

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 for independent testing
- Documentation

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Cost
- (B) Weight and Volume
- (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 H₂: 2 kWh/kg
- Useable energy density from H₂: 1.5 kWh/L
- Storage system cost: \$4/kWh
- Cycle life: 1,000 cycles
- Minimum and maximum delivery temperature: -30/85°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 ₄ -LiNH ₂ -MgH ₂
Specific Energy	kWh/kg	2.0	1.1*
Energy Density	kWh/L	1.5	0.8*

Accomplishments

- Completed investigation of the ternary LiNH₂-MgH₂-LiBH₄ system, finding new compositions near 0.6 LiNH₂-0.3 MgH₂-0.1 LiBH₄ which show improved hydrogen absorption/desorption kinetics over binary systems such as 2 LiNH₂-MgH₂.
- Completed a theoretical investigation of the phase diagram and thermodynamic properties of the Li-Mg-N-H system using first-principles density functional calculations.
- Completed investigation of mixed alanates both experimentally and by modeling, however, no improvement was found over NaAlH₄/Ti.

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 LaNi_5H_6), or require high temperature to release hydrogen (such as 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

Mixed Alanates

Ten phase diagrams containing ternary mixtures of Li-, Na-, K-, Mg- and/or Ca-alanate were screened experimentally. Samples were synthesized by hydriding mixtures of Al and alkali/alkaline earth metal hydrides. While many phases, including hexahydrides, were observed none of the systems performed better than NaAlH_4/Ti .

In a comprehensive search of this system, VHTS was used to scan 981 six-component mixtures containing Li, Na, K, Be, Mg and Ca-alanate. Only seven new phases were discovered with negative heats of mixing. Figure 1 shows the predicted heats of mixing and the composition of these phases. Although they are predicted to be stable with respect to mixing, they are not stable with respect to decomposition at room temperature. In general, the low heats of mixing in the alanates appear to be due to the packing of the tetrahedral (AlH_4) groups in crystals of alanates which leads to structures with only one type of cation site. Based on these results, the investigation into mixed alanates has been discontinued.

Amide – Borohydride – Metal Hydride Systems

The next phase of the research moved to more complex systems based on combinations of components with high hydrogen content such as amides, alanates, and borohydrides. A generalized phase diagram is

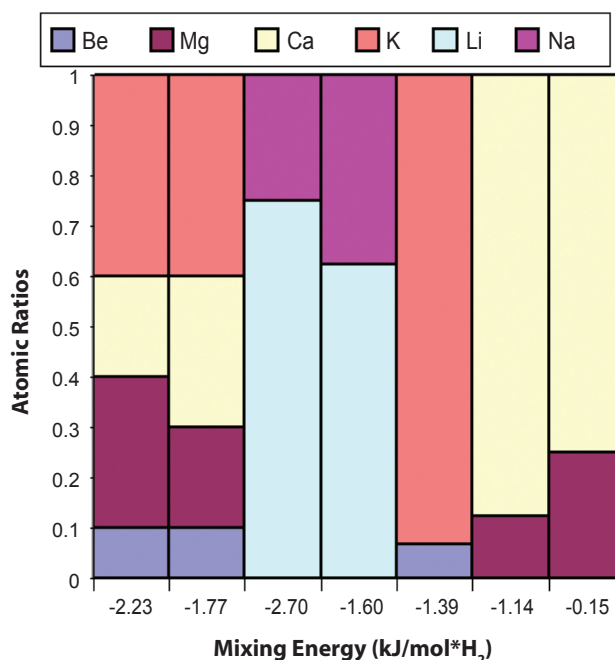


FIGURE 1. Predicted Heats of Mixing and Composition of the Most Stable Mixed Alanate Phases Evaluated by VHTS

shown in Figure 2. The first undertaking within this general phase diagram was the LiBH_4 - LiNH_2 - MgH_2 system. The three binary sub-systems associated with this phase diagram have all been examined previously in the literature (LiBH_4 - MgH_2 [1], LiNH_2 - MgH_2 [2], LiNH_2 - LiBH_4 [3]), but the ternary system has not been reported.

Samples for the LiBH_4 - LiNH_2 - MgH_2 phase diagram were synthesized in 0.1 mol-fraction steps by ball-milling. H_2 content was measured by temperature programmed desorption using a ramp rate of $2^\circ\text{C}/\text{min}$ from room temperature to 220°C followed by a hold of 1 hour. The reversible H_2 content was obtained by rehydriding the samples after the first desorption and measuring a second desorption. It should be emphasized that these measurements are kinetic by nature and do not represent equilibrium hydrogen storage capacities. As shown in Figure 3, the best material in this system is a ternary composition of the formulation $0.6 \text{LiNH}_2:0.3 \text{MgH}_2:0.1 \text{LiBH}_4$, with 3.4 wt% reversible hydrogen. Evaluation of a similar material of composition $5 \text{LiNH}_2:2.2 \text{MgH}_2:\text{LiBH}_4$ in the high throughput assay desorbed almost 7 wt% at 350°C , but became irreversible after heating to 300°C , as shown in Figure 4, suggesting a useful operating range below 240°C . Evaluation of the entire phase diagram in the high throughput unit sequentially desorbing to 220°C , 285°C , 350°C , and 350°C , with intervening 125°C rehydriding steps did not reveal any new reversible materials, the only reversibility being observed for materials approaching MgH_2 .

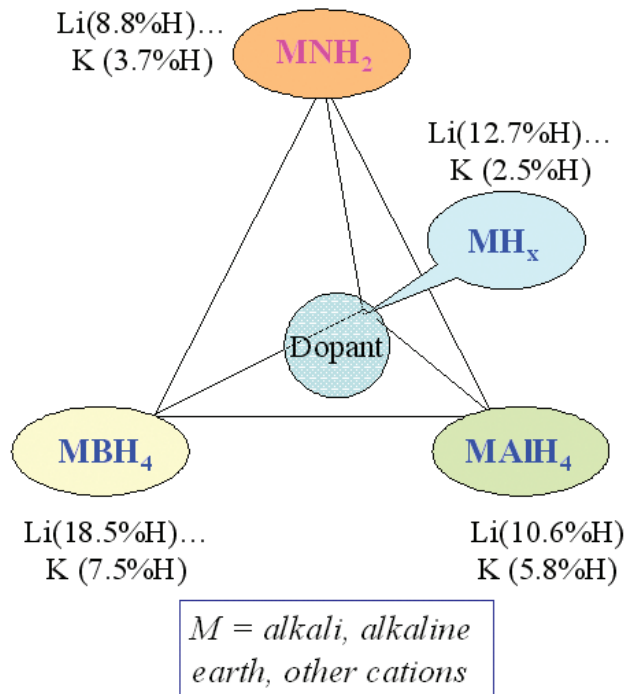


FIGURE 2. General Phase Diagram for Hydrogen Storage Materials to be Investigated

X-ray diffraction was used to determine the phases present in hydrided and dehydrided ($5 \text{ LiNH}_2 \cdot 2.2 \text{ MgH}_2 \cdot \text{LiBH}_4$) material. $\text{Li}_4\text{BH}_4(\text{NH}_2)_3$ was observed throughout the cycles, in varying amounts. The hydrided materials consisted of mostly $\text{Mg}(\text{NH}_2)_2$, while the dehydrided materials consisted mostly of $\text{Li}_2\text{Mg}(\text{NH})_2$ with some $\text{Li}_2\text{NH}/\text{LiNH}_2$. The presence of the $\text{Mg}(\text{NH}_2)_2/\text{Li}_2\text{Mg}(\text{NH})_2$ couple is similar to the active species in the binary $2 \text{ LiNH}_2\text{-MgH}_2$ system, with the notable absence of significant LiH . Yet the optimum ternary system with the extra LiBH_4 performs better kinetically. Measurements of the purity of the desorbed hydrogen to check for volatile N, B species is underway.

High-Throughput Combinatorial Capability

The high throughput assay has been operational since late last year and it has been used in the work described above. The high throughput synthesis system is scheduled for shipping in late June and will be set up in July 2006.

First Principles Modeling

The Li-Mg-N-H system has attracted enormous attention recently due to reports of high reversible H_2 capacity and thermodynamics favorable for storage under ambient temperatures and pressures [4-6]. Using first-principles density functional calculations, we have obtained structural properties, lattice dynamics,

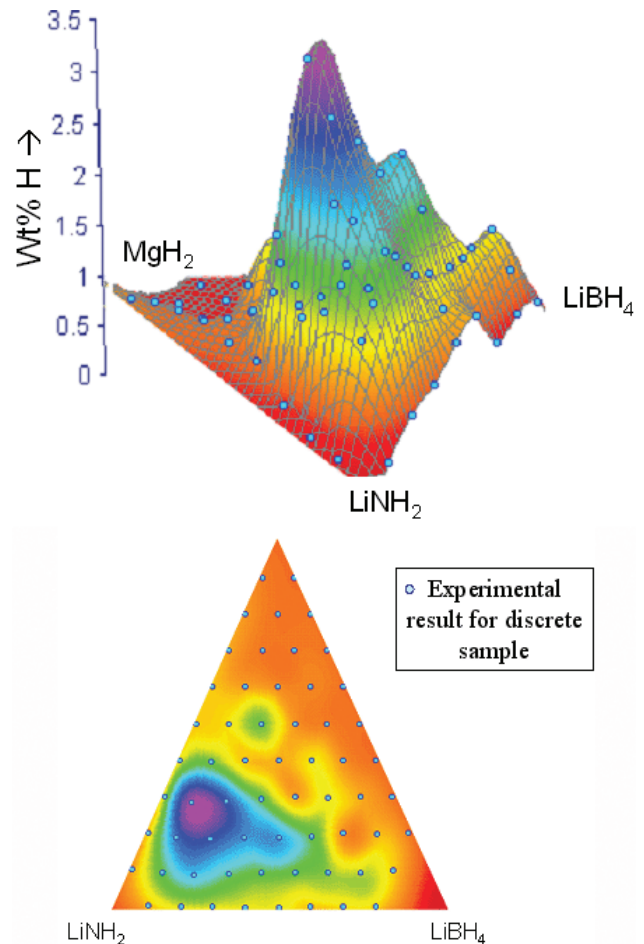


FIGURE 3. $\text{LiNH}_2 + \text{MgH}_2 + \text{LiBH}_4$; Experimental Medium Throughput Results for Reversible wt% Hydrogen (Desorption #2 to 220°C)

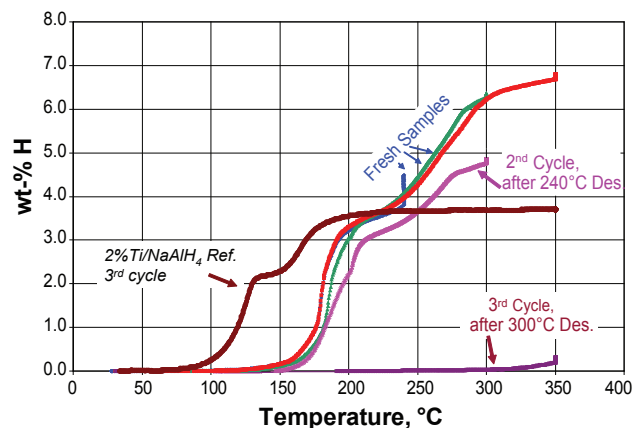


FIGURE 4. Hydrogen storage capacity of fresh $5 \text{ LiNH}_2 : 2.2 \text{ MgH}_2 : \text{LiBH}_4$ at 240°C, 300°C, and 350°C and in sequential desorptions. The material is no longer reversible after desorption at 300°C.

and hydrogenation enthalpies and entropies of the known ordered compounds in this system. First-principles calculations indicate that the reversible H_2

storage density is thermodynamically limited due to the formation of the mixed $\text{Li}_2\text{Mg}(\text{NH})_2$ imide. The lowest decomposition enthalpy for this compound is achieved in the following reaction: $\text{Li}_2\text{Mg}(\text{NH})_2 + 2 \text{LiH} + \text{Mg}_3\text{N}_2 \rightarrow 4 \text{LiMgN} + 2 \text{H}_2$, which has an enthalpy of 92 kJ/mol- H_2 (without zero-point vibrational energies), and is well outside the targeted range of 20-50 kJ/mol- H_2 .

Conclusions and Future Directions

The mixed alanate results have not been promising and the focus of this work has shifted to systems that include additional high hydrogen capacity components, including amides and borohydrides. A new reversible composition has been found in LiNH_2 - MgH_2 - LiBH_4 phase diagram that has better low-temperature kinetics than the known 2 LiNH_2 - MgH_2 system. Future directions will include transition-metal modified borohydride systems. The general composition of these materials can be described as M-TM-BH_4 - NH_2 - AlH_4 - 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 to pursue of these complicated systems. The first-principles computational work will be extended to perform a similar comprehensive investigation of thermodynamics in the LiBH_4 - MgH_2 - LiNH_2 system.

FY 2006 Publications/Presentations

1. "High Throughput Screening of Complex Metal Hydrides for Hydrogen Storage," Fall Materials Research Society Meeting, Symposium A5.5, Boston, Nov. 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. "Discovery Of Novel Complex Metal Hydrides For Hydrogen Storage Through Molecular Modeling And Combinatorial Methods," Presentation to FreedomCAR Tech-Team, Detroit, MI, January 12, 2006, presented by J.W.A. Sachtler.
4. "Discovery of Novel Complex Metal Hydrides for Hydrogen Storage Through Molecular Modeling And Combinatorial Methods," U.S. DOE Hydrogen Program Annual Merit Review, May 18, 2006, Presented by G.J. Lewis.
5. "Predictions of New Hydrogen Storage Compounds and Mixtures," invited talk given at the Theory Focus Session on Hydrogen Storage Materials, held in conjunction with the U.S. DOE Hydrogen Program Annual Merit Review, May 18, 2006, V. Ozolins.
6. "First-Principles Computational Search for Reversible Room-Temperature Hydrides," poster presented at the U.S. DOE Hydrogen Program Annual Merit Review, May 16-19, 2006, V. Ozolins.

References

1. J. J. Vajo et.al., J. Phys. Chem. B, 109, 3719 (2005).
2. Z. Xiong et. al., Adv. Mater., 16, 1522 (2004).
3. F. E. Pinkerton et. al., J. Chem. Phys. B, 109, 6 (2005).
4. Chen et al., Nature, 381, 302 (2002).
5. W. Luo and S. Sickafoose, J. Alloys and Compounds, 407, 274 (2006).
6. Y. Nakamori et al., 204, 396 (2005).