

IV.A.1b Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage

Ping Liu (Primary Contact), John J. Vajo
 HRL Laboratories, LLC
 3011 Malibu Canyon Road
 Malibu, CA 90265
 Phone: (310) 317-5474; Fax: (310) 317-5840
 E-mail: pliu@hrl.com

DOE Technology Development Manager:
 Ned Stetson
 Phone: (202) 586-9995; Fax: (202) 586-9811
 E-mail: Ned.Stetson@ee.doe.gov

DOE Project Officer: Paul Bakke
 Phone: (303) 275-4916; Fax: (303) 275-4753
 E-mail: Paul.Bakke@go.doe.gov

Contract Number: DE-FC36-05GO1506

Project Start Date: March 1, 2005

Project End Date: February 28, 2010

Technical Targets

Destabilized System	Benchmark	2007 Status	2007/08 Progress
LiBH ₄ /MgH ₂ @C aerogel 11.4 wt%, 0.095 kg/L without aerogel, est. T _{1 bar} = 170°C	Could meet 2010 system weight and volume capacity goals (assuming 25% aerogel and 25% system penalties)	Lowered LiBH ₄ dehydrogenation temp. by 70°C in C-scaffold	Reduced capacity penalty to 40% Measured 10x equilibrium pressure Incorporated Mg into aerogel Measured >60x reaction rate
LiBH ₄ /Mg ₂ NiH ₄ 8.3 wt%, est. T _{1 bar} = 150°C	Could meet 2010 system capacity goal (but only small system penalty)		Reversible capacity of ~6.5% at 350°C Slight degradation observed

Objectives

- To identify and test new high capacity Li- and Mg-based destabilized hydrides
 - Screen candidate LiBH₄ + MgX destabilized systems and evaluate energetics and kinetics; down-select systems for additional work.
- Evaluate sorption kinetics and thermodynamics of LiBH₄ and Mg in carbon aerogel scaffolds
 - Investigate effects of pore size and pore size distribution on reaction rates of LiBH₄.
 - Incorporate Mg into the aerogel and measure its kinetics.

Technical Barriers

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

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charging and Discharge Rates

Accomplishments

- Screened new LiBH₄/MgX systems, X = Si and Ni:
 - Observed new Ni-based destabilized system with reversible capacity of ~6.5%.
 - Observed the formation of ternary borides, pointing to potential new direction of discovery.
- Quantified rates for LiBH₄ dehydrogenation in aerogel:
 - At 300°C, rate in aerogel is 60X rate for control sample.
 - Incorporated Mg into aerogel at reduced temperature to minimize degradation of aerogel (in progress).
 - Measured dehydrogenation rates for Mg@ aerogel – with Ni wetting layer/catalyst, the rate at 250°C comparable to best catalyzed bulk samples.
- Began to understand effects of pore size and pore size distribution – smaller pores lower reaction temperatures; hydrogen access is important.



Introduction

This project is developing solid-state materials consisting of light elements to meet the capacity goals set forth by the DOE for on-board vehicle hydrogen storage systems. While many light element compounds are

known to have high hydrogen storage capacities, most of these materials are too thermodynamically stable and, consequently, the temperatures for hydrogen delivery are too high. In addition, hydrogen exchange is often too slow for practical use. In this project we are developing new material systems that can deliver hydrogen at lower temperatures and at higher rates. These advancements are made possible by tuning the thermodynamics and kinetics of the hydrogenation/dehydrogenation reactions.

Approach

HRL's technical approach has two principal components: 1) hydride destabilization by alloy or compound formation in the dehydrogenated state is used to develop new chemical systems that overcome the thermodynamic constraints imposed by high bond energies in light metal systems, and 2) nano-engineering of reactants is utilized to reduce the effective diffusion distances and thereby increase the rate of hydrogen exchange.

The first component of our approach, hydride destabilization, is built upon the idea that if the dehydrogenation product of a light metal hydride can react with another material to form a more stable phase, the overall enthalpy of the reaction will be lowered, thereby decreasing the temperature for hydrogen exchange. The modified system can cycle between the hydride and the new stable phase instead of the pure metal. The thermodynamics of the reaction can be tuned with the use of materials that afford phases of different stability. Although the addition of a destabilizing agent imposes a gravimetric capacity penalty, it is possible to minimize this penalty by using metal hydrides or other light element compounds as destabilizing agents.

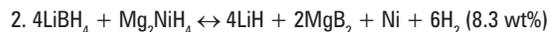
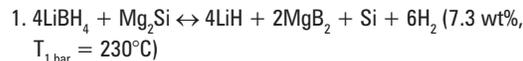
The second component of our approach addresses the kinetics limitations to hydrogen exchange reactions in light metal hydrides. We are using catalysts as well as nanoscale reactants to improve the overall reaction kinetics. Nanoscale reactants can reduce solid-state diffusion distances and their high surface/volume ratio can improve catalytic activity. In particular, we are investigating the use of nanoporous "scaffolds" as structure-directing agents for forming nanoscale metal hydride reactants. This approach has the additional advantage of mitigating potential problems that can arise from agglomeration and sintering of the nanostructured material during hydrogen cycling.

Results

There were two main objectives for this project in Fiscal Year 2007/2008: (1) continue to screen new LiBH_4/MgX destabilized systems and evaluate their energetics, and (2) investigate the effects of pore size and

pore size distribution of carbon aerogel scaffolds on the hydrogen sorption kinetics of LiBH_4 and Mg.

Work to screen new destabilized systems focused on systems with a general formula of LiBH_4/MgX . Two systems were studied which were postulated to have the following reactions:



Reaction 1 was studied beginning with a ball milled mixture of $\text{LiH} + 0.5\text{MgB}_2 + 0.25\text{Si} + 0.03\text{TiCl}_3$. The mixture adsorbed 5.5 wt% H_2 during hydrogenation at 100 bar H_2 , 350°C, 2 hr. Formation of LiBH_4 and Mg_2Si was verified by X-ray diffraction (XRD) measurements (data not shown). Upon dehydrogenation, at temperatures up to 450°C, the LiBH_4 decomposed but the Mg_2Si did not react. Thus, the reaction was not reversible. This behavior is similar to the behavior observed in the MgH_2/Si destabilized system and further indicates the extreme kinetic stability of Mg_2Si .

Reaction 2 was studied beginning with a milled mixture of $\text{LiH} + 0.5\text{MgB}_2 + 0.25\text{Ni} + 0.03\text{TiCl}_3$. Hydrogenation at 100 bar, 350°C, 2 hr led to the uptake of 6.2 wt% H_2 . XRD, Fourier transform infrared, and nuclear magnetic resonance (NMR, performed at Caltech/JPL) measurements, after hydrogenation, indicated the presence of LiBH_4 and Mg_2NiH_4 (data not shown). Dehydrogenation was performed into a hydrogen overpressure of 4 bar. During heating to 450°C, 7 wt% hydrogen was desorbed, see Figure 1. The difference between the amount of hydrogen absorbed (6.2 wt%) and the amount desorbed (7 wt%) is within

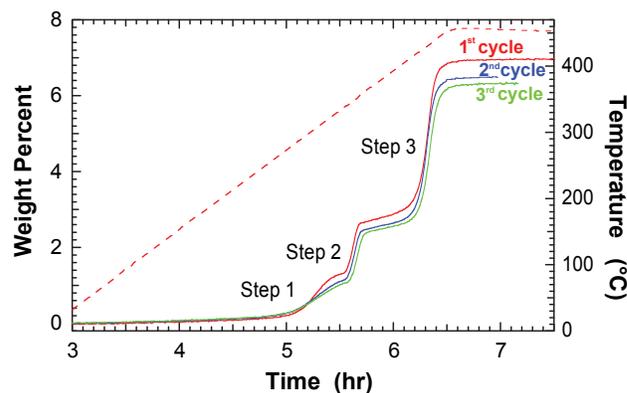


FIGURE 1. Dehydrogenation following hydrogenation of milled $\text{LiH} + 0.5\text{MgB}_2 + 0.25\text{Ni} + 0.03\text{TiCl}_3$. Milling was performed at 400 rpm for 1 hr. Hydrogenation was performed in 100 bar hydrogen at 350°C for 2 hr. Dehydrogenation was conducted into a hydrogen pressure of 4 bar. Solid curves show desorbed hydrogen (left axis). Dashed curve shows the temperature (right axis). The system cycles with a capacity of ~6.5 wt% H_2 and some degradation over 3 cycles.

the uncertainty of the high-pressure hydrogenation measurements. After dehydrogenation, XRD suggested that MgB_2 was formed, although the measurement was not conclusive (data not shown). In addition, the XRD showed that a ternary boride phase was formed with a composition of MgNi_3B_2 , $\text{Mg}_{2.99}\text{Ni}_{7.52}\text{B}_6$ or $\text{Li}_{2.39}\text{Ni}_{5.01}\text{B}_4$. These phases have nearly identical powder XRD patterns and, thus, it has not been possible to tell which phase or combination of phases was formed. NMR measurements confirmed the presence of MgB_2 and also, tentatively, identified a new boride phase. Currently, we are attempting to synthesize directly the ternary borides listed above to calibrate the NMR spectra. Based on this preliminary characterization, a possible reaction is as follows:



As shown in Figure 1, three hydrogenation/dehydrogenation cycles were performed. Some degradation was observed but the results indicate that the reaction is reversible and that the boride is participating in the cycling (XRD results, not shown). This result is significant because except for MgB_2 , other borides cannot be cycled readily. Moreover, other Li or Mg/transition metal ternary borides may exist that could lead to new destabilization reactions.

The dehydrogenation cycles (Figure 1) show that the reaction occurs in three steps. Steps 2 and 3 correspond closely to the two steps seen in the $\text{LiBH}_4/\text{MgH}_2$ reaction, i.e. without Ni. Step 1 occurs at a lower temperature (280 – 330°C) than the first step in the $\text{LiBH}_4/\text{MgH}_2$ reaction (360°C). Understanding this reaction step may indicate ways to improve the reaction kinetics.

Future work to fully characterize the compounds produced in this reaction, identify the reaction steps, and explore the utility of the ternary borides phases in other possible destabilization reactions is planned.

To optimize the beneficial effect of incorporating hydride materials into nanoporous scaffolds, dehydrogenation rates were measured for LiBH_4 in carbon aerogels with 4 nm and 25 nm pore sizes and compared to earlier measurements on samples with 13 nm pores. The 4 nm sample was prepared at Lawrence Livermore National Laboratory (LLNL, Ted Baumann) while the 13 nm and 25 nm samples were prepared at HRL. Isothermal dehydrogenation measurements and pore size distributions are shown in Figure 2. Dehydrogenation of LiBH_4 was performed at 300°C into a large volume, which kept the pressure below 0.1 bar. Maintaining the pressure low insured that the dehydrogenation was not inhibited by equilibrium. The 13 nm sample has the highest dehydrogenation rate, ~12.5 wt% LiBH_4 /hr, while the 4 nm and 25 nm samples have lower rates, 7.8 wt% LiBH_4 /hr and 6.8 wt% LiBH_4 /hr, respectively. Comparing the 13 nm

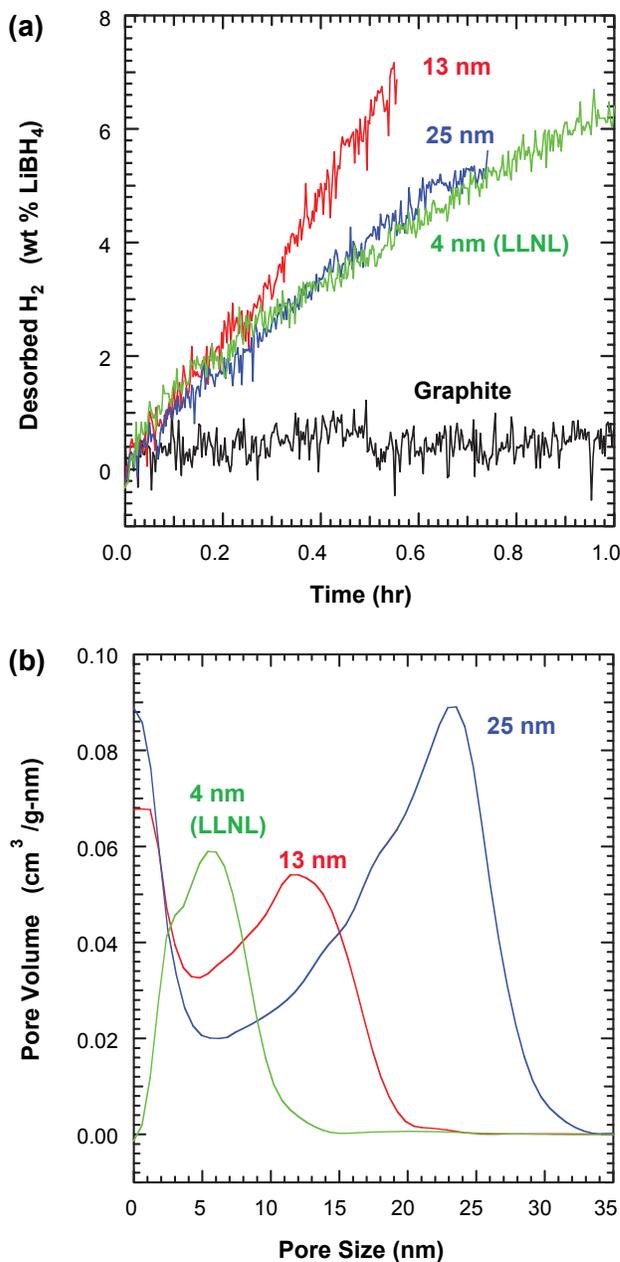


FIGURE 2. Effect of aerogel pore size and pore size distribution on the dehydrogenation rate of LiBH_4 . Panel (a) shows the hydrogen desorbed in wt% LiBH_4 vs. time at 300°C for LiBH_4 in 4 nm, 13 nm, and 25 nm aerogels and for LiBH_4 mixed with graphite. Panel (b) shows the pore size distributions for the aerogel samples.

and 25 nm samples suggest that the kinetics are favored in smaller pores. This is the same trend that was seen previously using thermogravimetric analysis reaction temperatures. However, this trend does not extend to the 4 nm sample. In this case, the lack of micropores <2 nm (see Figure 2b) in the 4 nm sample, may indicate the dehydrogenation nucleates in micropores. Alternatively, the lack of any relatively large pores may indicate the need for unfilled conduits for hydrogen

transport. A third possibility is the influence of surface chemistry originating from slightly different synthesis routes at LLNL and HRL. We are working (together with Ted) to prepare additional samples designed to discriminate between these possibilities.

In addition to incorporating LiBH_4 within the aerogel, considerable effort was also devoted to incorporating Mg with the ultimate goal of testing the full $\text{LiBH}_4/\text{MgH}_2$ destabilized system an aerogel. In 2006/2007 we succeeded in incorporating Mg from molten Mg into aerogels by using a Ni wetting layer. This layer was produced by reduction of a Ni salt, impregnated from an acetone solution. However, the processing temperature of 900°C led to the formation of graphite as indicated by XRD. The XRD measurements were confirmed by transmission electron microscopy (TEM, performed by Channing Ahn, Caltech), which showed considerable breakdown of the aerogel structure, see Figure 3a. By using larger particle size Mg, the impediments to obtaining an acceptable melt imposed by the surface oxide layer on the Mg particles were reduced and good incorporation was achieved at 700°C . Although a small graphite diffraction feature was still discernable by XRD (data not shown), TEM images of samples with 10 wt% Mg were indistinguishable from unfilled samples (Figure 3b).

The effect of incorporation into the aerogel on the dehydrogenation rate of MgH_2 was examined using isothermal measurements. Figure 4 shows dehydrogenation at 250°C for 10 wt% Mg incorporated into a 13 nm aerogel using Ni and Cu wetting layers, and for a sample with 3.3 wt% Mg that was prepared without a wetting layer. The dehydrogenation rate for the sample containing the Ni wetting layer is 26 wt% Mg/hr. This rate, which excludes the weight of the aerogel, is comparable to the best rates obtained for Mg milled with catalysts. There are several reports of dehydrogenation rates between 20 and 30 wt%/hr and one report of a rate of 50 wt%/hr. The rate measured for the sample prepared using a Cu wetting layer is lower, 5.5 wt% Mg/hr, which indicates the catalytic effect of the Ni. Without a wetting layer, the dehydrogenation is lower still, 2.2 wt%/hr. This rate is higher than the rates obtainable for bulk MgH_2 without catalysts, for which there very few reports at 250°C .

In addition to kinetics, the equilibrium pressure for Mg/ MgH_2 was measured to look for any thermodynamic effect from the aerogel. A relatively large sample of 10 wt% Mg in a Ni-doped 13 nm aerogel was dehydrogenated into a relatively small volume. The small volume insured that the desorbed hydrogen would raise the hydrogen pressure sufficiently to achieve equilibrium. At 250°C , with 2 wt% H_2 desorbed, dehydrogenation stopped and the pressure equilibrated at 0.4 bar (data not shown). To verify that the sample was indeed at equilibrium, the desorption volume was

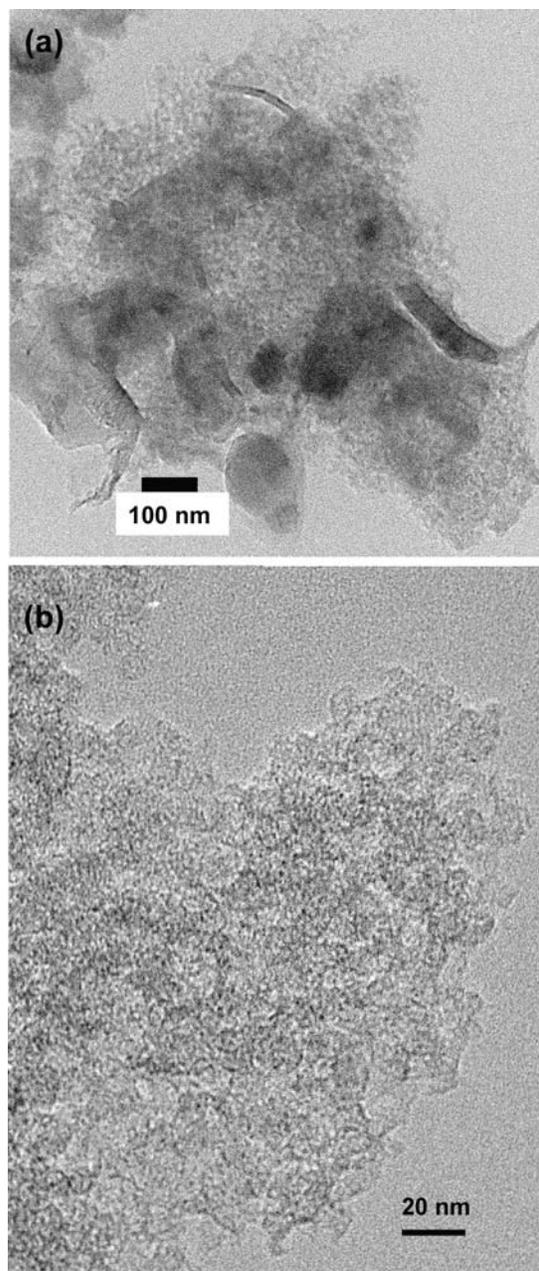


FIGURE 3. Transmission electron micrographs for 13 nm aerogels containing 10 wt% Mg. For panel (a), the Mg was incorporated into the aerogel from a melt at 900°C . This temperature caused degradation of the aerogel structure. For panel (b), the Mg was incorporated at 700°C . The micrograph appears unchanged from an empty aerogel.

pumped briefly (1 min); upon resealing the volume, desorption resumed confirming that equilibrium had been attained. The equilibrium pressure (0.4 bar) is nearly identical to the value obtained from the Sandia database (0.41 bar) indicating that for this sample there was no change in the thermodynamics as a result of incorporation into the aerogel.

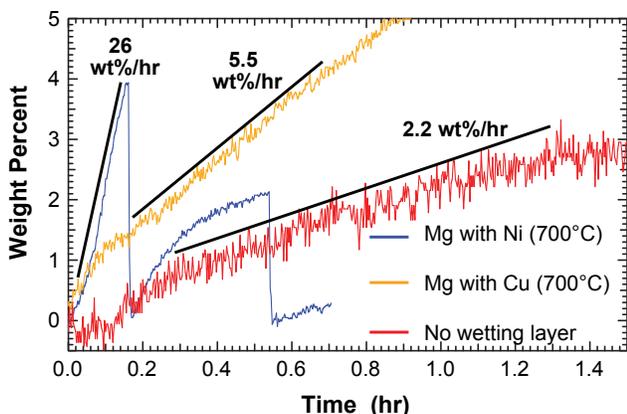


FIGURE 4. Dehydrogenation at 250°C of MgH_2 incorporated into aerogels using different wetting layers. For Ni and Cu wetting layers, the aerogel contain 10 wt% Mg and the dehydrogenation rates are 26 wt% Mg/hr and 5.5 wt% Mg/hr, respectively. Without a wetting layer, 3.3 wt% Mg was incorporated and the dehydrogenation rate is 2.2 wt% Mg/hr.

These results for aerogels with Mg incorporated using a Ni wetting/catalyst layer at 700°C indicate that these samples can be used testing the full $\text{LiBH}_4/\text{MgH}_2$ destabilized system in the aerogel. However, the process is time consuming and the yield is low. Currently, we are planning to use samples prepared at the University of Hawaii, that contain MgH_2 incorporated from an organo-magnesium precursor at ~150°C, which is much lower than the temperature used in the HRL process.

Conclusions and Future Directions

The major conclusions from FY 2007/2008 are:

- The LiBH_4/MgX destabilized system with $\text{X} = \text{Si}$ is not reversible upon dehydrogenation.
- The LiBH_4/MgX destabilized system with $\text{X} = \text{Ni}$ is reversible with a storage capacity of ~6.5 wt% hydrogen and appears to involve a ternary boride phase.
- A decrease in pore size increases the rate of dehydrogenation of LiBH_4 , although the dependence is complicated. For very small pores, access of the hydrogen may become limiting.
- Incorporation of Mg into aerogels improves the rate of hydrogen exchange.

Future directions are:

- Further characterization of the LiBH_4/MgX system with $\text{X} = \text{Ni}$.
- Continue to optimize the aerogel pore structure.
- Test the full $\text{LiBH}_4/\text{MgH}_2$ destabilized system in the aerogel using MgH_2 @aerogel sample obtained from the University of Hawaii.

FY 2008 Publications/Presentations

1. J.J. Vajo, A.F. Gross, R.D. Stephens, T.T. Salguero, S.L. Van Atta, and P. Liu, "Hydride Chemistry in Nanoporous Scaffolds", Invited presentation, International Symposium on Materials Issues in a Hydrogen Economy, November 12-15, 2007, Richmond, Virginia.
2. A.F. Gross, S.L. Skeith, P. Liu, and J.J. Vajo, "Fabrication and Characterization of Nanoscale MgH_2 for Hydrogen Storage Applications" MRS Fall Meeting, November 2007, Boston, MA.
3. J.J. Vajo, A.F. Gross, R.D. Stephens, T.T. Salguero, S.L. Van Atta, and Ping Liu, "Nanoscale Hydrides in Porous Carbon Scaffolds", Invited presentation, APS Spring Meeting, March 2008, New Orleans, LA.
4. J. J. Vajo, "Hydrogen Storage for Transportation Applications", Invited presentation, ASM International San Fernando Valley Chapter: Alternative Energy Mini Symposium, April 2008, Northridge, CA.
5. A.F. Gross, J.J. Vajo, S.L. Skeith, and G.L. Olson, "Enhanced Hydrogen Storage Kinetics of LiBH_4 in Nanoporous Carbon Scaffolds", *J. Phys. Chem. C*, 2008, 112, 5651-5657.