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

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Objectives

- To identify and test new high capacity Li- and Mg-based destabilized hydride systems:
  - Investigate involvement of ternary borides in the $LiBH_4/Mg_2NiH_4$ system.
  - Study the kinetics and thermodynamics of the $LiBH_4/Mg_2NiH_4$ system focusing on the low temperature dehydrogenation step.
- Explore use of nanoconfinement to improve the kinetics of complex hydrides:
  - Incorporate complete $LiBH_4/MgH_2$ destabilized system into carbon aerogel and characterize the hydrogen exchange kinetics.
  - Investigate effects of pore size and pore size distribution on reaction rates of $LiBH_4$.

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

Technical Targets

Destabilized System	Benchmark	2008 Status	2008/09 Progress
$LiBH_4/MgH_2$ @C aerogel 11.4 wt%, 0.095 kg/L without aerogel, est. $T_{1\,bar}=170°C$	Could meet updated 2015 system weight and volume capacity goals (assuming 25% aerogel and 35% system penalties)	For $LiBH_4$ @ C aerogel, reduced capacity penalty to 40% Measured 10x equilibrium pressure Incorporated Mg into aerogel Measured >60x reaction rate	Incorporated complete destabilized system into aerogel Reaction temperature lowered but with degradation Mesoporous carbon synthesized and shows promise for improved kinetics
$LiBH_4 / Mg_2NiH_4$ 8.3 wt%, est. $T_{1\,bar}=150°C$	Could meet updated 2015 system capacity goal (with 35% system penalty)	Reversible capacity of ~6.5% at 350°C Slight degradation observed	Measured T_{1bar} of 65°C for low temperature step Hydrogenation of ternary boride confirmed

Accomplishments

- Investigated $LiBH_4/Mg_2NiH_4$ system:
  - Observed first kinetically destabilized system.
  - Confirmed the formation of ternary borides.
  - Synthesized ternary borides and observed their hydrogenation.
- Incorporated $LiBH_4/MgH_2$ destabilized system into scaffold:
  - Observed lower dehydrogenation temperature but with poor cycling.
  - Tentatively assigned poor cycling to poor mixing of components.
  - Developed synthetic capability of mesoporous carbon at HRL.
  - Observed effect of pore architecture on reaction rate.

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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 Years 2008/2009: (1) evaluate the $LiBH_4/Mg_2NiH_4$ destabilized system developed in 2007/2008 to elucidate

its reaction mechanism, in particular, to clarify the role of ternary borides which could provide a new direction for hydrogen storage material discovery; and (2) incorporate the complete destabilized system of $LiBH_4/MgH_2$ into carbon aerogel scaffolds and evaluate the effect of nanoconfinement on reaction kinetics; continue to investigate the effects of pore size and pore size distribution of carbon scaffolds on hydrogen sorption kinetics.

In the previous year, we discovered and performed preliminary characterization of a new destabilized reaction between $LiBH_4$ and Mg_2NiH_4. Nuclear magnetic resonance (NMR) and X-ray diffraction (XRD) studies of the dehydrogenation product revealed the formation of ternary borides although their exact identity was unknown due to identical XRD patterns for many ternary boride compounds. Work in this year focused on 1) characterization of a low temperature hydrogen desorption step that might indicate kinetic destabilization; 2) chemical synthesis of ternary borides and confirmation of their roles in hydrogenation; and 3) obtaining data on the reaction thermodynamics after the reaction is identified.

Kinetic Destabilization – In the well known destabilized system of $LiBH_4/MgH_2$, MgH_2 first dehydrogenates to form Mg which in turn reacts with $LiBH_4$ to form MgB_2, LiH and hydrogen. Despite an estimated T_{1bar} of 170°C, the reaction in reality does not take place until after the dehydrogenation of MgH_2, which has a T_{1bar} of 280°C. In other words, kinetic pathways prevent the realization of the full benefit of thermodynamic destabilization. In contrast, the $LiBH_4/Mg_2NiH_4$ system does not appear to go through this multi-step process. Figure 1 shows the hydrogen desorption profile of a $0.8LiBH_4/Mg_2NiH_4$ mixture into 4 bar of hydrogen overpressure. Also included for comparison are profiles for Mg_2NiH_4 desorption into 4 bar of hydrogen and $LiBH_4$ into vacuum. There
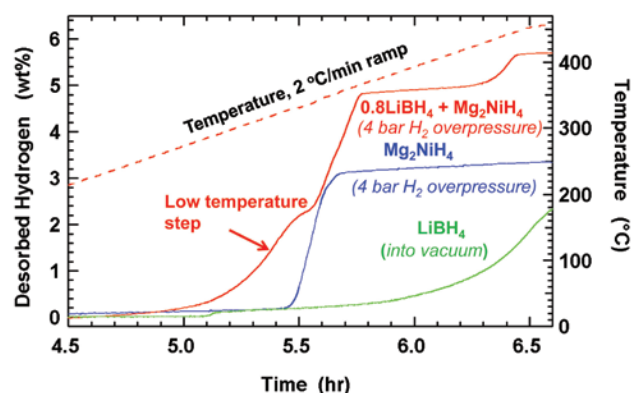

FIGURE 1. Dehydrogenation profiles of $LiBH_4$ into vacuum and Mg_2NiH_4 as well as a $0.8LiBH_4 + Mg_2NiH_4$ mixture into 4 bar of hydrogen overpressure. The low temperature step for the mixture is absent from either of the components.

are three distinct steps for the destabilized system. Of particular interest is the low temperature step between 250 and 325°C. This low temperature step does not occur for either Mg_2NiH_4 or $LiBH_4$ individually (dehydrogenation of $LiBH_4$ would have taken place at even higher temperature into 4 bar of hydrogen than into vacuum). This observation argues that the two components reacted directly prior to their own decomposition, i.e., this is a kinetically destabilized system. As far as we know, this is the first example of such a system. Its identification is important since kinetic destabilization is required to ever realize useful reaction rates at temperatures approaching the thermodynamic (T_{1bar}) value.

Reversible Hydrogenation of Ternary Borides – Another important feature of the new destabilized reaction is the formation of ternary borides. In the previous year, XRD results confirmed their formation, but it was not possible to identify their exact composition, nor was it clear whether they were responsible for reversible hydrogen storage. In this year, by direct synthesis, we investigated potential ternary $MgNi_xB_2$ borides with x = 0.5 to 3. ^{11}B NMR results obtained by Sonjong Hwang at Caltech showed that single-phase compounds exist for x = ~1.5 to 3. In order to examine the hydrogenation of the ternary boride, a mixture of $MgNi_{2.5}B_2$, MgH_2 and LiH in the mole ratios of 1:4:2 was mechanically milled and hydrogenated at 300°C under 100 bar of hydrogen. Subsequent dehydrogenation was performed under 4 bar of hydrogen by ramping the temperature to 400°C. Calibrated ^{11}B NMR spectra (not shown) performed after hydrogenation indicated clearly that the ternary boride was participating in a reversible reaction to form $LiBH_4$. In combination with hydrogen exchange reaction studies, the destabilized reaction is most likely the following:

$$4LiBH_4 + 5Mg_2NiH_4 \rightarrow 2MgNi_{2.5}B_2 + 8MgH_2 + 4LiH + 2.5wt\%H_2$$
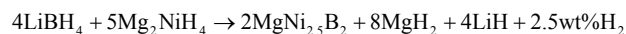
Preliminary Thermodynamic Characterization – Since lower reaction temperature was observed for the $LiBH_4/Mg_2NiH_4$ system, we proceeded to measure the thermodynamic properties of the system. Figure 2 shows the van't Hoff behavior for the system as compared to several other reversible complex hydride materials. A dehydrogenated mixture was hydrogenated at a given temperature and hydrogen overpressure and subsequently dehydrogenated. The hydrogenation overpressure was gradually raised until hydrogen uptake was confirmed by release of hydrogen during the subsequent desorption. For example, after holding at 310°C for one day, no hydrogenation was observed for hydrogen pressures ranging from 10 to 75 bar. When the hydrogen pressure was raised to 100 bar, desorption showed 1.3 wt% of reversible hydrogen uptake which was similar to the uptake obtained at 350°C and 100 bar.
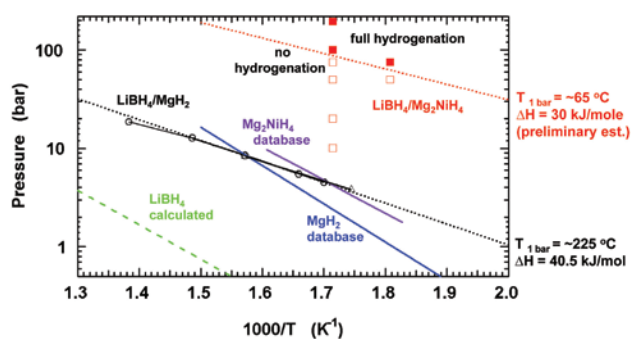
FIGURE 2. Preliminary results of van't Hoff plots for $0.8LiBH_4/Mg_2NiH_4$. Dehydrogenated mixtures were first hydrogenated at a given temperature under certain hydrogen overpressure followed by dehydrogenation. The hydrogen overpressure for hydrogenation was increased until hydrogen absorption was observed during subsequent dehydrogenation. Empty squares indicate no hydrogenation and filled squares indicate hydrogenation. van't Hoff plots for related compounds are also included for comparison.
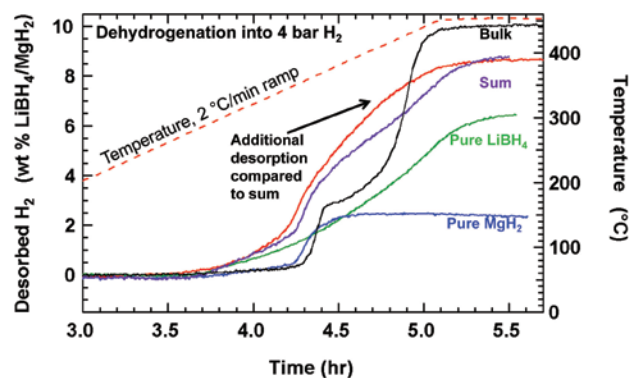
This result indicates that the equilibrium pressure of hydrogen at 310°C is between 75 and 100 bar. A similar sequence was performed at 280°C. These preliminary results allowed us to establish an approximate van't Hoff plot. The reaction was found to have a ΔH value of 30 kJ/mol and a T_{1bar} of 65°C. These values represent marked improvements over the $LiBH_4/MgH_2$ system with ΔH of 40.5 kJ/mol and T_{1bar} of 170°C.

In summary, $LiBH_4/Mg_2NiH_4$ is the first known kinetically coupled destabilized system, forms a ternary boride during dehydrogenation, and exhibits low ΔH and T_{1bar} values. Despite its limited reversible capacity of 2.5 wt%, these attributes point to a potential new direction for material discovery that involves ternary borides. Future work includes more complete assessment of the thermodynamics of the system as well as search of other systems of higher storage capacity.

Our second objective for the year focuses on further exploring the use of nanoconfinement in porous carbon scaffolds to improve the kinetics of hydrogen exchange reactions. In order to incorporate the $LiBH_4/MgH_2$ destabilized system in carbon aerogels, HRL has been working on the incorporation of MgH_2 since last year. Molten Mg was incorporated with a preloading of Ni in the aerogel to enhance wetting. Unfortunately, the high temperature process resulted in low Mg loading as well as non-negligible destruction of aerogel structure. Craig Jensen's group at the University of Hawaii (UH) recently developed a new synthetic procedure for MgH_2 using a reaction between hydrogen and dibutyl magnesium, which greatly facilitates MgH_2 incorporation into carbon aerogel at temperatures as low as 150°C. We measured the hydrogen exchange reaction rate of an MgH_2@C sample and found its kinetics to be similar to the HRL sample prepared with the melt-in process. Equilibrium

pressure of the sample at 250°C was 0.36 bar, very similar to the reported bulk value of 0.4 bar, indicative of no thermodynamic effect due to nanoconfinement.

We used the $MgH_2@C$ sample from UH and incorporated an appropriate amount of $LiBH_4$ to complete the destabilized system. The final sample was 19.9 wt% $LiBH_4$, 12 wt% MgH_2, and 68.1 wt% carbon. The molar ratio of $LiBH_4$: MgH_2 was 1.96. Figure 3 shows its dehydrogenation profile as compared to a catalyzed ball milled bulk sample. The aerogel sample shows a much lower temperature for the onset of dehydrogenation (300 vs 350°C) with the transition between the two dehydrogenation steps less well defined. This reduction in dehydrogenation temperature demonstrates the expected benefit of nanoconfinement on the hydrogen exchange kinetics. Unfortunately, there is a significant degradation of hydrogen storage capacity for the 2nd and the 3rd cycles (results not shown). One possible explanation is that MgH_2 and $LiBH_4$ are not well mixed in the pores of the aerogel. In other words, they may occupy different pores of the aerogel and go through hydrogen exchange reactions separately. The reduction in the onset temperature of dehydrogenation is similar to what would be observed with a $LiBH_4$ loaded carbon aerogel. Since $LiBH_4$ is not fully reversible even when incorporated in the aerogel, the degradation in storage capacity would be expected. This hypothesis is supported by two additional observations: 1) the sum of the hydrogen desorption profiles of pure MgH_2 and pure $LiBH_4$ is very close to that of the combined system as also shown in Figure 3. The lower desorption temperature of the destabilized system can be attributed to the lower decomposition temperature of $LiBH_4$ in the aerogel; and 2) dehydrogenation products at 325°C, i.e., before MgH_2 decomposition occurs under 4 bar H_2 have no MgB_2 as confirmed by NMR analysis. This result further argues that the low temperature decomposition step does not involve a coupled reaction between $LiBH_4$ and MgH_2 which would likely lead to the formation of MgB_2. Work is in progress to develop synthetic method to enable simultaneous incorporation of both Mg and Li compounds in the aerogel to ensure uniform mixing.
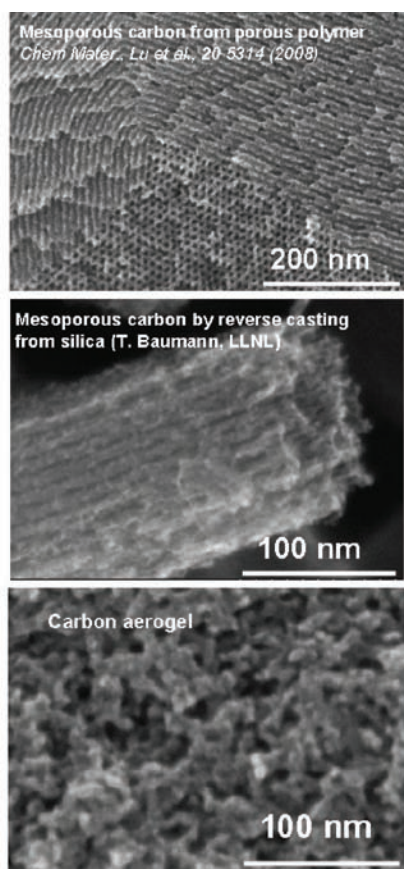
We have also continued to evaluate additional carbon scaffolds in search of the maximum kinetic impact while minimizing the volume and weight penalty. Shown in Figure 4a are scanning electron microscope (SEM) images of three representative carbon materials with distinct microstructures. The mesoporous carbon synthesized from porous polymer (HRL meso-C) has long, straight but not interconnected pores while the mesoporous carbon synthesized by reverse casting from mesoporous silica has long, straight but interconnected pores. The carbon aerogel, on the other hand, has isotropic random pores. These differences in architecture have a direct impact on hydrogen desorption kinetics as shown in Figure 4b. HRL meso-C has an initial rate very similar to those of aerogel and the reverse cast mesoporous carbon. However, unlike all the other materials, its rate gradually decreases with time. We could explain these observations by attributing them to the effect of the one dimensional porous architecture. As the dehydrogenation proceeds the reaction products of LiH and B gradually accumulate in the pores which impede the release of hydrogen. In contrast, carbon aerogels and the reverse cast mesoporous carbon both have three dimensional porous architectures which would ensure continued hydrogen access. These results provide further evidence that porous architecture, in addition to pore size and pore volume, is an important factor in its effectiveness in kinetic enhancement.
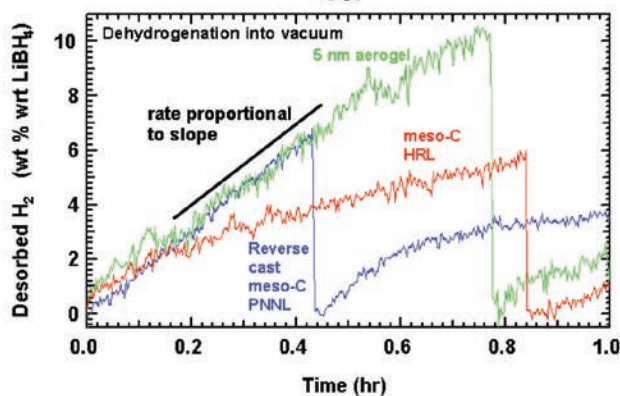
Conclusions and Future Directions

The major conclusions from FY 2008/2009 are:

- The $LiBH_4/Mg_2NiH_4$ destabilized system is the first to exhibit kinetic destabilization. The reaction involves reversible hydrogen exchange with ternary borides. Preliminary thermodynamic characterization gives a ΔH of 30 kJ/mol and a T_{1bar} of 65°C, two of the lowest values reported for any borohydride based hydrogen storage system;

- The complete destabilized system of $LiBH_4/MgH_2$ has been incorporated into carbon aerogels. It shows reduced dehydrogenation temperature but poor cycling stability. Poor mixing of the two hydrides in the nanopores is most likely the cause; and

- Pore architecture, in addition to pore size of carbon scaffold has a significant impact on hydrogen exchange reaction kinetics. Interconnectivity between the pores is important to maintain fast reaction rate.

FIGURE 3. Hydrogen desorption profiles of the $LiBH_4/MgH_2$ destabilized system, pure MgH_2, and pure $LiBH_4$ in carbon aerogels with a peak pore size of 13 nm. The profile for the destabilized system is very similar to the sum of the profiles from the components. Also included for comparison is the profile for the bulk destabilized system.

4a

4b

FIGURE 4. (a) SEM images of mesoporous carbon synthesized from porous polymer (HRL meso-C) and reverse casting from mesoporous silica (by Lawrence Livermore National Laboratory, LLNL) and a carbon aerogel; (b) hydrogen desorption profiles for the carbon aerogel, HRL meso-C, and a mesoporous carbon from reverse casting prepared by the Pacific Northwest National Laboratory which is similar to the LLNL material.

Future directions are:

- Complete thermodynamic characterization of the $LiBH_4/Mg_2NiH_4$ system;
- Search for other destabilized systems involving ternary borides with higher capacities;
- Develop synthetic methods to achieve simultaneous incorporation of $LiBH_4$ and MgH_2 for improved mixing; characterize its hydrogen exchange reaction kinetics; and
- Continue to optimize carbon scaffold pore structure.

FY 2009 Publications/Presentations

1. 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.,* **112**, 5651–5657 (2008).

2. A.F. Gross, C.C. Ahn, S.L. Van Atta, P. Liu, J.J. Vajo, "Fabrication and hydrogen sorption behavior of nanoparticulate MgH_2 confined in a porous carbon host", *Nanotechnology*, **20**, 204005 (special issue focused on nanoscale phenomenon in hydrogen storage).

3. J. Graetz, S. Chaudhuri, T.T. Salguero, J.J. Vajo, M.S. Meyer, F.E. Pinkerton, "Local bonding and atomic enviroments in Ni-catalyzed complex hydrides" *Nanotechnology*, **20**, 204007 (special issue focused on nanoscale phenomenon in hydrogen storage).

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5. S.T. Kelly, B.M. Clemens, S.L. Van Atta, J.J. Vajo, G.L. Olson, "Kinetic limitations of the Mg_2Si system for reversible hydrogen storage" *Nanotechnology,* **20**, 204017 (special issue focused on nanoscale phenomenon in hydrogen storage).

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7. H. Wu, W. Zhou, K. Wang, T.J. Udovic, J.J. Rush, T. Yildirum, L.A. Bendersky, A.F. Gross, S.L. Van Atta, J.J. Vajo, F.E. Pinkerton, "Size effects on hydrogen storage properties of nanoscaffolded $Li_3BN_2H_8$" , *Nanotechnology*, **20**, 204002 (special issue focused on nanoscale phenomenon in hydrogen storage).

8. R.D. Stephens, A.F. Gross, S.L. Van Atta, J.J. Vajo and F.E. Pinkerton, "The kinetic enhancement of hydrogen cycling in $NaAlH_4$ by melt infusion into nanoporous carbon aerogel", *Nanotechnology* , **20**, 204018 (special issue focused on nanoscale phenomenon in hydrogen storage).

9. J.J. Vajo, "Hydrogen storage for transportation applications", Invited presentation, ASM International San Ferando Valley Chapter: Alternative Energy Mini Symposium, April 2008, Northridge, CA.

10. J.J. Vajo, W. Li, P. Liu, "Thermodynamic and kinetic destabilization in LiBH$_4$-based hydride systems", American Physical Society Meeting, March, 2009, Pittsburg, PA.

11. W. Li, J.J. Vajo, R.W. Cumberland, P. Liu, S.-J. Hwang, C. Kim, "Reversible low temperature hydrogen storage using ternary borides", American Physical Society Meeting, March, 2009, Pittsburg, PA.

12. W. Li, J.J. Vajo, P. Liu, "Magnesium based metal borides for reversible hydrogen storage at low temperature" Patent application filed March 2009.