskey*[c]**
a) Department of Physics and Astronomy, The University of Georgia
b) Department of Chemistry and Biochemistry, University of California – Santa Cruz
c) Department of Physics and Astronomy, Washington State University

Program Scope

By tailoring the structural properties of nanomaterials, the thermodynamics and kinetics of hydrogen adsorption can be designed to satisfy the future hydrogen storage requirements. A fundamental understanding of hydrogen-nanostructure interactions also depends largely on the ability to fabricate nanostructures with the desired structural properties.

Our program goal is to use a novel nanofabrication technique, glancing angle deposition (GLAD), to design and produce metal hydride nanorods and nanowires with different topography, structure, and composition, and to probe how hydrogen interact with different metal hydride nanostructures using in-situ Raman and IR spectroscopic techniques. We hope to investigate the following important issues for hydrogen storage applications: (1) How would different nanoscale structures change the hydrogen storage behavior? (2) Would nanoscale catalysts, incorporated into nanostructured hydrogen storage materials in different forms, greatly enhance the storage behavior? (3) Is there a cost-effective fabrication technique to integrate nanoscale hydrogen storage materials and catalysts?

Our specific aims are:

- Fabricating metal hydride nanostructures with different diameter, separation, alignment, and shape
- Fabricating metal hydride nanostructures with different catalysts and dopants
- Fabricating multilayer metal hydride nanostructures
- Characterizing hydrogen sorption thermodynamics, kinetics and hydrogen-nanostructure interactions

Recent Progress

Currently most of our efforts are focusing on the very initial stage of the project, especially on the further proof-of-concept stage.

(1) ***Designed a unique GLAD fabrication system with two e-beam sources and a glove box.*** Due to the reactive nature of the metal hydride materials, we have designed a very unique deposition system (Fig. 1) that integrates the vacuum chamber and a glovebox together so that the as-deposited nanostructure will not be exposed to any oxygen. This guarantees that we are probing the metal–hydrogen interaction rather than metal oxide-hydrogen interaction. The two e-beam sources will be used for in-situ catalyst and nanostructure fabrication, or multilayer structure fabrication. The system will be delivered to UGA in late May, 2006.

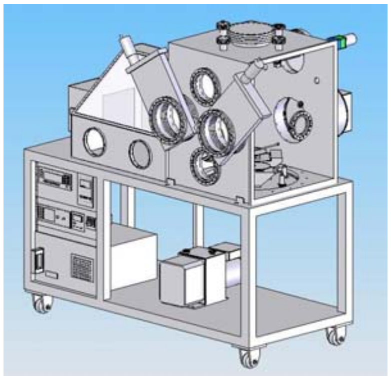

Fig. 1 The unique GLAD system designed for this project.

(2) ***Preparing multilayered nanospring and decorated nanorods (poster).*** To demonstrate the feasibility of

the GLAD technique, we have performed several experiments using the existing lab equipment to fabricate multilayered nano-spring structure, as well as decorated nanorod structures. Figure 2 shows the sketch of the Ni/Si nanospring structure and their SEM and TEM characterization. The magnetic property of this unique structure has been characterized using a vibrating sample magnetometer (VSM). The Au nanoparticle decorated Si nanorod array has also been fabricated.

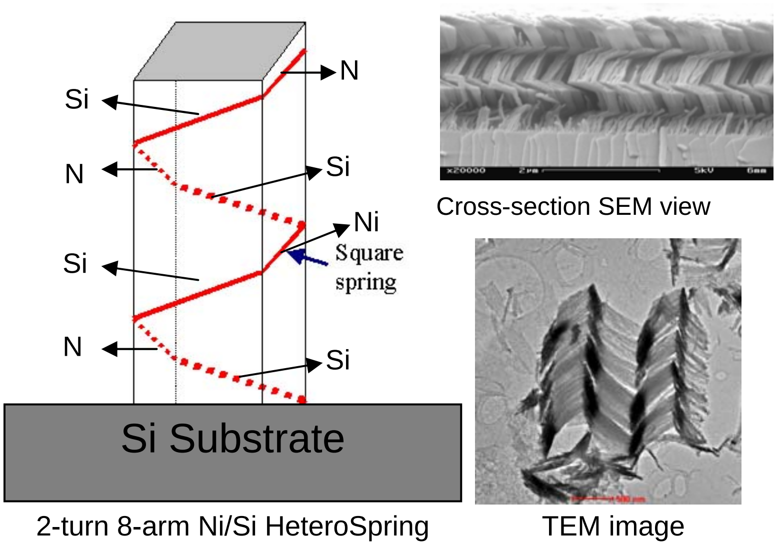

Fig. 2 The Si/Ni nanospring structure fabricated by GLAD.

(3) ***Investigating how the substrate rotation speed affects the growth of low melting point metallic materials.*** The surface diffusion rate of adatoms on a substrate is one of the dominate effects that determine the GLAD growth mechanism. Since Mg is a low melting point metallic material, the adatom surface diffusion is relatively fast. This may play a major role in nanostructure fabrication. With the current lab setup, we have investigated Ag (also a low-melting point metal) nanorod growth for rotation rate of 0 rev/s, 0.05 rev/s, 0.5 rev/s, and 5rev/s, and different morphologies have appeared when characterized by SEM and optical absorbance spectroscopy.

(4) ***Developing vibrational spectroscopic experiments to characterize how the hydrogen is stored in these materials.*** An understanding of the microscopic structure, hydrogen complex concentration, and its interaction with the host material will aid in improving the development of these materials. These will be elucidated using spectroscopic techniques of infrared (IR) and Raman spectroscopy over a range of temperatures and pressures. Currently, the PI Zhang group at UCSC has been conducting hydrogen detection experiments on a model metal hydride of $NaBH_4$. As seen in Fig. 3, we are able to detect hydrogen metal vibrations using a normal Raman scattering technique under standard conditions.

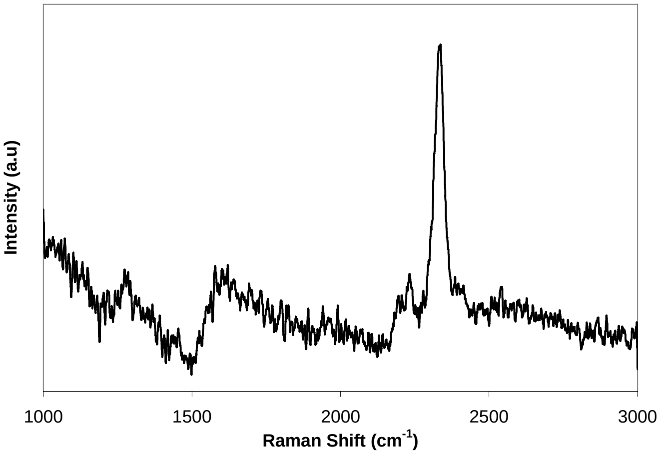

Fig. 3 Raman spectrum of $NaBH_4$ excited with 532 nm laser. The peak at 2230 cm^{-1} and 2340 cm^{-1} represents the asymmetric bending and symmetric stretching vibrations of the molecule, respectively.

The PI McCluskey group is investigating the interaction of hydrogen with ZnO nanoparticles. We synthesized ZnO nanoparticles using wet-chemistry techniques. A transmission electron microscopy (TEM) image (Fig. 4) shows that the average diameter of the nanoparticles is ~15 nm. XRD measurements indicate a wurtzite crystal structure. The nano-powder was pressed into thin pellets (~0.2 mm) for analysis. We found that annealing pellets in hydrogen at a moderate temperature (350°C) results in a dramatic increase in electrical conductivity and free-carrier absorption (Fig. 4). Bulk ZnO, annealed under similar conditions, does not result in these changes. The difference is likely due to the high surface-to-volume ratio of the nanoparticles. These new results will be submitted to Journal of Applied Physics.

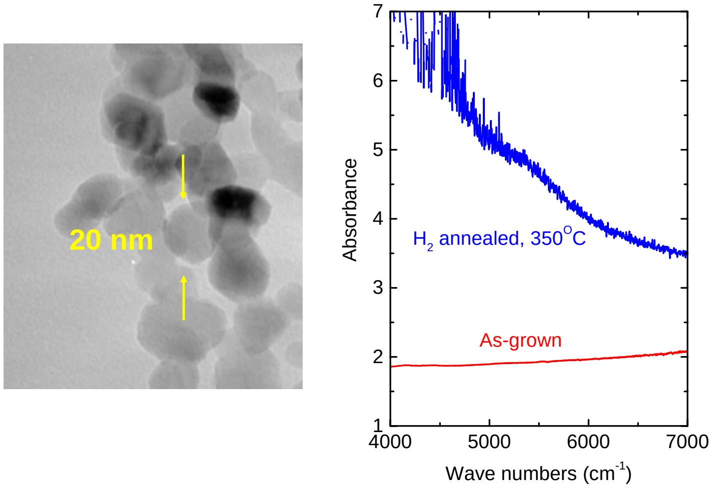

Fig. 4 TEM image of ZnO nanoparticles and Free-carrier absorption of as-grown and hydrogen-annealed ZnO nanoparticles.

Future Plans

With the completion of the unique GLAD deposition system, we will concentrate on the metal hydride nanostructure fabrication and characterization. We will fabricate metal hydride nanostructures with different diameter, separation, alignment, and shape, and with different catalysts and dopants, and multilayers, and perform vibrational spectroscopy characterization during the hydration process. The thermal dynamic behavior of the metal hydride nanostructures will be characterized at Savannah River National Laboratory, and the further characterization of hydrogen-metal hydride nanostructure interaction will be performed by neutron scattering at NIST.

Publications since the beginning of the project

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2. W.M. Hlaing Oo, M.D. McCluskey, and L. Bergman, “Hydrogen in ZnO Nanoparticles,” in preparation.

The Molecular Design Basis for Hydrogen Storage in Clathrate Hydrates

Principal Investigator: Vijay T. John, Tulane University
Co-Principal Investigators: Henry L. Ashbaugh, Tulane University, Gary L. McPherson, Tulane University, Camille Y. Jones, Hamilton College.

Program Scope

Our research objective is to develop new clathrate hydrates as inclusion compounds for hydrogen storage at moderate pressure (<100 bar), approaching 10 wt % hydrogen loading, and at ambient or near-ambient temperatures. This research is focused on a new paradigm in the treatment of clathrate molecular additive design to reinforce the lattice structure of clathrate materials. Specifically, we seek to determine if semi-clathrate materials are capable of encapsulating hydrogen for storage. In semi-clathrate materials, a portion of the guest chemically binds to the host framework, effectively replacing a water molecule in the lattice.[1] The remainder of the guest is then free to interact with the lattice through either van der Waals forces or hydrogen bonding. The strong hydrogen bonding lattice-guest interactions act as an "anchor" to rigidly hold the guest and reduced the translational and rotational degrees of freedom thus increasing the bulk material thermodynamic stability. There are several examples in the literature of semi-clathrate guest interactions with host lattices containing alcohols, phosphine oxides, phosphine sulfides, amines, amides, carbonyls, and aldehyde functional groups. There are also examples of ion pairs acting as host-guest stabilizers.

The research involves a collaboration between the investigators on this project, and a team at Los Alamos National Laboratory (R. Currier and S. Obrey) who are developing novel hydrotrope additives that dramatically reduce the pressure requirements for clathrate formation. The theoretical aspects of the research are complemented by computational studies which is lead by H. Ashbaugh. The research is strongly enhanced by collaboration from C. Jones (Hamilton College) whose expertise is the use of neutron scattering and computational methods for the study of the structure and dynamics of lattice inclusion compounds and molecular solids.

Recent Progress

Research in this project has not yielded any results yet. Due to the effects of hurricane Katrina in New Orleans, the investigators at Tulane have been significantly delayed in starting the work. The University was closed for the Fall of 2005 and the current semester is focused on bringing laboratories back to full operation and rebuilding research. Additionally the intensive teaching schedules to make up for the lost semester have affected faculty progress on research. The PI has just completed hiring research personnel (a post doctoral scholar and Ph.D. student) for the project and is working on setting up the high pressure equipment to characterize hydrogen storage. It is anticipated that results will be forthcoming only in the late summer or Fall of 06.

Future Plans

The following are specific project tasks.

1. Classical thermodynamics and phase behavior of semi-clathrates in the presence of hydrogen. Here we will screen a variety of semi-clathrates for their ability to store hydrogen
2. The Use of Confined Media for Rapid Clathrate Formation. We will evaluate semiclathrate formation in water-in-oil microemulsions (reversed micelles) which have extremely high surface areas for gas-water contact.
3. Characterization of semi-clathrates and hydrogen uptake through neutron scattering (small angle neutron scattering and neutron diffraction) and spectroscopy. We will also undertake novel cryoelectron microscopy techniques to capture the morphology of semi-clathrate structures.
4. Theoretical and Simulation Studies of Semi-Clathrate Stability.

Publications

No publications have resulted from this project to date.

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First Principles Based Simulation of Hydrogen Interactions in Complex Hydrides

Qingfeng Ge (PI) and Jianjun Liu

Department of Chemistry and Biochemistry
Southern Illinois University Carbondale
1245 Lincoln Drive, Carbondale, IL 62901, qge@chem.siu.edu

Project Scope

Our goal is to develop a multiscale approach to model desorption and adsorption of hydrogen in complex metal hydrides. In this initial stage of the project, we started by using density-functional-theory quantum chemical calculations to study the structure of complex metal hydrides and the interactions of hydrogen with the metal atoms in these hydrides. We analyzed the crystal structure of $LiAlH_4$, $NaAlH_4$, $KAlH_4$ as well as $LiBH_4$ and determined the stability of different crystal surfaces of these hydrides. We further studied the thermodynamics of hydrogen desorption from the surfaces by creating hydrogen vacancies on the surfaces. We identified a precursor state for the formation of $TiAl_3$ complex in Ti-doped $NaAlH_4$ and explored its possible roles in reversible hydrogen desorption/adsorption.

Recent Progress

(a) Density functional theory analysis of intrinsic surface properties of complex metal hydride.[1]

Effective on-board hydrogen storage systems are required to have appropriate thermodynamics, fast kinetics, and high storage capacities and densities. Among various possible hydrogen storage technologies, solid-state method offers perhaps the best opportunities for meeting the requirements of on-board application. In particular, alanate-based complex metal hydrides show great promises for meeting the requirements. The alanates release hydrogen through a series of decomposition / recombination reactions,

$$\mathrm{MeAlH_4} \rightleftharpoons \frac{1}{3}\mathrm{Me_3AlH_6} + \frac{2}{3}\mathrm{Al} + \mathrm{H_2} \qquad \text{(R1)}$$

$$\frac{1}{3}\mathrm{Me_3AlH_6} \rightleftharpoons \mathrm{MeH} + \frac{1}{3}\mathrm{Al} + \frac{1}{2}\mathrm{H_2} \qquad \text{(R2)}$$

$$\mathrm{MeH} \rightleftharpoons \mathrm{Me} + \frac{1}{2}\mathrm{H_2} \qquad \text{(R3)}$$

where Me represents Li, Na, or K. For the most widely studied $NaAlH_4$, the first two combined reactions give a theoretical reversible hydrogen-storage capacity of 5.6 wt% at the temperatures lower than 250°C out of a total content of 7.5 wt%. For $LiAlH_4$ and $KAlH_4$, the first two steps would produce a theoretical reversible hydrogen capacity of 7.9% and 4.3%, respectively. The mechanism involves a series of complex steps of heterogeneous reactions and phase transitions. This mechanism is significantly different from the hydrogen storage mechanism in the conventional metal hydrides in which hydrogen atoms are the only mobile species. In this project, low-index surfaces, (001), (010), (100), and (101), have been created by constructing slabs from the relaxed bulk $MeAlH_4$ structures. All the surfaces have been built without breaking Al–H bond of the AlH_4^- unit. The thickness of the slab in each case is about 12 Å and the vacuum region separating the slab from its periodic images is larger than 15 Å. The surface energy, in J/m^2, is calculated by the following formula:

$$\sigma_{surf} = \frac{1}{2A}(E_{stoi} - nE_{bulk}) \qquad (1)$$

where A is the area of the surface unit cell, E_{stoi} and E_{bulk} are the total energy of a stoichiometric slab and the total energy of one formula MeAlH4 in the bulk, respectively. The number of $MeAlH_4$ formula in the slab is represented by n. The results are summarized the Table 1.

In order for alkali alanate to release hydrogen, the Al – H bonds in the compound have to be broken. Therefore, the properties of the defected surfaces formed by removing H atoms from the surfaces have been studied. In general, the formation energy of H vacancies is defined as,

$$\Delta E_{vac} = \frac{1}{2n}(E_{vac} - E_{stoi} + nE_{H_2}) \qquad (2)$$

where E_{vac} is the total energy of the slab with hydrogen vacancy and is a measure of hydrogen desorption energy from the surface the these alanates. The formation energy was averaged over the vacancies in the same unit cell and the factor of 2 accounts for the two-sided slab. E_{H_2} is the total energy of a free H_2 molecule calculated in a large box. The calculated energy costs to create the defects are summarized in Table 2.

Table 1. DFT-GGA surface energy of $LiAlH_4$, $NaAlH_4$ and $KAlH_4$.

	(001)	(010)	(100)	(101)
$LiAlH_4$	0.205	0.176	0.160	0.192
$NaAlH_4$	0.146	0.327	0.327	0.246
$KAlH_4$	0.104	0.132	0.157	/

Table 2. Hydrogen desorption energy (eV) from the surfaces of $LiAlH_4$, $NaAlH_4$ and $KAlH_4$.

	(001)	(010)	(100)	(101)
$LiAlH_4$	1.324	1.472	1.293	1.319
$NaAlH_4$	1.390	1.227	1.308	1.299
$KAlH_4$	1.349	1.369	1.338	/

The energy cost to create a single H vacancy represents the low-limit of the activation energy for hydrogen desorption from an ideal surface. By comparing with our results from an earlier study of $LiBH_4$ study,[2] we found that this energy correlates strongly with the intrinsic H-M bond energy, i.e. H-B >> H-Al (340 vs 284 kJ/mol for gas phase molecules), in the complex hydrides but correlates weakly with the alkali ions.

(b) A precursor state for formation of $TiAl_3$ complex in reversible hydrogen desorption/adsorption from Ti-doped $NaAlH_4$.[3]

Extensive experimental studies of Ti-doped $NaAlH_4$ have led to considerable improvement in the kinetics and cycling performance at the conditions that are relevant to the practical operation of a proton exchange membrane fuel cell. Despite of the progresses, the mechanism and process that the $NaAlH_4$ system is catalyzed by a small amount of Ti is not well understood. In general, the heterogeneous reactions such as hydrogen release and uptake in Ti-doped $NaAlH_4$ are complex and difficult to study. We first established the preferred site of Ti in Ti-doped $NaAlH_4$(001) and focused on three types of sites: (1) Ti is adsorbed on the surface and linked with two neighboring AlH_4^- hydrides; (2) Ti replaces Na^+ in the lattice, making Na^+ displace upward or downward; (3) Ti is located in the interstitial sites and connected with three hydrides. Our results clearly show that Ti in the interstitial sites, with a binding energy of 4.182 eV, is most stable among all these structures. In the relaxed structures, the Ti atom occupies the interstitial space among three hydrides and is bound directly with three Al atoms, as shown in Figure 1(a). This interstitial space is accessible directly from the surface. The stronger affinity of Ti toward H than Al makes Ti strip hydrogen from Al. We refer it to as $TiAl_3H_x$ for simplicity but note that Ti-H bonds are formed

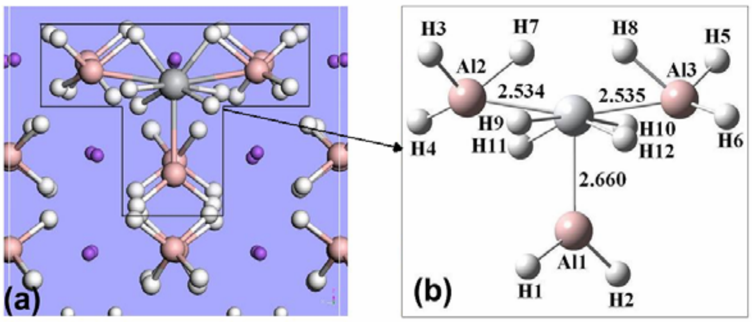


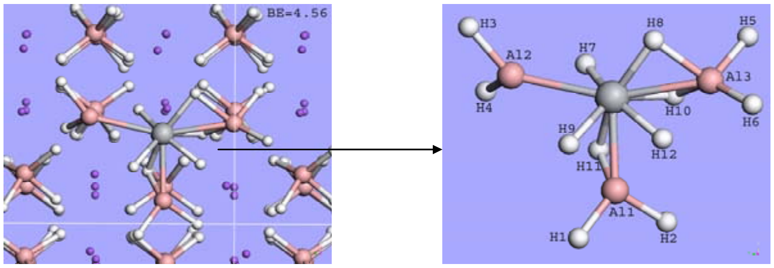
Figure 1. (a) GGA-relaxed structure of Ti-doped $NaAlH_4$(001) with Ti in the interstitial space; (b) Detailed local structure of the $TiAl_3H_x$ (x=12) complex shown in (a).

in the complex structure. The detailed local structure of a $TiAl_3H_x$ complex with x=12 is shown in Figure 1(b). We then studied the energetics of hydrogen desorption on the basis of the most stable structure determined above. Herein, we define desorption energy as the total energy difference between the Ti-doped stoichiometric slab and the sum of the slab with hydrogen atoms removed and hydrogen molecules. Hydrogen desorption energies with hydrogen atoms from different positions of the complex structure shown in figure 1b were summarized in Table 3. For comparison, we also calculated the energy cost to desorb a pair of hydrogen atoms from the same AlH_4^- unit on the (001) surface of pure $NaAlH_4$. This energy is 1.383 eV per H_2 molecules. Clearly, to desorb hydrogen from the Ti-containing complex is energetically favorable over the direct desorption from pure $NaAlH_4$. Furthermore, the energy required to desorb the first 4 hydrogen molecules from the complex is ~3.3 eV, indicating that the heat released from doping the Ti atoms would be sufficient to maintain the energy balance.

Table 3. DFT-GGA hydrogen desorption energies with different combinations of hydrogen atoms in the local structure $TiAl_3H_x$ (x=12) shown in Figure 1b.

Combination of hydrogen atoms	Desorption energy (eV/H_2 molecule)
H1,H2	0.515
H3,H4,H5,H6	0.921
H9,H10	0.934
H11,H12	1.265
H7,H8	2.067

The complex $TiAl_3H_x$ structure may play important roles in the reversible hydrogen release/uptake in Ti-doped $NaAlH_4$. Similar structures were also found in Ti-doped $NaAlH_4$(010) surface, as shown in figure 2. Our calculations showed that desorption of two bottom hydrogen atoms and four side hydrogen atoms caused hydrogen atoms of the neighboring AlH_4^- units to migrate to the Al atoms of the complex. This process is illustrated in figure 3 in which two side hydrogen atoms (H5 and H6) in figure 1(b)) were removed.[4] After the relaxation, direct bonding interactions between Al atoms in the complex and the neighboring AlH_4^- units starts to develop. This will enable hydrogen migration across different hydrides units. The migration of hydrogen during relaxation after desorbing hydrogen indicates that the barrier for hydrogen diffusion across different AlH_4^- units is small. The small diffusion barrier of hydrogen from surrounding AlH_4^- units to the complex structure helps to sustain the hydrogen desorption until the hydrogen in the surrounding region become sufficiently depleted. Complete dehydrogenation will lead to the formation of $TiAl_3$ dispersed in a predominantly Al phase. Rehydrogenation may start at the dispersed $TiAl_3$ complex with the formation of $TiAl_3H_x$ complex structure. As the structure became saturated with hydrogen, diffusion of hydrogen from $TiAl_3H_x$ to the neighboring Al site may take place. Alternatively, Ti may migrate to a new Al dominated site and form a new $TiAl_3$ complex. Hydrogenation will be repeated at the new complex structure. All these arguments support that the $TiAl_3H_x$ complex structure is active in dehydrogenation/hydrogenation processes. Furthermore, this complex does not exclude the presence of Ti hydrides during hydrogenation and reformation of $NaAlH_4$. The high desorption energy of two bridging hydrogen atoms bound



Figgure 2. (a) GGA-relaxed structure of Ti-doped $NaAlH_4$(0101) with Ti in the interstitial space; (b) Detailed local structure of the $TiAl_3H_x$ (x=12) complex shown in (a).

to Ti and two side Al atoms may provide explanation of the Ti-hydrides observed experimentally, We are currently working on mapping out the reaction pathways for hydrogen desorption through this complex and determining the transition states and reaction barriers for hydrogen migration and desorption. The understanding from these studies will not only help us to establish the mechanism for this particular system but also to understand the mechanism of similar heterogeneous reactions.

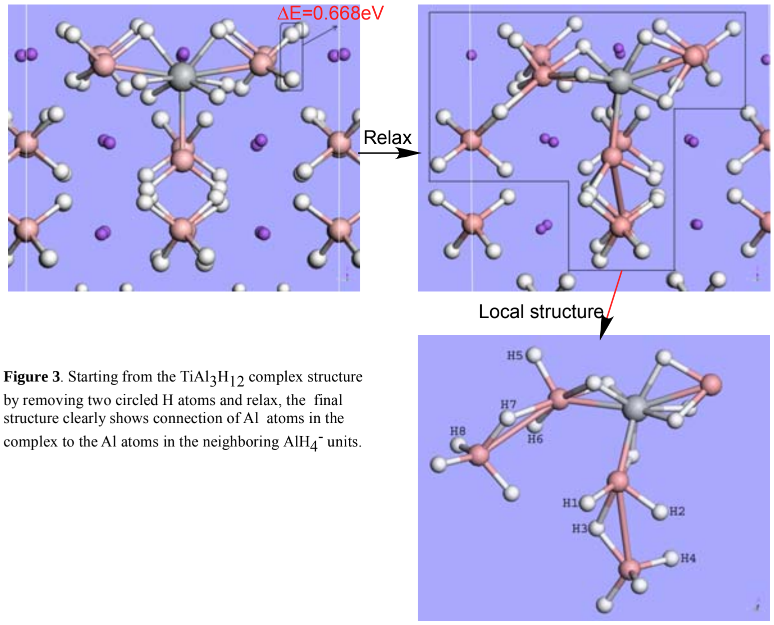


Figure 3. Starting from the $TiAl_3H_{12}$ complex structure by removing two circled H atoms and relax, the final structure clearly shows connection of Al atoms in the complex to the Al atoms in the neighboring AlH_4^- units.

Future Plans

Based on the results obtained in the initial stage of the research, we plan to further explore the role of Ti in hydrogen desorption and adsorption of Ti-$NaAlH_4$. Our preliminary *ab initio* molecular dynamics (MD) study shows some promising results in this direction. For example, octahedral coordinated Al moieties that may lead to AlH_6^- formation were identified during the molecular dynamics runs. More extensive *ab initio* MD calculations would allow us to develop a more complete picture of the potential energy surface. Therefore, we will

(a) Perform more electronic structural calculations for Ti-doped $NaAlH_4$ to establish the mechanism of hydrogen desorption.
(b) Carry out more extensive *ab initio* MD calculations for Ti-doped $NaAlH_4$ to understand the dynamic nature of the heterogeneous process and to establish a working model for hydrogen desorption/adsorption in complex metal hydrides.
(c) Extend the research to $LiAlH_4$ and $LiBH_4$ and to examine the effect of dopants such as Ti on those complex metal hydrides.
(d) Examine particle size effect by calculating hydrogen interactions in the clusters of Ti-doped $NaAlH_4$ with vary sizes.
(e) Attempt large scale tight-binding MD simulation and/or dynamic Monte Carlo simulation based on the understanding developed at molecular scale.

We hope the understanding achieved through these research activities will help to develop advanced materials with greatly enhanced performance for efficient hydrogen storage.

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Dehydrogenation of Boron-Nanoclusters

Aashani Tillekaratne and Michael Trenary
Department of Chemistry
University of Illinois at Chicago
845 W Taylor Street
Chicago, IL 60302 mtrenary@uic.edu

Program Scope

This new research program is designed to test the hypothesis that at a certain length scale the three-dimensional boron structural units found in certain boron-rich solids can be reversibly hydrogenated in the presence of a suitable catalyst to form boranes and/or carboranes with similar three-dimensional boron units. Of the elements lighter than carbon, only boron forms a rich array of compounds with high hydrogen weight percentages. The ability of boron hydrides to release their hydrogen and for the remaining boron nanoclusters to reabsorb hydrogen is being investigated. To promote the hydrogenation-dehydrogenation reactions, the boron clusters are being studied while in contact with a platinum surface, as platinum is a well-known hydrogenation-dehydrogenation catalyst. Since the reactions are intrinsically surface processes, a variety of surface science methods are being used, including reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD). The PI's laboratory is well equipped to obtain RAIR spectra of molecules present at submonolayer coverages with exceptional sensitivity and resolution [1, 2]. The overall program entails the following components:

- RAIRS and TPD are being used to study the adsorption, chemical stability, and dissociation of decaborane, $B_{10}H_{14}$, on a Pt(111) surface under ultrahigh vacuum conditions.
- Analogous to the $B_{10}H_{14}$/Pt(111) studies, other boron cage molecules such as carborane, $C_2B_{10}H_{12}$, will also be investigated by the same techniques.
- A new apparatus that will allow RAIRS studies of hydrogenation-dehydrogenation reactions under high H_2(g) pressure conditions is being constructed.
- A second apparatus that will allow transmission IR studies of hydrogen interactions with boron nanowires prepared ex-situ is also being constructed.
- The interpretation of the experimental spectra is being aided with density functional theory calculations of small model clusters.

Recent Activity

Figure 1 shows the structure of a decaborance molecule, which has the structure of an 11-sided deltahedron lacking one boron atom and as is typical of the polyhedral boranes, it possesses terminal B-H bonds and bridging H-B-H bonds. Figure 2 shows hydrogen temperature programmed desorption (TPD) data after dosing decaborane onto the surface at low temperatures. It reveals that the molecule is dehydrogenated on the

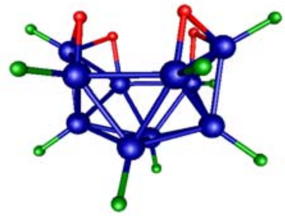

Figure 1: Structure of decaborane showing terminal hydrogens(green) and bridging hydrogens(red).

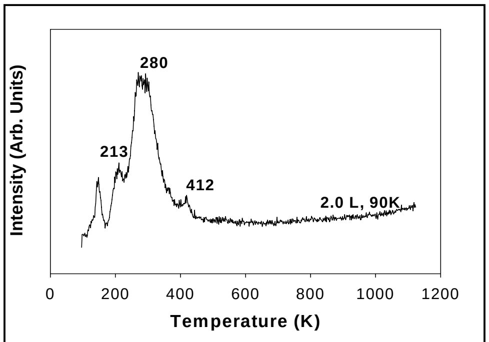

Figure 2: Hydrogen TPD after dosing 2.0 L of $B_{10}H_{14}$ at 90 K.

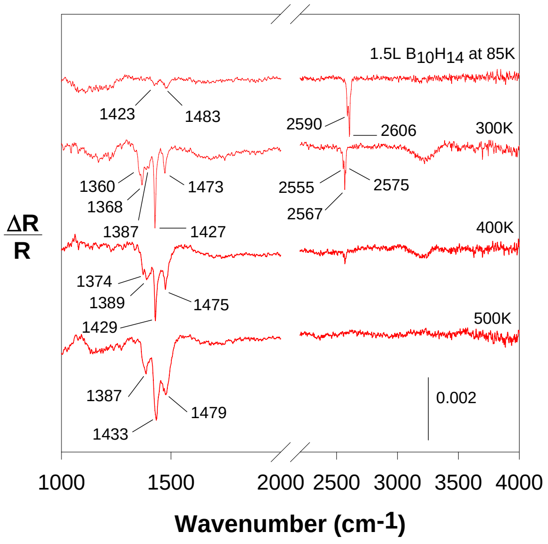

Figure 3: RAIR spectra of B10H14 on Pt(111)

surface in stages, with the final hydrogen loss occurring at 412 K. The lower temperature peaks are probably due to fragmentation associated with the desorption of a mulitlayer of decaborane, which gives rise to a peak at 255 K. More information on the thermal evolution of decaborane on Pt(111) is revealed by the RAIR spectra shown in Figure 3. After a 1.5 L (1 L = 1×10^{-6} Torr sec) exposure at 85 K, peaks in the BH stretch region at 2590 and 2606 cm^{-1}, and peaks at 1423 and 1483 cm^{-1} that correspond to deformations of the boron cage structure appear. As the sample is annealed to increasingly higher temperatures, the changes in the spectra reveal that the molecule undergoes dramatic changes associated with dehydrogenation. The 300 K anneal results in a new set of B-H stretch peaks at 2555, and 2567, with a shoulder at 2575 cm^{-1} along with a new set of more intense peaks in the boron cage region. The latter peaks persist even after the BH stretch peaks completely disappear after the 500 K anneal. The most obvious interpretation is that while hydrogen is removed from the molecule, the boron cage remains intact covering the surface with small nanoscale boron clusters. Moreover, the latter entities clearly have a high stability on the surface. Information on the structure of the boron clusters will be obtained by comparing the spectra to spectra calculated using DFT for clusters of various assumed structures. Experiments to determine if the boron structures can be hydrogenated are ongoing.

Future Plans

a) Dehydrogenation of Carborane on Pt(111)

Following the decaborane studies described above, we will shift to studies of the surface chemistry of 1,2-*closo*-dicarbadodecaborane, $C_2B_{10}H_{12}$, (also known as *ortho*-carborane, or just carborane) under ultrahigh vacuum conditions. This compound is an air stable solid with a modest vapor pressure at room temperature that can be easily dosed onto surfaces using standard techniques. It has the structure of a distorted icosahedron with similar B-B bond lengths as in the distorted CB_{11} icosahedra that form the basic structural unit of boron carbide. Although carboranes have been used as precursors for the deposition of boron carbide thin films [3], their dehydrogenation chemistry has not been explored on surfaces. More importantly, it has not been established in previous studies if the boron cage structure of carborane remains intact in the course of the chemical reactions leading from molecular carborane to boron carbide films. Similarly, the ability of boron carbide thin films to be rehydrogenated to carborane-like entities has not been studied.

b) RAIRS Studies under High H_2 Pressures

To fully explore the hydrogenation chemistry of boron cage structures, a new apparatus will be constructed that will allow RAIRS experiments under an ambient pressure of hydrogen up to one atmosphere. As a homonuclear diatomic molecule, $H_2(g)$ does not absorb infrared radiation and the presence of gas phase hydrogen will not interfere with the RAIRS studies. The new apparatus will permit the investigation of surface hydrogenation/dehydrogenation reactions at an unprecedented level of detail. To help identify the surface species present, the experimental RAIRS spectra will be compared with spectra calculated for likely surface species using density functional theory calculations, as is currently done in the PI's laboratory [4].

c) Transmission IR Studies of Boron Nanowires and Nanoribbons

In a third phase of the project, the hydrogenation chemistry of boron nanowires and nanoribbons will be studied using transmission IR. An apparatus similar to one currently used elsewhere [5] for transmission IR studies of carbon nanotubes is being constructed. In these studies the boron nanostructured materials will be prepared in a simple CVD apparatus as developed elsewhere [6, 7] and then pressed into a high transparency tungsten mesh, which is in good thermal contact with a sample holder. The IR spectra will then be studied over a wide range of temperatures from 77 to over 1000 K. The ability to heat the structures to high temperatures in vacuum, will permit any surface oxide to desorb, thus exposing boron dangling bonds at the surface. These bonds should readily react with hydrogen to form a hydrogen-terminated surface. The B-H bonds can then be characterized with IR spectroscopy. Given the strong IR absorption coefficients associated with B-H bonds [8], and the high surface areas associated with the nanostructured material, we expect to have excellent signal-to-noise ratios in the BH stretch region. The studies will not only allow us to characterize the hydrogenated surface, but also to measure spectra as a function of annealing temperature to thereby establish the thermal stability of the hydrogenated structures.

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NMR studies of metal-hydrides: $MgScH_x$

Mark S. Conradi[1], Robert C. Bowman, Jr.[2], Timothy Ivancic[1], Michael P. Mendenhall[1], Peter H. Notten[3], and W. P. Kalisvaart[4]
[1]Washington University, Department of Physics, St. Louis, MO
[2]Caltech and Jet Propulsion Lab, Pasadena, CA
[3]Philips Research, Eindhoven, NL
[4]Eindhoven University of Technology, NL

Program Scope

Our research program focuses on *in situ* NMR studies of solid-state hydrogen storage systems. In particular, NMR measurements at the high temperatures and/or high pressures of the dehydriding and rehydriding reactions offer the best opportunity of detecting and identifying the mobile species that must be present, as well as the chemical intermediate species that are crucial to the reactions. For example, we expect to identify mobile H atoms in partially dehydrided $NaAlH_4$. From high-field measurements on the nuclear spins of catalytically active species like Ti and Sc, we will determine the local environment of the catalyst atoms in terms of the neighboring nuclear spins, using spin-echo double resonance.

Recent Progress

(a) Kinetics of hydrogen atom hopping in Mg-Sc alloy hydride.

(Poster presentation by Mark Conradi)

Background: The research group of Notten at Philips has recently shown Mg-Sc metastable alloys to be effective systems for hydrogen storage and metal-hydride battery electrodes[1-3]. The motivation behind this alloy system is to capture desirable features of both end-members. At one end, MgH_2 has a high hydrogen storage capacity of 8 wt%. However, the binding is of ionic character and this is believed to result in the very slow diffusion kinetics of H in MgH_2. The equilibrium H_2 pressure is on the low side at 1 atm at T = 278 C, but this is not a severe disability for electrochemical applications. At the other end is ScH_2 with approximately 4 wt% storage but the superior diffusion kinetics typical of interstitial metallic hydrides. The H_2 equilibrium pressure of the two-phase plateau region is very low at 1 Torr at 740 C.

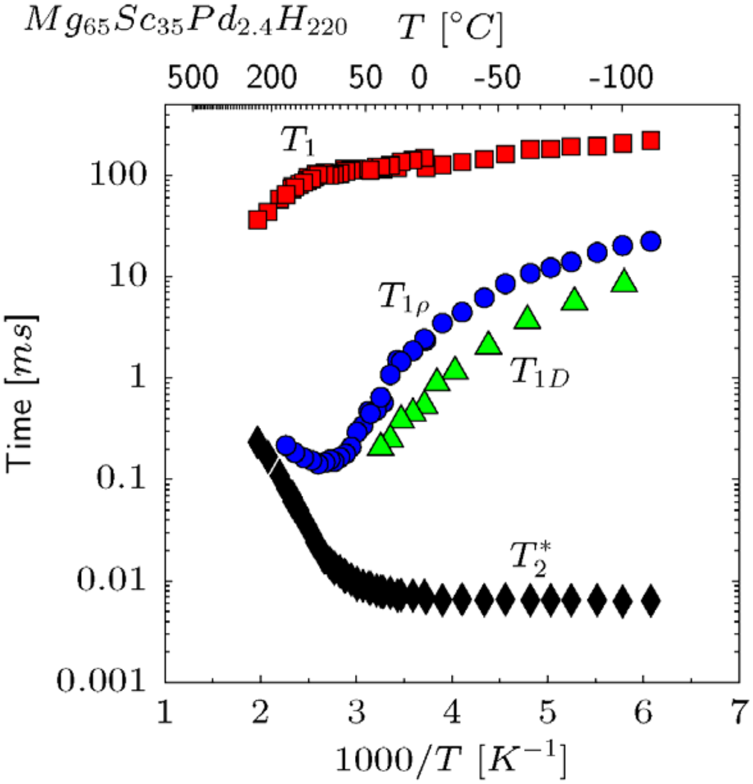
The Mg-Sc alloy hydrides take on the fluorite structure[3], as does ScH_2, for Mg fractions $\leq 80\%$. At higher Mg fractions the structure is rutile-like as for MgH_2 and it appears the charging kinetics suffer markedly as a result. The alloys show high storage capacity of 6.7 wt%, in approximate agreement with the simplistic (local) view that each Mg supports 2H and each Sc supports 3H; here the expanded lattice is believed to allow the additional H on Sc beyond the usual ScH_2. Mg-Ti alloys have similar behavior to Mg-Sc, but should be much less costly[4]. However, even in thin films for electrochemical applications, the charge/discharge kinetics of $MgScH_x$ are slower than one would like. The kinetic bottleneck may be slow diffusion of H through the alloy or slow kinetics at the electrode surface (despite use of a Pd overlayer).

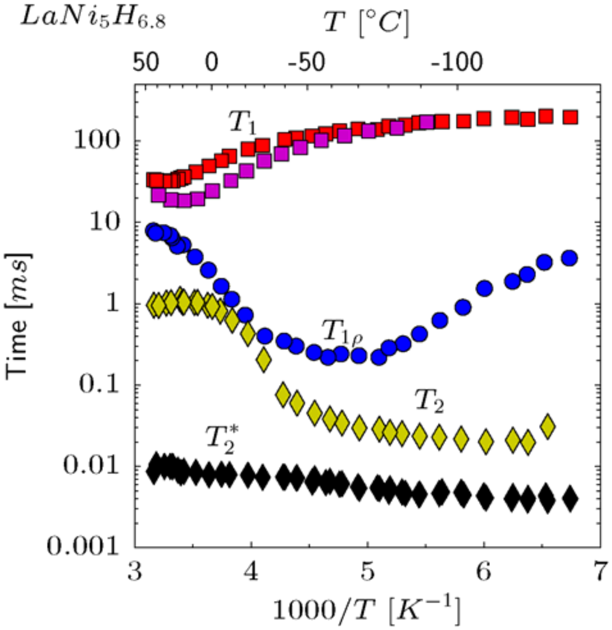
While gearing-up for *in situ* studies of complex hydrides, we have measured and report here the temperature dependence of the H hopping rate ω_H in $MgScH_x$, as determined by NMR relaxation times.

Methods: Bulk $Mg_{65}Sc_{35}Pd_{2.4}$ was synthesized by WPK at TUE and loaded with H_2 to $x = [H]/[M] = 2.2$ from the gas phase. Samples were loaded into glass NMR tubes under 0.9 atm of N_2 and sealed at a neck with a flame. RF field penetration into the powdered metallic sample was judged to be good from measurements of rf pulse lengths for π/2 and π nutations, compared to a water reference sample.

Relaxation times were measured with a homebuilt pulsed, superheterodyne NMR spectrometer with 4 transmitter phases and quadrature-detected receiver. The transmitter power to the probe was about 80 W. Pulse sequences were generated with a combination of TTL hardware and a Pulse Blaster card. The NMR acquisition and analysis software was written locally. T_1 was determined with inversion-recovery and repeated-saturation-recovery schemes. T_2 was measured from the decays of free-induction signals (T^*_2), two-pulse (Hahn) echoes, and CPMG echo trains. Continuous (not chopped) spin-locking with $\gamma B_1/2\pi = 50$ kHz was used to measure $T_{1\rho}$. The relaxation of the dipolar-ordered state (T_{1D}, essentially $T_{1\rho}$ in zero amplitude field) was measured using a phase-alternated version of the Jeener-Broekaert three-pulse method.

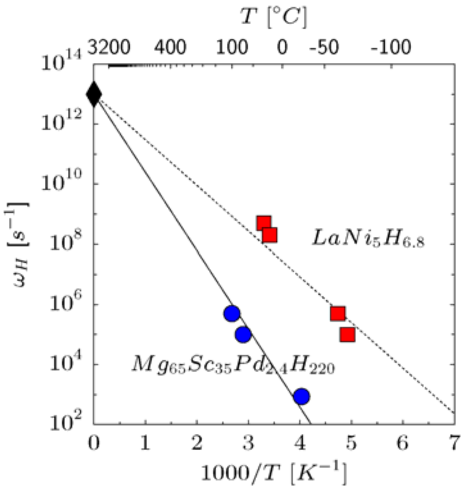
Results: The relaxation times for $Mg_{65}Sc_{35}Pd_{2.4}H_{220}$ are presented as a function of reciprocal temperature in the figure below. The data can be understood by realizing that T_2 begins to increase (motional averaging) when the H atomic hopping rate ω_H is about 10^5 s^{-1}. The $T_{1\rho}$ minimum corresponds to $\omega_H = 5 \times 10^5$ s^{-1}, and a T_1 minimum at 21 MHz would reflect $\omega_H = 2 \times 10^8$ s^{-1}, but evidently the available temperature range is too low to reach such a fast rate of H motion. One sample was heated to 300 C for about one hour and suffered irreversible changes (e.g., T_1 was different upon returning to 25 C). The time T_{1D} is, to within a factor of two, equal to the mean hopping time, $1/\omega_H$, a strong-collision result.





For comparison, similar data for $LaNi_5H_{6.8}$ are presented in the above figure. This material was synthesized at JPL and hydrided at WU by MPM. Comparing the figures, it is obvious that specific features such as the $T_{1\rho}$ minimum occur at much higher temperatures in $MgScH_x$ than in $LaNi_5H_{6.8}$. Thus, at a given temperature the H motion in $MgScH_x$ is much slower (by factor of ~3000) than in $LaNi_5H_x$. This demonstrates that slow internal kinetics are a substantial reason for the slow kinetics of MgSc film electrodes.

The relaxation map of the lower figure shows the log of ω_H as a function of reciprocal temperature for both materials. The data points are from a T_1 minimum, $T_{1\rho}$ minima, and the onset of line narrowing (lengthening of T_2). In each case, the attempt frequency ω_a is approximated as 10^{13} s^{-1}, corresponding to $1/T = 0$, providing an additional point on each line. The straight line fits correspond to $\omega_H = \omega_a \exp(-\Delta E/kT)$; the activation energies $\Delta E/k$ are 6000 K and 3500 K for $MgScH_x$ and $LaNi_5H_x$, respectively. This approach is more reliable than obtaining activation energies from the temperature dependence of one relaxation time (e.g., T_1 or $T_{1\rho}$) in cases with broad distributions of hopping rates at a fixed temperature (particularly true of $LaNi_5H_x$).



Future Plans

The study of new interstitial metallic alloys will be extended to Mg-Ti[4], because Ti is so much less costly than Sc. Only a small quantity of Mg-Ti is expected to be available, requiring measurement in a microcoil at high field strength. The H kinetics in Mg-Sc hydride will also be studied as a function of the Mg:Sc ratio, to test the view that the rutile-fluorite structural transition controls the H hopping rate. When $MgScD_x$ is available, deuterium magic-angle spinning NMR will be used to try to resolve distinct resonance lines for distinct hydrogenic sites.

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