

VI.A.5 DOE Metal Hydride Center of Excellence

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California Institute of Technology

Carnegie Mellon University

General Electric – Global Research

HRL, LLC

Intematix Corp.

Jet Propulsion Laboratory (JPL)

National Institute of Standards and Technology (NIST)

Oak Ridge National Laboratory (ORNL)

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Projected End Date: Project continuation and direction determined annually by DOE

Introduction

The DOE Metal Hydride Center of Excellence (MHCoe) consists of 8 universities (Caltech, Carnegie Mellon, Stanford, University of Hawaii, University Illinois, University of Nevada, Reno (UNR), University of Pittsburgh, and University of Utah), 3 industrial partners (GE Global Research, HRL, and Intematix), and 6 national/federal laboratories (BNL, JPL, NIST, ORNL, SNL and SRNL). SNL is the lead laboratory of the Center to provide leadership for the Center and a management structure to assist and advise the DOE. Furthermore, technical assistance will be provided to the DOE as needed in the area of program planning, management, implementation and execution of tasks.

The goal of the MHCoe is to discover and develop efficient, safe and cost-effective reversible hydrogen storage materials for vehicle applications. To achieve this goal, we have assembled an interdisciplinary team of the best researchers to address each critical component of this technical “Grand Challenge.” These components are: (1) materials development and discovery including rapid experimental development efforts, (2) fundamental modeling and science to identify hydrogen-materials interactions and to provide direction for the screening efforts, (3) materials synthesis and improved performance through compositional, structural,

catalytic, and nano-synthesis modification, (4) rigorous testing of hydrogen storage and delivery properties to support the fundamental science and to enable a critical and timely evaluation of materials research directions, and finally (5) strong engineering science and process development capabilities to accelerate the transition of the best hydrogen storage materials and systems to a commercial reality.

The MHCoe brings together scientists and institutions with strong and focused capabilities in each of the research areas shown in Figure 1. The core philosophy of this Center of Excellence is to provide a collaborative teaming environment that enables each member to have the full support of other members to solve interlinking problems through a coordinated effort. This allows each team member to focus on and be a resource to others in their individual area of expertise. It also shows the complementary and leveraging relationships among Center partners.

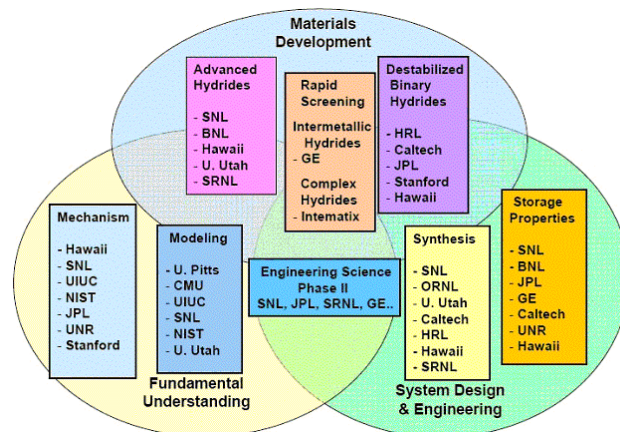


Figure 1. Topic Schematics of the DOE Metal Hydride Center of Excellence

Objective

To bring the best research teams in the nation together to work on a coordinated effort to solve the “Grand Challenge” of developing practical and cost-effective materials and systems for on-board hydrogen storage. Our specific Metal Hydride Center of Excellence goals are:

- To develop new reversible hydrogen storage materials that meet or exceed DOE/FreedomCAR 2010 and 2015 system goals
- To deliver a 1-kg hydrogen storage system prototype to DOE by 2010

Technical Barriers

This project addresses the following technical barriers from the On-Board Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Reversible Solid-State Material Storage Systems (Regenerated On Board)

- A. Cost. Low-cost materials and components for hydrogen storage systems are needed, as well as low-cost, high-volume manufacturing methods.
- B. Weight and Volume. Materials and components are needed that allow compact, lightweight, hydrogen storage systems while enabling greater than 300-mile range in all light-duty vehicle platforms. Reducing weight and volume of thermal management components is required.
- C. Efficiency. The energy required to get hydrogen in and out of the material is an issue for reversible solid-state materials. Thermal management for charging and releasing hydrogen from the storage system needs to be optimized to increase overall efficiency.
- D. Durability. Materials and components are needed that allow hydrogen storage systems with a lifetime of 1,500 cycles and tolerance to fuel contaminants.
- E. Refueling Time. There is a need to develop hydrogen storage systems with refueling times of less than three minutes for 5-kg of hydrogen, over the lifetime of the system. Thermal management during refueling is a critical issue that must be addressed.

- G. System Life-Cycle Assessments. Assessments of the full life cycle, cost, efficiency, and environmental impact for hydrogen storage systems are lacking.

Technical Targets Addressed by the MHCoe

The MHCoe has adopted a multi-prong approach to the development of new hydrogen storage materials that meet the DOE 2010 and ultimately the 2015 targets for on-board hydrogen storage. While all of the critical targets detailed in the multi-year R, D&D plan will be addressed, the main focus will be on meeting the following specific targets:

- By 2010, develop and verify on-board hydrogen storage materials achieving storage system targets of 2 kWh/kg (6 wt. %), 1.5 kWh/L, fill time of 3 minutes for 5-kg of hydrogen, and \$4/kWh.
- By 2015, develop and verify on-board hydrogen storage materials achieving storage system targets of 3 kWh/kg (9 wt. %), 2.7 kWh/L, fill time of 2.5 minutes for 5-kg of hydrogen, and \$2/kWh.

Table 1. Some Examples of MHCoe Progress Toward Meeting DOE On-Board Hydrogen Storage System Targets (**Examples are based on materials only, not system values)

Storage Parameter	Units	2010 Target	2015 Target	**Na-Alanates	**Li/Mg-Amides	**LiBH ₄ - MgH ₂
Specific Energy by Weight	kWh/kg	2.0	3.0	1.3	1.8	3.6
Specific Energy by Volume	kWh/L	1.5	2.7	1.3	2.0	4.6
Hydriding Temperature (Current status)	°C			120	200	350

Overall Approach of the MHCoe

The MHCoe is tasked with developing hydrogen storage materials that meet or exceed the DOE/FreedomCAR and Fuel targets for an on-board hydrogen storage system. This is a critical task for the DOE to be able to reach its goal of enabling an informed industry commercialization decision for hydrogen fuel cell vehicles by 2015.

The MHCoe employs a multi-prong approach focused in the following areas:

- The discovery of new hydrogen storage material through combinatorial, high-throughput synthesis and testing.
- The development of advanced reversible light-weight materials based on known high-capacity hydrides.
- The application of irreversible high-capacity hydrides through reversible destabilization reactions.
- Experimental characterization of the material and system hydrogen storage properties using techniques such as electron diffraction, X-ray and neutron diffraction, Raman, infrared (IR), nuclear magnetic resonance (NMR), low energy electron microscopy (LEEM), scanning tunneling microscopy (STM), secondary electron microscopy (SEM), low energy ion scattering (LEIS), electron spin resonance (ESR).
- First principles and thermodynamic modeling to aid in understanding fundamental hydrogen uptake and release processes and aid in the discovery of new materials.
- The investigation of the mechanisms of hydrogen uptake and release through experimental analysis in coordination with modeling efforts.
- The development of new synthesis and doping routes to improve both kinetics and capacity.

- Determination of important engineering materials properties of new hydrogen storage materials to ensure that they will meet the system storage targets.

This work is coordinated and performed in collaboration with other members of the MHCoe to apply a wide range of expertise in the development of hydrogen storage materials and systems.

FY 2005 Accomplishments of the MHCoe

The Center's project work has just started in FY 2005. Specific progress on current projects and proposed work by the center partners is describe below.

- Identified aluminum hydride (AlH_3 , theoretical material capacity of 10 wt%) as a promising candidate for meeting DOE's 2010 hydrogen storage goals. Found that the desorption temperature of the as-received α - AlH_3 , which typically ranged from 175-200°C, could be lowered to 100-150°C when the material was mechanically milled with a LiH dopant (BNL and SNL).
- Refinement and scale-up of synthesis of Si, Mg and MgH_2 in nanophase form using a cryo-melting gas condensation technique (CalTech).
- Demonstrated that a high-throughput screening tool based on thermography can screen hydrogen absorption & desorption with a sensitivity down to 0.3 wt% hydrogen (GE).
- $\text{LiBH}_4/\text{Mg(X)}$ appears to represent a class of promising high capacity destabilized systems with partial to complete reversibility demonstrated for X = H, F, and S. However, these systems also display slow kinetics; future work will focus on enhanced reaction rates in nanoscale materials (HRL).
- Validated combinatorial molecular beam epitaxy (MBE) and ion beam sputtering (IBS) systems for synthesizing thin film complex hydrides containing air-sensitive elements, such as Li, Na, Mg (Intematix).
- 5.2 wt% reversible hydrogen storage was achieved through the development of a destabilized Mg-modified Li-imide material (SNL).

Future Directions of the MHCoe for FY 2006

The development of an advanced solid-state storage system that meets the 2010 DOE target will be undertaken with partners working together in the following focus areas:

- Establish materials screening criteria based on system-level analyses which include, but are not limited to, performance targets, cost, reliability, and safety.
- Rapid screening combinatorial chemistry for the discovery of new storage materials.
- Advanced hydrides development to achieve practical reversible storage of known high-capacity hydrides.
- Destabilization at reasonable temperatures of high hydrogen content materials through the designed reaction of multi-component systems.
- Experimental characterization of hydrogen storage materials performance and systems performance.
- Advancing the fundamental understanding of hydrogen uptake and release in advanced materials.
- Modeling to aid in understanding the fundamental processes and to guide materials improvement.
- The development of novel synthesis routes to produce new materials, nano-crystalline materials and eventually practical scale up to production.
- Engineering materials properties and storage systems development.

VI.A.5a Brookhaven National Laboratory (BNL)

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Projected End Date: Project continuation and direction determined annually by DOE

Partner Approach

In pursuit of the targets listed below, BNL will continue to work with the members of “Grand Challenge” partnership. BNL will concentrate on understanding the fundamental and system-level issues of using alane (AlH_3) as a storage medium. In this effort BNL collaborates with Savannah River, the University of Hawaii and SNL. The overall targets are below, assuming favorable decisions at go/no-go decision points.

- Develop an on-board fuel tank delivery system for better than 6% (system-level) gravimetric and 0.07 kg- H_2 /L (system-level) volumetric energy capacities.
- Design a fuel tank storage system to cost <\$133/kg- H_2 with a hydrogen fuel flow > 0.02 g/s, a delivery pressure of 4 atm(s) and an operating temperature of 80°/100°C.
- Produce 1 kilogram of an AlH_3 material that has a gravimetric storage capacity > 8% kg- H_2 /kg and a volumetric storage capacity of > 0.10 kg- H_2 /L.
- Development of an economic, energy efficient and practical AlH_3 regeneration process.

Partner Results for FY 2005

BNL, in collaboration with Dr. Gary Sandrock (who was supported by SNL), investigated the accelerated thermal decomposition of doped α - AlH_3 . The results were very encouraging. We found that the desorption temperature of the as-received α - AlH_3 , which typically ranged from 175-200°C, could be lowered to 100-150°C when the material was mechanically milled with a LiH dopant. This was demonstrated by temperature-programmed-desorption experiments. The lower temperatures were achieved with higher loadings of LiH. However, at high dopant levels the storage content was reduced to about 7 wt%. Recent work has been concerned with the synthesis of α - AlH_3 using the technique developed by Brower *et al.* The pure α -phase was obtained this past year, and could be readily decomposed at 100°C without ball milling or the addition of a dopant. The measured H storage content was 9.7 wt%. There is no inherent barrier to achieving even lower temperatures that would be well within the DOE 2010 target range, but further research is needed to achieve these targets.

More recently, we have been collaborating with HRL to study various catalysts in the doped $\text{LiBH}_4/\text{MgH}_2$ system. X-ray absorption spectroscopy was used to determine the location and valence of the catalyst immediately after ball milling and at different stages of hydrogen cycling. Our recent experiments on doped sodium alanate have shown that the Ti atoms are well dispersed in this system and form Ti-Al clusters on/near the surface. The presence of a transition metal atom lowers the potential energy barrier to the formation of the aluminum hydride species, which in turn enhances the hydrogenation/dehydrogenation kinetics. Preliminary absorption studies on the doped borohydrides have revealed a number of similarities with the alanates.

In addition, as a member of the Metal Hydride Center of Excellence, BNL this last year has supplied the following research samples: α - AlH_3 to partners at SNL and JPL, de-hydrated Al powder to SRNL and the alloy Mg_2Cu to HRL.

Partner FY 2006 Plans

- Task 1 – Aluminum Hydride (AlH₃) Synthesis
- Task 2 – AlH₃ Properties
- Task 3 – Scale (1 kg) AlH₃ Tank Study
- Task 4 – AlH₃ Theory & Refueling Models
- Task 5 – Collaborations and Reporting

Conclusions of Partner Effort for FY 2005

- Identified aluminum hydride (AlH₃, theoretical material capacity of 10 wt%) as a promising candidate for meeting DOE's 2010 hydrogen storage goals. Found that the desorption temperature of the as-received α -AlH₃, which typically ranged from 175-200°C, could be lowered to 100-150°C when the material was mechanically milled with a LiH dopant.

BNL FY 2005 Publications/Presentations

1. J. Graetz, Y. Lee, J. J. Reilly, S. Park and T. Vogt, "Structure and thermodynamics of the mixed alkali alanates", *Phys. Rev. B*, **71** 184115 (2005).
2. J. Graetz and J. J. Reilly, "Nanoscale energy storage materials produced by hydrogen-driven metallurgical reactions", *Adv. Eng. Mat.*, invited article, in press (2005).
3. G. Sandrock, J. Reilly, J. Graetz, W.-M. Zhou, J. Johnson and J. Wegrzyn, "Accelerated thermal decomposition of AlH₃ for hydrogen-fueled vehicles", *Appl. Phys. A*, **80** 687 (2005).
4. 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).
5. J. Graetz et al. "New Reversible Complex Metal Hydrides", *March Meeting of American Physical Society*, 2005.
6. G. Sandrock et al. "Doping of AlH₃ with alkali metal hydrides for enhanced decomposition kinetics", *March Meeting of the American Physical Society*, 2005.
7. J. J. Reilly et al. "The Potential of Aluminum Hydride for Vehicular Hydrogen Storage" *IPHE International Hydrogen Storage Conference*, 2005.
8. J. Graetz et al. "X-ray absorption study of Ti-doped sodium aluminum hydride", *Fall Meeting of the Materials Research Society*, Dec. 2004.
9. J. J. Reilly et al. "The Use of Hydrogen-Driven Metallurgical Reactions (HDMR) to Produce Reactive, Nano-Scale and Nano-Composite Materials", *Fall Meeting of the Materials Research Society*, Dec. 2004.
10. G. Sandrock et al. "Preparation of Nanoscale/Nanocomposite Materials Using Hydrogen-Driven Metallurgical Reactions (HDMR)" *International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications*, Sept. 2004.

VI.A.5b California Institute of Technology

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Start Date: October 2004

Projected End Date: Project continuation and direction determined annually by DOE

Partner Approach

The California Institute of Technology is working with partner institutions within the MHCoe to address issues related to the kinetics of thermodynamically tuned reversible hydrogen storage systems. We are using a variation of the gas condensation technique and a variant known as cryo-melting in order to synthesize hydride and hydride precursors at size scales that are at least an order of magnitude smaller than can be achieved by mechanical attrition or ball-milling.

Partner institutions and investigators within the MHCoe include Jet Propulsion Laboratory (Robert C. Bowman, Jr.), HRL Laboratories (John Vajo and Greg Olson), University of Hawaii (Craig Jensen), Stanford (Bruce Clemens), Univ. Pittsburgh (J. Karl Johnson), National Institute of Standards and Technology (NIST) (Terry Udovic), and external collaboration with CECM-CNRS, Vitry, France (Yannick Champion).

Partner Results for FY 2005

- Synthesis of nano Si via cryo-melting and gas condensation and nano Mg via gas condensation.
- Improvements to gas condensation filament design to minimize filament burnout.
- Disproportionation reaction of Mg_2Si during gas condensation/consolidation.

Partner FY 2006 Plans

We have already been working on the direct synthesis of nano Mg_2Si in order to determine whether the present inability to rehydrogenate this material under conditions that are presently employed, is a kinetic problem, and thus solvable by use of appropriately small particle sizes, or one in which fundamental issues related to the covalent bonding of Si to Mg presents a difficult obstacle to rehydrogenation. We note that recent work by Michelle Gupta's group in Orsay has for the first time, successfully rehydrogenated Mg starting from a Mg_2Si material by mechanical attrition in 20 bar of H_2 gas. We anticipate that the insights drawn from this work will enable us to pursue more practical schemes for the rehydrogenation process.

Our attempts at the direct synthesis of this material in nanophase form by gas condensation appears to result in complete disproportionation of the starting material. We have not seen this behavior in LiAl, nor in NiAl systems. This adds credence to the possibility of ultimately being able to dissociate Mg_2Si back into MgH_2 and Si. We plan to investigate other Li based complex hydride compositions. We plan to work on scale-up of our process for producing nanoparticles so that meaningful reaction/kinetic phenomena can be easily evaluated.

Conclusions of Partner Effort for FY 2005

While FY 2005 research has not yet come to an end, we plan to complete the following before the end of FY 2005:

- Refinement and scale-up of synthesis of Si, Mg and MgH₂ in nanophase form.
- Transmission electron microscope (TEM) analysis of in-house and vendor supplied material.
- Initial kinetic evaluation of reactivity and hydrogenation behavior of hydrides in nanophase form.

California Institute of Technology FY 2005 Publications/Presentations

1. 2005 DOE Hydrogen Program Annual Review, "Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage"

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Contract Number: DE-FC36-05GO15062

Start Date: March 2005

Projected End Date: May 2009

Partner Approach

GE will discover and develop a high capacity (> 6 wt%) lightweight hydride that is practical and inexpensive for reversible vehicular hydrogen storage and delivery systems, capable of meeting or exceeding the 2010 DOE/FreedomCAR targets. As a partner for the DOE MHCoe, GE will use our unique high-throughput/combinatorial approaches, state-of-the art research tools and facility, and most importantly an innovative team of researchers to discover a high-capacity hydride. Our research applies a proven methodology to investigate large numbers of lightweight intermetallics, both theoretically and experimentally, quickly screen their hydrogen storage capabilities, and gain a detailed understanding of the critical hydrogen storage performance characteristics. Once a promising material has been found, scale-up and processing studies will commence in anticipation of possible commercialization.

GE will leverage the hydride materials and system engineering expertise at Sandia National Laboratories (SNL). We plan to have system requirement flow down discussion with SNL very early on in the program. GE's system-level materials characterization will complement SNL's system scale-up design. The synchrotron diffraction at Brookhaven National Laboratory (BNL) and the neutron diffraction at NIST will be extensively used by GE to evaluate the structure and physical hydrogen storage mechanism of new intermetallic hydrides. Our long-lasting collaboration with NIST on thermodynamic modeling and phase diagram calculation will be extended to this program. We will also work with the MHCoe modeling team to integrate modeling results into new hydride discovery.

Partner Results for FY 2005

Our FY 2005 objectives are: 1) to develop a high-efficiency combinatorial synthesis and high-throughput screening methodology for metal hydride discovery; and, 2) identify hydrides from combinatorial samples and validate them through gram-quantity sample tests. During the course of our study, we have accomplished the first objective and are in the process of meeting the second objective.

- Demonstrated that our high-throughput screening tool based on thermography can screen hydrogen absorption and desorption with a sensitivity down to 0.3 wt% hydrogen, see Figure 1;
- Identified the reaction pathway and crystal structures of $\text{Li}_2\text{Mg}(\text{NH})_2$ using our unique in-situ high temperature high pressure cell and both synchrotron x-ray diffraction at BNL and neutron diffraction at NIST, see Figure 2;
- Performed systematic screening of compounds in the Al-Li-Si ternary system;
- Synthesized AlH_3 that is a starting material for synthesis of many lightweight intermetallics.

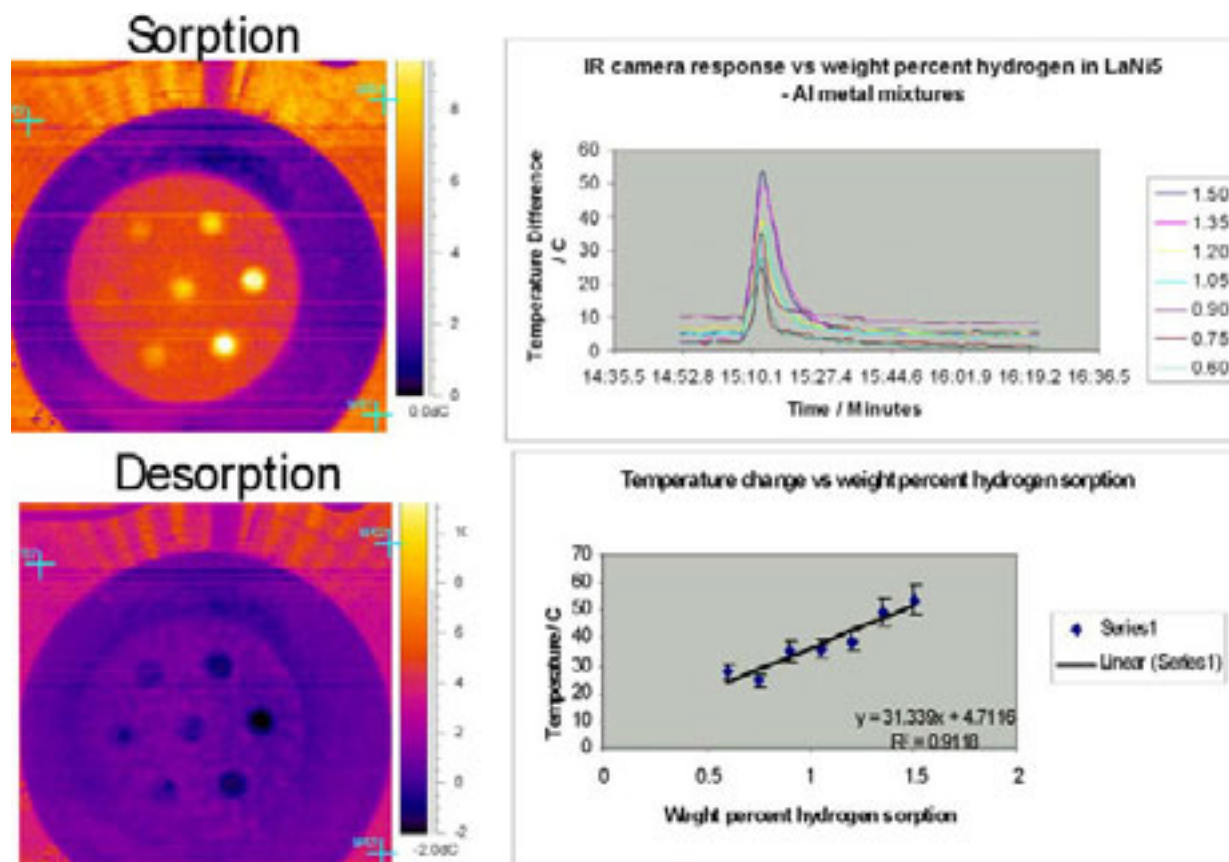


Figure 1. Benchmark Study of the Thermography High-Throughput Screening Tool for Hydride Discovery The IR camera can monitor the temperature change vs time for various hydrogen concentration during sorption (heat generation) and desorption (heat absorption). Reaction kinetic parameter can be derived by the time dependent measurements. Calibration curve for hydrogen sorption in LaNi_5 mixtures. The overall detection limit is approximately 0.3 wt%.

Partner FY 2006 Plans

- Continue to make combinatorial samples and screen the lightweight intermetallic composition space (continue with the hydride discovery task, Task 1);
- Use our unique in-situ cell to study the reaction pathway and identify crystal structure of new hydrides;
- Synthesize lab quantities of compounds identified from combi screening to validate the methodology (begin Task 2, materials synthesis);
- Prepare Task 3: system-level materials evaluation models and setup.

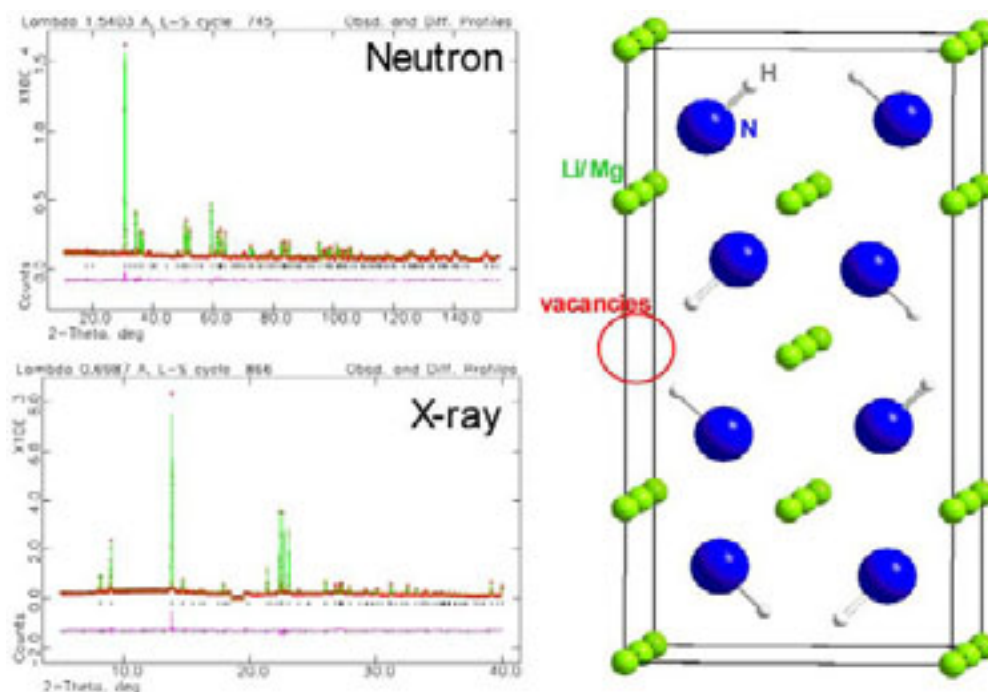
Special Recognitions & Awards/Patents Issued

1. Three members of our metal hydride team, J.-C. Zhao, Yan Gao, and Gosia Rubinsztajn were presented with GE Management Awards for excellence in metal hydride research.

General Electric FY 2005 Publications/Presentations

1. Poster presentation at the IPHE Hydrogen Storage International Conference (June 2005, Lucca, Italy): "Chemical and morphological changes of Ti-catalyzed NaAlH_4 during hydrogen storage"
2. Poster presentation at the IPHE Hydrogen Storage International Conference (June 2005, Lucca, Italy): "Phase formation and reaction pathway of $\text{Mg}(\text{NH}_2)_2 + 2 \text{LiH}$ mixtures for reversible hydrogen storage"

- Poster presentation at Gordon Research Conference on Hydrogen – Metal Systems (July 2005, Maine):
“Recent progress in high throughput screening for new hydrogen storage materials”
- Poster presentation at Gordon Research Conference on Hydrogen – Metal Systems (July 2005, Maine):
“Phase formation and reaction pathway of $\text{Mg}(\text{NH}_2)_2 + 2 \text{LiH}$ mixtures for reversible hydrogen storage”



Space Group	<i>Iba2</i> (#45)					
Lattice Parameters	$a = 9.7880 \text{ \AA}$	$b = 4.9931 \text{ \AA}$	$c = 5.2023 \text{ \AA}$			
	$\alpha = 90^\circ$	$\beta = 90^\circ$	$\gamma = 90^\circ$			
	$V = 254 \text{ \AA}^3$	$Z = 4$	$d_{\text{calc}} = 1.8 \text{ g/cm}^3$			
Atomic positions	Occ.	Wyckoff	x	y	z	U_{iso}
Li/Mg1	0.61/0.39	4a	0	$\frac{1}{2}$	0.46638	0.00307
Li/Mg2	0.67/0.33	8c	0.24025	-0.03680	-0.01834	0.00307
N	1.00	8c	0.13545	0.27816	0.22782	0.01797
H/D	0.29/0.71	8c	0.06333	0.14320	0.18212	0.03544
R factors		R_p	R_{wp}	χ^2		
(w/o background)		3.01 %	3.61 %	1.391		
Refinement software	GSAS					

Figure 2. Identification of the reaction pathway and crystal structures of $\text{Li}_2\text{Mg}(\text{NH})_2$ using our unique in-situ high temperature high pressure cell and both synchrotron x-ray diffraction at BNL and neutron diffraction at NIST. There are three different structure types for $\text{Li}_2\text{Mg}(\text{NH})_2$ depending on the temperature. The low-temperature α - $\text{Li}_2\text{Mg}(\text{NH})_2$ is shown here.

VI.A.5d HRL Laboratories, LLC

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Contract Number: DE-FC36-05GO15067

Start Date: March 2005

Projected End Date: February 2008

Partner Approach

The approach adopted in this project has two principal components. First, hydride destabilization is used to overcome the thermodynamic constraints imposed by high bond energies in light metal systems. Destabilization occurs when a stable reaction intermediate alters the sorption reaction pathway, resulting in a dramatic reduction in the reaction enthalpy and an attendant decrease in reaction temperature. Second, to overcome the intolerably slow reaction kinetics in most bulk light metal hydride systems, we are using nanoscale reactants and catalysts formed by direct (bottom-up) synthesis to reduce diffusion distances and enhance the net reaction rate.

Our initial efforts are being directed toward demonstrating reversibility in MgH_2/Si —a prototype for a wide range of destabilized hydride reaction systems. We are extending that work to include new Li- and Mg-based destabilized systems with higher gravimetric and volumetric capacities. Nanoparticle synthesis, thermodynamic and kinetic modeling, and detailed materials characterization are being conducted in collaboration with numerous MHCoe partners, including Caltech, Stanford, JPL, the University of Hawaii, the University of Utah, Carnegie Mellon and the University of Pittsburgh, the University of Illinois, and NIST.

Partner FY 2006 Plans

- Demonstrate reversibility in the nanostructured MgH_2/Si destabilized system and characterize hydrogen diffusion kinetics, phase nucleation mechanisms, and catalysis in MgH_2/Si . Characterize behavior at high pressures and temperatures in nanoscale materials.
- Develop and implement nanoscale engineering approaches to improve hydrogen sorption kinetics in the high capacity $\text{LiBH}_4/\text{MgH}_2$ and $\text{LiBH}_4/\text{Mg(X)}$ destabilized hydride systems. Explore use of nanoscale metal catalysts to enhance hydrogen dissociation and reaction rates in nanoparticles.
- Evaluate sintering and agglomeration of nanoscale materials during hydrogen cycling, and develop mitigation strategies involving framework structures and H-permeable coatings.

Conclusions for Partner Effort for FY 2005

- Serious kinetic limitations exist for hydrogenation of nanometer Mg_2Si thin films and micrometer scale particles. Work is in progress to evaluate the kinetics of nanometer scale particles and to discriminate between diffusion and phase nucleation barriers during the hydrogenation process.
- $\text{LiBH}_4/\text{Mg(X)}$ appears to represent a class of promising high capacity destabilized systems with partial to complete reversibility demonstrated for $X = \text{H}, \text{F}, \text{and S}$. However, these systems also display slow kinetics; future work will focus on enhanced reaction rates in nanoscale materials.

HRL Laboratories FY 2005 Publications/Presentations

1. G.L. Olson and J. J. Vajo, *Thermodynamically Tuned Nanophase Materials* (Oral and poster presentations) at 2005 DOE Annual Review (Arlington, VA May 23-26, 2005).
2. J.J. Vajo, *Destabilization of Strongly Bound Hydrides for Hydrogen Storage Applications*, invited presentation at 2005 Gordon Research Conference on Hydrogen-Metal Systems (Waterville, ME, July 10-15, 2005).
3. G.L. Olson, J.J. Vajo, A.G. Gross, T.M. Salguero, S.L. Skeith, and B.M. Clemens (Stanford U.), *Nanostructure Engineering for Improved Reaction Rates in Destabilized Hydrides*, poster presentation at 2005 Gordon Research Conference on Hydrogen-Metal Systems (Waterville, ME, July 10-15, 2005).

VI.A.5e Intematix Corporation

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Contract Number: DE-FC36-05GO15070

Start Date: March 2005

Projected End Date: February 2010

Partner Approach

Intematix concentrates on cost-effective and time-efficient combinatorial synthesis and high-throughput screening of effective reversible metal hydrides and catalysts. The materials development tasks focus on instrumentation and application of high throughput materials research in complex metal hydrides. Establishment and validation of high throughput synthesis and screening tools are performed during the first phase of the projected period (the first 2.5 years). Full work flow of high throughput investigation of advanced hydrogen storage materials will be enabled in the second phase of the project.

The major efforts of this project are devoted to the following tasks:

- Validation of combinatorial synthesis techniques and high-throughput screening of metal hydrides and catalysts;
- Synthesis and screening of thin-film complex hydrides/catalysts libraries;
- Synthesis and screening of nanoparticle complex hydrides/catalysts libraries;
- Characterization of material properties of lead hydrides/catalysts.

Partner Results for FY 2005

- Validated combinatorial molecular beam epitaxy (MBE) and ion beam sputtering (IBS) systems for synthesizing thin film complex hydrides containing air-sensitive elements, such as Li, Na, Mg. Integrated an oxygen-free glove box for *in situ* sample transfer and characterization with the MBE system.
- Developed a combinatorial nanoparticle synthesis system (CNP) as the third proprietary combinatorial materials synthesis technique with the advantages of small particle size ~10-50 nm, narrow particle-size distribution.
- Designed and constructed a high-pressure (1 to 150 atm), high-temperature (up to 400°C) optical testing chamber for hydriding and dehydriding parallel screening.

Partner FY 2006 Plans

- Catalysts screening
 - Identify key parameters for high throughput *in situ* optical screening
 - Demonstrate effectiveness of catalyst screening methodology for model reaction
- Validate the capability of CNP for synthesizing metal hydride/catalyst nanoparticles

Conclusions of Partner Effort for FY 2005

- Completed instrumentation validation for combinatorial synthesis of complex metal hydrides and catalysts
- Initiated high throughput screening and characterization of metal hydrides

VI.A.5f Jet Propulsion Laboratory (JPL)

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Contract Number: NAS7-03001, Task Order: NMO715781

Start Date: April 2005

Projected End Date: Project continuation and direction determined annually by DOE

Partner Approach

- Validation of initial storage properties, reversibility, and cycling durability:
 - Nanophase, destabilized hydrides based upon LiH, MgH₂, LiBH₄ & other candidates produced at HRL, Caltech, & other MHCoe partners.
 - Complex hydrides (e.g., amides/imides, borohydrides, & AlH₃-hydrides) provided by SNL, BNL, the University of Hawaii, GE Global, and other MHCoe partners.
- Support development of low weight and thermal efficient hydride storage vessels and demonstrate their compatibility with complex and destabilized hydrides.
- Perform Magic Angle Spinning - Nuclear Magnetic Resonance (MAS-NMR) measurements to assess the phase compositions and chemical bonding parameters.
- Characterize phases and structures by XRD, neutron scattering and diffraction methods in collaboration with MHCoe partners (i.e., NIST, Caltech and BNL).

Partner Results for FY 2005

- Assessed phases and reversibility of model LiH-Si, LiH-Ge, and MgH₂-Si systems.
- Performed MAS-NMR studies on phase composition of AlH₃ and Li/Mg amides.
- Initiated modification of hydride testing facility for accelerated cycling studies to start screenings of Li/Mg amides, MgH₂/LiBH₄ or other promising samples.

Partner FY 2006 Plans

- Complete degradation studies of first destabilized nanophase system (MgH₂/LiBH₄).
- Evaluate degradation behavior during cycling of first selected MHCoe materials.
- Develop a conceptual design of prototype hydride sorbent bed that improves capacity and thermal efficiency over current configurations.
- Perform first generation thermal model analyses on a prototype bed design.
- Complete first phase NMR studies on LiH-AlH₃ & Li/Mg amides.

JPL FY 2005 Publications/Presentations

1. R.C. Bowman, Jr., S.-J. Hwang, C. C. Ahn, A. Dailly, J. J. Vajo, T. J. Udovic, M. Hartman, and J. J. Rush, "Studies of Thermodynamics and Phases Produced in the Destabilized LiH-Si System" an invited presentation at the Nordic Energy Research Meeting, Krusenberg, Sweden, 17-18 June 2005.

VI.A.5g National Institute of Standards & Technology (NIST)

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Start Date: April 2005

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Partner Approach

The key to improved hydrogen-storage materials is a detailed understanding of the atomic-scale locations and lattice interactions of the hydrogen. We are applying our state-of-the-art neutron measurement capabilities and expertise at the NIST Center for Neutron Research (NCNR) to the promising materials being developed by the MHCoe. In addition, we are performing Calphad thermodynamic modeling to provide critical assessments of hydrogen content, heats of reaction, and phase-reaction sequences during hydrogen charge-discharge cycling of MHCoe-developed metal-hydride systems. This work will enable MHCoe partners to obtain unique insights into the atomic- and molecular-scale properties that are responsible for the hydrogen-storage properties of these candidate materials.

Partner Results for FY 2005

- Investigated vibrational spectroscopy, structure, and H content of phases present in the LiH/Si system (with JPL, Caltech, HRL).
 - Found preliminary neutron spectroscopic (See Figure 1) and diffraction (See Figure 2) evidence for previously unknown ternary Li-Si-H phase recently indicated by XRD and NMR measurements from JPL/Caltech/HRL.
 - Obtained unknown H contents of different LiH/Si samples received from JPL using neutron prompt gamma activation analysis.

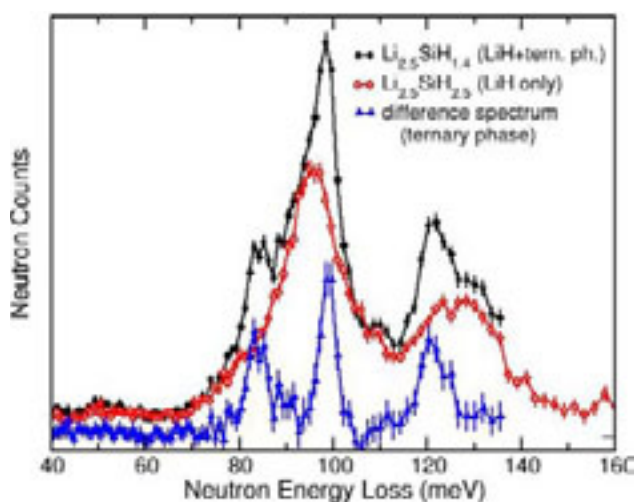


Figure 1. Neutron Vibrational Spectrum of Unknown $\text{Li}_x\text{Si}_y\text{H}_z$ Ternary Phase in $\text{Li}_{2.5}\text{SiH}_{1.4}$ at 3.5 K

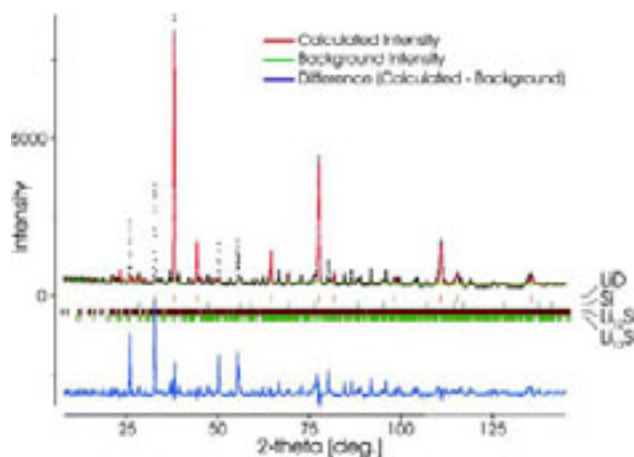


Figure 2. Neutron Powder Diffraction Pattern of Unknown $\text{Li}_x\text{Si}_y\text{D}_z$ Ternary Phase in $\text{Li}_{2.5}\text{SiD}_{1.4}$ at 295 K

- Investigated the reaction, $\text{MgH}_2 + \frac{1}{2} \text{Si} \leftrightarrow \frac{1}{2} \text{Mg}_2\text{Si} + \text{H}_2$, using Calphad thermodynamic modeling (with HRL).
 - Evaluation of different existing databases showed qualitative agreement between 11.5°C and 62.6°C at 0.1 MPa.
 - SGTE database was selected for future calculations.
 - P–T dependence was calculated.

Partner FY 2006 Plans

- Characterize the effects of ball-milling on the structure and hydrogen-bonding potentials in Ti-doped and undoped NaAlH_4 (with the University of Hawaii).
- Characterize structures of mixed-alkali alanates (with SNL).
- Characterize structures and H dynamics for the Li–Mg–B–H system, possibly using ^7Li and ^{11}B .
- Continue to provide neutron metrology to other MHCoe partners on any new hydrogen-storage materials of interest.
- Develop Calphad compatible fugacity/pressure function for H_2 .
- Evaluate literature for thermochemical data for the Li–Mg–B–H system (with HRL).
- Construct thermodynamic database for the Li–Mg–B–H system.
- Devise strategy for obtaining missing quantities of the Li–Mg–B–H system.

Conclusions of Partner Effort for FY 2005

- Neutron diffraction, neutron vibrational spectroscopy, and prompt-gamma activation analysis have demonstrated themselves as three key techniques for characterizing new hydrogen-storage materials investigated by the MHCoe (e.g., for the ternary Li-Si-H system).
- The results of neutron metrology are most useful when performed in conjunction with first-principles calculations.
- Calphad modeling has demonstrated itself as a valuable predictor of thermodynamic properties of new hydrogen-storage materials investigated by the MHCoe (e.g., for the ternary Mg-Si-H system).

VI.A.5h Oak Ridge National Laboratory (ORNL)

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Projected End Date: Project continuation and direction determined annually by DOE

Partner Approach

The objective of the work at ORNL is to develop the chemistry for a hydrogen storage system based on complex hydrides, chosen mostly from alanates and amides of the light elements in the periodic table, in a form that produces materials suitable for the study of practical aspects of hydrogen release and uptake when subjected to the appropriate temperature and hydrogen pressure. ORNL is conducting research on the development of synthetic methods and on the discovery of new hydrides. ORNL is collaborating with MHCoe partners by developing synthetic methods that will produce materials that will achieve the DOE/FreedomCAR performance targets for 2010. Our research on chemical synthesis takes advantage of expertise in solution-based synthesis including reaction in liquid ammonia to develop novel light weight compounds. The synthetic approach that is being followed incorporates strategies such as the use of solvents, catalysts, and complexation agents that lead to the production of highly reversible materials. An emphasis is placed on the microstructure of the products and the incorporation of well dispersed catalysts that have been shown to be critical in the performance of this type of materials for the uptake and release of hydrogen.

The objective of the ORNL work is to explore materials synthesis of new and known materials using synthetic methods appropriate for scale-up to production and practical application. Alanates have a large (~50%) change in lattice dimensions upon hydriding and de-hydriding. A nanoscale to mesoscale superstructure within a storage canister will be needed to maintain bed dimensions, allow for heat transfer, and improve kinetics of hydrogen transfer with scale-up. Although the methods of mechanical alloying (high energy ball milling) have provided the most active hydrogen storage systems, solvent processing will be needed if the reactor bed has a preformed superstructure

Partner Results for FY 2005

Technical progress in the FY 2005 centered on getting an ORNL Research Safety Summary approved for conducting experimental work, developing and setting up facilities for the synthesis and characterization of materials, and developing strategies to incorporate titanium catalysts in lithium and sodium alanates.

- Prepared alanates of Li, Na, and Mg using $\text{AlH}_3 \cdot \text{OR}_2$ as a reactant in ether solvents
- Incorporated of titanium catalyst as organometallic complexes of the form $\text{TiR}_{(4-n)}(\text{AlH}_4)_n$ where R is an alkyl or aryl group that is thermally labile

Partner FY 2006 Plans

Research at ORNL in FY 2006 will be conducted in two general tasks: (1) development of synthetic methods in support of MHCoe collaborators and (2) discovery of new complex metal hydrides.

Within the first general task the ORNL team will utilize its expertise in the synthesis of metallo-organic compounds by solution based synthetic methods. Current plans call for using solution based methods for the preparation of Ti-catalyzed magnesium alanate. The ORNL team will follow the progress of reactions with pressure measurements and with a mass spectrometer to better understand the reactions that are occurring and to determine whether undesirable carbon containing precursor materials are retained by the solid. A number of soluble metallo-organic compounds of the early transition series (titanium to be emphasized) will be tested as catalysts. Synthetic methodology will utilize ethers as solvents as well as liquid ammonia-based synthesis with the objective of finding systems in which the solvent can be easily removed from the solid. In general, methods related to the preparation of known or previously identified AlH_4^- solids based on using $\text{AlH}_3 \cdot \text{OR}_2$ as a reactant will be investigated.

Our collaborators at SNL have reported success with Mg modified Li amide, and this suggests that multi-element metal hydrides may be needed to meet 2010 goals. It is anticipated that a solution based processing may facilitate the preparation of these materials. The observation that TiN was an effective catalyst for sodium alanate lends hope that Ti and V alkylamides may be precursors to catalytically active doping agents to make metal amides reversible hydrogen storing agents. The chemistry of alkylamides, reacting with gaseous or liquid ammonia, will be pursued in some detail to search for effective metal amide storage agents. Li, Na, Mg, and Al species will be investigated.

Samples prepared in these two subtasks will be characterized in preliminary studies of hydrogen desorption and sorption at ORNL. Selected materials that appear satisfactory for further studies will be provided to MHCoe partners for further evaluation.

ORNL FY 2005 Publications/Presentations

1. "Novel Synthetic Approaches for the Preparation of Complex Hydrides for Hydrogen Storage," G. M. Brown and J. H. Schneibel, Poster presentation at the DOE 2005 Hydrogen Annual Review, Washington DC, May 23, 2005

VI.A.5i Sandia National Laboratories

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Projected End Date: Project continuation and direction determined annually by DOE

Partner Objectives

- Develop new hydrogen storage materials with > 6 wt% system hydrogen capacity at below 100°C.
- Improve the kinetics of absorption and desorption and thermodynamic plateau pressures of new complex hydrides and modified amides.
- Gain a better understanding of the fundamental processes that control hydrogen uptake and release in these advanced materials through both modeling and experimental efforts.
- Improve processing and catalytic doping techniques in the synthesis of these materials.
- Pursue the engineering science for eventual development of hydrogen storage/delivery systems through analysis of materials engineering properties, durability, safety and compatibility of advanced materials.

Partner Approach

- We are employing a multi-task approach to advanced materials development through research and development in each of the following areas:
- The discovery of new complex hydrides that achieve higher capacities.
- The development of advanced Mg/Li-amides that operate under lower temperature conditions than the current reversible Li-amides.
- The use of new synthesis and doping processes to improve both kinetics and capacity.
- Experimental characterization of the material properties using techniques such as electron diffraction, X-ray and neutron diffraction, Raman, IR, NMR, LEEM, STM, SEM, LEIS, and ESR.
- The investigation of the mechanisms of hydrogen uptake and release through experimental analysis and modeling.
- Determination of important engineering materials properties of new hydrogen storage materials to ensure that they will meet the system storage targets.

This work is coordinated and performed in collaboration with other members of the MHCoe to apply a wide range of expertise in the development of hydrogen storage materials and systems.

Partner FY 2005 Accomplishments

- A new Li/K-alanate compound has been synthesized using our high-pressure facilities.
- 5.2 wt% reversible hydrogen storage was achieved through the development of a destabilized Mg-modified Li-imide material.
- Mg-modified Li-amide was tested over 100 cycles with a hydrogen storage capacity degradation of approx. 0.005% per cycle, which appears promising for an un-optimized sample.
- Ammonia emission from Mg-modified Li-amides were investigated and was found to be correlated to the status of mixing, desorbing temperature and amounts of excess LiH.

- First-principles modeling led to a proposed mechanism that may explain the catalytic role of transition metal dopants in increasing the kinetics of complex hydride hydrogen storage materials.
- Experimental analysis of fundamental properties on Na-alanates, Li/Mg-amides as well as the iteration of hydrogen with Ti-doped aluminum surfaces, has been carried out.
- New bulk-synthesis routes for the preparation of amides and complex hydrides have been proposed and successfully tested.
- Thermal conductivity measurements have been completed on lithium/magnesium-amide materials.

Partner Future Directions

- Serve as the lead laboratory for DOE MHCoe to coordinate, focus and expedite Center activities among partners toward achieving DOE 2010 FreedomCAR goals and to advise DOE regarding Center business.
- Continue explore new high wt% complex hydrides via high pressure/high temperature processes.
- Optimize Li-Mg-H based materials for faster kinetics and lower temperatures. Destabilize the low pressure reaction of lithium imides to expand the storage capacity of Li-Mg-H to > 9 wt%.
- Initiate modeling and mechanisms studies on Li-Mg-H, B-Li-H and Al-H based materials.
- Develop modeling tool box to help experimentalists search for storage materials with optimal system design properties.
- Improve the wet chemistry process to produce pure storage materials and/or intermediaries with nano-size particles.
- Continue to measure engineering properties of hydrogen storage materials, e.g., thermal conductivities, volume expansion, tap density, etc., of newly developed potential candidates.
- Continue to study performance degradation and reliability of candidate storage materials.
- Initiate investigation on reactions related to safety.

Partner Results in Specific Topic Areas

New Reversible Solid-State Hydrogen Storage Materials:

Novel, light-weight, high-capacity metal hydrides are synthesized as potential candidates for on-board hydrogen storage materials. During FY 2005 a family of alanate materials, i.e. bi-alkali alanates, with hydrogen capacities of 6 wt% or more were investigated. The methods used for preparation in the solid state include ball milling and sintering in a high-pressure (HP) station (<136 MPa, <675 K). A HP vessel is employed that enables six separate samples to be prepared concurrently. This is an effective tool for screening for new hydrides in a multitude of ternary systems. The reaction parameters, i.e. molar ratio, pressure, temperature and reaction time are systematically varied until an optimized yield is obtained.

Bialkali alanates of Li-K, Li-Mg, Li-Ca, Li-Ti, and Mg-Ti of different molar ratios were synthesized by hand mixing or ball milling before pressed into pellets and tested in the HP hydride station. A new K-Li bialkali alanate was discovered at 600 K and 68 MPa. Its structural features are shown in Figure 1 based on

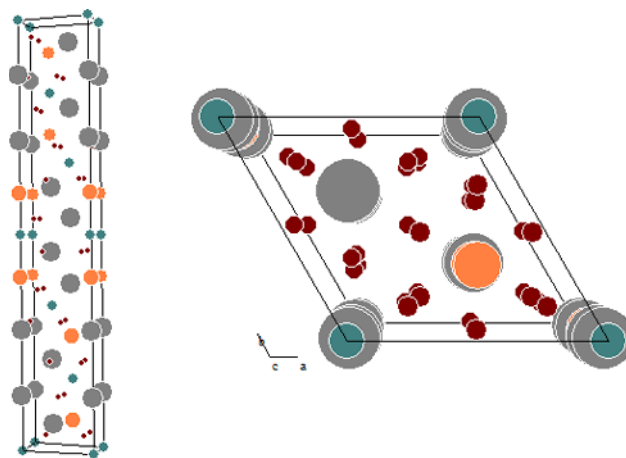


Figure 1. Preliminary Crystal Structure Model of K_2LiAlH_6 (K – Gray, Li – Orange, Al – Green and H – Brown)

X-ray powder diffraction measurements. The hydrogen atom's positions are not yet verified by synchrotron data, but it is likely that the structure is similar to the HP form of K_2LiAlF_6 . It desorbs about 3 wt% hydrogen at 513 K after two activation cycles, but the kinetics are slow. A new high-yield synthesis route for Mg_2FeH_6 (5.5 wt% reversible hydrogen storage capacity) was also developed. Samples were sent to Professor Klaus Yvon's group at the University of Geneva in Switzerland for further analysis as a part of our collaborative participation in the IEA project Task 17.

Development of Advanced Mg/Li-Amides:

Preliminary results of Mg-substituted Li-amides reported last year had demonstrated its reversible hydrogen storage capacity > 5 wt%. This year, thermodynamic and crystal structural characterizations are being pursued to gain a better understand of the reaction mechanism of this system. It is anticipated that this will lead to the development of more advanced H-storage materials. In particular this knowledge will help to optimize the starting compositions and to develop additives that will improve sorption capacity and kinetics.

Absorption-desorption isotherm measurements at 493, 473 and 453 K had been completed (see Figure 2). These measurements indicated that H-capacity within this temperature range is 5.2 wt%, with hydrogen

desorption pressure of 4.4 MPa at 493 K, and 2.8 MPa at 473 K.

The starting composition was selected as $2LiNH_2+MgH_2$.

However, this converts readily to $Mg(NH_2)_2+2LiH$ when heated to 473 K for more than 2 hours.

Following this initial step, the reversible sorption process takes place between the following compositions $Mg(NH_2)_2+2LiH \rightleftharpoons Li_2Mg(NH_2)_2$. Test of 100 sorption cycles was completed for this system at 473 K (see Figure 3). These early cycling experiments indicate an 11% capacity loss over 100 cycles without any optimization of the starting composition or the addition of catalysts.

Preliminary results on other samples during the first desorption cycle indicate the presence of ammonia at levels < 40 ppm. Adequate milling and mixing of the samples may play an important role in the reversible hydrogen sorption processes.

Assembly of a high pressure/high temperature diffuse-reflectance infrared Fourier Transform spectroscopy (DRIFTS) reactor and

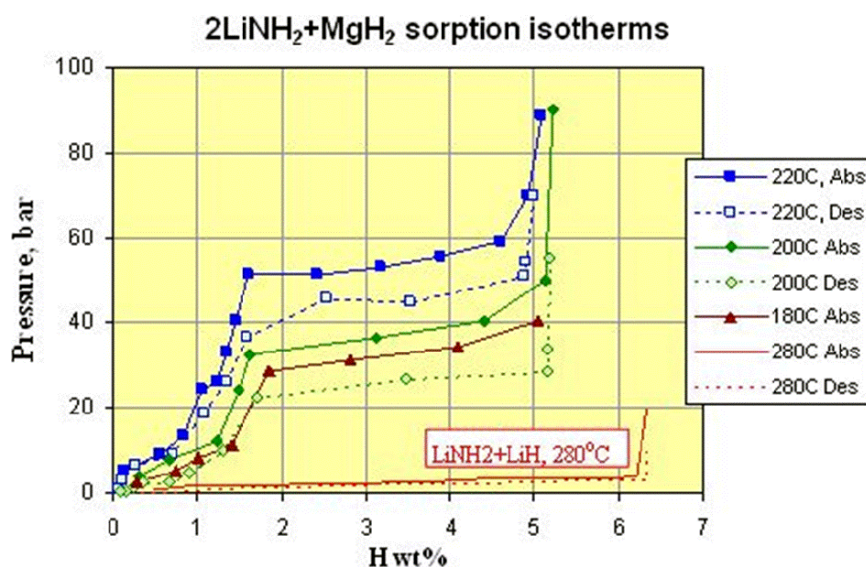


Figure 2. Isotherms for $(2LiNH_2+MgH_2)$

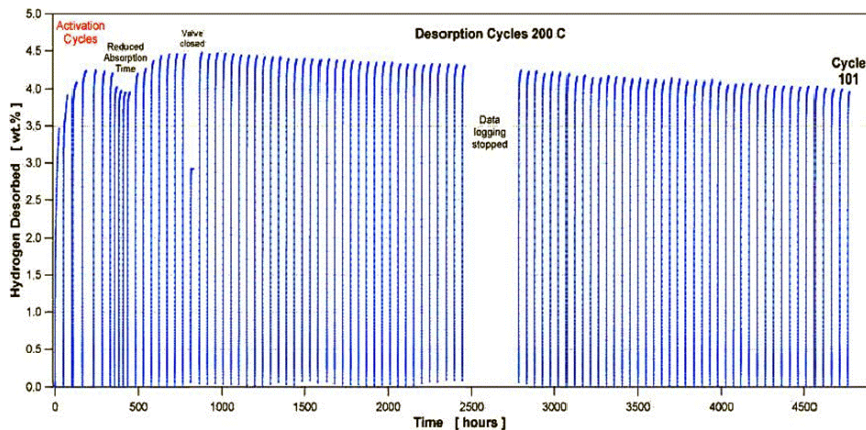


Figure 3. Cycle Life Test for $(2LiNH_2+MgH_2)$

accompanying thermal desorption capability were completed to investigate the hydrogen capacity and thermal desorption characteristics of mixed $\text{LiNH}_2:\text{MgH}_2$ at temperatures between 298 and 475 K desorbing into a 1,000 torr ambient environment. Samples were also hydrogen cycled, with re-hydriding at a pressure of 8 MPa pure hydrogen and temperature of 433 K over time intervals between minutes and hours. Unique infrared spectral features were observed for the mixed $\text{LiNH}_2:\text{MgH}_2$ system during TPD which indicate the emergence of new surface species as a result of thermal cycling. These spectral features were not present in the *as milled* material and coincide with the formation and volatilization of ammonia. Initial indications suggest that the newly milled material reverts to some other more stable form after the first hydrogen desorption cycle.

Fundamental Understanding of the Mechanisms of Hydrogen/Materials Interactions Modeling Efforts:

Aluminum is one of the decomposition products of alanates and thus is always present in the actual storage material. Al (100) is a surface of intermediate surface energy and should not reconstruct upon hydrogen exposure. We find that Ti and Sc atoms generally prefer to reside in an ordered $\frac{1}{2}$ monolayer (ML) sub-surface substitutional array or alloy (see inset in Figure 4). The sub-surface transition metals bind strongly to surface Al atoms, activating them to form strong covalent bonds with adsorbates like H. This indirect effect of Ti and Sc leads to the formation of a relatively stable surface

Ti-Al-hydride layer at high hydrogen pressures. Ti and Sc directly exposed at the surface and Al atoms with Ti neighbors have lower barriers for H_2 dissociation and recombination.

The proposed mechanism (see Figure 4) might explain the catalytic role of transition metal dopants in speeding up the kinetics of complex hydride hydrogen storage materials. This work also suggests a new class of near surface alloys of simple and transition metals with favorable catalytic properties for hydrogen chemistry. These surface alloys combine usually mutually exclusive properties of the constituent metals, relatively low H binding energy and low H_2 dissociation and recombination barriers. This unusual combination benefits the H_2 dissociation to produce adsorbed H atoms and the reaction of H with other surface species.

Our mechanism does not discriminate between different alanates like LiAlH_4 and NaAlH_4 . The main difference between these cases should be the concentration of relatively mobile cations on the Al surface. As established in calculations, they are attracted to the Ti and H covered Al surface and serve as site blocking agents, reducing the rates of H sorption, but not the barriers.

The identification of hydrogen dissociation and recombination at the surface as the main obstacle to hydrogen uptake and release has major consequences for interpretation of experiments. For example, it indicates that thin oxide films that naturally cover actual materials before H cycling or milling can dramatically slow the kinetics. Kinetic effects have to be discriminated from thermodynamic effects - which is often difficult. Thus we have started a program to reliably predict the thermodynamics of hydriding and dehydriding. The first static calculations concern Na, Li, and Mg alanates. The capability to include the vibrational entropy is currently under way.

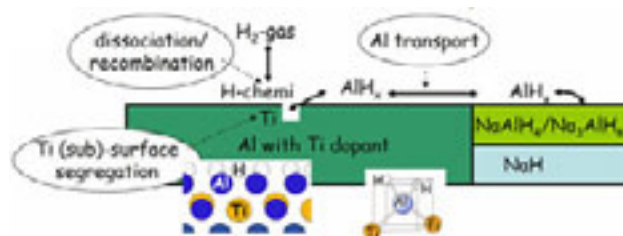


Figure 4. Conceptual Diagram of the Mechanism of Transition Metal Enhanced Kinetics of H Sorption on Alanate H Storage Materials

The behavior of Ti on Al surfaces is being studied to ascertain whether or not this inexpensive material can be employed as a catalyst to promote hydrogen uptake in Al and lead to the formation AlH_3 . Calculations indicate that Ti, which normally does not accumulate (i.e., segregate) on Al surfaces, may be stabilized at or near the Al surface in the presence of hydrogen. The project seeks experimental confirmation of this prediction. To do so, well-characterized test surfaces are being prepared and examined using a highly sensitive surface analysis method (low-energy ion scattering and direct recoil spectroscopy, LEIS/DRS) that can measure the surface abundance of both Ti and H on Al surfaces. A probe ion beam is directed at a test surface and the energy of scattered and recoiled ions is measured. Signals from surface Ti, Al, and H atoms are detected, as illustrated in Figure 5. The surface composition is monitored as a function Ti doping level, H flux intensity, and temperature. If the presence of H stabilizes Ti on the surface, a correlation between the H and Ti signals will occur. Preliminary data suggest the Ti surface concentration may increase in the presence of H_2 .

We also investigated the bonding characteristics of MH_x anions, which represent a large class of the new complex ionic hydrides by measuring the lattice vibrations in NaAlH_4 using Raman scattering and understand them from first principles methods. We succeeded in determining the zone center phonons for sodium alanate by polarized Raman scattering studies. The results demonstrate that the lattice modes separate neatly into two categories, (1) crystal modes, in which the AlH_4 anion can be regarded as a rigid unit, and moves in conjunction with Na cations, and (2) AlH_4 anion modes, which represent the Al-H bending and stretching that is characteristic of a polar-covalently bonded AlH_4 molecular anion. These results clearly indicate that the building blocks for the complex hydrides may be viewed as molecular anions, the stability of which may determine to a large extent the kinetics of sorption reactions.

Advanced Methods for Synthesis of New Storage Materials:

Currently, the ball-milling method is widely used to prepare alanate hydrogen storage materials. This method has practical limitations, especially for large-scale production. In addition, materials properties, such as chemical homogeneity, grain sizes and surface areas, and impurity levels, are difficult to control. Furthermore, nanostructured metal hydrides with high surface areas are desirable to improve the thermodynamics and kinetic properties of the hydrogen storage materials. Such nanoscale materials cannot be obtained through ball milling. Thus, we are exploring chemical routes for the bulk production of a variety of nanostructured, nanoporous metal hydrides, metal alanates (MAlH_x), and amides (MNH_2) for hydrogen storage applications.

Two approaches will be investigated. The first will focus on a unique low temperature precipitation route to generate nanoparticles, utilizing liquid ammonia to maximize hydrogen content, and potentially producing amide derivatives as well as alanates. The use of amides will help to sequester the nanomaterials and will be labile enough to allow for the necessary reactivity. If the ammonia-based surfactants prove to be too volatile,

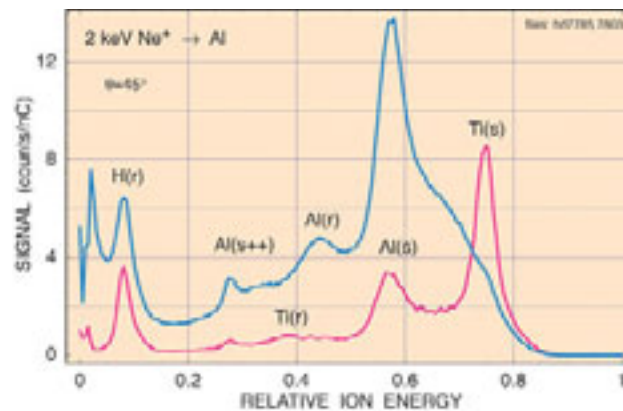


Figure 5. Example of experimental data. These are ion energy spectra of 2 keV Ne^+ scattered from an Al surface before and after doping with Ti at room temperature. The main peaks arise from scattering of the Ne^+ from Al and Ti atoms on the surface. The peak intensities indicate the population of the various types of atoms on the surface of the sample. Evaporating Ti on the surface initially covers most of the Al atoms. A signal from hydrogen atoms present on the surface is also visible. These peak intensities are monitored as various treatments of the sample are made and provide an atomic snapshot of the surface condition.

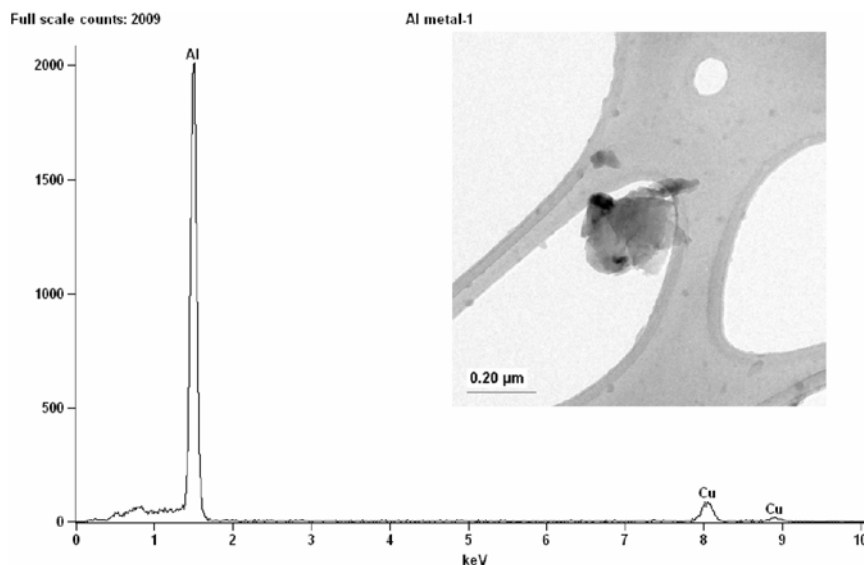


Figure 6. 200 nm Al Particles and EDS Analysis

several alternative amine-based surfactants will also be explored. The starting precursors will also be doped with a variety of alternative alkali metals to increase the number of defects present in the material thus allowing for maximum reactivity.

The second route will be based on cluster building through carefully controlled molecular formation and atomistic architecture based on hyper-oligomerization of unsaturated metal centers. In particular we will carefully construct complex alkali metal hydride clusters using templating approaches disseminated in the literature. This controlled construction will allow us to fine-tune the reactivity of the compounds through controlled doping and molecular design. These species will necessarily be active since they will not have surfactants present. These two approaches will have great potential for improved chemical homogeneity and purity, and will provide the opportunity to control the grain size and pore structure from molecular, to nanometer and micrometer scale. These routes will also enable more efficient, uniform, potentially in-situ incorporation of catalysts. Rational synthesis of nanostructured and nanoporous metal hydrides will lead to improved thermodynamics and faster hydrogen adsorption/desorption kinetics. In addition, greater robustness and resistance to thermal and mechanical stress and to moisture and air exposure are anticipated. To test the proposed synthesis routes we have successfully synthesized nano-Al (see Figure 6). Most recently we have been able to synthesize Mg and Al amide from solvent-free systems.

Engineering Properties Characterization of Advanced Hydrogen Storage Materials:

Quantification of material engineering properties is required to perform detailed optimization of hydrogen storage system designs to meet the DOE 2010 hydrogen storage targets.

A custom hardware and an absorption/desorption test station reported last year are being used to perform experiments to measure material properties of newly developed materials. Using a high pressure vessel equipped with a thermal conductivity probe, metal hydride material are brought to conditions required for hydrogen absorption or desorption. After an absorption or desorption is completed, the material is cooled to room temperature where transient probe temperature measurements are taken. Transient temperature data is post-processed to calculate values for the thermal conductivity of the material.

Thermal conductivity experiments with approximately 119 grams of lithium amide combined with magnesium hydride material were performed during 5 sorption cycles. Transient temperature rise measurements for fully absorbed and fully desorbed at pressures between 10^{-2} torr vacuum and 10 MPa (H_2)

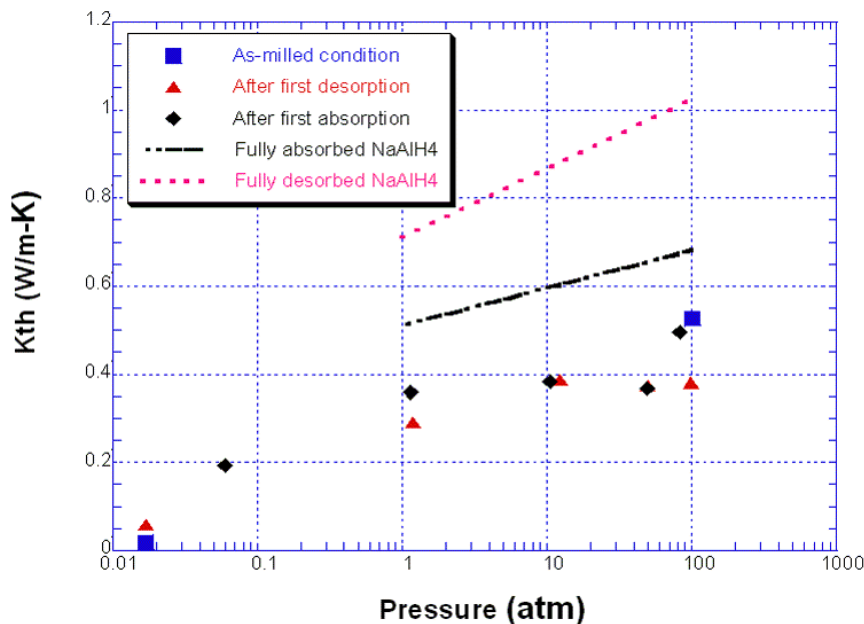


Figure 7. Thermal Conductivity of Li-Mg-N-H Samples as a Function of Composition and Gas Pressure

had also been completed. Based on these tests thermal conductivity for the lithium amide, magnesium hydride material with 0.54 g/cm^3 bulk density were determined to be: 0.3 to 0.5 W/m-K (in the absorbed state) and 0.25 to 0.45 W/m-K (in the desorbed state). These values are lower than those of sodium alanates (see Figure 7). This is not unreasonable because there is always free aluminum mixed in the alanates, while amides have no metallic species to help improve its thermal conductivities.

Sandia National Laboratories Special Recognitions & Awards/Patents Issued

1. U.S. Patent # 6793909 B2, Direct Synthesis Of Catalyzed Hydride Compounds, Sept 21 2004.

Sandia National Laboratories FY 2005 Publications

1. W. Luo, "(LiNH₂-MgH₂): a viable hydrogen storage system", J. Alloys and Compounds, 381, 284-287 (2004)
2. W. Luo, K. Gross, "A kinetics model of hydrogen absorption and desorption in Ti-doped NaAlH₄", J. Alloys and Compounds, 385, 224-231 (2004)
3. Z. Xiong, J. Hu, G. Wu, P. Chen, W. Luo, K. Gross, J. Wang, "Thermodynamic and kinetic investigation on the ternary imide of Li₂MgN₂H₂", J. Alloys and Compounds, in press.
4. E. H. Majzoub, K. F. McCarty, and V. Ozolins, "Lattice dynamics of NaAlH₄ from high-temperature single-crystal Raman scattering and ab initio calculations: Evidence of highly stable AlH₄ anions," Phys. Rev. B 71, 024118 (2005)
5. R. Bastasz, J.W. Medlin, J.A. Whaley, R. Beikler, and E. Taglauer, "Deuterium adsorption on W(100) studied by LEIS and DRS," Surface Science, volume 571 (2004) pp 31-40.
6. J. Wang and E. Ronnebro, "Hydride Developments for Hydrogen Storage," Proceedings of the 2005 Spring TMS conference, p. 19, (2005)
7. E. H. Majzoub, J. L. Herberg, R. Stumpf, S. Spangler, R.S. Maxwell, "XRD and NMR investigation of Ti-compound formation in solution-doping of sodium aluminum hydrides: solubility of Ti in NaAlH₄ crystals grown in THF," J. of Alloys and Compounds 388, 81 (2004)
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1. R. Bastasz and J.A. Whaley, "LEIS and DRS: Diagnostic tools for studying hydrogen on surfaces," MRS Spring Meeting, Symposium on Materials and Technology for Hydrogen Storage and Generation, San Francisco, March 30, 2005.
2. K. Gross, W. Luo, "Sorption Properties of novel hydrogen storage materials", International Symposium on Metal Hydrogen Systems, Krakow, Poland, Sept. 6-9, 2004,
3. K. Gross and G. Thomas, "Hydrogen Storage Where We Are Now and Where We Need to Go", American Physical Society Annual Meeting, Montréal Canada March 20-26, 2004.
4. K. Gross and D. Dedrick, "Advances in Hydrides for Hydrogen Storage", American Physical Society Annual Meeting, Montréal Canada March 20-26, 2004.
5. K. Gross, "Advances in Alanates for Hydrogen Storage," NHA Annual Meeting 2004
6. K. Gross, W. Luo, "Properties of advanced hydrogen storage materials", Material Research Society Annual Meeting, Boston, MA, Nov. 29-Dec.2, 2004.
7. W. Luo, "Towards a viable hydrogen storage system for transportation application", International Symposium on Metal Hydrogen Systems, Krakow, Poland, Sept. 6-9, 2004,
8. W. Luo "Towards a Viable Hydrogen Storage System for Transportation Application", Material Solution Conference and Exposition", Columbus, OH, Oct. 18-21, 2004.
9. W. Luo, K. Gross, E. Ronnebro, J. Wang, "Destabilization of metal hydrides by forming nitrogen-containing compounds", American Physical Society Annual Meeting, Los Angeles, CA, March 21-25, 2005.
10. W. Luo, K. Gross, E. Ronnebro, J. Wang, "Metal-N-H: new promising hydrogen storage materials", NHA Meeting, Washington DC, March 28-Apr.1, 2005
11. E. Majzoub, "X-ray Diffraction and Raman Spectroscopy Investigation of Titanium Substitution in Sodium Aluminum Hydride," TMS Annual Meeting 2004
12. E. Majzoub, "In-situ Raman Spectra of $NaAlH_4$: Evidence of Highly Stable AlH_4 Anions," MRS 2004
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VI.A.5j Savannah River National Laboratory (SRNL)

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Start Date: April 2005

Projected End Date: Project continuation and direction determined annually by DOE

Partner Approach

The objective of this research is to develop rechargeable aluminum hydride (AlH_3) for hydrogen storage to meet the DOE on-board hydrogen transportation goals. Specific objectives include: 1) design and fabricate a novel high pressure cell to efficiently charge aluminum hydride (AlH_3 -alane), 2) test and evaluate feasibility of cell for alane charging, and 3) characterize and analyze charged alane materials for structure, purity and yield. Collaborations include the University of Hawaii, Brookhaven National Laboratory and Sandia National Laboratory.

Partner Results for FY 2005

Design and fabrication of Alane charging/discharging cell:

- Completed cell design (SRNL patent pending)
- Complete cell fabrication, install cell in SRNL high pressure laboratory and initiate charging tests by the end of FY 2005

Preliminary analyses on samples obtained from BNL, the University of Hawaii and UTRC:

- SEM investigation has been conducted (see Figure 1)

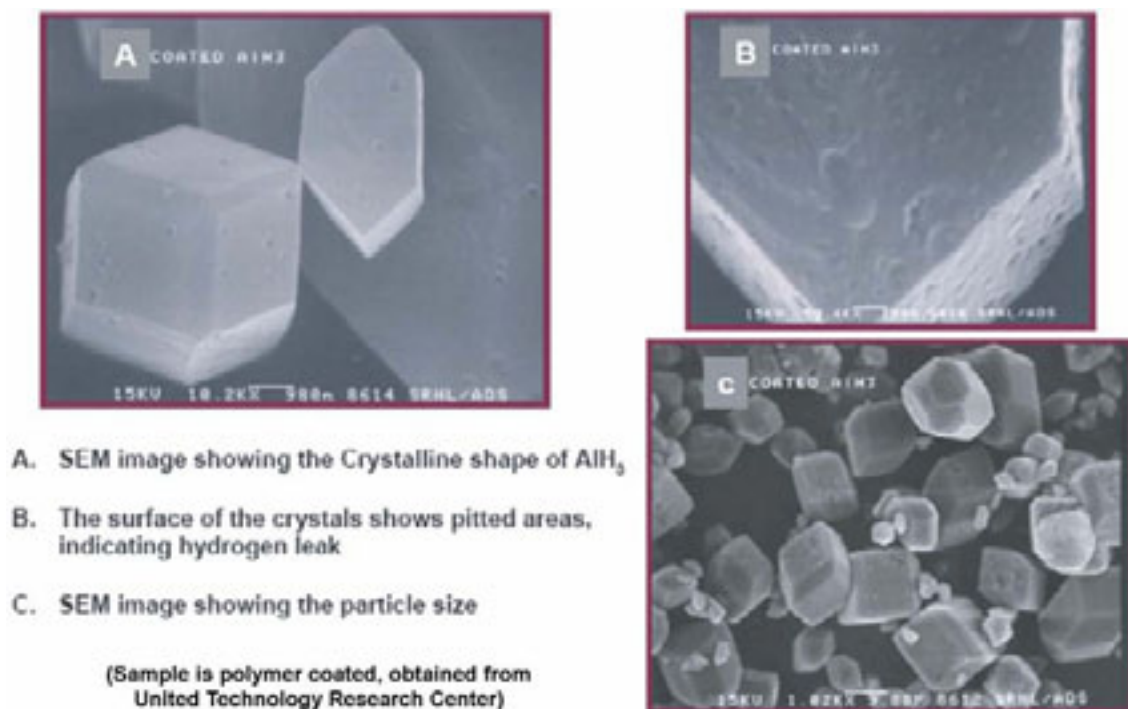


Figure 1 Scanning Electron Microscopy Images of Alane

- X-ray analysis of both α and γ phases of AlH_3 has been performed, see Figures 2 and 3
- Thermal programmed desorption evaluation of AlH_3 has been conducted, see Figure 4

Partner FY 2006 Plans

High Pressure Cell Testing and Material Synthesis:

Charging tests will continue and synthesis operations will be initiated. Catalysts will be added to increase material yield and increase material stability. The key to the first year effort is the development of stable alane materials.

Characterization: Structural characterization will continue to identify material purity and yield. X-ray diffraction (XRD) and differential scanning calorimetry (DSC) will be the primary tools. XRD will be used to determine phase structure, lattice parameters and a preliminary assessment of the volume fractions of the material produced.

Conclusions of Partner Effort for FY 2005

- Competing reaction can lead to unstable phases
- Innovative methods are being developed by SRNL to convert Al to stable AlH_3
- Heat of reaction has been determined to be 7.57 ~ 7.6 kJ/mol
- Ball milling allows hydrogen to desorb at lower temperature
- Aged particle surfaces showed pitted areas, indicating that hydrogen leaks over time
- The hydrogen recovered from aged AlH_3 indicated that these leaks are not significant

SRNL FY 2005 Publications/Presentations

- Development of Reversible Hydrogen Storage Alane, R. Zidan, DOE Annual Review Meeting 2005
- Novel Hydrides, R. Zidan, IPHE Conference Lucca, Italy 2005
- Development and Characterization of Novel Hydrides, R. Zidan, Gordon Research Conference, July, 2005

SRNL Special Recognitions & Awards/Patents Issued

- Alane High Pressure Cell design (SRNL patent pending)



Figure 2. Structure Characterization –XRD α phase

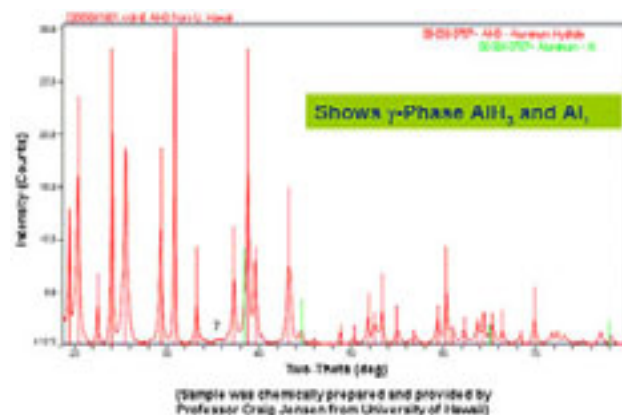


Figure 3. Structure Characterization –XRD γ Phase

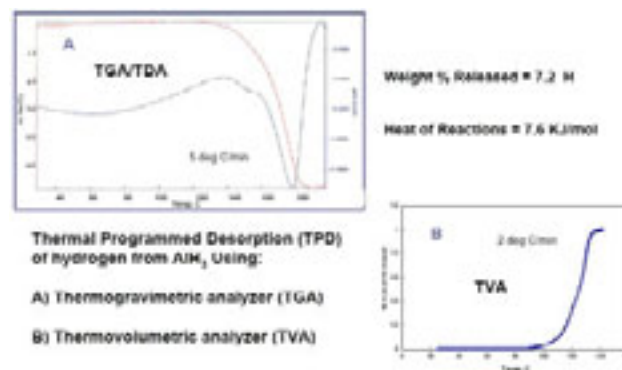


Figure 4. Hydrogen Release from Alane

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Contract Number: DE-FC36-05GO15069

Start Date: March 2005

Projected End Date: February 2010

Partner Approach

In order to investigate the kinetics and structural changes associated with reversible hydrogen storage in model metal hydride material systems, we use the flexibility of physical vapor deposition and thin film characterization to produce specifically engineered model systems. In addition, we model the hydrogen charging and discharging kinetics of nanoscale metal hydride systems. Information from these models and from the aforementioned characterization techniques guides material selection and engineering for future model nanoscale material systems.

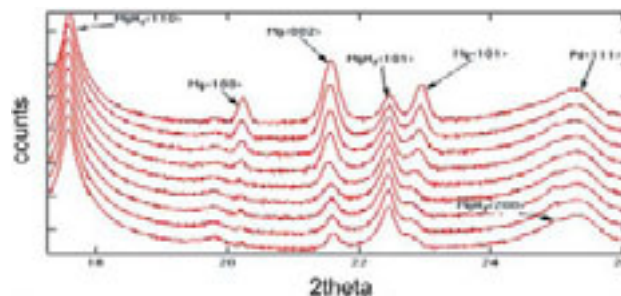


Figure 1. SSRL Discharging Experiment Data

Partner Results for FY 2005

- Fabricated and charged thin film model systems using magnesium and palladium
- Discharging experiment performed at Stanford Synchrotron Radiation Laboratory (SSRL)
- Developed continuum model for nanoparticle thermodynamics and solid solubility

Partner FY 2006 Plans

For FY 2006, we will continue to investigate the kinetics and thermodynamic processes associated with hydrogen charging and discharging in metal hydride material systems. We will continue performing experiments utilizing thin film characterization techniques and increase our efforts to model these processes while exploring other novel metal hydride material systems (chosen in collaboration with the HRL team). We will also develop a method for fabricating nanoparticles of our material systems and use our recently acquired Sievert's apparatus to examine the hydrogen absorption properties of these nanoparticles, allowing us to understand the thermodynamic effects of reduced size.

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Start Date: March 2005

Projected End Date: February 2010

Partner Approach

- Characterization of the active Ti species in Ti-doped NaAlH₄ through electron paramagnetic resonance (EPR) studies (collaboration with the University of Denver).
- Elucidation of mechanism of action of dopants in Ti-doped NaAlH₄, Na₃AlH₆ and LiBH₄/MgH₂ through anelastic spectroscopy (collaboration with the University of Rome), position annihilation studies (collaboration with AIST, Tskuba, Japan) and nuclear magnetic resonance spectroscopy.
- Determine if the thermodynamics of the reversible dehydrogenation of Ti-doped NaAlH₄ are effected by doping through differential scanning calorimetry studies (collaboration with the University of South Florida).
- Determine the effects of doping on the hydrogen cycling kinetics of *thermodynamically tuned* binary hydrides (i.e., LiBH₄/MgH₂) in collaboration with HRL, JPL, CalTech, and Stanford University.
- Structure-reactivity correlation studies of the different phases of AlH₃ through X-ray and neutron diffraction studies and kinetic studies in collaboration with SRNL, Institute for Energy Research, Norway and Tohoku University).

Partner Results for FY 2005

- Determination through isotopic labeling experiments that the point defects in Ti-doped NaAlH₄ are hydrogen containing species and development of a point defect based model for the reversible dehydrogenation of NaAlH₄ according to the anelastic spectroscopic data.
- Direct characterization of the Ti species in Ti-NaAlH₄ by EPR.
- Preparation and characterization of all known as well as novel phases of AlH₃.

Partner FY 2006 Plans

- Apply methods developed for the study and evaluation of doped alanates for the development of advanced complex hydrides and related materials with the potential application in a system that meets the DOE 2010 system storage targets.
- Preparation of advanced complex hydrides and related materials with the potential application in a system that meets the DOE 2010 system storage targets.

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Contract Number: DE-FC36-05GO15064

Start Date: March 2005

Projected End Date: February 2010

Partner Approach

We will employ state-of-the-art characterization tools to investigate the microstructural and microchemical changes that occur in candidate material systems during the uptake and release of hydrogen. This investigation will provide fundamental insight to the processes governing hydrogen uptake and release.

We will use first-principles electronic-structure and thermodynamic techniques to predict and assess meta-stable and stable phases via first-principles electronic-structure and thermodynamic techniques. Electronic-structure calculations will be used to enhance the understanding of MHCoe experimental characterization results on candidate systems. These efforts will enable a more efficient approach to designing a new system with the required properties.

Partnerships have been formed with the following groups: SNL, HRL, the University of Pittsburgh, Carnegie Mellon University, and UNR.

Partner Results for FY 2005

- Developed an approach for preparing environment sensitive samples for examination in the TEM. This has included a preliminary assessment of the sensitivity of these materials to the environment and to the stability of the particles under exposure to the electron beam. Figure 1 compares the microstructure of undoped NaAlH_4 under the electron beam for 60 sec.
- Begun study on the chemical composition of different material systems as supplied by partners. This is the first step in conducting a series of studies on the change in structure and chemistry during the outgassing cycle. Figure 2 shows a chemical analysis obtained from a MgSi alloy that was received from HRL. This material was prepared by ball-milling. The elemental maps show the non-uniformity of the elemental distribution
- Developed a unique cluster expansion toolkit for alloys to study thermodynamic stability. Initial database construction completed; a screen shot from the database is shown as Figure 3. The "Structural Database" allows one to navigate site and use search features via various descriptors (e.g., structures, lattices, etc.). Pertinent electronic-structure information can be uploaded by partners, once authorship to the database is permitted. The database is currently being tested before being opened for use by the Center partners.

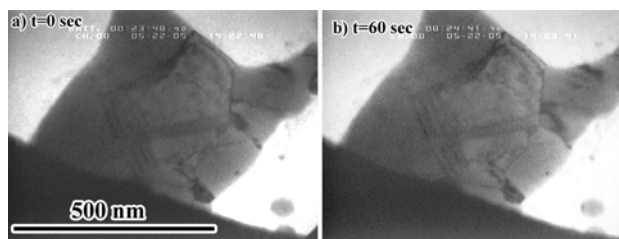


Figure 1. Bright-field Images Showing Stability of Undoped NaAlH_4 under the Electron Beam over 60 sec

- Electronic-structure calculations on the bulk phase of LiBH_4 in the ground-state orthorhombic phase and room temperature hexagonal phase were completed, along with H_2 , hexagonal MgB_2 , MgH_2 and LiH .

To validate the reliability of the calculations, we verified that the phase transition in LiBH_4 system was accurately reproduced from DFT-GGA.

- Experiment: hexagonal phase occurs at $T_c = 381$ K.
- VASP calculated LiBH_4 : $E_{\text{hex}} - E_{\text{ortho}} = 38.5$ meV/atom
- Solid-on-solid transformation has same entropy and phonons, except for BH_4 cages in room temperature hexagonal phase, which can rotate independently from each other by no more than $2\pi/3$ radians, giving phase space probability of $P = 3/2\pi$. Rotational entropy can be estimated as $S_{\text{rot}} = -\ln P \sim 0.177$ k_B /atom.
- Hence, from thermodynamics, $T_c \sim (E_{\text{hex}} - E_{\text{ortho}}) / (1 + S_{\text{rot}}) = 38.5 / 1.177 = 32.7$ meV, or 379 K.

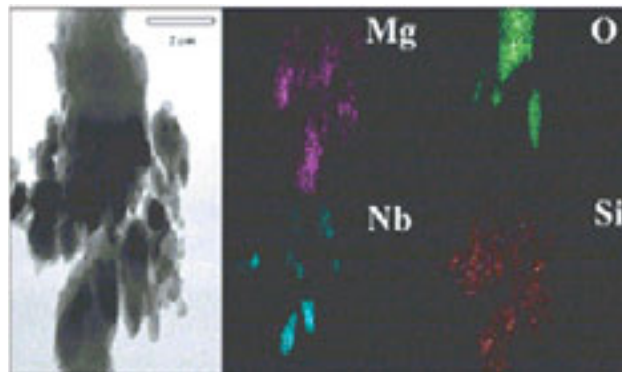


Figure 2. Chemical Maps of Ball-Milled Nb-Doped $\text{MgH}_2 + \frac{1}{2}$ Si Milled for 1 hr, Showing Inhomogenous Mixing

Partner FY 2006 Plans

For FY 2006 we will initiate studies of the microchemical and microstructural changes occurring in different candidate systems. In addition to EDS analysis, electron energy loss spectroscopy will be used to examine the chemistry and where appropriate to examine the nature of the bonding through examination of the near edge structure. Preliminary analysis on a Ti-doped sodium alanate shows that the Ti peak can be detected. A new partnership with the University of Hawaii will be initiated to assist their effort to elucidate the microchemical and microstructural processes controlling the uptake and release of hydrogen in candidate systems.

The Structural Database

Home Structures Lattices Symbols Elements Methods Authors Comments

Logon:
Username:
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Search results by:

Keyword: Case insensitive

Structures
First found 2 structures, displaying 1 through 15

	Name	Energy (eV/atom)	FE (eV/atom)	Error (eV/atom)	Pressure (kbars)	Stoichiometry	Composition	# Atoms	# Types	Author
<input type="checkbox"/>	LiBH4-hex	-4.190185	null	.01	-.67	2:8:2	B H Li	12	3	Nikolai Zarkevich
<input type="checkbox"/>	LiBH4-ort	-4.22446	null	.01	-.82	4:16:4	B H Li	24	3	Nikolai Zarkevich

Figure 3. Screen Capture Showing Elements in the Database

The database following completion of tests will be made available for use by partners. Initial thermodynamic modules have been completed, and, as a test, were used at the 2005 Summer School on First-Principles Thermodynamics via Cluster Expansion, which was supported by the National Science Foundation. These modules will be made available to partners. Further studies on the electronic-structure calculations on the bulk phase of LiBH_4 in the ground-state orthorhombic phase and room temperature hexagonal phase were completed, along with H_2 , hexagonal MgB_2 , MgH_2 and LiH will be conducted with input from the HRL group. The results of these studies may require experimental verification. Additional calculations will be performed with input from partners regarding key issues.

Conclusions of Partner Effort for FY 2005

- Developed a successful approach for examining environment sensitive materials in state-of-the-art analytical equipment.
- Developed database system.
- Initiated studies of the phases and phase stabilities in LiBH_4 .

University of Illinois FY 2005 Publications/Presentations

1. Poster presented at the Hydrogen Program Review, Washington, DC, May 2005.

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Start Date: April 2005

Projected End Date: March 2009

Partner Approach

The main issue to be addressed in this program is to determine the effect of gaseous contaminants such as O₂, CO, H₂O, and others upon recharging of hydrogen in complex hydrides. Thermal cycling studies will be performed to observe any degradation of hydriding/dehydriding properties (thermodynamic studies), determine mechanisms (neutron and X-ray diffraction analyses) and model the phase diagrams of complex hydrides. These studies will give both a better understanding of the physical and thermodynamic properties of complex hydrides, and determine the practical feasibility of using the hydrides with a fuel cell and other systems. This will aid in the design of a reversible-hydride hydrogen storage system that meets or exceeds DOE/FreedomCAR targets for 2010.

Our approach is to conduct this research in two phases. In Phase 1, we will evaluate multiple complex hydride materials that have been selected by our team. We have designed and are now fabricating cycling apparatus that will be connected to our existing automated Sievert's apparatus at UNR. The initial tests will be performed on Mg substituted Li amides/imides, samples of these will be obtained from SNL. We will also perform preliminary screening of samples that will be sent by other groups, and from our group, by first obtaining isotherms, after which promising materials will be selected for more detailed thermodynamic and crystal structure studies and extrinsic stability experiments by long-term hydrogen cycling (and test for short-term pressure hydrogen aging). We anticipate collaborating with JPL, the University of Utah, and University of Illinois. In Phase 1, we will also perform structural characterization by neutron scattering and X-ray diffraction to determine hydriding mechanisms selected hydrides from our MHCoe team. Finally, complex hydrides with optimum hydrogen capacities at reasonable pressures are expected to emerge from these studies. In Phase 2; we will assist our MHCoe team in moving towards the selection of 1 to 3 hydrogen storage materials by providing characterization and performance testing on the potential materials. These materials will be submitted to the DOE for independent evaluation.

Partner Results for FY 2005

- The fabrication of the thermal cycling apparatus, with data acquisition hardware and software, that will be used to understand the effect of contaminant gases, has been started. After completion of fabrication, this apparatus will be interfaced to an existing UNR fully automated Sievert's apparatus. We expect to obtain Li(Mg) amide from SNL for testing.
- The kinetics of hydrogenation/dehydrogenation of Li₃N has been explained as a pathway involving LiNH₂ (amide) and Li₂NH (imide). However, commercially available Li₃N, from different vendors, generally have two mixed phases. It is of interest to know if the presence of two different structures of Li₃N will affect the hydriding properties. Neutron scattering studies performed on commercial material showed

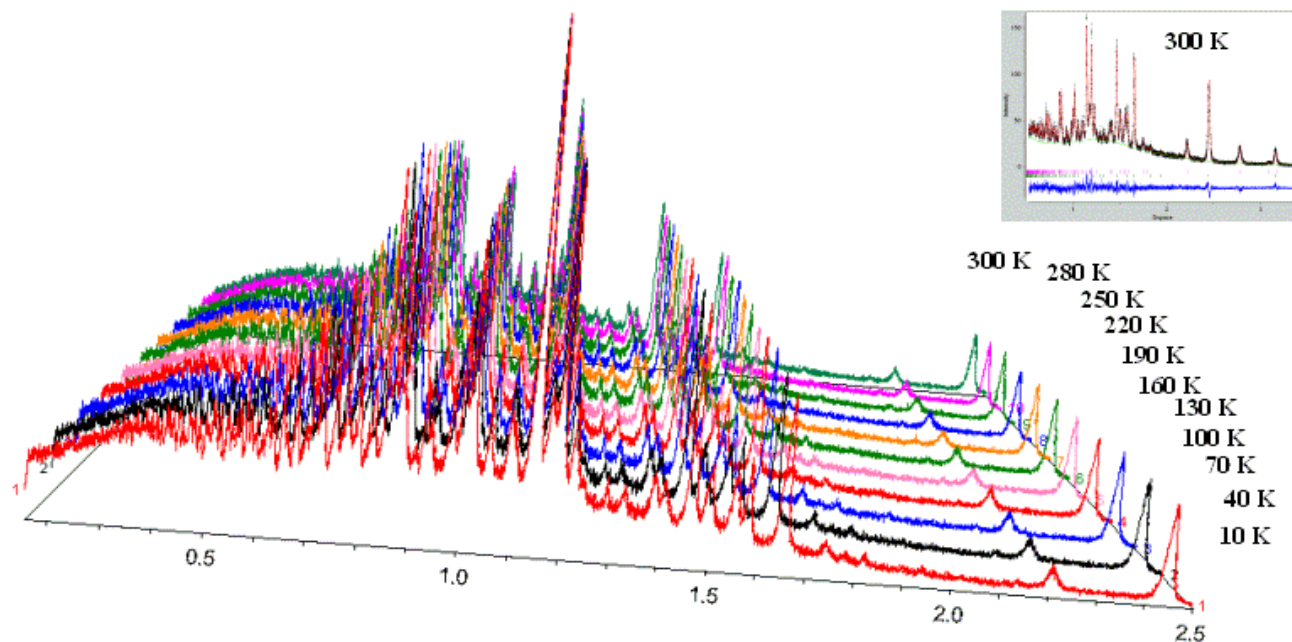


Figure 1. Neutron Diffraction Patterns of Li_3N Sample from 10 K to 300 K Show α and β Phase Mixtures

presence of these two phases; low temperature ambient pressure α - Li_3N phase (major fraction) and high pressure retained $\sim\beta$ Li_3N (minor fraction) from one of the vendors. Neutron diffraction patterns of the mixed (α and β) Li_3N phases are shown in Figure 1.

- Detailed lattice parameters, volumes, c/a ratio, lattice expansions and atom positions for α and β Li_3N phases are obtained by using GSAS program [1-2] (Figure 2 and 3). There is a discontinuity at 300 K in the lattice expansions as well as volumes. The procedure used were different for these experiments from (a) 10 - 300 K (sample loading in He glove box), and (b) 300 - 573 K (sample loading in nitrogen glove box). It is suggested that the differences in lattice parameters is due to exposure of sample to nitrogen at 300 K due to the use of nitrogen in case (b).
- Total volume expansions of β Li_3N phase (2.46%) are larger than α phase (1.6%) from 10 K to 523 K. Neutron diffraction data of Li_3N show there is a phase transition between 523 K and 573 K.
- Neutron diffraction data of LiAlD_4 sample show the monoclinic structure with $P2_1/c$ space group for 10 K to 300 K. Lattice expansion of LiAlD_4 from 10 K to 300 K show *anisotropic expansions* in lattice parameters; the Bragg peaks of 200, 212 and 130 reflections do not show appreciable change in position, whereas the 013 Bragg peak of LiAlD_4 is shifted significantly with the change in temperature from 10 K to 300 K. This anisotropy is also true for volume expansions.

Partner FY 2006 Plans

Phase I Research: Pioneering work of Chen et al. [4-5] showed Li_3N hydriding in their P-C-T's. Luo [6] developed modified complex $\text{LiNH}_2\text{-MgH}_2$ that appear as promising material. We plan to examine the effect of gaseous impurities such as CO , O_2 , and H_2O in ppm levels in hydrogen on the thermodynamics by thermal cycling at UNR, as soon as the apparatus is completed. X-ray diffraction studies will be performed at UNR. Additional experiments will be performed using a special environmental stage to perform neutron scattering studies at IPNS (Argonne National Laboratories). We expect to gain understanding of the structural details and occupancy of the deuterium atoms as a function of loading. We will use the UNR portable Sievert's apparatus to control the hydrogen or deuterium loading at different temperatures. Neutron data will be taken after each loading until the materials are completely hydrided. These procedures will be repeated at different temperatures (RT to $\sim 400^\circ\text{C}$).

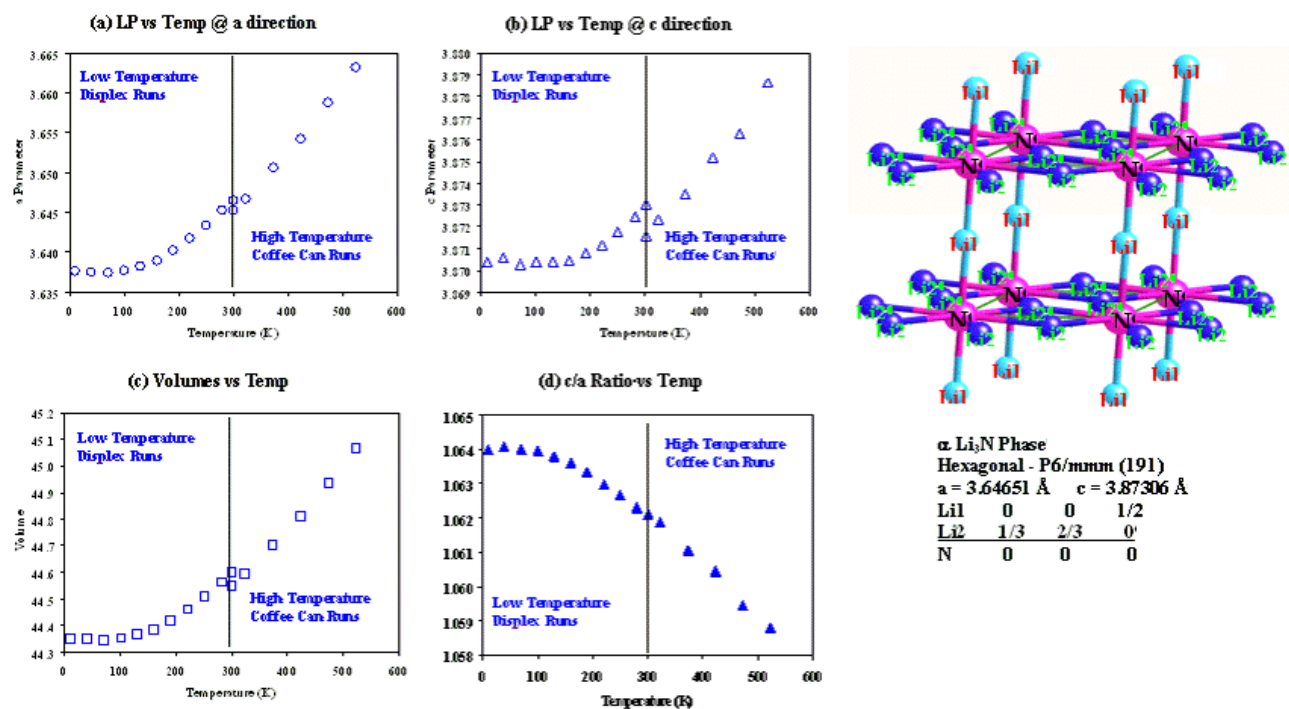


Figure 2. Lattice Parameter, Volume and c/a ratio as a Function of Temperature Plots of α Li₃N Phase at 10 - 523 K Temperature Range (The c/a ratios are decreasing from 1.0640 to 1.0588.)

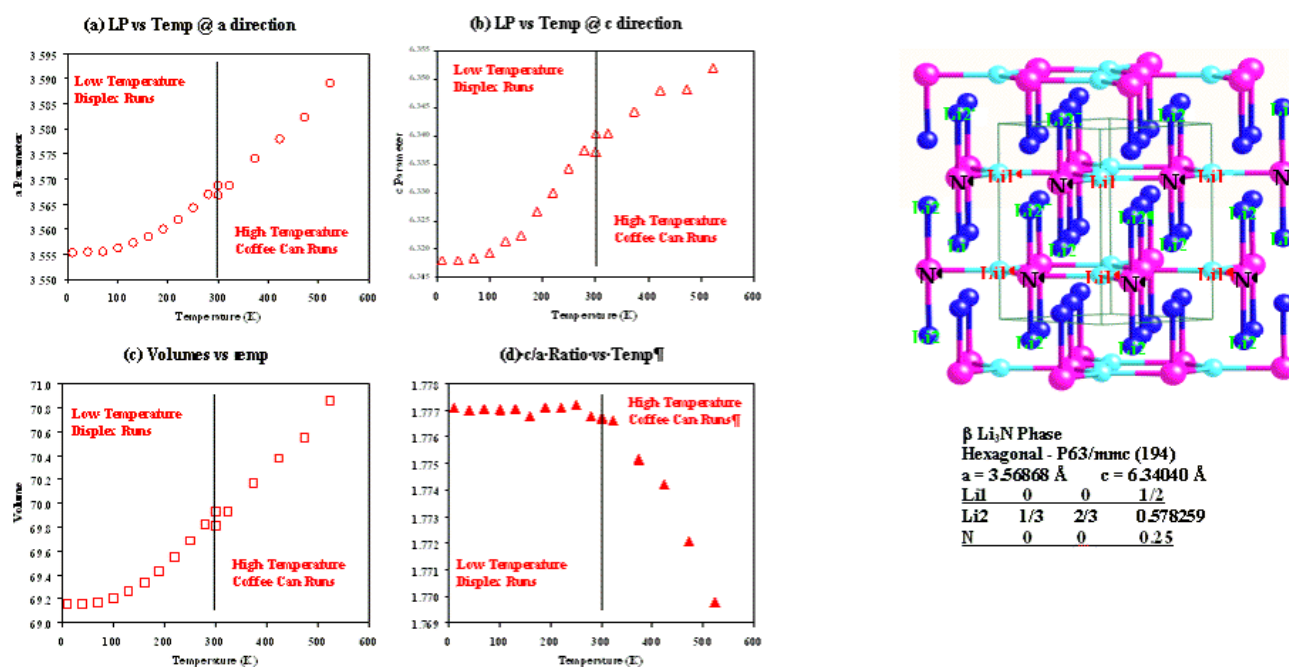


Figure 3. Lattice Parameter, Volume and c/a ratio as Function of Temperature Plots of β Li₃N Phase at 10 - 523 K Temperature Range (The c/a ratios remain the same from 10- 300 K, and then decreases from 1.7771 to 1.7698 from 300-523 K.)

Conclusions of Partner Effort for FY 2005

- Crystal structure studies of Li_3N showed the axial ratio c/a for the α phase decreases monotonically from 10 to 523 K, whereas the β phase does not show any decrease in the c/a ratio until 300 K; beyond which decreases rapidly until 523 K.
- Thermal expansion of LiAlD_4 showed significant anisotropy in expansion in the 013 plane; the 200, 21-2, and 130 spacings did not change appreciably.

University of Nevada, Reno FY 2005 Publications/Presentations

1. Hydrogen Program Review poster presentation in Washington D.C., May 2005.
2. Poster presented at the IPHE International Hydrogen Storage Technology Conference (Lucca, Italy), June 2005.

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Contract Number: DE-FC36-05GO15066

Start Date: March 2005

Projected End Date: February 2010

Partner Approach

Goals

We propose to complement experimental efforts of HRL, GE and other MHCoe partners involved in this effort by using density functional theory (DFT) methods coupled with Monte Carlo techniques to predict the heats of formation and finite temperature phase stability information for a variety of alloys of interest. The HRL team investigating alloyed materials also includes the California Institute of Technology, the University of Hawaii, Stanford University/SSRL and JPL. The HRL team has already studied the destabilization of LiBH_4 for reversible hydrogen storage using MgH_2 as a destabilizing additive [1]. They also reported that alloying with Si is shown to destabilize the strongly bound hydrides LiH and MgH_2 [2]. Combinatorial chemistry methods at GE will be used to generate a range of different alloys. We will also collaborate with GE's experimental team.

Methods

The feasibility of using plane wave DFT to quantitatively examine the heats of formation of metal hydrides has recently been demonstrated by Smithson *et al* [3]. We will initially focus on stoichiometric alloys such as A_4BH_x , where A is a low-Z metal such as Li or Mg. For a series of candidate crystal structures, we will optimize the lattice and cell parameters of each alloy both with and without hydrogen present to determine the heat of formation of the hydride. In addition to providing numerical predictions for specific materials of interest, this initial work will also allow us to explore means to correlate the heat of formation of the hydride with fundamental properties such as the electronic structure of the alloy. Smithson *et al* found that the formation energy of elemental hydrides was closely related to the *d*-band structure of the initial metal.³ Very similar observations have been used to correlate adsorption energies for a variety of atomic and molecular adsorbates on metal surfaces.

For alloys identified as promising in our initial calculations and in the experimental work of our MHCoe partners, we will perform more detailed studies to assess the possible roles of structural disorder and phase segregation. Structural disorder will be examined by performing plane wave DFT calculations with substitutionally disordered supercells [4] and comparing the stability of these materials to their ordered stoichiometric counterparts. If structural disorder is found to play a crucial role in the properties of the most favorable materials, methods are available to use DFT to assess the short range order [5] and quantify its effect on hydride formation energies. Phase segregation will be studied by separately optimizing the structures of candidate phases.

Partner Results for FY 2005

- We have computed structural (lattice parameters) and energetic (total energies) for a number of different alloys using gradient generalized approximation (GGA) density functional theory (DFT)
- The energies were used to compute enthalpy of reaction for four different destabilization reactions
- Calculations were compared with experiments to assess the accuracy of GGA DFT for these systems
- We have computed adsorption energetics and geometries of H₂ adsorbing on the surface of Mg₂Si

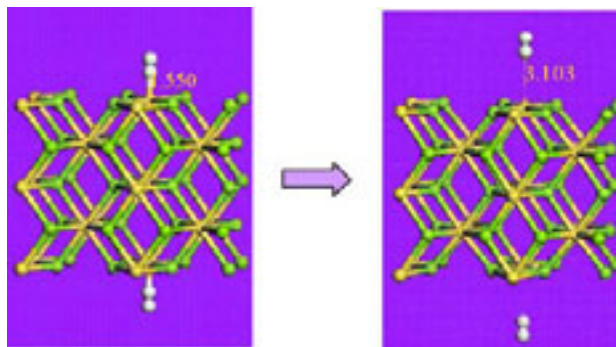


Figure 1. Adsorption of H₂ on the Mg₂Si Surface (The adsorption does not lead to dissociation. This result agrees with experiments, which indicates that Mg₂Si does not hydrogenate.)

Partner FY 2006 Plans

- Compute hydrogen partial pressures as a function of temperature for selected destabilized metal hydrides
- Calculate dissociation pathways for H₂ on Mg₂Si
- Calculate binding energies and adsorption barriers for atomic H on Mg₂Si
- Compute diffusion pathways for H in bulk Mg₂Si
- Consider catalytic pathways to facilitate the reversibility of Mg₂Si + 2H₂ → 2MgH₂ + Si
- Compute thermodynamic properties of new materials as needed based on continuing collaboration with HRL, GE, Stanford, and other MHCoe partners.
- Compute dissociation pathway for H₂ on Mg surfaces
- Compute diffusion pathways for H in bulk Mg

Conclusions of Partner Effort for FY 2005

- We have verified the accuracy of GGA-DFT for computing structural properties and energies of metal hydrides and destabilized alloys.
- Molecular hydrogen adsorbs very weakly through physisorption (van der Waals interactions) on the Mg₂Si surface. The binding energies are on the order of 0.1 eV. Dissociation of H₂ on the Mg₂Si surface must have a substantial energy barrier.

University of Pittsburgh FY 2005 Publications/Presentations

1. DOE Hydrogen Program Review, May 2005

References

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Partner Approach

The project undertaken by the University of Utah team aims to improve kinetics of hydrogen release/uptake reactions by using nanoscaled powders. The nanoscaled powders will be produced by a chemical vapor synthesis (CVS) process. The primary advantage of CVS process is that it yields materials with homogeneity at atomic level. CVS process is also very flexible for fine tuning chemical formula of materials. The synthesis process will also be used for discovery of new solid hydrides that have hydrogen storage properties.

The University of Utah team has established intra-center partnership with other members of the center. The Utah team will collaborate with SNL on the study of the influence of processing variables on the performance of hydrogen storage materials. The Utah team will also assist HRL on synthesis of MgH_2 alloys with Si via the chemical vapor reaction process.

Partner Results for FY 2005

- This is a new project that is still in the start-up mode.
- Installed several laboratory equipment and instrumentations
- The CVS synthesis furnace set-up has been designed and is in the process of fabrication.

Partner FY 2006 Plans

It is anticipated that at the beginning of FY 2006, we will have already established basic vapor phase reaction system and capabilities. Therefore, the focus for FY 2006 will be to make nano sized powders of selected materials and optimize the reaction system for better performance.

Specifically, we plan to make the following materials as starting materials for synthesis of complex metal hydrides:

- Ti-doped nanosized aluminum (Al) powder for synthesis of AlH_3 , $NaAlH_4$, $LiAlH_4$, and $Mg(AlH_4)_2$,
- Ti-doped lithium nitride for synthesis of lithium amide,
- Nanosized Mg_2Si for the study of thermodynamically tuned MgH_2 .