

IV.A.1g 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 investigation of the hydrogen storage properties of magnesium nano-confined in carbon aerogels.
- 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, AlH_3 , and/or 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 Hydrogen, Fuel Cells and Infrastructure 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 of for the full reversible dehydrogenation of $\text{Mg}(\text{BH}_4)_2$ 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 (WTT) energy efficiency that approaches 60% and thus meets U.S. DOE targets.

Accomplishments

Nano-Confined Mg in Carbon Aerogels

- Confirmed MgH_2 incorporation in aerogel by transmission electron microscopy (TEM) imaging, energy dispersive X-ray spectroscopy, and X-ray diffraction (XRD).
- Obtained 23 wt% MgH_2 loadings in carbon aerogels with larger pore sizes.
- Determined the rate of dehydrogenation at 252°C is >5 times faster than the initial rate found for ball milled MgH_2 and that it remains approximately the same over four cycles of dehydrogenation/rehydrogenation.
- Established that thermodynamics of the dehydrogenation of MgH_2 are not altered by nano-confinement.

Novel Borohydrides

- Achieved full, ~14 wt% re-hydrogenation of MgB_2 to $\text{Mg}(\text{BH}_4)_2$ through a high pressure method that avoids formation of highly stable, $\text{MgB}_{12}\text{H}_{12}$.
- Confirmed that the only major product of high pressure hydrogenation is $\text{Mg}(\text{BH}_4)_2$ by magic angle spinning (MAS) ^{11}B nuclear magnetic resonance (NMR) spectroscopy.

- Filed patent application for method for hydrogenation of MgB_2 to $\text{Mg}(\text{BH}_4)_2$.

Hydrogenation in Non-Conventional Solvents

- Developed a method for the room temperature, direct hydrogenation of Ti-doped LiH/Al in liquefied dimethyl ether under 100 bar of H_2 .
- Optimized synthesis process such that charged, Ti-doped LiAlH_4 is obtained in >95% yield.
- Determined the WTT energy efficiency our direct synthesis process approaches the 60% U.S. DOE target.
- Filed patent application for our direct synthesis process.



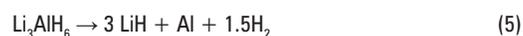
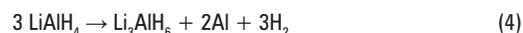
Introduction

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 goal, we are exploring new approaches for homogeneous incorporation of high hydrogen capacity metal hydrides into carbon aerogels. Intercalation into these nano-porous materials may change the thermodynamics and/or enhance the kinetics of the reversible hydrogenation thus bringing previously non-viable, metal hydrides such as MgH_2 into the realm of practical hydrogen storage materials.

We are also developing high hydrogen capacity borohydrides 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. However, in the course of our studies, we found a method whereby the fully reversible dehydrogenation $\text{Mg}(\text{BH}_4)_2$ to MgB_2 can be achieved. In consideration of the >14 wt% hydrogen that is potentially cyclable with this system, it has become the focus of our efforts on borohydrides.

The dehydrogenation of AlH_3 to Al gives 10 wt% H_2 . With additives, controllable dehydrogenation is possible at acceptable rates below 100°C. The low (<10 kJ/mol H_2) ΔH_{dehyd} mandates very high pressures for charging at ambient or higher temperatures. Supercritical fluids (SCFs) have different physical properties than gases. It has been found that requisite pressures hydrogenations are reduced in SCFs (i.e. hydrogenations of organic molecules and NaH/Al to NaAlH_4). In collaboration with the University of New Brunswick, we are developing new approaches utilizing supercritical fluids recharging AlH_3 .

We are also exploring the direct synthesis of LiAlH_4 in liquefied dimethyl ether, Me_2O . LiAlH_4 releases hydrogen according to the two reactions seen in equations 4 and 5. Although the second reaction is endothermic ($\Delta H = +25$ kJ/mol H_2), the first reaction



is exothermic ($\Delta H = -10$ kJ/mol H_2) [1]. 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 of Eq. 4 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, Ashby *et al.* reported that a mixture of LiH and activated Al in THF or diglyme solvent reacted with 350 bar H_2 at 120°C to produce LiAlH_4 [2]. An improvement of the synthesis of the tetrahydrofuran (THF) adduct has recently achieved by researchers at Brookhaven National Laboratory by using Ti additives to significantly lower the required pressure and temperature [3]. A variation of this synthesis was previously reported by Ritter *et al.* in a procedure that involves the high-energy ball milling of a LiH/Al mixture under H_2 pressure in the presence of THF [4]. 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). Ashby noted that it is very difficult to remove the final vestiges of THF. The prolonged baking *in vacuo* required to remove THF will necessarily compromise the integrity of a Ti-activated product. Clearly, the key to practically is the identification of a solvent that 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.

Approach

We have developed a novel approach for the intercalation of Mg in carbon aerogel materials. This procedure achieves high, cyclable magnesium loadings in carbon aerogels without host degradation. Since this method is performed at relatively low temperatures, the pore size of the aerogel material is preserved without degradation. The high loadings are allowing us to conduct highly reliable studies of the effects of nano-confinement on the kinetics and thermodynamics of the dehydrogenation of MgH_2 .

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; increase stability; and for some, complexes such as $\text{Na}_2\text{Zr}(\text{BH}_4)_6$, very low levels of diborane evolution during the dehydrogenation. Our studies 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 ball-milled mixtures of MgB_2 and catalytic additives undergo full hydrogenation to $\text{Mg}(\text{BH}_4)_2$ at high pressures. We are currently conducting detailed studies of the reversible dehydrogenation >12 wt% H_2 from $\text{Mg}(\text{BH}_4)_2$.

Our previous efforts have resulted in the development a SCF medium for the hydrogenation of Al that facilitates the hydrogenation of Al to AlH_3 in ~5% yield. Attempts to achieve higher yields by conducting the hydrogenation in alternative SCFs and utilizing variety initiator and catalysts are currently underway.

We are also exploring the synthesis of LiAlH_4 in liquefied Me_2O . Dimethyl ether should perform 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).

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

Previously we reported high (9-16 wt%) MgH_2 loadings of carbon aerogel without host degradation are obtained using organometallic method. TEM imaging studies of our magnesium nano-confined aerogel have been completed in collaboration with the California Institute of Technology. These studies point to the nano-size of the Mg and MgH_2 particles. We also examined the effect of pore size of carbon scaffold materials on the MgH_2 loading. Results showed that higher MgH_2

loadings can be obtained with materials that have larger pore sizes (Table 1).

TABLE 1. Effect of Increasing Pore Size on MgH_2 Loading

Scaffold	Activated Carbon	13 nm Carbon Aerogel	25 nm Carbon Aerogel
Pore Size (nm)	<2	13	25
Pore Volume (cm^3/g)	0.58	0.80	1.38
MgH_2 Loading (wt%)	4.2	17	23

We have found that the rate of dehydrogenation of the nano-confined MgH_2 at 252°C is >5 times faster than the initial rate found for ball milled MgH_2 and comparable to those found for nano-confined MgH_2 in carbon aerogels that was prepared by alternative methods at HRL (Figure 1). We have also conducted comparative cycling studies of MgH_2 incorporated into aerogel granules and aerogel powder. Dehydrogenation was carried out at 325°C under vacuum and hydrogenation was performed under 9-13.5 MPa at 177 - 325°C for 6-20 hours. We found that with aerogel granules, the dehydrogenation rates remained approximately the same over four cycles and that they contained about 12 wt% reversible MgH_2 (Figures 2 and 3). Cycling tests of aerogel powder showed an obvious degradation of the dehydrogenation kinetics, and aggregation of Mg was observed.

To improve the kinetics of dehydrogenation and re-hydrogenation of the nano-confined MgH_2 we incorporated Ti-catalyst in the carbon aerogel. The Ti(0) catalyst was synthesized in situ through the reaction of $\text{TiCl}_4 \cdot 2\text{THF}$ with LiAlH_4 . We developed two procedures to carry out this synthesis. The first involved initial preparation of Ti(0) incorporated aerogel that was next loaded with MgBu_2 and finally hydrogenated to MgH_2 . The second procedure involved the reciprocal impregnation of Ti(0) into MgH_2 . We found that the

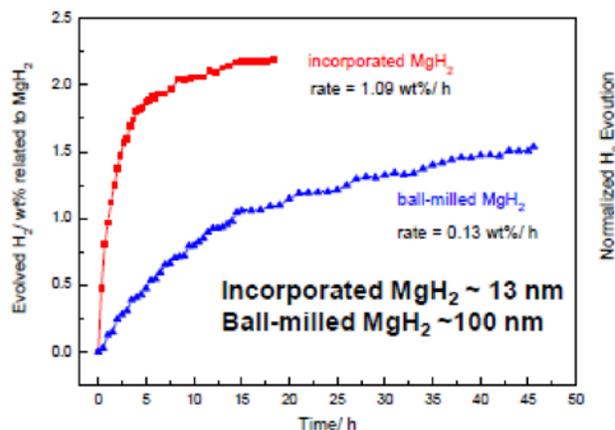


FIGURE 1. The rate of dehydrogenation at 252°C is >5 times faster than the initial rate found for ball milled MgH_2 .

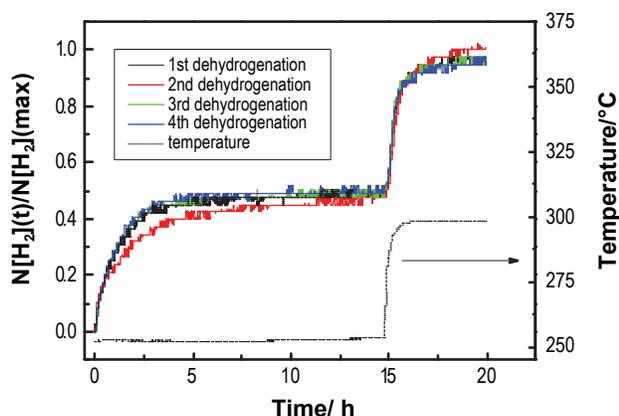


FIGURE 2. Reversible dehydrogenation kinetics of Mg intercalated carbon aerogels through four cycles.

initially prepared materials containing Ti catalyst did not show any kinetic improvement. In fact, the amount of H_2 evolution actually decreased when compared to the material without the Ti species.

We have started measurements of pressure-composition isotherms to accurately determine if the thermodynamic properties of MgH_2 are changed upon nano-confinement. The equilibrium pressure of MgH_2 nano-confined in 13 nm aerogel at 250°C agrees with database value of 0.9 atm for bulk MgH_2 . This preliminary result indicates that the enthalpy of dehydrogenation of the nano-confined MgH_2 is 70 kJ/mol which is not significantly different than that of bulk MgH_2 .

Task 5. Synthesis and Evaluation of Novel Borohydrides

We have found that the alkali metal salts of anionic transition metal borohydride complexes such $LiMn(BH_4)_4$ undergo rapid dehydrogenation at moderate (<150°C) temperatures while evolving high (>3) wt% of hydrogen. In some cases, only very minor the amounts of the undesirable, diborane side product are produced. However, we have not found the 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 various ball-milled mixtures alkali metal borides or hydrides; transition metal hydrides and borides; and catalytic additives proved unsuccessful. However, hydrogen uptake was found to occur in experiments with mixtures of MgB_2 ; transition metal hydrides; and catalytic additive. Analysis of the product mixture by XRD showed that the transition metal component was unreactive while the MgB_2 was hydrogenated to $Mg(BH_4)_2$. The same result was achieved when starting with ball-milled mixtures of MgB_2 and the catalytic additive at 400°C and 900 atm. A previous effort

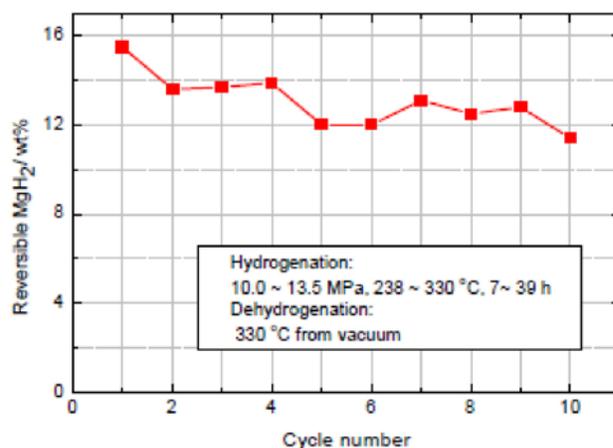
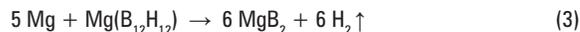
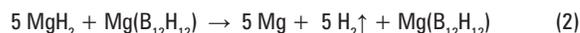
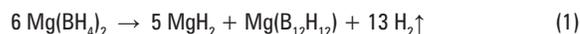


FIGURE 3. The MgH_2 intercalated carbon aerogel contains about 12 wt% of reversible MgH_2 .

within the Metal Hydride Center of Excellence headed by researchers at General Electric showed $Mg(BH_4)_2$ undergoes stepwise dehydrogenation to give MgB_2 while releasing 14.8 wt% H_2 as seen in equations 1-3. Thermodynamic considerations indicate that it



should be possible to hydrogenate MgB_2 to $Mg(BH_4)_2$ at moderate temperatures and pressures. However, experimentally it has proven possible to reverse only the processes in equations 2 and 3 at temperatures lower than 500°C. It has been suggested that this is due to the high kinetic stabilization of $MgB_{12}H_{12}$. Thus our finding of full hydrogenation to $Mg(BH_4)_2$ is a breakthrough in the effort to develop this compound as a hydrogen storage material. We have also confirmed its identity by MAS¹¹B NMR spectroscopy. This analysis is very important as previous studies of the hydrogenation of MgB have found that the obtained $MgB_{12}H_{12}$ is amorphous and thus cannot be detected by XRD. By contrast, ¹¹B NMR is able to detect all boron-containing materials in the product mixture. As seen in Figure 4, only one major boron-containing product is observed. The chemical shift of -41 ppm allows its clear identification as $Mg(BH_4)_2$ as the shift exactly matches that which we have observed for an authentic sample of $Mg(BH_4)_2$. Only a very minor signal is observed for $MgB_{12}H_{12}$, at -24 ppm indicating that it represents <5% of the product mixture. It is not clear at this point if the high-pressure low-pressure reaction proceed by the same pathway. Thus the minor amount of $MgB_{12}H_{12}$ that was obtained could be either a small amount of an unreacted intermediate in the catalyzed dehydrogenation pathway or, alternatively, it could be a

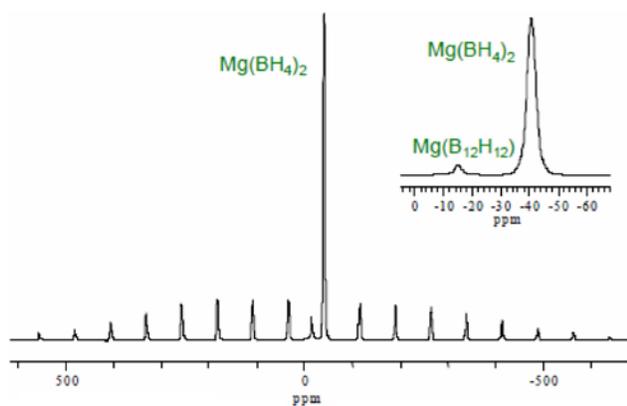


FIGURE 4. MAS ^{11}B NMR $\text{MgB}_2 + 2 \text{ mol\%}$ additive hydrogenated under 950 bar at 400°C .

small amount of product resulting from the competing, standard uncatalyzed pathway.

As seen in Figure 5, thermal desorption of $\text{Mg}(\text{BH}_4)_2$ synthesized from high pressure hydrogenation of MgB_2 yields 11.5 wt% hydrogen. If the catalyst contribution to sample weight is not taken into consideration, 12.7 wt% hydrogen is realized, representing about 86% conversion of MgB_2 to $\text{Mg}(\text{BH}_4)_2$. XRD analysis of the synthesized product shows the presence of MgO , which contributes to the low weight percent hydrogen.

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

A variety of alternative SCFs, initiators and catalysts were screened in attempts to improve the yield of AlH_3 from the hydrogenation of Al in SCFs. However, we have been unable to improve upon the ~5% (surface only?) yield we reported last year.

In a more promising development, we have found that LiAlH_4 can be synthesized in liquefied dimethyl ether (Me_2O) at room temperature from the hydrogenation of a mixture of LiH and Al in the presence of very low amounts of Ti catalyst (0.5-0.2 mol%). The method requires only moderate pressures of H_2 (80-100 bar). On completion of reaction, the volatile Me_2O solvent and excess H_2 are vented leaving only fine, dry Ti -doped LiAlH_4 that, as seen in Figure 6, can be clearly identified by XRD. We have found that improved yields are obtained upon lowering the Ti doping level. As seen in Figure 7, the amount of hydrogen obtained from the materials synthesized by our methods upon heating between 80 and 150°C dramatically increases as the doping level is decreased from 2.0 to 0.2 mol%. At the lower Ti loading a $>7 \text{ wt\%}$ H_2 is obtained which corresponds to a yield of ca. 95% [5]. Thus we have found a highly efficient method of the direct synthesis of LiAlH_4 at low pressure and room temperature. In further consideration that the energy for compression of Me_2O and H_2 is about 1/5

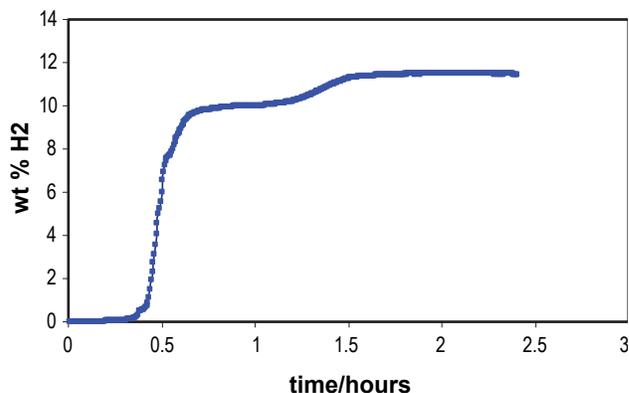


FIGURE 5. Thermal desorption curve for high pressure, direct synthesized $\text{Mg}(\text{BH}_4)_2$.

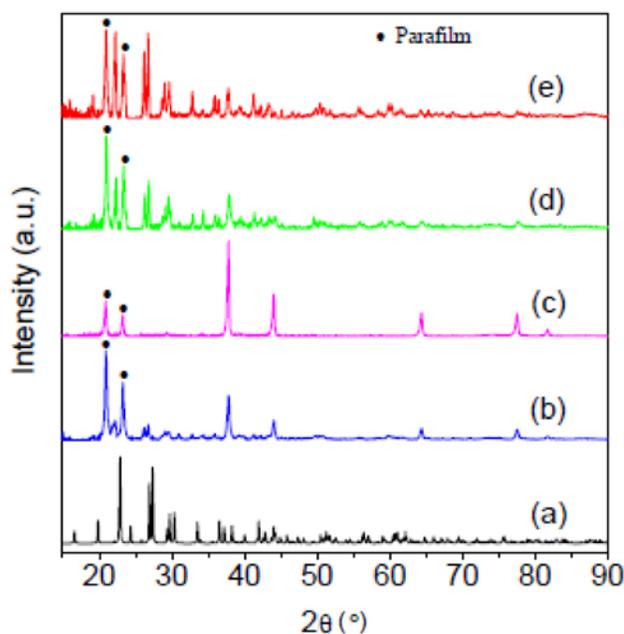


FIGURE 6. XRD patterns of LiAlH_4 samples: (a) International Centre for Diffraction Data[®] ref; (b) ball milled (2.0 mol% TiCl_3); (c) fully dehydrogenated (0.2 mol% TiCl_3); (d) rehydrogenated (2.0 mol% TiCl_3); (e) rehydrogenated (0.2 mol% TiCl_3).

that of H_2 and that LiAlH_4 has a high solubility in Me_2O , a preliminary analysis conducted at Argonne National Laboratory has indicated that WTT energy efficiency of our regeneration process is great than 60% and thus in line with U.S. DOE targets.

Conclusions

In summary, using our low temperature, “neat organometallic” method, we have achieved high, 9-16 wt% Mg loadings in carbon aerogels without host degradation. Higher MgH_2 loadings obtained with

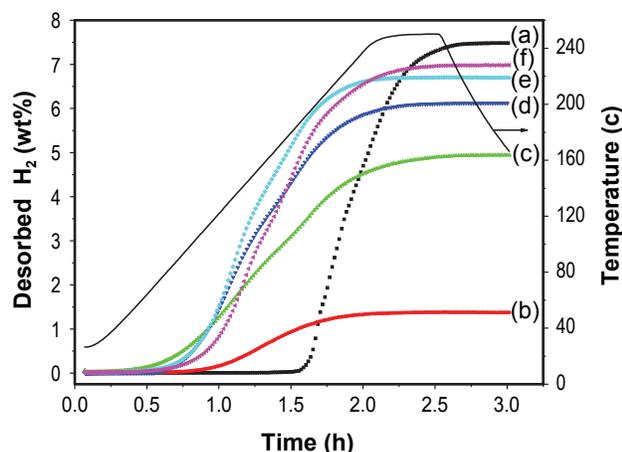


FIGURE 7. Temperature-programmed desorption plots for LiAlH_4 samples: (a) as-received; (b) ball milled with 2.0 mol% TiCl_3 ; (c) rehydrogenated (2.0 mol% TiCl_3); (d) rehydrogenated (1.0 mol% TiCl_3); (e) rehydrogenated (0.5 mol% TiCl_3); and (f) rehydrogenated (0.2 mol% TiCl_3).

materials that have larger pore sizes. In addition, our studies have concluded that nano-confinement of MgH_2 improves the dehydrogenation kinetics, but does not appear to effect its thermodynamic properties, most notably, the enthalpy of dehydrogenation.

We have also achieved the full re-hydrogenation of MgB_2 to $\text{Mg}(\text{BH}_4)_2$ through a high pressure method that avoids formation of highly stable, $\text{MgB}_{12}\text{H}_{12}$ that typically precludes a full, 14 wt% hydrogenation. This result was first indicated by XRD and also confirmed by MAS ^{11}B NMR spectroscopy studies which show that the only major product of the hydrogenation is $\text{Mg}(\text{BH}_4)_2$.

Finally, we have developed a method whereby 95% yields of fully charged, Ti-doped LiAlH_4 are obtained from the direct hydrogenation of Ti-doped LiH/Al . The method involves room temperature hydrogenation in liquefied dimethyl ether under 100 bar of H_2 . The WTT energy efficiency of a LiAlH_4 -based hydrogen system utilizing liquid dimethyl ether as a re-hydrogenation medium approaches the 60% US DOE target.

Future Directions

Nano-confined Mg in Carbon Aerogels

- Determining dehydrogenation and re-hydrogenation kinetics of aerogels loaded with both MgH_2 and Ti-catalyst.
- Obtain pressure-concentration-temperature isotherms to confirm nano-confinement has no effect on the ΔH_{dehyd} of MgH_2 .

Anionic Borohydrides

- Exploring variations in reactions conditions to improve yield of lower pressure, full hydrogenation of MgB_2 to $\text{Mg}(\text{BH}_4)_2$.
- Continue studies of the catalyzed and un-catalyzed hydrogenation of MgB_2 utilizing MAS ^{11}B NMR to determine the mechanism in order to improve kinetics.

Hydrogenation in Non-Conventional Solvents

- Maximizing the extended cycling capacity of Ti-doped LiAlH_4 through variation of the dopant concentration and recharging conditions in liquid Me_2O .
- Further detailed evaluation of WTT energy efficiency of the direct synthesis of LiAlH_4 in liquid in collaboration with Argonne National Laboratory.
- Continuing exploration of improving levels of hydrogenation of alane using alternative SCFs and variety of initiators/catalysts.
- Exploring SCF synthesis of $\text{Mg}(\text{AlH}_4)_2$.

Patent Applications

1. "Hydrogen Storage Materials, Metal Hydrides, and Complex Hydrides prepared Using Low-Boiling Point Solvents." G. Sean McGrady and Craig M. Jensen U.S. Patent Application 60/945,650, filed 6/08.
2. "Reversible Hydrogen Storage with Magnesium Borohydride." Eva Ronnebro, Godwin Severa, and Craig M. Jensen, U.S. Patent Application 61/093,937, filed 11/08.

FY 2009 Publications/Presentations

Publications

1. "Synthesis and Hydrogen Storage Properties of 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 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 H_2 Release and Uptake by Ti-doped LiAlH_4 for High Performance Hydrogen Storage." X. Liu, G.S. McGrady, H.W. Langmi, and C.M. Jensen; *J. Am. Chem. Soc.* **2009**, *113*, 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** in press. (invited contribution for special volume on Organometallics for Energy Conversion).
5. “Reversible Vacancy Formation and Recovery During Dehydrogenation-Hydrogenation Cycling of Ti-doped NaAlH_4 .” K. Sakaki, M.T. Kuba, Y. Nakamura, C.M. Jensen, and E. Akiba; submitted to *Phys. Rev. Lett.* **2009**.”

Presentations

1. “Novel Borohydrides for Hydrogen Storage Materials”, International Energy Agency, Task 22, Hydrogen Storage Experts Workshop; Rome, Italy, October 6–10, 2009.
2. “High Pressure Hydrogenation of Magnesium Boride to Magnesium Borohydride at Moderate Temperatures”, Study of Matter under Extreme Conditions 2009, High Pressure Society of America, Western Caribbean, March 28 – April 3, 2009.
3. “Novel Borohydrides for Hydrogen Storage Materials” International Energy Agency, Task 22, Hydrogen Storage Experts Workshop; JejuIsland, Korea, April 19–23, 2009.

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5. Xi. Liu, G.S. McGrady, H.W. Langmi, C.M. Jensen; *J. Am. Chem. Soc.* 113 (2009) 5032.