

IV.A.3 Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity

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Objectives

- Design coupled reactions of complex hydride compounds with co-reactants to yield a reversible hydrogen storage gravimetric capacity of ≥ 7.5 wt%.
- Demonstrate sorption kinetics for reversible generation of ≥ 7.5 wt% hydrogen from newly designed hydrogen storage media under viable temperatures and pressures.

Technical Barriers

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

- (A) System Weight and Volume
- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

TABLE 1. UTRC Progress Toward Meeting DOE On-Board Hydrogen Storage Targets

Storage Parameter	Units	2007 Target	Material Result To Date
Specific Energy	kWh/kg	1.5	2.3-2.9*
Energy Density	kWh/L	1.2	0.7-1.3**
Desorption Temperature	°C	< 100	150-340***

*Relation of material results to system targets depends on system design, the material is nominally 50-60% of system mass, and capacities should be adjusted accordingly.

**Enhanced settling technique on $\text{LiMg}(\text{AlH}_4)_3$, and M-B-N-H systems A & B.

***Results for $\text{LiMg}(\text{AlH}_4)_3$. M-B-N-H Systems A and B have onset T's of < 100°C.

Accomplishments

- Developed integrated methods for coupled complex reaction strategy: structure refinement, thermodynamic predictions, reaction design and thermodynamic optimization.
- Identified and evaluated three new complex compounds with theoretical potential for greater than 7.0 wt% hydrogen storage capacity.
- Implemented reaction design with co-reactants and complex modification to: improve complex stability by reducing dehydrogenation exotherms up to a factor of four, lower H discharge onset temperatures below 100°C and prevent NH_3 side-product formation.
- Demonstrated progress towards volumetric targets, up to 1.3 kWh/L theoretical capacity, using enhanced densification method.

Introduction

This project team is integrating first principles and thermodynamic modeling with three different synthetic methods to develop hydrogen storage media with retrievable hydrogen contents of greater than 7.5 wt% H_2 and 0.05 kg H_2 /L, and discharge rates greater than 0.02 g/s/kW. The development of hydrogen storage media with greater than 7.5 wt% gravimetric capacity would meet the 2007 DOE goal of 4.5 wt% capacity, assuming a system component weight penalty of 40%.

Approach

The project is focused on identifying fully hydrided phases having the formula: $AK_wAE_xTM^+i_y(P^{zj}H_2)_{(w+2x+iy)}$ where $z = |1 \pm j|$, formed in the multi-dimensional phase spaces between alkali (AK) and/or alkaline earth (AE) hydrides, transition metals (TM), p-metal hydrides (alane, borane, or ammonia) (P), and molecular hydrogen (H_2). These new complex hydride phases are being isolated and verified with multiple experimental methodologies: (i) solid state processing, (ii) molten state processing, (iii) solution-based processing, and (iv) structural characterization. First principles atomic and thermodynamic modeling are being used iteratively with experimental methods to design, refine, and evaluate coupled high hydrogen capacity reactions of new complex hydrides and co-reactants to reversibly generate greater than 7.5 wt% H_2 . The project activities include performance evaluations to select compositions for further development, spectroscopic mechanistic studies and first-principles screening simulations to optimize dehydrogenation and hydrogenation catalysis, safety and compatibility analyses, and preliminary scoping for synthesis scaleup and business case development.

Results

Atomic-Thermodynamic Modeling

A modified search strategy coupling quaternary complex hydride reactions with co-reactants was instituted in FY 2006. First principles thermodynamic predictions were used to supplement experimental thermodynamic databases for the thermodynamic modeling of a wider range of potential hydrogen retrieval reaction scenarios. The survey compositional scope was expanded, requiring thermodynamic predictions of over 60 complex alanate, boronate, and amine phases as well as lower order phases within the Li-Mg-Na-Al-B-N-H septenary system, and of over 40 co-reactant phases within related quaternary compositional systems. The modified strategy prompted the implementation of new modeling methods for: a) structure refinement, b) reaction design, and c) thermodynamic optimization. Input models for the crystallographic refinement and atomic-thermodynamic simulation of new phase structures were globally optimized with a simulated annealing method. Combined thermochemical reaction and Gibbs energy minimization calculations were used to survey and design coupled reactions that exchange a high amount of hydrogen between solid and gas phases. A new tool was developed to optimize the elemental stoichiometry within a compositional space at selected temperature/pressure conditions, for the highest theoretical hydrogen storage capacity. These methods, in combination with the established density

functional theory structural minimization, first principles thermodynamic property prediction, and thermodynamic phase diagram modeling methods, constituted a complete repertoire of virtual tools for guiding the experimental discovery and design of high hydrogen capacity systems.

Materials Synthesis and Testing

A. Li_3AlH_6

During the FY 2005 study of the Na-Li-Mg-Tm-Al-H system, evidence was found that the following reaction releasing 5.6 wt% theoretical hydrogen may be reversible at 80-100°C and 190 bar:



In this study, two approaches were taken to synthesize Li_3AlH_6 by solid-state processing using the following reactions:



In the absence of a catalyst, x-ray diffraction (XRD) results showed the formation of Li_3AlH_6 after 3 hours of SPEX milling by using both approaches. When 4 mol% $TiCl_3$ or 2 mol% $TiCl_3/AlCl_3$ were added as catalysts, most of the Li_3AlH_6 decomposed after 3 hours of SPEX milling in both cases. The desorption reaction occurred readily in the presence of the catalyst. The subsequent rehydrogenation at 80-120°C, 170 bar for 24 hours did not result in hydrogen absorption, indicating the Ti-modified compound is not reversible at moderate temperatures and pressures.

B. $LiMg(AlH_4)_3$

$LiMg(AlH_4)_3$ is a mixed alkaline and alkaline earth alanate with a theoretical storage capacity of 7.77-8.20 wt%, depending on the decomposition products formed. It was synthesized by Albemarle using a solution-based method. The as-synthesized material was tested for isothermal desorption at 100, 150, and 340°C, under 1 bar H_2 pressure. At 100°C, 4 wt% H_2 was released at a slow rate (see Figure 1). XRD characterization of the dehydrogenated material showed new peaks attributed to $LiMgAlH_6$, along with LiH , MgH_2 , and Al . The desorption rate increased significantly at 150°C, with 6.9-7.0 wt% H_2 released. At 150°C, the probable $LiMgAlH_6$ phase disappeared. An additional 1.8 wt% H_2 was released at 340°C, yielding a total capacity of 8.7 wt% H_2 . The intermetallic phase, $Al_{3.11}Mg_2$, was formed at 340°C. The results indicated that the following reactions occurred during desorption:

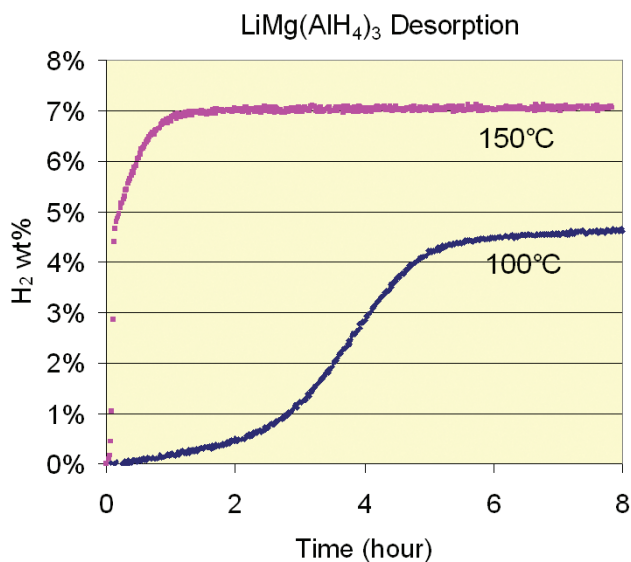
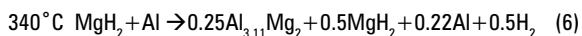
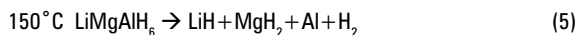
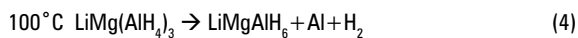


FIGURE 1. H_2 Desorption of $\text{LiMg}(\text{AlH}_4)_3$ at 100 and 150°C

The average first hour H_2 desorption rates are listed in Table 2 in comparison with 4% TiCl_3 catalyzed NaAlH_4 . The desorption rate of the as-synthesized $\text{LiMg}(\text{AlH}_4)_3$ at 150°C is double that of catalyzed NaAlH_4 .

TABLE 2. First hour average desorption rate.

Compound	100°C	150°C
$\text{LiMg}(\text{AlH}_4)_3$	0.16%	6.79%
4% TiCl_3 catalyzed NaAlH_4	2.10%	3.34%

The reverse hydrogen absorption was tested at 110 bar and 120°C after desorption at 150°C . Absorption of H_2 did not occur up to 24 hours. The differential scanning calorimetry (DSC) of $\text{LiMg}(\text{AlH}_4)_3$ showed two exothermic (140.3°C and 168.2°C) and one endothermic (192.6°C) events, indicating that $\text{LiMg}(\text{AlH}_4)_3$ desorption reactions at temperatures below 170°C were irreversible. Further progress on this system is contingent on pending structural analyses and thermodynamic predictions.

C. Metal-B-N-H System A

Metal (M)-B-N-H system A was synthesized by Albemarle using solution-based synthetic methods.

Thermogravimetric analysis–mass spectrometry (TGA-MS) showed two hydrogen peaks at 214°C and 285°C (see Figure 2). In addition to hydrogen, ammonia was also released at temperatures above 100°C . In order to reduce the generation of ammonia, a co-reactant was mechanically mixed with M-B-N-H system A. This designed reaction has the potential of releasing >8 wt% H_2 . The TGA-MS of the designed reaction showed three hydrogen peaks at 128°C , 238°C , and 444°C (see Figure 3). Only a trace amount of ammonia was detected at temperatures above 450°C . This indicated that the introduction of co-reactant significantly reduced

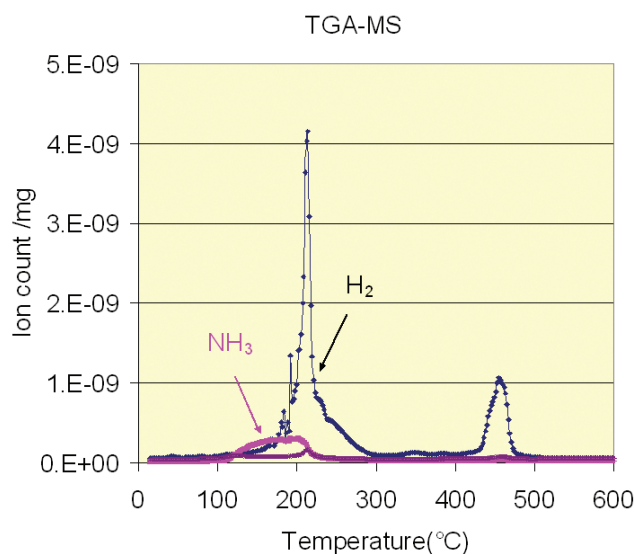


FIGURE 2. Thermogravimetric Analysis – Mass Spectrometry of Metal-B-N-H System A

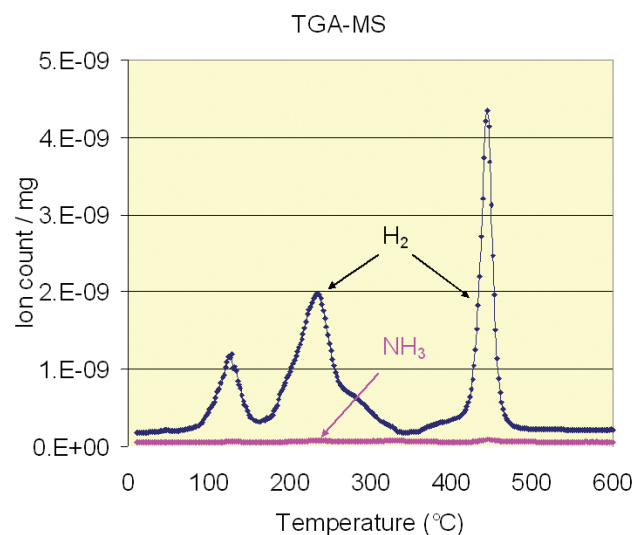


FIGURE 3. Thermogravimetric Analysis – Mass Spectrometry of Metal-B-N-H System A with Co-Reactant

ammonia generation. Also, the onset temperature for H₂ release was lower than that of the original material. The isothermal desorption test showed that >7.5 wt% hydrogen was released at temperatures up to 350°C. No rehydrogenation of the dehydrided material was observed under 195 bar of hydrogen. Further complex modification is being pursued to improve M-B-N-H system A reversibility.

D. Metal-B-N-H System B

A Metal-B-N-H system B compound was synthesized by a solution-based method. The DSC of this compound showed an exothermic peak at 147°C, releasing 1006 J/g of heat. A modification of the composition resulted in the reduction of the reaction exotherm to 261.5 J/g without appreciably reducing H capacity, while eliminating side-product formation. The modified compound released >4 wt% H₂ at 150°C in the first half hour of desorption, and a total of 5.9 wt% in 10 hours. No significant hydrogen absorption was observed during rehydriding under 80-120°C, 68 bar pressure.

Conclusions

- Implemented an expanded repertoire of virtual methodologies to guide the experimental discovery and design of two coupled complex hydride systems.
- Demonstrated feasibility of meeting DOE 2007 gravimetric and volumetric targets with desorption studies of three new complex hydride systems.

Future Directions

- Screen one additional metal borohydride high capacity composition. Design coupled reactions and/or complex modification to refine reversible hydrogen capacity of all promising candidate systems.
- Downselect best system by October 2006 and accelerate kinetics with activating agent.
- Conduct safety and compatibility tests. Outline plans for synthesis scaleup and business case development.

FY 2006 Publications/Presentations

1. S. M. Opalka, O. M. Løvrik, H. W. Brinks, P.W. Saxe, and B. C. Hauback, "Integrated experimental-theoretical investigation of the Na-Li-Al-H system," submitted J. Am. Chem. Soc.
2. C. Qiu, S. M. Opalka, G. B. Olson, and D. L. Anton, "Thermodynamic modeling of the sodium alanates and the Na-Al-H system," accepted for publication in Int. J. Mat. Res.
3. O. M. Løvrik and S. M. Opalka, "The stability of Ti in NaAlH₄," Applied Physics Letters 88, 161917-1-3(2006). Also published in the May 1, 2006 issue of Virtual Journal of Nanoscale Science & Technology. <http://www.vjnano.org>.
4. O. M. Løvrik, O. Swang, and S. M. Opalka, "Modelling alkali alanates for hydrogen storage by density-functional band-structure calculations," J. Mater. Res., 20(12) 3199-3213 (2005).
5. C. Qiu, S. M. Opalka, G. B. Olson, and D. L. Anton, "The Na-H System: from first principles calculations to thermodynamic Modeling," Int. J. Mat. Res. 97 845 (2006).
6. S. M. Opalka, T. H. Vanderspurt, S. C. Emerson, D. A. Mosher, Y. She, X. Tang, and D. L. Anton, "Theoretical contributions towards the development of storage media and related materials for hydrogen processing", invited presentation, 2006 TMS Annual Meeting, San Antonio, Texas, March 13-16, 2006.
7. C. Qiu, G. B. Olson, S. M. Opalka, and D. L. Anton, "Thermodynamic modeling of sodium alanates and the effect of Ti," presentation, 2005 Fall MRS Meeting, Boston, MA, Nov. 29-Dec. 3, 2005.
8. O. M. Løvrik, O. Swang, S. M. Opalka, and P. N. Molin, "Alanates for hydrogen storage – density functional calculations of structural, electronic, and thermodynamic properties," invited presentation 2005 Fall MRS Meeting, Boston, MA, Nov. 29-Dec. 3, 2005.
9. S. M. Opalka, D. A. Mosher, X. Tang, D. L. Anton, R. Zidan, K. Shanahan, J. Strickler, F.-J. Wu, O. M. Løvrik, H. Brinks, and B. Hauback, "Complex hydride compounds with enhanced hydrogen storage capacity," presentation, SemiAnnual Workshop of the IEA Hydrogen Implementing Agreement Task 17 – Solid and Liquid State Hydrogen Storage at Tateshina, Japan, October 23-27, 2005.
10. C. Qiu, S. M. Opalka, D. L. Anton, G. B. Olson, "Thermodynamic modeling of sodium alanates," Materials for the Hydrogen Economy Symposium, presentation, Materials Science & Technology 2005, Pittsburgh, PA, September 25-28, 2005.
11. S. M. Opalka, O. M. Løvrik, H. W. Brinks, B. Hauback, P. W. Saxe, and D. L. Anton, "Combined experimental-theoretical investigations of the Na-Li-Al-H system," presentation, Materials Science & Technology 2005, Pittsburgh, PA, September 25-28, 2005.