

## IV.A.2 Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods

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### Objectives

Discovery of complex metal hydrides through molecular modeling and combinatorial methods which will enable a hydrogen storage system that meets DOE 2010 performance goals. The deliverables include:

- Optimized material
- Accompanying documentation

### Technical Barriers

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

- (A) System Weight and Volume
- (B) System Cost
- (D) Durability/Operability
- (E) Charging/Discharging Rates

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

### Technical Targets

This project uses virtual high-throughput screening by computer modeling and combinatorial experimentation to identify promising metal hydrides for vehicular on-board hydrogen storage applications meeting DOE 2010 system targets:

- Useable specific-energy from H<sub>2</sub>: 2 kWh/kg
- Useable energy density from H<sub>2</sub>: 1.5 kWh/L
- Storage system cost: 4 \$/kWh net
- Cycle life: 1,000 cycles
- Minimum and maximum delivery temperature: -40/85°C
- System fill time: 3 minutes for a 5-kg hydrogen system.

UOP Progress Toward Meeting DOE On-Board Hydrogen Storage Targets  
(Data is based on material only, not system)

Storage Parameter	Units	2010 Target	LiBH <sub>4</sub> -LiNH <sub>2</sub> -MgH <sub>2</sub>
Specific Energy	kWh/kg	2.0	1.1
Energy Density	kWh/L	1.5	0.8

### Accomplishments

- Nearly 900 samples prepared, characterized by X-ray diffraction (XRD) and evaluated for hydrogen storage properties. Unfortunately, none of the materials met DOE targets for hydrogen storage, especially in terms of reversibility.
- The High Throughput Synthesis System was brought on-line this year and is being used for combinatorial catalytic doping experiments.
- Completed a Virtual High Throughput screen of ~1,200 mixtures containing LiBH<sub>4</sub>, NaBH<sub>4</sub>, Mg(BH<sub>4</sub>)<sub>2</sub>, Ca(BH<sub>4</sub>)<sub>2</sub> and Zn(BH<sub>4</sub>)<sub>2</sub>. Unfortunately, no heats of mixing were large enough to stabilize any mixture versus dehydrogenating.
- Carried out a comprehensive theoretical investigation of the quinary Ca-Li-Mg-B-H and Li-Mg-B-N-H systems; identified decomposition pathways of Li<sub>4</sub>BN<sub>3</sub>H<sub>10</sub>.
- Screened destabilized reactions based upon LiBH<sub>4</sub> and Ca(BH<sub>4</sub>)<sub>2</sub>; identified thermodynamically promising, but kinetically inhibited reactions;

formulated general rules for designing thermodynamically correct destabilized reactions.



## Introduction

Metal hydrides have the potential for reversible on-board hydrogen storage with hydrogen release at low temperatures and pressures. However, known hydrides are either too heavy (such as  $\text{LaNi}_5\text{H}_6$ ), or require high temperature to release hydrogen (such as  $\text{MgH}_2$ ). This project will systematically survey complex hydrides to discover a material which would enable a hydrogen storage system that meets DOE's 2010 goals.

## Approach

The team is applying combinatorial experimentation and molecular modeling to discover materials with optimum thermodynamics and kinetics for on-board hydrogen storage. Virtual high-throughput screening (VHTS) exploits the capability of molecular modeling to estimate the thermodynamics on the computer more quickly than can be measured in the laboratory. First-principles calculations are being used to predict thermodynamic properties of these new materials. Even more importantly, the coupling of combinatorial experiments with molecular modeling of structural and thermodynamic properties is providing insights into the underlying mechanisms of action in these complex materials, permitting the design of hydrogen storage materials which would never have been envisioned otherwise.

## Results

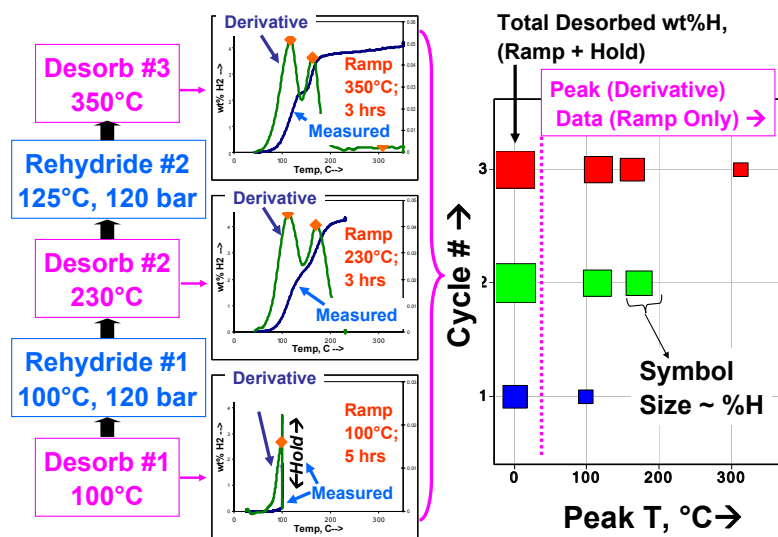
### High Throughput Experimentation

Our investigation of the  $\text{LiNH}_2 - \text{LiBH}_4 - \text{MgH}_2$  phase diagram last year highly influenced the future direction of our project. In that study, the best storage material was derived from a combination of all three components,  $0.6 \text{ LiNH}_2 - 0.3 \text{ MgH}_2 - 0.1 \text{ LiBH}_4$ , but the active reversible storage species were  $\text{Li}_2\text{Mg}(\text{NH})_2$  and  $\text{Mg}(\text{NH}_2)_2$ , which can be derived from  $2 \text{ LiNH}_2 + \text{MgH}_2$ . The addition of the  $\text{LiBH}_4$  greatly enhanced the kinetics of this system, which we speculate to be due to the formation of  $\text{Li}_4(\text{NH}_2)_3\text{BH}_4$ , which was observed in varying amounts at the various stages of the adsorption/desorption reaction via XRD. It is well known from the studies in the GM laboratories that this

phase melts above  $100^\circ\text{C}$ . The presence of this molten phase enabled easier transport of the species involved in this reaction whereas before one had to rely on solid state reaction. Because  $\text{LiNH}_2$  (8.7 wt% H) and  $\text{LiBH}_4$  (18.5 wt% H) are excellent sources of hydrogen on a gravimetric basis and together could form ionic liquids that could provide access to new metastable materials via the softer chemistry, we chose to pursue phase diagrams based on  $\text{LiNH}_2$  and  $\text{LiBH}_4$  in combination with a third major component, usually a transition metal such as Mg, Al, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, or Zr. Synthesis strategies that included metathesis were employed to generate transition metal borohydrides, transition metal amides, and mixed transition metal borohydride-amides in each phase diagram.

The samples were tested by performing several temperature programmed desorption-rehydrating cycles. The standard protocol is shown in Figure 1. The sequence started with a low temperature desorption to avoid damaging sensitive samples, then was stepped up in successive cycles to higher temperatures to access less reactive hydrogen.

Among the samples studied, hydrogen capacities of up to 2.5 wt% were recorded during  $100^\circ\text{C}$  desorption cycles. Some of the low temperature capacities suffered from hydrogen loss during milling. During desorption in the mid range ( $230^\circ\text{C}$ ) up to 7.2 wt% hydrogen was observed. While this is in the range of DOE targets, these results were not reversible. Desorption cycles carried out at  $350^\circ\text{C}$  yielded hydrogen capacities up to 6.3 wt% and were also found to be less than reversible. It should be kept in mind that there was no effort to purify these samples, i.e., they often contained byproducts such as  $\text{LiCl}$  that could not contribute to



**FIGURE 1.** Illustration of the Peak Derivative Detection from the Cumulative wt% H versus Temperature Measurements from Three Desorption Cycles for 2%Ti/NaAlH<sub>4</sub>, as well as a Visual Representation of the Results

hydrogen desorption, diminishing the observed hydrogen storage content. Also, the high-throughput hydrogen capacities assume that all of the gas is hydrogen. Gas analysis to check for ammonia or diborane in the desorbed hydrogen was performed separately for interesting samples.

### Anionic Transition Metal Borohydride Complexes

Recently, lithium and other Group I and II borohydrides have been explored as hydrogen storage materials. However, the dehydrogenation of these compounds is plagued by severe kinetic limitations, competing side reactions, and/or irreversibility. Many transition metal borohydride complexes have highly attractive gravimetric hydrogen densities. However, most well known transition metal borohydride complexes such as  $Zr(BH_4)_4$  and  $Zn(BH_4)_2$  are volatile or desorb diborane under the conditions required for dehydrogenation and cannot be rehydrided under practical conditions.

We have synthesized Group I salts of anionic transition metal borohydride complexes to circumvent these problems. These materials maintain a high hydrogen capacity while the anionic character offers reduced volatility and increased stability. In addition, different thermodynamic parameters might allow reversibility and eliminate production of diborane during dehydrogenation.

Anionic transition metal borohydrides (mainly of zinc, manganese, and zirconium) have been synthesized by the ball milling of transition metal chlorides with Group I borohydrides and by the ball milling of neutral transition metal borohydrides with Group I borohydrides. The above reactions were monitored by X-ray diffraction and infrared spectroscopy. Also, characterization of the products was possible by magnetic angle spinning (MAS)  $^{11}B$  nuclear magnetic resonance (NMR) spectroscopy. The dehydrogenation properties of the synthesized complexes were studied. The complexes all eliminated 2-7 weight percent hydrogen at around 100°C. It was found that tandem hydrogen/diborane evolution occurs with anionic zinc borohydride complexes. On the other hand, hydrogen evolved from  $M'Mn(BH_4)_3$  at low temperatures without tandem diborane production and no diborane was observed with hydrogen evolved from anionic zirconium borohydrides. It was also found that the nature of the cation influences the desorption temperature of complexes like  $M_2Zn(BH_4)_4$ .

### High-Throughput Combinatorial Capability

The high throughput assay has performed over 1,000 hydrogen storage capacity measurements this last year. The high throughput synthesis system, which is capable of robotically manipulating powders and liquids,

is now operational. The system has been utilized for a combinatorial dopant study on two host materials in order to improve kinetics and reversibility.

### High Throughput Informatics

The Hydrogen Synthesis Materials Interface tool has been completed to upload synthesis information to the database, describing milling and other unit operations. The Desorption Data Utility (DDU) tool has been developed and validated for computing and visualizing primary data such as wt%  $H_2$  and desorption descriptors from the output of the testing systems. In order to extract desorption peak information from the cumulative wt% H versus temperature measurements, new methods were developed to differentiate the desorption profiles and identify the peak data. Figure 1 shows an example of desorption curves for 2%Ti/NaAlH<sub>4</sub> from three cycles with derivative peaks generated by the DDU, as well as a novel visualization that covers multiple desorption peaks from multiple cycles in a single graph.

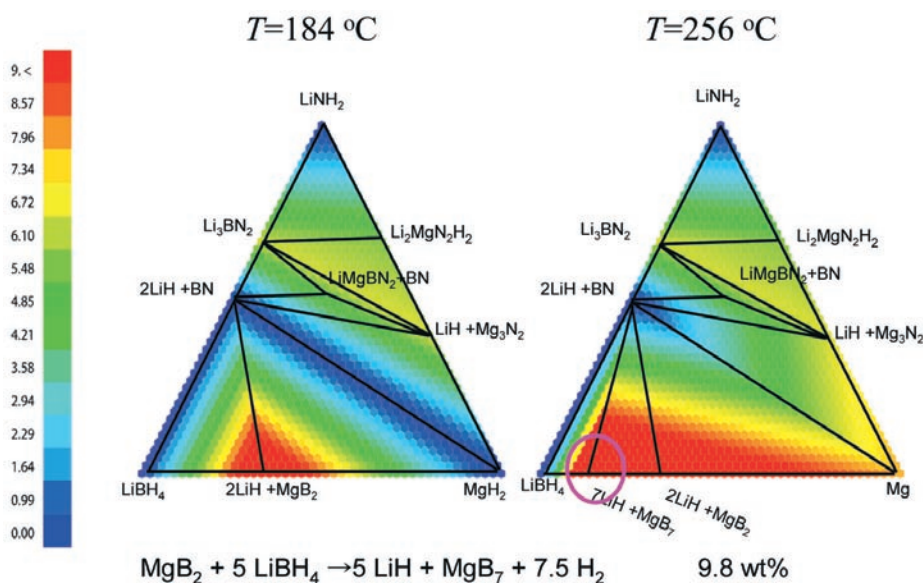
### Virtual High-Throughput Screening

A new force-field was developed to model mixtures of alkali, alkaline earth and transition metal borohydrides. The scan of ~1,200 mixtures containing  $LiBH_4$ ,  $NaBH_4$ ,  $Mg(BH_4)_2$ ,  $Ca(BH_4)_2$  and  $Zn(BH_4)_2$  has been completed. Unfortunately, no heats of mixing were large enough to stabilize any mixture versus dehydriding. These calculations assumed that current predicted structures are close to the lowest energy structure. An additional 15 kJ/mol\* $H_2$  would be needed to stabilize any of these mixtures.

### First Principles Modeling

In order to predict thermodynamically allowed reactions in multicomponent systems, we have developed a general first-principles framework [1] based on the minimization of the grand canonical Gibbs free energy of an open system that can exchange hydrogen with a reservoir of  $H_2$  gas. Using the density functional theory (DFT) free energies (including vibrations) of all possible multinary phases and linear programming, our method can predict all thermodynamically favored hydrogenation reactions and pinpoint the temperatures and compositions with the greatest promise for reversible storage. Our results for the quaternary Li-Mg-B-N-H system help to understand the experimental data and predict new reactions (see Figure 2).

Using first-principles free energy calculations we explored whether destabilization of the strongly-bound  $LiBH_4$  and  $Ca(BH_4)_2$  borohydrides is possible by mixing with various metal hydrides. By screening through ~20 candidate reactions, we identify new reactions having both favorable thermodynamics and high hydrogen



**FIGURE 2.** Calculated phase diagram of the  $\text{LiBH}_4$ - $\text{LiNH}_2$ - $\text{MgH}_2$  system. Color shading indicates the total amount of hydrogen released, as wt% of the starting mixture. The region corresponding to the indicated reaction is marked with a purple circle.

densities of  $<7\text{--}9 \text{ wt}\% \text{ H}_2$  and  $<100 \text{ g H}_2/\text{L}$ . Compared to other recent predictions, the proposed reactions have the advantage of consisting of known compounds with established synthesis routes. Via several examples, we have demonstrated that chemical intuition alone is not sufficient to identify valid reaction pathways, and proposed three guidelines to facilitate more robust predictions of destabilized reactions [2].

## Conclusions and Future Directions

A great many compositions have been tested in the last year and some of them show good fresh hydrogen storage capacity, but the problem is they fall short with respect to reversibility. Active phases that might represent a minority of the sample need to be investigated further. Because very mild conditions have been employed so far in the rehydrating phase of the desorption/absorption cycles, new rehydrating conditions should be applied to many of the materials that showed promising desorption properties in an attempt to attain reversibility. Our work so far has been conducted with limited addition of dopants to improve reaction kinetics and reversibility. The combinatorial application of dopants to promising materials would also be part of our future work. Another aspect of our work involves the chemistry that is used to synthesize the hydrogen storage materials. Many materials released hydrogen during milling before they could even be tested. Softer synthetic methods such as solution or ionic liquid synthesis, and the addition of stabilizing components are strategies that would be part of our future work. Future directions in materials screening

will also continue to focus on transition-metal modified borohydride-containing systems. The development of reversible borohydride components for a hydrogen storage system is important because of their gravimetric advantage. Our initial results for alkali transition metal borohydrides has shown that these systems are more stable and have improved properties over transition metal borohydrides. The general composition of these materials can be described as  $\text{M-TM-BH}_4\text{-NH}_2\text{-AlH}_4\text{-H}$ , where M is an alkali/alkaline earth metal and TM stands for transition metals. The goal here is to lower the desorption temperature and improve reversibility compared to the known alkali and alkaline earth borohydrides. The high throughput approach will enable the pursuit of these complicated systems.

The VHTS screening of mixtures of complex hydride has shown that simple mixtures of these materials will not stabilize unstable alanates or borohydrides enough to be reversible under reasonable conditions. This has led us to focus on systems where the cations and anions react to form new charged species to yield greater stabilization. For example, the reaction between alkali borohydrides and transition metal borohydrides yield complex anions with the general formula  $\text{M}(\text{BH}_4)_n^{-(n-x)}$ , where x is the oxidation state of M.

Our theoretical work has demonstrated how to correctly design new reactions with thermodynamic properties in the targeted range for reversible on-board storage. However, most of the predicted new reactions are severely inhibited kinetically. Future research in this area should focus on finding new ways of accelerating the solid-state kinetics of hydrogen storage reactions.



## FY 2007 Publications/Presentations

1. “High Throughput Screening of Complex Metal Hydrides for Hydrogen Storage,” Fall Materials Research Society Meeting, Symposium A5.5, Boston, November 30, 2006, Gregory J. Lewis, J. W. Adriaan Sachtler, John J. Low, David A. Lesch, Syed A. Faheem, Paul M. Dosek, Lisa M. Knight, and Craig M. Jensen.
2. “High Throughput Screening of Complex Metal Hydrides for Hydrogen Storage,” submitted to MRS Proceedings, Gregory J. Lewis, J. W. Adriaan Sachtler, John J. Low, David A. Lesch, Syed A. Faheem, Paul M. Dosek, Lisa M. Knight, and Craig M. Jensen.
3. “A Novel Li-Based Hydrogen Storage System,” Presentation at MH2006 conference, Kanaapali, HI, October 1–6, 2006, by Jun Yang, Andrea Sudik, Donald Siegel, Devin Halliday, Andy Drews, Roc Carter, Christopher Wolverton, Gregory J. Lewis, J. W. A. Sachtler, John J. Low, Syed A. Faheem, David A. Lesch, and Vidvuds Ozolins.
4. “Global Optimization of Complex Anionic Hydride Crystal Structures,” Presentation at MH2006 conference, Kanaapali, HI, October 1–6, 2006, by E.H. Mazoub and V. Ozolins.
5. “High Throughput Screening of a Novel Ternary Complex Hydride System,” Presentation at MH2006 conference, Kanaapali, HI, October 1–6, 2006, by G.J. Lewis, J.W.A. Sachtler, J.J. Low, D.A. Lesch, S.A. Faheem, P.M. Dosek, L.M. Knight, L. Halloran, C.M. Jensen, Jun Yang, Andrea Sudik, Donald Siegel, Chris Wolverton, Vidvuds Ozolins, Shu Zhang.
6. “Transition Metal Borohydride Complexes as Reversible Hydrogen Storage Materials,” Presentation at MH2006 conference, Kanaapali, HI, October 1–6, 2006, by G. Severa, J. Eliseo, and C.M. Jensen.
7. “Developments in Advanced Borohydride Materials for Hydrogen Storage,” Poster at MH2006 conference, Kanaapali, HI, October 1–6, 2006, by Jennifer R. Eliseo and C.M. Jensen.
8. “High Throughput Screening of Complex Hydrides for Hydrogen Storage,” Poster at MH2006 conference, Kanaapali, HI, October 1–6, 2006, by J.W.A. Sachtler, G.J. Lewis, J.J. Low, D.A. Lesch, S.A. Faheem, P.M. Dosek, L.M. Knight, and C.M. Jensen.
9. “Virtual High Throughput Screening of Complex Hydrides for Hydrogen Storage,” Poster at MH2006 conference, Kanaapali, HI, October 1–6, 2006, by John J. Low, J.W. Adriaan Sachtler, Gregory J. Lewis, David A. Lesch, and Craig M. Jensen.
10. “First-Principles Studies of Thermodynamic and Structural Properties of the Li-Mg-N-H System,” Presentation at MH2006 conference, Kanaapali, HI, October 1–6, 2006, by A. Akbarzadeh, C. Wolverton, and V. Ozolins.
11. “High Throughput Screening of the Ternary  $\text{LiNH}_2$  –  $\text{MgH}_2$  –  $\text{LiBH}_4$  Phase Diagram,” Journal of Alloys and Compounds, doi:10.1016/j.jallcom.2007.04.028, G. J. Lewis, J.W.A. Sachtler, J.J. Low, D.A. Lesch, S.A. Faheem, P.M. Dosek, L.M. Knight, L. Halloran, C.M. Jensen, Jun Yang, Andrea Sudik, Donald J. Siegel, Devin Halliday, Andy Drews, Roc Carter, Christopher Wolverton, Vidvuds Ozolins, and Shu Zhang.
12. “First-Principles Studies of Thermodynamic and Structural Properties of the Li-Mg-N-H System,” Presentation at the MRS Fall Meeting in Boston, MA, November 27 – December 1, 2006, by A. Akbarzadeh, C. Wolverton, and V. Ozolins.
13. “Hydrogen storage in calcium alanate: First-principles thermodynamics and crystal structures,” Phys. Rev. B 75, 064101 (2007), C. Wolverton and V. Ozolins.
14. “First-principles determination of multicomponent hydride phase diagrams: Application to the Li-Mg-N-H system,” submitted to Advanced Materials (2007), A. Akbarzadeh, V. Ozolins, and C. Wolverton.

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1. A. Akbarzadeh, V. Ozolins, and C. Wolverton, “First-principles studies of multicomponent hydride phase diagrams: Applications to the Li-Mg-N-H system,” submitted to Advanced Materials (2007).
2. D. Siegel, C. Wolverton, and V. Ozolins, “New Hydrogen Storage Reactions Based on Destabilized Borohydrides,” submitted to Phys. Rev. Lett. (2007).