

## IV.A.1 Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity

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### Subcontractors:

- Albemarle Corporation, Baton Rouge, LA
- Institutt for Energiteknikk (IFE), Kjeller, Norway
- QuesTek Innovations LLC, Evanston, IL
- Savannah River National Laboratory (SRNL), Aiken, SC

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### Objectives

- Deploy integrated methods to design and optimize hydrogen storage media based on mixed metal borohydride compositions capable of  $\geq 7.5$  wt%  $H_2$  reversible capacity.
- Assess potential volumetric capacity of new complex hydride compositions with respect to the 2007 DOE system volumetric goal of 36 kg  $H_2/m^3 H_2$  capacity.

### Technical Barriers

This project addresses the following technical barriers from the Reversible Solid-State Materials Storage Systems section 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

### Technical Targets

TABLE 1. UTRC Progress Toward Hydrogen Storage System Targets\*

Target	Units	2007 System Targets	2005 to 2006 Best Alanate $LiMg(AIH_4)_3$ System	2006 to 2007 Best Borohydride $Mg(BH_4)_2 \cdot 2NH_3$ System
Gravimetric Capacity	kWh/kg (kg $H_2$ /kg)	1.5 (0.045)	2.1 / 1.3 (0.070 / 0.042)	3.0 / 1.8 (0.091 / 0.055)
Volumetric Capacity	kWh/L (kg $H_2$ /L)	1.2 (0.036)	0.5 / 0.38*** (0.015 / 0.011)	1.5 / 1.1 (0.044 / 0.033)
Desorption Rate** & T	g/s/kW °C	0.02 (<100)	0.019 165	0.037 100-300

\* For system design with material 60% of system mass & 75% of system volume.  
 \*\* Calculated results based on 5 kg storage for 75 kW fuel cell.  
 \*\*\*  $LiMg(AIH_4)_3$  in as received condition – ball milling could improve densification.

### Accomplishments

- Synthesized several ligand-stabilized  $Mg(BH_4)_2$  complexes with up to 16 wt%  $H_2$  capacity by solution-based processing (SBP) and solid-state processing (SSP). Identified varying  $H_2$  desorption mechanisms of these complexes through integrated experimental analyses, performance testing, and first principles atomic-thermodynamic modeling.
- Identified and evaluated quaternary borohydride systems from SSP of alkali, transition metal, and borohydride precursors, with the potential for up to 11.7 wt%  $H_2$  capacity.
- Demonstrated several ligand-stabilized alkali (Ak)-transition metal (Tm)-boron (B)-hydrogen (H) systems from SBP with very low discharge temperatures, excellent kinetics and partial reversibility, having the potential for up to 7.3 wt% capacity.
- Surveyed Ak-metal (M)-B-H systems using first principles modeling to identify solubility limits of some stable constituents and to predict the influence of metastable constituents on reducing dehydrogenation endothermicity.



### Introduction

The project team has integrated three different synthesis methods with first principles and thermodynamic modeling to develop hydrogen storage

materials with retrievable hydrogen capacities of greater than 7.5 wt% H<sub>2</sub>, 50 kg H<sub>2</sub>/m<sup>3</sup>, and discharge rates greater than 0.02 g/s/kW. The development of hydrogen storage media with greater than 7.5 wt% gravimetric H<sub>2</sub> capacity would meet the 2007 DOE system goal of 4.5 wt% H<sub>2</sub> capacity, assuming a system component weight penalty of 40 %.

## Approach

The project approach evolved dynamically in response to both reviewer recommendations and recent findings. The original approach was to combine atomic modeling methodologies with parallel synthesis trials to survey quaternary systems for new high capacity complex hydride compositions. This approach was expanded in the second year to pursue reversible high capacity coupled reactions of quaternary complex hydrides with co-reactants. A triad of first principles modeling, thermodynamics, and experimental methodologies were iteratively implemented to identify, refine, and evaluate new high capacity systems. In the third year, the new promising quaternary or ligand-stabilized high capacity systems were synthesized using three different methods and mechanistically investigated by both first principles atomic-thermodynamic modeling and experimental characterization.

## Results

### Project Overview

Table 2 provides an overview of the broad compositional systems and methods applied to survey over nine quaternary systems, including six alanate systems and three borohydride systems in the entire program. These include mixed alkali, alkali-alkaline earth, alkali-

**TABLE 2.** Overview of Project Scope

System	Compositions	Method
Alanates	Na-Li-Al-H	FPM*, SSP*, MSP***
	Na-Tm-Al-H	FPM*, SSP*, SBP**, MSP***
	Li-Tm-Al-H	FPM*, SSP*, SBP**, MSP***
	Na-Mg-Al-H	FPM*, SSP*, SBP**, MSP***
	Li-Mg-Al-H	FPM*, SSP*, SBP**
	Li-Na-Mg-Tm <sup>a</sup> -H	SSP*, MSP***
Borohydrides	Tm-B-H w/ ligands & coreactants	SBP**
	Mg-B-H w/ & w/o ligands or coreactants	FPM*, SSP*, SBP**, SASSP***
	Ak-Tm-B-H w/ & w/o ligands	FPM*, SSP*, SBP**

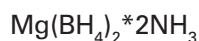
Ak = alkali, Tm = transition metal, Tm<sup>a</sup> = (Ti, V, Cr, Mn, Ni, Co, Fe)

\* UTRC – first principles modeling (FPM), solid state processing (SSP)

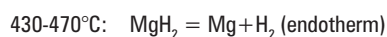
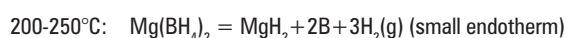
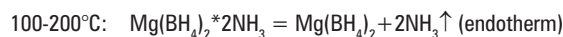
\*\* Albemarle – solution based processing (SBP)

\*\*\* SRNL – molten state processing (MSP), solvent assisted SSP (SASSP)

transition metal alanates and borohydrides. Promising candidates described in the following paragraphs were investigated with a variety of characterization methods to identify material structure, elucidate reaction mechanisms and evaluate performance.



It was found that the nature of the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> ligand-stabilized borohydride complex synthesized by SBP changed with synthesis conditions and/or with aging. Depending on the synthesis conditions, the compound could have two different dissociation mechanisms, one of which involves the release of NH<sub>3</sub> and has a theoretical hydrogen capacity of 9 wt%:



The second mechanism is an amine-borane (NH<sub>3</sub>-BH<sub>3</sub>) like dissociation reaction, possibly forming MgH<sub>2</sub> and BN. This mechanism releases 16 wt% H<sub>2</sub>:

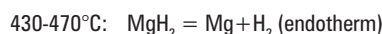
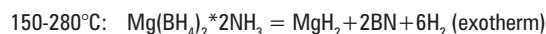
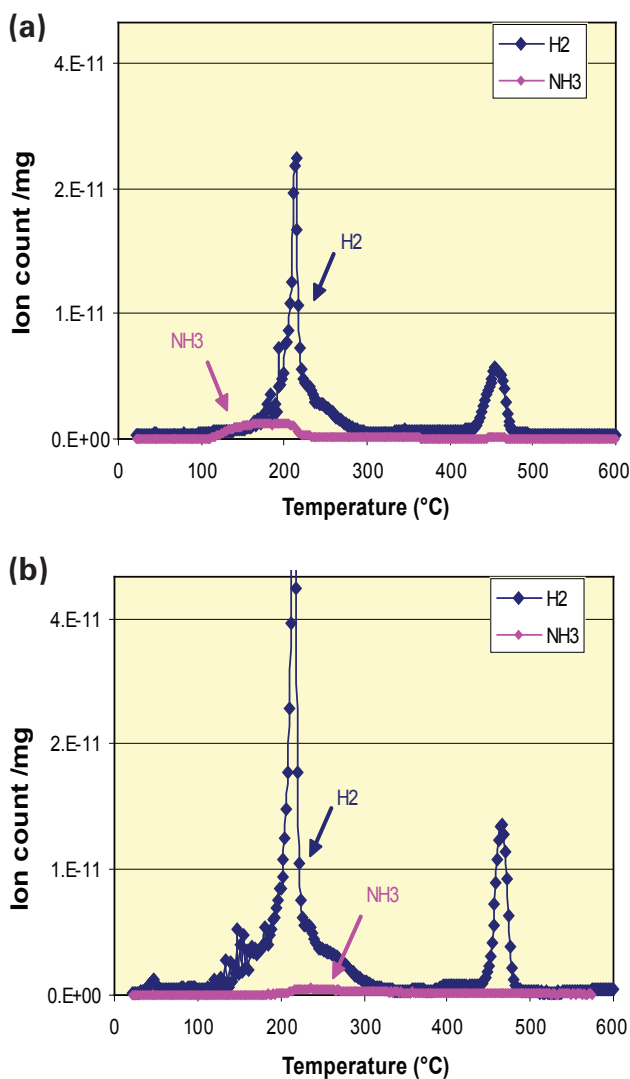


Figure 1a shows the thermogravimetric analysis-mass spectrometer (TGA-MS) of Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> material A, indicating the release of predominately NH<sub>3</sub>, followed by H<sub>2</sub> release between 100-150°C according to the first mechanism. Figure 1b shows the TGA-MS of Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> material B synthesized under slightly different conditions, with minimal NH<sub>3</sub> release, but increased H<sub>2</sub> evolution following mainly the second mechanism.

Atomic modeling was used to investigate the range of possible structures that could be formed with the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> complex and the change in possible decomposition reaction mechanisms with structure. Ground state minimizations and molecular dynamics were used to iteratively refine structures having varying NH<sub>3</sub> coordination with Mg. The stability of the Mg(BH<sub>4</sub>)<sub>2</sub>·2NH<sub>3</sub> compound was found to increase with inclusion of the NH<sub>3</sub> groups in the inner-Mg coordination sphere, which in turn correlated with lowering of the dimensionality of the Mg(BH<sub>4</sub>)<sub>2</sub> network. In the most stable case, two NH<sub>3</sub> ligands directly associate with Mg to form a tetrahedrally coordinated complex, Mg(BH<sub>4</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>, which is not networked with adjacent complexes. Here, with increasing complex stability, the metal hydride decomposition mechanism becomes more energetically prohibitive and the amine-borane mechanism becomes more likely.

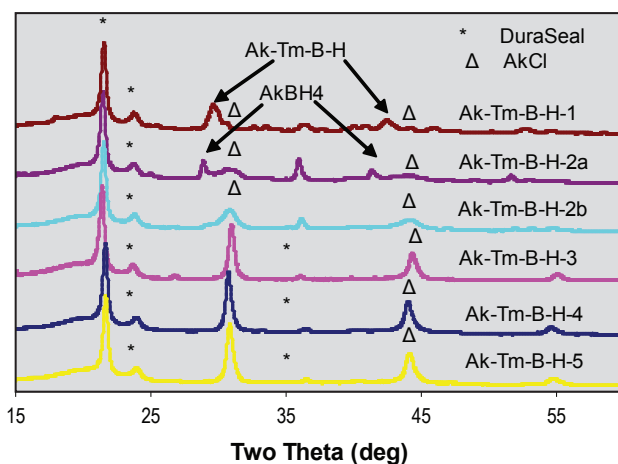


**FIGURE 1.** Thermogravimetric Analysis-Mass Spectrometry of  $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ : (a) Material A, (b) Material B

### New Quaternary Ak-Tm-B-H System

A series of compounds in the Ak-Tm-B-H system were synthesized by combining Ak and Tm precursors using solid-state processing to form new quaternary high capacity compositions. The theoretical gravimetric capacity of the Ak-Tm-B-H quaternary systems ranges from 8-13 wt%  $\text{H}_2$ . The X-ray diffraction (XRD) analysis of the reaction products shows the disappearance of precursor peaks (Figure 2). New peaks were only observed in one composition (Ak-Tm-B-H-1). The majority of compositions were predominantly amorphous in structure.

TGA-MS analysis of the reaction products showed that the  $\text{H}_2$  desorption temperature was decreased in the Ak-Tm-B-H systems, compared with a ternary  $\text{AkBH}_4$  system. In the latter,  $\text{H}_2$  release starts around 300°C, but significant  $\text{H}_2$  desorption does not occur until the



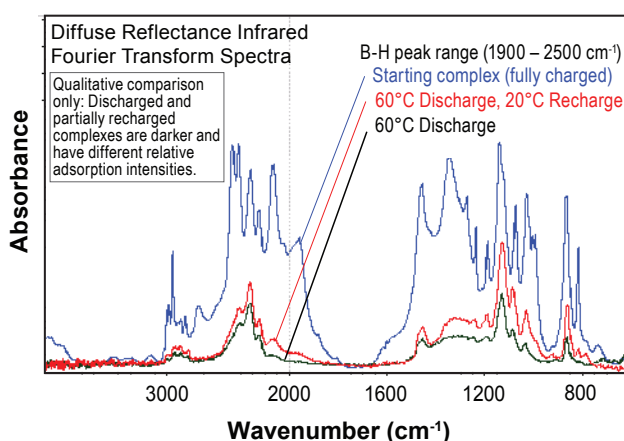
**FIGURE 2.** XRD of Quaternary Ak-Tm-B-H Systems

temperature reaches 500°C. The various Ak-Tm-B-H compositions showed a wide range of dehydrogenation stability, where the lowest  $\text{H}_2$  desorption started at about 120°C. Only trace amounts of  $\text{B}_x\text{H}_y$  gaseous species were detected in the outgas.

The  $\text{H}_2$  desorption measurements for the various Ak-Tm-B-H compounds indicated up to 12 wt% of  $\text{H}_2$  was generated at 400°C, when the removable LiCl side-reaction product weight was excluded in the capacity calculation. However, the most active material can only be partially recharged up to 2 wt%  $\text{H}_2$  at 220-300°C and 195 bar  $\text{H}_2$  pressure. The reversibility of this system is limited due to stable product formation.

First principles modeling was used to investigate Ak-metal (M)-B-H quaternary structures formed from a wider range of M constituents. Ground state minimizations were iteratively conducted with molecular dynamics to develop the most stable low symmetry pseudo-amorphous models. For the more stable quaternary systems, varying M stoichiometries were simulated to determine compositional ranges where quaternary compositions were more stable than the corresponding known ternary Ak-B-H compounds. The resulting ionic and electronic structures were analyzed to identify correlations between the compound stability and electronic properties, serving as a basis for guiding further formulation development.

A new ligand-stabilized Ak-Tm-B-H compound produced by SBP has the potential for up to 7.3 wt% capacity, including the solvent ligand weight (the capacity would be ~12 wt% without the ligands). The synthesis has a very high yield using inexpensive starting materials. The complex discharges  $\text{H}_2$  coupled with ligand release at temperatures as low as 60°C, and partially recharges as low as 20°C in the presence of the released ligand. Evidence of this reversibility was obtained with diffuse reflectance infrared Fourier transform spectra (DRIFTS) analyses, which is sensitive



**FIGURE 3.** Diffuse Reflectance Infrared Fourier Transform Spectra of Ligand-Stabilized Ak-Tm-B-H System

to various B-H vibrational frequencies (Figure 3). The dark color of the dehydrogenated complex indicates transition metal reduction, which most likely limits the reversible capacity and cyclability.

## Conclusions

Two high capacity systems,  $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$  and Ak-Tm-B-H systems, with up to 11.7 wt%  $\text{H}_2$  and 40 kg  $\text{H}_2/\text{m}^3$  capacity and partial reversibility have been synthesized and characterized. These compounds have high hydrogen storage capacity, improved kinetics, and small  $\text{B}_x\text{H}_y$  outgassing. However, they also have limited reversibility most likely due to the formation of stable desorption products. First principles modeling was utilized to screen a wider range of compositions for metastable and stable constituents. Several approaches have been identified for further synthesis and refinement of reversible alkaline earth systems.

## Future Directions

- Complete evaluation of hydrogen release mechanisms from  $\text{Mg}(\text{BH}_4)_2$  ligand complexes.
- Complete optimization of reversibility of Ak-Tm-B-H system.
- Final contract reporting and publications.

## Presentations/Publications

1. H. Grove, H. W. Brinks, R. H. Heyn, F.-J. Wu, S. M. Opalka, X. Tang, B. L. Laube, B. C. Hauback, "The structure of  $\text{LiMg}(\text{AlD}_4)_3$ ," *J. Alloys Compd.*, in press, doi:10.1016/j.jallcom.2007.01.150.
2. X. Tang, S. M. Opalka, B. L. Laube, F. - J. Wu, J. R. Strickler, D. L. Anton, "Hydrogen Storage Properties of Na-Li-Mg-Al-H Complex Hydrides," *J. Alloys Compd.*, in press, doi:10.1016/j.jallcom.2006.12.089.

3. S. M. Opalka, O. M. Løvvik, H. W. Brinks, P.W. Saxe, and B. C. Hauback, "Integrated Experimental-Theoretical Investigation of the Na-Li-Al-H System," *Inorg. Chem.* 46(4), 1401-1409 (2007).
4. C. Qiu, S. M. Opalka, G. B. Olson, and D. L. Anton, "Thermodynamic modeling of the sodium alanates and the Na-Al-H System," *Int. J. Mat. Res.* 97, 1484-1494 (2006).
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, 845-853 (2006).
6. X. Tang, B. L. Laube, D. L. Anton, S.-J. Hwang, and R. C. Bowman, "Stability studies of aluminum hydride," presentation at American Physical Society Meeting, Denver, CO, March 5-9, 2007.
7. A. C. Stowe, P. A. Berseth, A. Jurgensen, D. L. Anton, R. Zidan, "Thermodynamic considerations in the synthesis of complex metal hydrides via mechanosynthetic techniques," presentation at American Physical Society Meeting, Denver, CO, March 5-9, 2007.
8. S. M. Opalka, O. M. Løvvik, and P. W. Saxe, "Atomic simulations of alane phase transformations and dehydrogenation mechanisms," presentation at American Physical Society Meeting, Denver, CO, March 5-9, 2007.
9. O. M. Løvvik and S. M. Opalka, "Theory of complex hydrides," invited presentation *Int. Symp. on Metal Hydrogen Systems*, Lahaina, HI, October 1-6, 2006.
10. X. Tang, S. M. Opalka, B. L. Laube, F. - J. Wu, J. R. Strickler, D. L. Anton, "Hydrogen Storage Properties of Na-Li-Mg-Al-H Complex Hydrides," presentation *Int. Symp. on Metal-Hydrogen Systems*, Lahaina, HI, October 1-6, 2006.
11. H. Grove, H. W. Brinks, R. H. Heyn, X. Tang, S. M. Opalka, and B. C. Hauback, "Syntheses and structural studies of  $\text{LiMg}(\text{AlD}_4)_3$ ," *Int. Symp. on Metal-Hydrogen Systems*, Lahaina, HI, October 1-6, 2006.
12. O. M. Løvvik and S. M. Opalka, "Density-functional calculations of new alanates," invited presentation at *Int. Symp. on Materials Issues in Hydrogen Production and Storage*, Santa Barbara, CA, August 20-25, 2006.