IV.A.3 Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides

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Fiscal Year (FY) 2011 Objectives

The objective of this project is to develop a new class of reversible materials that have the potential to meet the DOE 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 LiH/Al to $LiAlH_4$ 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 7-17 wt% hydrogen. We have developed a system for the full reversible dehydrogenation of $Mg(BH_4)_2$ to 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 LiH/Al to Ti-doped $LiAlH_4$ (7 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 energy efficiency that approaches 60% and thus approaches DOE targets.

Accomplishments

We have provided the first example of the reversible, solid state dehydrogenation of a borohydride at temperatures below 350°C (200°C, 100 atm).

✧   ✧   ✧   ✧   ✧

Introduction

The development of high capacity, hydrogen storage materials that can be recharged under moderate conditions is a key barrier to the utilization of hydrogen as an onboard energy carrier. Towards this end we have examined anionic borohydride complexes as hydrogen storage materials. Our initial focus was on anionic transition metal complexes. 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. Our efforts are currently focused on determining whether the thermodynamic parameters of these complexes will allow them to undergo reversible dehydrogenation. In the course of these investigations we have found that that ball-milled mixtures of MgB_2 and catalytic additives undergo full hydrogenation to $Mg(BH_4)_2$ at high pressures. In consideration of the >14 wt% hydrogen that is potentially cyclable with this system, it has become the focus of our efforts in the area of borohydride complexes.

In collaboration with the University of New Brunswick (UNB), we are also developing new approaches utilizing supercritical fluids and non-conventional solvents for the direct synthesis of AlH_3 and $LiAlH_4$. $LiAlH_4$ releases hydrogen according to the two reactions seen in equations 1 and 2. Although the second reaction is endothermic ($\Delta H = +25$ kJ/mol H_2), the first reaction is exothermic

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2 \qquad (1)$$

$$Li_3AlH_6 \rightarrow 3LiH + Al + 1.5H_2 \qquad (2)$$
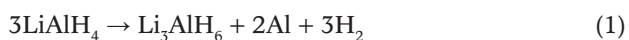
($\Delta H = -10$ kJ/mol H_2). Since entropic change is strongly positive for hydrogen release, the first reaction is thermodynamically irreversible under all practical conditions and it has been widely accepted that $LiAlH_4$ cannot be recharged and there have been no reports of its use for reversible hydrogen storage. However, the unfavorable thermodynamics may be altered by carrying out the reaction in solution, with the solvation of $LiAlH_4$ contributing to an (ideally) endothermic ΔH value. As early as 1963, [1] reported that a mixture of LiH and activated Al in tetrahydrofuran (THF) or diglyme solvent reacted with 350 bar H_2 at 120°C to produce $LiAlH_4$. Improved syntheses of the THF adduct has recently been reported by [2] and researchers at Brookhaven National Laboratory by using Ti additives to significantly lower the required pressure and temperature. While the methods of both Ashby and Ritter result in the ultimate formation of $LiAlH_4$ from LiH, Al and H_2, they are impractical because of the requirements of high temperature, high pressure, and/or mechanical energy during the synthesis as well as subsequent heating removal the THF solvent (vacuum drying at 60°C for several hours). As Ashby noted, it is very difficult to remove the final vestiges of THF and the prolonged baking in vacuo required to remove THF results in the dehydrogenation of the majority of a Ti-activated product. We have discovered that by the this difficulty can be circumvented by utilizing liquefied dimethyl ether as the reaction solvent as it is sufficiently coordinating to support the nascent $LiAlH_4$ in the reaction environment, yet which is also volatile enough to be removed easily once it has served this purpose. Our highly efficient, room temperature direct synthesis of $LiAlH_4$ in liquefied Me_2O shows great promise as a practical method for the re-hydrogenation of LiH/Al to $LiAlH_4$.

Approach

Having demonstrated the reversible elimination of over 11 wt% hydrogen from $Mg(BH_4)_2$, 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 X-ray diffraction and magic angle spinning boron-11 nuclear magnetic resonance spectroscopy (MAS ^{11}B NMR) and conducted quantitative thermal volumetric pressure-composition-temperature measurements.

We have found that nearly the entire 7.9 wt% theoretical cycling capacity can be restored in the first cycle of re-hydrogenation of Ti-doped LiH/Al in liquefied dimethyl ether at room temperature under 100 bar of Me_2O/H_2. Calculations show that this recharging process approaches 60% well-to-tank efficiency. Dimethyl ether performs well as the solvent for this reaction since it is more polar and

volatile than diethyl ether, it forms a strong complex with Li^+, and it evaporates quickly at room temperature (boiling point = -24°C). However, the cycling capacity dramatically drops off over the first five cycles of dehyrogenation/re-hydrogenation. In order to overcome this limitation, we have explored the extension of the maximum cycling capacity of Ti-doped $LiAlH_4$ through variation of the dopant concentration, recharging conditions, and variation dopants.

Results

Task 1. Characterization of the Active Titanium Species in Ti Doped $NaAlH_4$

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

This task has been completed.

Task 5. Synthesis and Evaluation of Novel Borohydrides

Our earlier studies found that it was possible to fully hydrogenate MgB_2 to $Mg(BH_4)_2$ under high hydrogen pressures. It was not clear from the results of these study whether $Mg[B_{12}H_{12}]$ is an intermediate in the reaction pathway that operates under these conditions. To answer this question, we have studied the early stages of the solid state dehydrogenation $Mg(BH_4)2$ in the solid state by ^{11}B NMR spectroscopy. The dehydrogenation of $Mg(BH_4)_2$, was followed by temperature programmed desorption/thermal gravimetric analysis over a set of isothermal temperatures (300, 350, 400°C) at various reaction times. The study was conducted with the concomitant analysis of the volatile gas species by temperature-programmed desorption/thermogravimetric analysis/mass spectroscopy (TPD/TGA/MS). Over this temperature range, a decrease of 6-10 mass% from the $Mg(BH_4)_2$ sample was observed with H_2 as the only volatile species detected by MS. At the end of each TPD experiment, the residual decomposition products were dissolved in aqueous media for analysis by solution phase NMR spectroscopy. Figure 1 shows representative [11]B[H] NMR spectra from samples heated to 300, 350 and 400°C. Four major resonances are observed in each spectra; boric acid at 5 ppm, $[B_{12}H_{12}]^{2-}$ at -15.6 ppm, $[B_{10}H_{10}]^{2-}$ at -29.2 ppm and $[B_3H_8]^-$ at -31 ppm. The results of these studies are summarized in Table 1. The major species observed in the ^{11}B NMR after hydrolysis of the thermal decomposition products is boric acid resulting from the hydrolysis of the unstable polyborane species
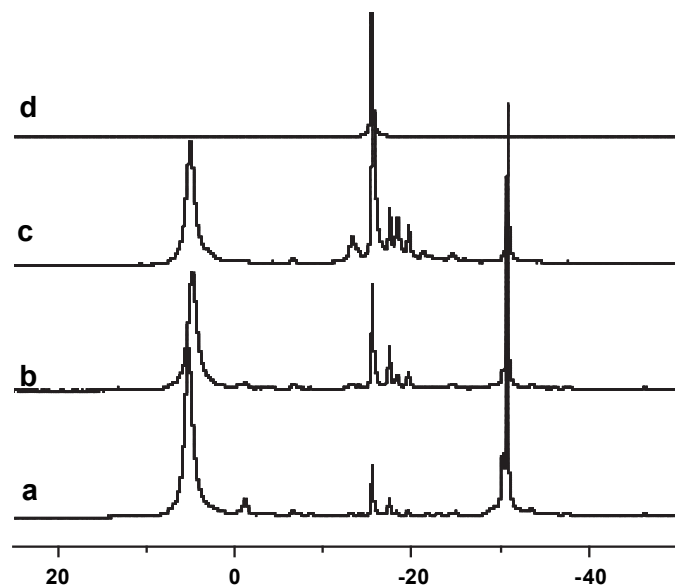
FIGURE 1. Solution $^{11}B\{H\}$ NMR of products resulting from dehydrogenated $Mg(BH_4)_2$ dissolved in aqueous solutions. a) $Mg(BH_4)_2$ heated to 300°C for 12 h, b) $Mg(BH_4)_2$ heated to 350°C for 6 h, c) $Mg(BH_4)_2$ heated to 400°C for 2 h, and d) $MgB_{12}H_{12}$.

TABLE 1. ^{11}B NMR analysis of the major products (mol%) formed in decomposition of $Mg(BH_4)_2$ followed by partial hydrolysis. Chemical shifts are reported relative to $BF_3 \cdot OEt_2$ at 0 ppm.

(δ ppm)	Species	300°C	350°C	400°C
5	$B(OH)_4^-$	86	87	83
-15.2	$(B_{12}H_{12})^{2-}$	0.4	1.5	4.5
-29.2	$(B_{10}H_{10})^{2-}$	0.8	0.2	0.0
-30.3	$(B_3H_8)^-$	12.6	9.0	6.5

formed during the decomposition of $Mg(BH_4)_2$. In addition to the unstable polyborane species a small amount of the stable dodecaborane $[B_{12}H_{12}]^{2-}$ is observed. However, the yield, ranging from 0.4 to 4.5 mol% is significantly less than the theoretical yield assuming complete conversion of $Mg(BH_4)_2$ to magnesium dodecaborane, ca. 16.6 mol% $(B_{12}H_{12})^{2-}$ (8.0 wt% H_2). It is also notable that a significant concentration of the triborane is present, especially at lower temperatures. The results of these studies indicated that the first step in the decomposition of $Mg(BH_4)_2$ involves the formation of a meta-stable triborane species, $Mg(B_3H_8)_2$. In order to verify this conclusion, we investigated the slow dehydrogenation of $Mg(BH_4)_2$ en vacuo at 200°C over a five-week period. Solid state and solution ^{11}B NMR spectra (solution NMR seen in Figure 2a) of the dehydrogenated product showed that there is much higher selectivity for the production of $Mg(B_3H_8)_2$ at this lower temperature.

We next probed the reversibility of the dehydrogenation of the $Mg(BH_4)_2$ to $Mg(B_3H_8)_2$. Experiments were carried

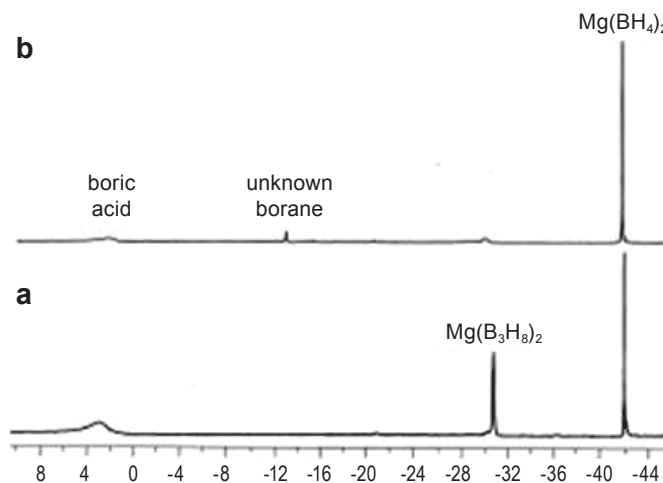**FIGURE 2.** $^{11}B\{^1H\}$ spectra of: (a) $Mg(BH_4)_2$ following solid state dehydrogenation at 200°C for five weeks and (b) re-hydrogention of under 120 atm of H_2 at 250°C for 48 h.

at 250°C under 120 atm of H_2. As seen in Figure 2b, ^{11}B NMR analysis consistently indicated that $Mg(B_3H_8)_2$ undergoes nearly complete conversion of the triborane back to $Mg(BH_4)_2$ after 48 h. This is the first example of the **reversible**, solid-state dehydrogenation of a borohydride occuring at temperatures below 350°C. However, it is also noted that the hydrogen cycling capacity associated with the reaction seen in equation 3 is only 2.5 wt%.

$$3Mg(BH_4)_2 \ \Leftrightarrow \ Mg(B_3H_8)_2 \ + 2MgH_2 \ + 2H_2 \qquad (3)$$
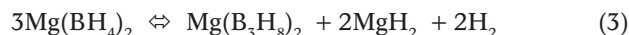
Our results suggests that the higher borane clusters form from the smaller clusters through a sequential borohydride insertions into growing polyboranes, in concert with the formation of hydrogen and the corresponding metal hydride. The stability of the corresponding metal hydride formed in the decomposition of borohydride may explain in part the observed reversibility for some borohydrides and the irreversibility of other borohydrides. The thermodynamics of the reaction, hydrogen desorption or hydrogen absorption, depends on the stability of the MH in addition to the stability of the polyborane intermediate. As such, formation of a more stable metal hydride, e.g., LiH compared to MgH_2, will make the thermodynamics for the reverse reaction less favorable. This mechanism provides an alternate explanation for incomplete reversibility in borohydrides as once $MgB_{12}H_{12}$ is formed, it is difficult to regenerate borohydride. Clearly hydrogen addition to arachnopoly-borane species (observed as boric acid after hydrolysis of the decomposed borohydride) is kinetically accessible whereas hydrogen addition to the thermodynamically stable closoborane species is kinetically inaccessible.

As part of effort of this project, we have synthesized and fully characterized the novel anionic transition metal borobyhydride complexes, $LiSc(BH_4)_4$, $NaSc(BH_4)_4$, $KSc(BH_4)_4$ and $Na_2Mn(BH_4)_4$. As seen in Table 2, we have

found that these complexes all release a significant wt% of hydrogen upon to heating to moderate temperatures, <200°C. Thus it was of interest to probe whether, like $Mg(BH_4)_4$, re-hydrogenation could be achieved following dehydrogention to lower boranes at moderate temperatures. Promising initial results were obtained with $KSc(BH_4)_4$ as the ^{11}B NMR spectrum of samples of following dehydrogenation for 24 h at 200°C are predominated by a peak at -32 ppm, which clearly indicates that triborane, $[B_3H_8]^{2-}$ is the only major product of the dehydrogenation. Attempts were made to re-hydrogenate the material back to the starting borohydride by placing the dehydrogenation samples under 120 atm of H_2 at 250°C for five days. The MAS ^{11}B NMR spectrum showed that a hydrogenated product did arise. However, the -10 ppm chemical of the observed product peak clearly does not match the -38 ppm shift of $KSc(BH_4)_4$ but rather that of KBH_4. In a previous DOE collaborative project with UOP, we screened the hydrogen storage potential lithium salts of transition metal borohydride complexes of the first transition metal series using a high throughput apparatus. This study also indicated that several of these complexes were stable at room temperature and released hydrogen at temperatures relevant to on-broad hydrogen storage applications. However, lithium copper borohydride was the only compound to show reversibility under moderate conditions. This finding stands unique as no other transition metal borohydride complex has been found to be regenerate the parent borohydride complex upon direct hydrogenation or show a stable, non-diminishing hydrogen cycling capacity. We have attempted to confirm that $Li_2Cu(BH_4)_4$ will undergo reversible dehydrogenation. A sample of the complex hydride was prepared by ball milling a 4:1 molar mixture of $CuCl_2$ and $LiBH_4$. Similar to the findings of the earlier preliminary study, we found that heating our sample of $Li_2Cu(BH_4)_4$ to 230°C for five h resulted the in the release of 2.9 wt% hydrogen. However, the results of attempted re-hydrogenation under 120 atm of H_2 at 100°C for 24 h have been variable and no firm conclusions have been reached to date.

Task 6. Recharging of Light Metal Hydrides in Supercritical and Non-Conventional Fluids

In an attempt to stabilize the cycling hydrogen capacity, we investigated the effect of the substitution of $TiCl_3$ with other dopants (e.g. $ScCl_3$ and $CeCl_3$). Doping of LiH/Al with 0.05 mol% $ScCl_3$ resulted in only partial hydrogenation

of the material (ca. 2 wt% H) while mixtures doped with same amount of $CeCl_3$ did not hydrogenation to any significant extend. When the level of dopant was increased to 1 mol%, the hydrogenated material was found to release approximately 6 wt% H upon dehydrogenation while the Ce-doped material did not show any signs of hydrogenation. These results indicate that for the $LiAlH_4$ system the catalytic performance of $ScCl_3$ supersedes that of $CeCl_3$, but does not reach that of $TiCl_3$.

Conclusions

We have established that the initial borane species produced in the dehydrogenation of $Mg(BH_4)_2$ is $Mg(B_3H_8)_2$. This conversion has been shown to be reversible at moderate temperature and pressure thus provides the first example of direct hydrogen cycling of a borohydride under moderate conditions. Although the 2.5 wt% cycling capacity does not meet current on-board storage targets, our results provide key experimental evidence that practical hydrogen storage based on a boron hydride is plausible. Heating to higher temperatures results in a series of BH condesation reactions leading to a complex mixture of polyboranes. Given the nature of the reaction pathways discussed in this work it is recommended that the stability of the corresponding metal hydride (as well as the polyborane) be considered in the design and development of borohydrides for reversible hydrogen storage.

Future Directions

Adjustment of conditions to maximize trade off between cycling capacity and temperature/pressures required for reversible dehydrogenation of $Mg(BH_4)_2$ and perhaps other borohydrides under moderate conditions.

References

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FY 2011 Publications/Presentations

Publications

1. "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.

2. "$NaSc(BH_4)_4$: A Novel Scandium Based Borohydride", Radovan Černy, 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.

TABLE 2. Temperatures and hydrogen wt% evolved during the first step in the dehydrogenation of novel anionic transition metal borohydride complexes.

Complex	T (°C)	wt% H (theoretical)
$LiSc(BH_4)_4$	175	3.5 (14.6)
$NaSc(BH_4)_4$	170	1.0 (12.8)
$KSc(BH_4)_4$	190	1.0 (11.3)
$Na_2Mn(BH_4)_4$	120	2.9 (6.9)

3. "Reversible Vacancy Formation and Recovery During Dehydrogenation-Hydrogenation Cycling of Ti-doped $NaAlH_4$", Kouji Sakaki, Meredith T. Kuba, Yumiko Nakamura, Craig M. Jensen, Etsuo Akiba; *J. Chem. Phys. C* **2010** *114*, 6869.

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5. "Thermal Desorption, Vibrational Spectroscopic, and DFT Computational Studies of the Complex Manganese Borohydrides, $Mn(BH_4)_2$ and $[Mn(BH_4)_4]^{2-}$", Godwin Severa, Hans Hagemann, Moïse Longhini, Jakub W. Kaminski, Tomasz A. Wesolowski, Craig M. Jensen; *J. Phys. Chem. C.* **2010**, *114*, 15516.

6. "Discovery of a New ^{27}Al Species in Hydrogen Reactions of $NaAlH_4$", 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**, 1, 2412.

7. "Synthesis and characterization of $KSc(BH_4)_4$," 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.* **2010**, *114*, 19540.

8. "Reversible Dehydrogenation of Magnesium Borohydride to Magnesium Triborane in the Solid State Under Moderate Conditions", Marina Chong, Ahbi Kamkamkar, Tom Autrey, Shin-ichi Orimo, Satish Jalisatgi, and Craig M. Jensen; (invited contribution for themed issue on Hydrogen) *Chem. Commun*. **2011**, *47*, 1330.

Presentations

1. "Development of Processes for the Reversible Dehydrogenation of High Hydrogen Capacity Complex Hydrides"; Godwin Severa, Marina Chong, Zhouhui Wang, Xiangfeng Liu, G. Sean McGrady, Henrietta Langmi, Ewa Rönnebro, Tom Autrey, Ahbi Kamkamkar, and Craig M. Jensen; International Conference on Materials Science and Technology; Puspiptek Serpong Indonesia; October 19–23, 2010.

2. "Development of Processes for the Reversible Dehydrogenation of High Hydrogen Capacity Complex Hydrides"; Godwin Severa, Marina Chong, Zhouhui Wang, Xiangfeng Liu, G. Sean McGrady, Henrietta Langmi, Ewa Rönnebro, Tom Autrey, Ahbi Kamkamkar, and Craig M. Jensen; Marie Curie Actions Conference on Nano- and Surface Science Approches to Production and Storage of Hydrogen; Noordwijkerhout, The Netherlands, November 14–19, 2010.

3. "Development of Processes for the Reversible Dehydrogenation of High Hydrogen Capacity Complex Hydrides"; Godwin Severa, Marina Chong, Zhouhui Wang, Xiangfeng Liu, G. Sean McGrady, Henrietta Langmi, Ewa Rönnebro, Tom Autrey, Ahbi Kamkamkar, and Craig M. Jensen; 3rd International Symospium on Materials Chemistry; Bhabha Atomic Research Centre, Mumbai, India, December 7–11, 2010.

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6. "Homogeneous Dehydrogenation of Liquid Organic Hydrogen Carriers Catalyzed by an Iridium PCP Pincer Complexs", Zhouhui Wang, Jack Belli, and Craig Jensen, Symposium Faraday Discussion 151: Hydrogen Storage Materials, Didcot, United Kingdom, April 18–20, 2011.

7. "Hydrogen Storage via Reversible Dehydrogenation of Magnesium Borohydride", Craig Jensen, Marina Chong, Tom Autrey, and Ahbi Kamkamkar, Symposium on Recent Developments in Hydrogen Storage at Materials Research Society Spring 2011 Meeting, San Francisco, April 26–28, 2011.