

## IV.A.1b Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides

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### Objectives

The objective of this project is to develop a new class of reversible materials that have the potential to meet the DOE 2010 kinetic and system gravimetric storage capacity targets. Current investigations include:

- The study of novel, high hydrogen capacity, borohydrides that can be reversibly dehydrogenated at low temperatures.
- The development of a method for the hydrogenation of Al to alane,  $\text{AlH}_3$ , and/or  $\text{LiH/Al}$  to  $\text{LiAlH}_4$  at moderate pressures in non-conventional solvents.

### Technical Barriers

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

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

### Technical Targets

The work on this project is currently exclusively devoted to materials that have demonstrated available hydrogen capacities of 7.9-15 wt% hydrogen. We have developed a system for the full reversible dehydrogenation of  $\text{Mg}(\text{BH}_4)_2$  to  $\text{MgB}_2$  that has shown a record 12 wt% reversible hydrogen capacity, but requires further development to meet kinetic performance targets within the target temperature. We have also developed a highly efficient method of the direct hydrogenation of  $\text{LiH/Al}$  to Ti-doped  $\text{LiAlH}_4$  (7.9 wt% hydrogen capacity, rapid dehydrogenation at 120-150°C) at moderate pressure and room temperature that has been estimated to have a well-to-tank (WTT) energy efficiency that approaches 60% and thus meets DOE targets.

### Accomplishments

#### Borohydrides

- Demonstration of the reversible hydrogenation of  $\text{MgB}_2$  to  $\text{Mg}(\text{BH}_4)_2$  with cycling of 12 wt% hydrogen.
- Nano-association of  $\text{Mg}(\text{BH}_4)_2$  in a carbon aerogel found to improve dehydrogenation kinetics.
- Mild conditions (<200°C, <100 atm) found for the reversible dehydrogenation of 2.4 wt% hydrogen from  $\text{Mg}(\text{BH}_4)_2$  as well as (~2.0 wt%) from  $\text{LiSc}(\text{BH}_4)_4$ ,  $\text{NaSc}(\text{BH}_4)_4$ , and  $\text{KSc}(\text{BH}_4)_4$ .

#### Hydrogenation in Non-Conventional Solvents

- Demonstration of the full recharging of Ti-doped  $\text{LiAlH}_4$  by the direct hydrogenation of Ti-doped  $\text{LiH/Al}$  in liquefied dimethyl ether at room temperature under 100 bar of  $\text{Me}_2\text{O}/\text{H}_2$ . Calculations show that this recharging process approaches 60% WTT efficiency.

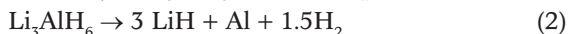


### Introduction

The development of high capacity hydrogen storage materials that can be recharged under moderate conditions is a key barrier to the realization of a hydrogen economy. Towards this end we have examined anionic transition metal borohydride complexes as hydrogen storage materials. The anionic character of these compounds was found to result in an increased stability and a reduced volatility when

compared to neutral transition metal borohydride complexes. We have found that group I and II salts of anionic transition metal borohydride complexes have several improvements over neutral transition metal borohydrides: including higher (9-13 wt%) hydrogen content, reduced volatility and increase stability. We have also found that the alkali metal salts of anionic transition metal borohydride complexes such  $\text{LiMn}(\text{BH}_4)_4$  undergo rapid dehydrogenation at moderate ( $<150^\circ\text{C}$ ) temperatures. In some cases, only very minor the amounts of the undesirable, diborane side product are produced. However, we have not found the full dehydrogenation of any of these materials to be reversible. In order to see if the re-hydrogenation can be achieved even at high pressures, we conducted experiments in the range of 900 bar in collaboration with Sandia National Laboratories. Experiments involving the attempted hydrogenation of mixtures of Group I hydrides and transition borides proved unsuccessful. However, hydrogen uptake was found to occur at  $400^\circ\text{C}$  and 900 atm in experiments in which  $\text{MgB}_2$  was present. Analysis of the product mixtures by X-ray diffraction (XRD) showed that the transition metal component was un-reactive while the  $\text{MgB}_2$  was hydrogenated to  $\text{Mg}(\text{BH}_4)_2$ . The hydrogenation also occurred when starting with only ball-milled  $\text{MgB}_2$ . Our experiments provided the first demonstration of the full reversibility  $\text{MgB}_2$  to  $\text{Mg}(\text{BH}_4)_2$ . In consideration of the  $>14$  wt% hydrogen that is potentially cyclable with this system, it has become the chief focus of our efforts in the area of borohydrides.

In collaboration with the University of New Brunswick, we are also developing new approaches utilizing supercritical fluids and non-conventional solvents for the direct synthesis of  $\text{AlH}_3$  and  $\text{LiAlH}_4$ .  $\text{LiAlH}_4$  releases 7.9 wt% hydrogen according to the two reactions seen in equations 1 and 2.



The second reaction is endothermic ( $\Delta H = +25$  kJ/mol  $\text{H}_2$ ) but the first reaction is exothermic ( $\Delta H = -10$  kJ/mol  $\text{H}_2$ ). Since entropic change is strongly positive for hydrogen release, the first reaction is thermodynamically irreversible under all practical conditions and it has been widely accepted that  $\text{LiAlH}_4$  cannot be recharged and there have been no reports of its use for reversible hydrogen storage. However, the unfavorable thermodynamics of Eq. 1 may be altered by carrying out the reaction in solution, with the solvation of  $\text{LiAlH}_4$  contributing to an endothermic  $\Delta H$  value. In 1963, Ashby et al. reported that a mixture of  $\text{LiH}$  and activated  $\text{Al}$  in tetrahydrofuran (THF) solvent reacted with 350 bar  $\text{H}_2$  at  $120^\circ\text{C}$  to produce  $\text{LiAlH}_4$ . While this method results in the ultimate formation of  $\text{LiAlH}_4$  from  $\text{LiH}$ ,  $\text{Al}$  and  $\text{H}_2$ , it is impractical because of the requirements of high temperature and high pressure

during the synthesis as well as subsequent heating for the removal the THF adduct. An improvement in the synthesis of the THF adduct was achieved by researchers at Brookhaven National Laboratory by using  $\text{Ti}$  additives to significantly lower the required pressure and temperature. However, the prolonged baking in vacuo that is required to remove THF results in the dehydrogenation of the majority of a  $\text{Ti}$ -activated product. We have discovered that this difficulty can be eliminated by utilizing liquefied dimethyl ether ( $\text{Me}_2\text{O}$ ) as the reaction solvent. It is sufficiently coordinating to support the nascent  $\text{LiAlH}_4$  in the reaction environment, yet also volatile enough to be removed easily once it has served this purpose. Through this approach,  $\text{LiAlH}_4$  can be synthesized at room temperature under moderate pressures of  $\text{H}_2$  (80-100 bar) in the presence of very low amounts of  $\text{Ti}$  catalyst (0.5-0.2 mol%). On completion of reaction, the volatile  $\text{Me}_2\text{O}$  solvent and excess  $\text{H}_2$  are vented leaving only fine, dry  $\text{Ti}$ -doped  $\text{LiAlH}_4$  in 95% yield. Thus we have found a highly efficient method for the direct synthesis of  $\text{LiAlH}_4$  at low pressure and room temperature. Preliminary analysis conducted at Argonne National Laboratory has indicated that WTT energy efficiency of our regeneration process is great than 60% and thus approaches the DOE targets.

## Approach

Having demonstrated the reversible elimination of over 11 wt% hydrogen from  $\text{Mg}(\text{BH}_4)_2$ , we wish to develop methods for hydrogen cycling in this system under less forcing conditions. In order to accomplish this, we required a more detailed understanding of the dehydrogenation reaction pathway. Thus we have monitored both the dehydrogenation and re-hydrogenation reactions by XRD and magic angle spinning boron-11 nuclear magnetic resonance spectroscopy (MAS  $^{11}\text{B}$  NMR) and conducted quantitative thermal volumetric pressure-composition-temperature measurements. We have also attempted to improve the kinetics and/or thermodynamics of the dehydrogenation of  $\text{Mg}(\text{BH}_4)_2$  through nano-confinement of the hydride in a carbon aerogel.

Our highly efficient, room temperature direct synthesis of  $\text{LiAlH}_4$  in liquefied  $\text{Me}_2\text{O}$  shows great promise as a practical method for the re-hydrogenation of  $\text{LiH}/\text{Al}$  to  $\text{LiAlH}_4$ . We have found that nearly the entire 7.9 wt% theoretical cycling capacity can be restored in the first cycle of re-hydrogenation. However, the cycling capacity dramatically drops off over the first five cycles of dehydrogenation/re-hydrogenation. In order to overcome this limitation, we have explored the extension of the maximum cycling capacity of  $\text{Ti}$ -doped  $\text{LiAlH}_4$  through variation of the dopant concentration, recharging conditions, and variation dopants.

## Results

### Task 1. Characterization of the Active Titanium Species in Ti Doped NaAlH<sub>4</sub>

This task has been completed.

### Task 2. Spectroscopic Studies of Complex Hydrides

This task has been completed.

### Task 3. Thermodynamic Properties of Complex Hydrides

This task has been completed.

### Task 4. Kinetic Enhancement of “Thermodynamically Tuned” Binary Hydrides

We have merged the Task 4 and 5 efforts and examined whether, as we found for MgH<sub>2</sub>, the kinetics of the dehydrogenation of Mg(BH<sub>4</sub>)<sub>2</sub> could be improved through nano-confinement. Following the exposure of the aerogel to the molten diethyl ether adduct of Mg(BH<sub>4</sub>)<sub>2</sub>, the coordinated diethyl ether was removed by heating at 220°C en vacuo for 3 h. Mg(BH<sub>4</sub>)<sub>2</sub> loadings of the aerogel 57–63 wt% were achieved by this method. Figure 1, provides a comparison of the XRD patterns of the Mg(BH<sub>4</sub>)<sub>2</sub> loaded aerogel with those observed for Mg(BH<sub>4</sub>)<sub>2</sub> powder that was scraped from the surface of the aerogel. The diffraction peaks of the Mg(BH<sub>4</sub>)<sub>2</sub> associated with the aerogel are clearly seen to be broader and much smaller. This indicates that the Mg(BH<sub>4</sub>)<sub>2</sub> associated with the aerogel has nano dimensions. As seen in Figure 2, the <sup>11</sup>B NMR spectrum of the Mg(BH<sub>4</sub>)<sub>2</sub> incorporated aero gel contains only a single peak at the chemical shift of -41.5 ppm, thus verifying that Mg(BH<sub>4</sub>)<sub>2</sub> is the only boron containing species present in the

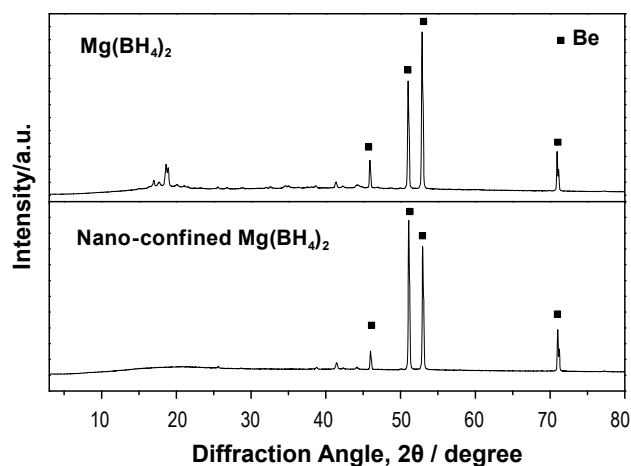


FIGURE 1. Comparison of the XRD patterns of co-synthesized, bulk and nano-Mg(BH<sub>4</sub>)<sub>2</sub>.

material. The nano-Mg(BH<sub>4</sub>)<sub>2</sub> showed good kinetics during the first dehydrogenation. As seen in Figure 3, 2.7 wt% H<sub>2</sub> was eliminated at 270°C in ca. 30 min. Overall, 4.94 wt% H<sub>2</sub> was evolved as the temperature was increased to 400°C. Re-hydrogenation was carried out under 11-13 MPa of H<sub>2</sub> at 300°C for 10 h. The observation of a much slower rate for the second cycle of dehydrogenation strongly suggests that the nano-Mg(BH<sub>4</sub>)<sub>2</sub> was not incorporated into the pores of the aerogel and was just associated with its surface.

### Task 5. Synthesis and Evaluation of Novel Borohydrides

In order to confirm the uptake of over 11 wt% hydrogen occurs in the high pressure hydrogenation of MgB<sub>2</sub>, the dehydrogenation of a sample of the Mg(BH<sub>4</sub>)<sub>2</sub> product was monitored using an automated thermal volumetric analyzer (Sievert's type apparatus). The dehydrogenation profile (seen in Figure 4) shows the release of 11.4 wt% hydrogen. Longer reaction times would quite likely result in higher levels of hydrogenation MgB<sub>2</sub> and thus cycling of 14 wt% hydrogen.

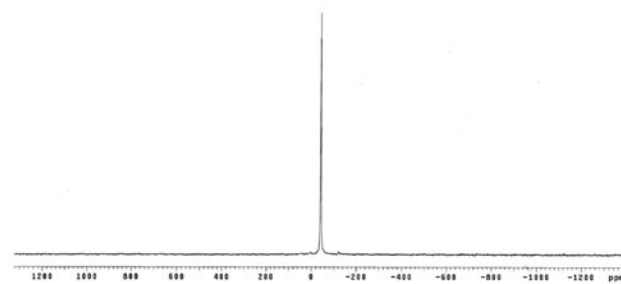


FIGURE 2. MAS <sup>11</sup>B NMR spectrum of carbon aerogel associated nano-Mg(BH<sub>4</sub>)<sub>2</sub>.

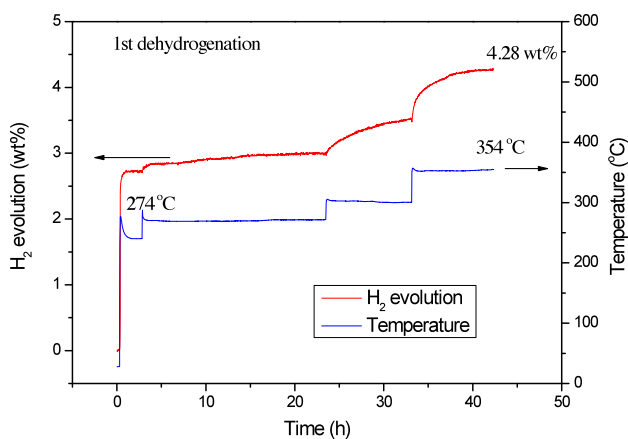
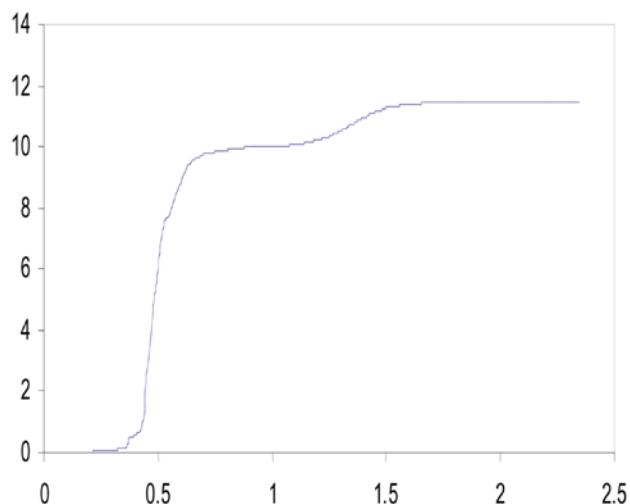


FIGURE 3. First dehydrogenation of carbon aerogel associated nano-Mg(BH<sub>4</sub>)<sub>2</sub>.



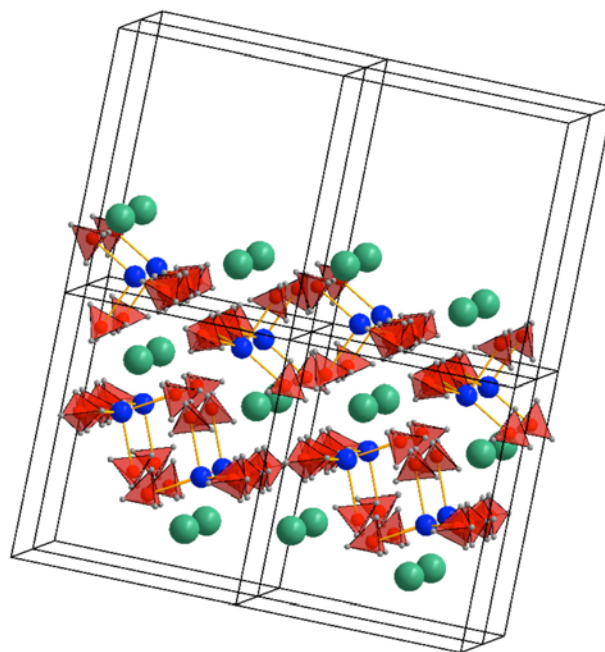
**FIGURE 4.** Thermal desorption profile of second dehydrogenation of  $\text{Mg}(\text{BH}_4)_2$ .

$^{11}\text{B}$  NMR studies of the dehydrogenation of  $\text{Mg}(\text{BH}_4)_2$  have revealed that the dehydrogenation process involves multiple steps. We have found that the early steps do not require heating above  $250^\circ\text{C}$  and result in the release of 2.4 wt% hydrogen. The products of the dehydrogenation at this lower temperature have not yet been fully characterized. However, it is clear at that, in contrast to the large mixture of boranes that results upon high temperature dehydrogenation, the products resulting from the low temperature dehydrogenation of only  $\text{MgH}_2$  and a single borane species. We have found that this species can be cleanly hydrogenated back to  $\text{Mg}(\text{BH}_4)_2$  at  $200^\circ\text{C}$  under 100 atm of hydrogen. This represents a major step towards practically from the extreme ( $400^\circ\text{C}$  and 900 atm) conditions under which we initially achieved re-hydrogenation of  $\text{Mg}(\text{BH}_4)_2$ .

The molecular structure of  $\text{KSc}(\text{BH}_4)_4$  (seen in Figure 5) was determined as part of our continuing collaboration with the University of Geneva. We have now determined the crystal structures of the Li, Na, and K salts of  $[\text{Sc}(\text{BH}_4)_4]^{1-}$ . We have found that heating  $\text{LiSc}(\text{BH}_4)_4$ ,  $\text{NaSc}(\text{BH}_4)_4$  and  $\text{KSc}(\text{BH}_4)_4$  to  $250^\circ\text{C}$  also results in the elimination of significant amounts of hydrogen (2.4, 2.1, and 1.8 wt%, respectively) and give rise to a product mixture that can be re-hydrogenated to the starting borohydride at  $200^\circ\text{C}$  under 100 atm of hydrogen.

#### Task 6. Recharging of Light Metal Hydrides in Non-Conventional Media

Cycle performance experiments were carried out for the  $\text{LiAlH}_4$  material doped with 0.05 mol%  $\text{TiCl}_3$ . The initial dehydrogenation of this material was seen to release 7.9 wt% hydrogen. Following the

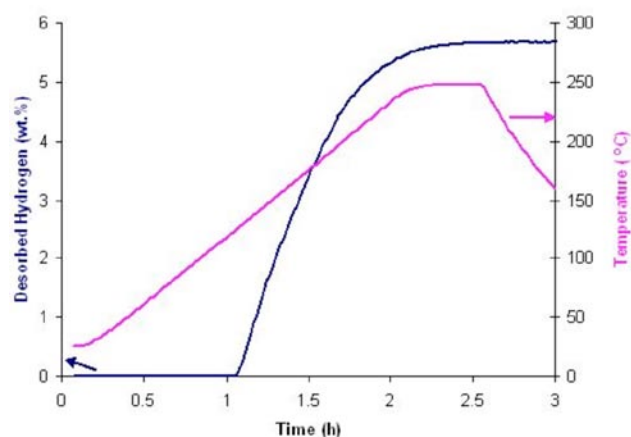


**FIGURE 5.** Crystal structure of  $\text{KSc}(\text{BH}_4)_4$  viewed approximately along the b axis showing the coordination of the  $[\text{BH}_4]^-$  tetrahedra (red) to Sc (blue).

first re-hydrogenation in liquid dimethyl ether, the dehydrogenation half cycle was again found to release 7.9 wt% hydrogen. However, this value dropped to 5.9 and 4.1 wt% H in the third and fourth dehydrogenation half cycles, respectively. In an attempt to stabilize the cycling hydrogen capacity, we investigated the effect of the substitution of  $\text{TiCl}_3$  with other dopants (e.g.  $\text{ScCl}_3$  and  $\text{CeCl}_3$ ). Our results indicate that the catalytic performance of  $\text{ScCl}_3$  supersedes that of  $\text{CeCl}_3$ , but does not reach that of  $\text{TiCl}_3$ . We also explored whether the use of  $\text{TiCl}_3$  supported on alumina ( $\text{Al}_2\text{O}_3$ ), would enhance hydrogen cycling performance. As seen in Figure 6, the Ti-supported catalysts were consistently found to lower the  $\text{H}_2$  desorption temperature of the hydride to  $\sim 125^\circ\text{C}$  (opposed to  $180^\circ\text{C}$  for the undoped  $\text{LiAlH}_4$ ). However, after dehydrogenation and subsequent re-hydrogenation, the hydrogen capacity dropped to 4.0 and 0.0 wt% in the second and third cycle respectively. Analysis of the sample after the third cycle dehydrogenation by transmission electron microscopy (TEM)/energy dispersive X-ray (EDX) showed that Ti was not uniformly distributed; there were areas where no Ti was detected (Figure 7). It is possible that Ti falls off the support upon cycling thereby reducing its effectiveness as a catalyst.

#### Conclusions

Our continuing studies of  $\text{Mg}(\text{BH}_4)_2$  have confirmed the uptake of over 11 wt% hydrogen occurs in the



**FIGURE 6.** First dehydrogenation profile of  $\text{LiAlH}_4$  doped with  $\text{TiCl}_3$  supported on  $\text{Al}_2\text{O}_3$ . The profile is similar to that observed with  $\text{LiAlH}_4$  doped with unsupported  $\text{TiCl}_3$ .

high pressure hydrogenation  $\text{MgB}_2$  to  $\text{Mg}(\text{BH}_4)_2$  and indicate that an optimized system might allow cycling of  $>14$  wt% hydrogen. Our attempts to lower the temperature required for the hydrogen cycling in the  $\text{Mg}(\text{BH}_4)_2/\text{MgB}_2$  system through catalytic enhancement and nano-confinement of the hydride did not prove successful. However, nano- $\text{Mg}(\text{BH}_4)_2$  was found to exhibit dehydrogenation kinetics that were significantly enhanced beyond those of bulk  $\text{Mg}(\text{BH}_4)_2$ .

$^{11}\text{B}$  NMR studies of the dehydrogenation of  $\text{Mg}(\text{BH}_4)_2$  at  $250^\circ\text{C}$  results in the release of 2.4 wt% hydrogen. The products that are obtained from the low temperature dehydrogenation can be cleanly hydrogenated back to  $\text{Mg}(\text{BH}_4)_2$  at  $200^\circ\text{C}$  under 100 atm of hydrogen. Dehydrogenation of  $\text{LiSc}(\text{BH}_4)_4$ ,  $\text{NaSc}(\text{BH}_4)_4$  and  $\text{KSc}(\text{BH}_4)_4$  under similar conditions also results the elimination of significant amounts of

hydrogen (2.4, 2.1, and 1.8 wt%, respectively) and give rise to product mixtures that can be re-hydrogenated to the starting borohydride at  $200^\circ\text{C}$  under 100 atm of hydrogen. Thus earlier studies of the dehydrogenation anionic transition metal borohydrides under more forcing conditions were premature in concluding that this family of hydrides are “irreversible.”

We have developed a method whereby 95% yields of fully charged, Ti-doped  $\text{LiAlH}_4$  are obtained from the direct hydrogenation of Ti-doped  $\text{LiH}/\text{Al}$  in liquefied  $\text{Me}_2\text{O}$ . Although the method is highly efficient method for the re-hydrogenation of  $\text{LiAlH}_4$ , cycling studies have shown the system’s hydrogen capacity dramatically drops off over the first five cycles of dehydrogenation/re-hydrogenation. Attempts to remedy this problem through substitution of  $\text{TiCl}_3$  other dopants (e.g.  $\text{ScCl}_3$  and  $\text{CeCl}_3$ ) and  $\text{TiCl}_3$  supported on alumina ( $\text{Al}_2\text{O}_3$ ) have not proven successful.

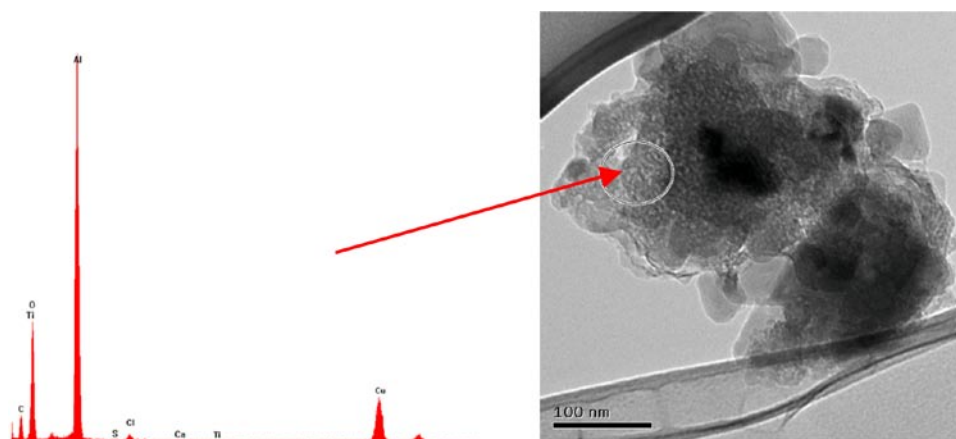
## Future Directions

### Borohydrides

- Adjustment of conditions to maximize trade off between cycling capacity and reaction conditions (temperature/pressures) required for reversible dehydrogenation of  $\text{Mg}(\text{BH}_4)_2$ ,  $\text{LiSc}(\text{BH}_4)_4$ ,  $\text{NaSc}(\text{BH}_4)_4$ , and  $\text{KSc}(\text{BH}_4)_4$ .

### Hydrogenation in Non-conventional Solvents

- Explore maintenance of cycling capacity of doped  $\text{LiAlH}_4$  through variation of the dopants.
- Further evaluation of WTT efficiency of the dimethoxyethane/ $\text{LiAlH}_4$  system to be examined in collaboration with Argonne National Laboratory.



**FIGURE 7.** TEM/EDX analysis of  $\text{TiCl}_3/\text{Al}_2\text{O}_3$ -doped  $\text{LiAlH}_4$  after third cycle dehydrogenation. Left: EDX spectrum taken from circled area in right figure. Right: TEM image; area in circle contains no Ti.

## FY 2010 Publications/Presentations

### Publications

1. “Synthesis and Hydrogen Storage Properties of  $\text{MgH}_2$  Incorporated Carbon Aerogel Scaffold.” S. Zhang, A.F. Gross, S.L. Van Atta, M. Lopez, P. Liu, C.C. Ahn, J.J. Vajo and C.M. Jensen; *Nanotechnology* **2009**, *20*, 204005. Invited contribution for issue on Nanoscale Phenomena in Hydrogen Storage).
2. “Nanostructure Observations of  $\text{AlH}_3$  during Dehydrating Reaction.” K. Ikeda, S. Muto, I.K. Tatsumi, M. Mejo, S. Kato, M. Biemann, A. Zuttel, C.M. Jensen and S. Orimo; *Nanotechnology* **2009**, *20*, 204004. (invited contribution for special issue on Nanoscale Phenomena in Hydrogen Storage).
3. “Facile  $\text{H}_2$  Release and Uptake by Ti-doped  $\text{LiAlH}_4$  for High Performance Hydrogen Storage.” X. Liu, G.S. McGrady, H.W. Langmi, and C.M. Jensen; *J. Am. Chem. Soc.* **2009**, *131*, 5032.
4. “Dehydrogenation of N-ethyl Perhydrocarbazole Catalyzed by PCP Pincer Iridium Complexes: Evaluation of a Homogenous Hydrogen Storage System.” Z. Wang, I. Tonks, J. Belli, and C.M. Jensen *J. Organomet. Chem.* **2009** *694*, 2854. (invited contribution for special volume on Organometallics for Energy Conversion).
5. “Direct Hydrogenation of Magnesium Boride to Magnesium Borohydride: Demonstration of >11 Weight Percent Reversible Hydrogen Storage” Godwin Severa, Ewa Rönnebro, Craig M. Jensen; *Chemical Commun.* **2010**, *46*, 421.
6. “ $\text{NaSc}(\text{BH}_4)_4$ : A Novel Scandium Based Borohydride. Radovan Černý, Godwin Severa, Dorthe Ravnsbæk, Yaroslav Filinchuk, Vincenza d’Anna, Hans Hagemann, Yngve Cerenius, Craig M. Jensen, and Torben R. Jensen; *J. Phys. Chem. C* **2010**, *114*, 1357.
9. “Reversible Vacancy Formation and Recovery During Dehydrogenation-Hydrogenation Cycling of Ti-doped  $\text{NaAlH}_4$ .” K. Sakaki, M.T. Kuba, Y. Nakamura, C.M. Jensen, and E. Akiba; *J. Phys. Chem. C* **2010**, *114*, 6869.
10. “Modification of the  $\text{H}_2$  Desorption Thermochemistry of  $\text{LiAlH}_4$  through Ti Doping.” Henrietta W. Langmi, G. Sean McGrady, Xiangfeng Liu, Craig M. Jensen; *J. Phys. Chem. C* **2010**, *114*, 10666.
11. “Discovery of a New  $^{27}\text{Al}$  Species in Hydrogen Reactions of  $\text{NaAlH}_4$ .” Timothy M. Ivancic, Son-Jong Hwang, Robert C. Bowman, Jr., Derek S. Birkmire, Craig M. Jensen, Terrence J. Udovic, Mark S. Conradi; *J. Phys. Chem. Lett.* **2010**, in press.
12. “Thermal Desorption, Vibrational Spectroscopic, and DFT Computational Studies of the Complex Manganese Borohydrides,  $\text{Mn}(\text{BH}_4)_2$  and  $[\text{Mn}(\text{BH}_4)_4]^{2-}$ ” Godwin Severa, Hans Hagemann, Moïse Longhini, Jakub W. Kaminski, Tomasz A. Wesolowski, Craig M. Jensen; *J. Phys. Chem. C* **2010**, in press.

13. “Alkali Metal Borohydrides Part 3: Synthesis and characterization of  $\text{KSc}(\text{BH}_4)_4$ .” Radovan Černý, Dorthe B. Ravnsbæk, Godwin Severa, Yaroslav Filinchuk, Vincenza d’Anna, Hans Hagemann, Dörthe Haase, Craig M. Jensen, Torben R. Jensen; *J. Phys. Chem. C* submitted.

### Presentations

1. “Development of Novel Borohydrides as Hydrogen Storage Materials”; Godwin Severa and Craig M. Jensen; 2009 Hydrogen-Metal Systems Gordon Research Conference; Barga, Italy; July 12–16, 2009.
2. “Dimethyl Ether Facilitated Facile Reversible Dehydrogenation of Ti-doped  $\text{LiAlH}_4$ ”; Xiangfeng Liu, G. Sean McGrady, Henrietta W. Langmi, Shane D. Beattie and Craig M. Jensen; 2009 Hydrogen-Metal Systems Gordon Research Conference; Barga, Italy; July 12–16, 2009.
3. “Synthesis and Hydrogen Storage Properties of Nano-confined  $\text{MgH}_2$  in Carbon Aerogel Scaffold” Shu Zhang, Adam Gross, Sky Van Atta, Ping Liu, Channing Ahn, John Vajo and Craig M. Jensen; 2009 Hydrogen-Metal Systems Gordon Research Conference; Barga, Italy; July 12–16, 2009.
4. “TEM Studies on Ti-Doped Alantates” L.F. Culnane, D.D. Graham, C.M. Jensen, I.M. Robertson; 2009 Hydrogen-Metal Systems Gordon Research Conference; Barga, Italy; July 12–16, 2009.
5. “Structure of  $\text{LiSc}(\text{BH}_4)_4$ : a novel salt of  $\text{Li}^+$  and Discrete  $\text{Sc}(\text{BH}_4)_4^-$  complex anions”; Hans Hagemann, Moïse Longhini, Jakub W. Kaminski, Tomasz A. Wesolowski, Radovan Černý, Nicolas Penin, Magnus H. Sørby, Bjørn C. Hauback, Godwin Severa, and Craig M. Jensen; American Crystallography Society; Toronto, Canada; July 24–27 2009.
6. “Hydrogenation of Magnesium Boride to Magnesium Borohydride at Moderate Temperatures” Craig M. Jensen, Godwin Severa, Ewa Ronnebro, Tom Autrey, and Shin-ichi Orimo; Symposium on Advances in Experimental and Computational Studies of Materials for Hydrogen Storage, Fuels Division, 300<sup>th</sup> meeting of the American Chemical Society, Washington, D.C., August 17–20, 2009.
7. “Novel Borohydrides as Hydrogen Storage Materials”; Craig M. Jensen. International Energy Agency, Task22, Hydrogen Storage Experts Workshop; Paris France; October 11–15, 2009.
8. “Catalysts in Complex Hydrides”; Craig M. Jensen. NANOMAT Workshop, University of Oslo, Norway; October 20, 2009.
9. “High Pressure Hydrogenation of Magnesium Boride to Magnesium Borohydride at Moderate Temperatures”; Godwin Severa, Ewa Ronnebro, and Craig M. Jensen. Symposium on Hydrogen Storage Technologies, Materials Research Society meeting, Boston, MA; November 30 – December 4, 2009.

**10.** “Development of Processes for the Reversible Dehydrogenation of High Hydrogen Capacity Complex”; Godwin Severa, Ewa Ronnebro, Xiangfeng Liu, G. Sean McGrady, Henrietta Langmi, and Craig M. Jensen; Conference on Materials for Energy Conversion, organized by the American Ceramic Society and American Materials Society, Cocoa Beach, Florida, USA, March 10–12, 2010.

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**12.** “Novel Borohydrides as Hydrogen Storage Materials”; Craig M. Jensen. International Energy Agency, Task22, Hydrogen Storage Experts Workshop; Death Valley, California, USA; April 11–15, 2010.

### Patents

**1.** “Direct Synthesis of Magnesium Borohydride; U.S. Patent Application 12/553,633; Ewa Ronnebro, Godwin Severa, and Craig M. Jensen; filed 09/03/09.