IV.A.5d Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage

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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 advances are made possible by tuning the thermodynamics and kinetics of the hydrogenation/dehydrogenation reactions.

The project at HRL Laboratories (HRL) is being conducted in close collaboration with other researchers from the DOE Metal Hydride Center of Excellence (MHCoE). We are participating in a sub-team comprising 10 organizations within the MHCoE that focuses specifically on the development of thermodynamically tuned destabilized materials for reversible storage.

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. In both approaches, we continuously seek collaboration with MHCoE partners with regard to theoretical support, catalyst screening, sample exchange, and technical discussions.

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 alloy, 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 stable alloy instead of the pure metal. The thermodynamics of the reaction can be tuned with the use of materials to afford alloys of different stability. Although the addition of a destabilizing agent imposes a gravimetric capacity penalty, it is possible to minimize the penalty by using metal hydrides or other light metal compounds as destabilizing agents.

The second component of our approach addresses the kinetics limitations of 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.

Objectives

There were two main objectives for this project in FY 2007:

(1) continue to evaluate new destabilized systems with more desirable hydrogen delivery temperatures; and
(2) use nanoengineering methods to improve reaction rates.

Results

We concluded our work on the MgH_2/Si system and devoted most of our effort to studying the hydrogen exchange reaction in $LiBH_4$ and MgH_2 when they are confined in nanoporous scaffolds.

We continued to expand our knowledge on new destabilized systems with a general formula of $LiBH_4/MgX$. Unfortunately, no reversibility was observed in the two systems we have investigated:

- $2LiBH_4 + MgCl_2 \leftrightarrow 2LiCl + MgB_2 + 4H_2$ (5.8 wt%, $T_{1\,bar}$ = -10°C)

  (There was no H_2 uptake from $2LiCl + MgB_2$ at 150 bar, up to 250°C, possibly because T_{1bar} is too low.)

- $4LiBH_4 + Mg_2Cu \leftrightarrow 4LiH + 2MgB_2 + Cu + 6H_2$ (6.0 wt%)

  (From $4LiBH_4 + Mg_2Cu$, only trace MgB_2 is formed, i.e., $4LiBH_4$ and Mg_2Cu did not react with each other.)

We believe that the first reaction did not reverse because the reaction kinetics was very slow at low temperatures, as dictated by its thermodynamics.

In FY 2007, much effort was devoted to improving reaction kinetics in two systems: MgH_2/Si and $LiBH_4$. MgH_2/Si was chosen in FY 2006 as a prototype destabilized system. The addition of Si dramatically reduces the T_{1bar} to 50°C due to the formation of the very stable alloy of Mg_2Si. The main goal of our effort was to demonstrate reversibility of the reaction, i.e., rehydrogenation of Mg_2Si. After considerable effort by HRL as well as our Center partners, no reversibility was observed and we made a no-go decision at the end of FY 2006. The various attempts to achieve rehydrogenation included:

- **Catalysis.** An array of bulk and nanosized metals and metal oxides were screened. While all of them improved the dehydrogenation reaction with nanoparticles of Ni being the best, no hydrogenation was observed.
- **Mechanical dispersion.** MgH_2 was milled with excess amount of Si to form highly dispersed nano-MgH_2. The temperature for onset of dehydrogenation decreased by up to 100°C but no hydrogenation was observed.
- **Mg_2Si Nanoparticles.** The particles were synthesized by using Si nanoparticles with self-propagating reactions or chemical vapor synthesis. But none of the materials could be rehydrogenated.
- **Mechano-Chemistry.** Extensive milling of Mg_2Si in 50 bar of hydrogen under a variety of conditions and with catalysts did not yield any rehydrogenation products.

A possible explanation for the difficulties in hydrogenating Mg_2Si is passivation of the Mg_2Si surface by hydrogen as suggested by Prof. Somorjai of University of California, Berkeley. After considering all the experimental attempts, we made a no-go decision at the end of FY 2006 on this system.

We devoted most of our FY 2007 effort in studying the effect of nanoconfinement by carbon aerogel on the hydrogen exchange reactions in $LiBH_4$ and MgH_2. In FY 2006, we showed that the dehydrogenation temperature of $LiBH_4$ could be lowered by up to 70°C when confined in carbon aerogel. In addition, the hydrogen exchange reaction also became more reversible, presumably because the dehydrogenation products (LiH and B) are in close contact due to the confinement of the nanopores. In FY 2007, we further explored the effect of nanoconfinement on both the thermodynamics and kinetics of the hydrogen exchange reaction.

The energetic states of the confined $LiBH_4$ were probed by differential scanning calorimetry (DSC) as shown in Figure 1. Also included for comparison are results from $LiBH_4$ – neat and mixed with graphite. The temperature for the orthorhombic to hexagonal structural change was noticeably lowered and the heat of transition was reduced from 4.3 to 2.3 kJ/mol. The melting point of the confined $LiBH_4$ was lowered by 30°C when compared to its bulk counterpart. These effects of confinement were consistent with peak broadening observed in X-ray diffraction (XRD) that indicated structural strain. Since the dehydrogenation reaction usually coincides with the melting of $LiBH_4$, the reduced melting point effectively lowers the dehydrogenation temperature.

The effect of nanoconfinement on hydrogen exchange rate was measured in a Sieverts apparatus by monitoring the pressure rise during the reaction. Figure 2 shows the results from an isothermal experiment at 300°C for $LiBH_4$ confined in an aerogel with a peak pore size of 13 nm. The hydrogen release rate for the aerogel sample was 50 times greater compared to the graphite control. Data in Table 1 also clearly show the correlation between pore size and dehydrogenation rates, temperature, and activation energy.
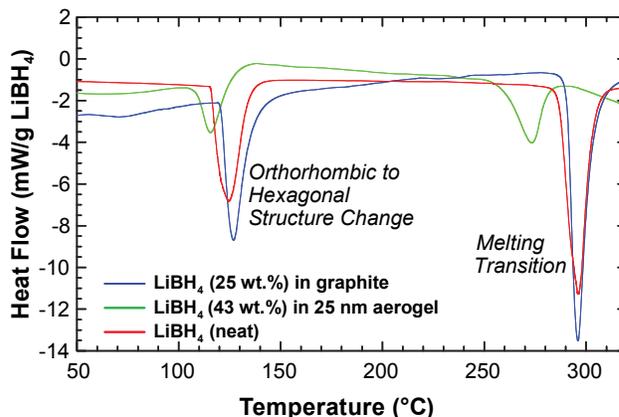
FIGURE 1. Enthalpies for Structural and Melting Transitions for Neat $LiBH_4$ and $LiBH_4$ Contained in a 25 nm Aerogel and Mixed with Graphite (The enthalpies for the neat and $LiBH_4$/graphite sample are similar and agree with values in the literature. The transition temperatures and enthalpies for the aerogel sample are lower.)
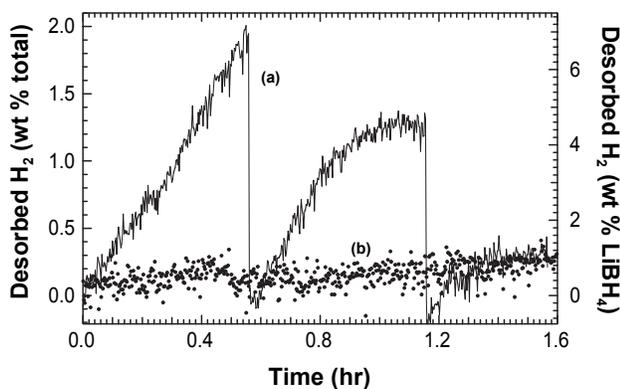
FIGURE 2. Dehydrogenation of LiBH$_4$ at 300°C (Curve a [solid line] shows dehydrogenation of LiBH$_4$ contained in a 13 nm carbon aerogel. Curve b [filled circles] shows dehydrogenation of LiBH$_4$ mixed with nonporous graphite. Left axis gives the amount of desorbed hydrogen relative to the total weight of the LiBH$_4$ and carbon composite. Right axis gives the desorbed amount relative to the LiBH$_4$ only. For Curve a, the steps at ~0.6 and ~1.2 hr occur because the desorbed hydrogen was briefly evacuated. The initial dehydrogenation rate is ~50 times greater for LiBH$_4$ in the aerogel as compared to the bulk material.)

TABLE 1. Dehydrogenation Parameters for LiBH$_4$ Incorporated in Nanoporous Carbon

Nanoporous Scaffold Material (pore size)	Dehydrogenation Temperature (°C)[a]	Activation Energy (kJ/mol LiBH$_4$)[b]	Dehydrogenation Rate at 300°C (wt%/hr)[c]
Activated carbon (~2 nm)	375	-	-
Aerogel (13 nm)	381	103±4	12.5
Aerogel (25 nm)	390	111±2	7.8
Graphite (nonporous)	453	146±3	0.22

a) TGA, 10°C/min temperature ramp, flowing argon
b) TGA, Ozawa analysis [1], errors indicate two standard deviations
c) Volumetric measurements, rate expressed with respect to the weight of LiBH$_4$, P(H$_2$) <0.05 bar

We also investigated possible changes in thermodynamics of the dehydrogenation reaction due to the effect of nanoconfinement. The equilibrium pressure during dehydrogenation is ~10 times higher for the aerogel sample at 300°C and ~4 wt% desorbed. While the measurement of the entire isotherm is yet to be completed, this is a strong indication that nanoconfinement does change the thermodynamics of the hydrogen exchange reaction.

An important consideration for practical application of the nanoconfinement approach is the weight and volume penalty on hydrogen capacity due to the porous host. We estimated in 2006 that a 25% mass penalty, which yields a material storing 10.2% of hydrogen, would be acceptable. This can be realized if the pore volume can be increased to 4 cm^3/g. We obtained a

carbon aerogel with a pore volume of 2.7 cm^3/g from Ted Baumann of Lawrence Livermore National Laboratory (LLNL), a partner in the DOE Sorption Center of Excellence. The material delivered 8 wt% of hydrogen and showed a lower dehydrogenation temperature than the bulk LiBH$_4$. It is strongly desirable, however, to use a material with a smaller pore size than this aerogel (around 40 nm) since our work indicates that smaller pore sizes lead to better kinetics. The challenge remains to synthesize a carbon aerogel with high pore volume but small pore sizes. We will continue to work with LLNL in 2008 in pursuit of this material.

Our ultimate goal of using nanoconfinement to facilitate hydrogen storage is to incorporate complete destabilized systems such as LiBH$_4$/MgH$_2$. To achieve this goal, it is necessary to incorporate Mg or MgH$_2$ into carbon aerogel. Unlike LiBH$_4$, which can be readily introduced through melting, Mg does not wet the carbon aerogel surface. After numerous failed attempts at introducing Mg by changing the surface energy of carbon aerogel surface, we have found that preloading the porous host with Ni metal facilitates the introduction of Mg. Figure 3 shows XRD patterns that confirm the presence of Mg in the carbon aerogel. Without Ni, no Mg was detected, even after heating Mg with carbon aerogel for 60 hrs at 900°C. Ni was introduced as Ni(NO$_3$)$_2$, which was subsequently reduced to Ni metal. The broad peaks are indicative of the small size of the highly dispersed particles. Heating Ni preloaded aerogel with Mg at 900°C led to successful introduction of Mg. We subsequently measured the hydrogen exchange rate of Mg in carbon aerogel in an isothermal experiment. As shown in Figure 4, a desorption rate of 20 wt%/hr was observed at 250°C, which was comparable to the best values reported in the literature [2,3].
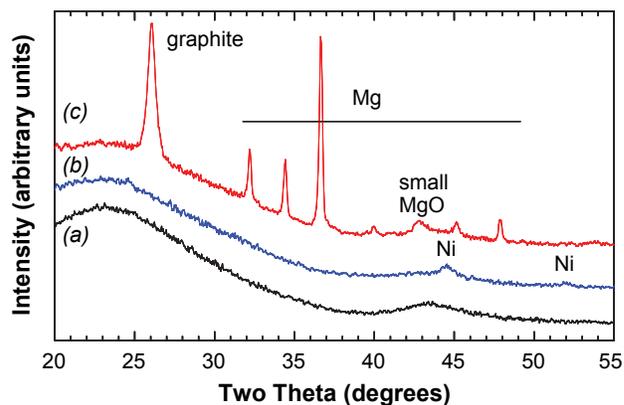
FIGURE 3. XRD of Mg in Carbon Aaerogel with a Peak Pore Size of 26 nm. (a) Aerogel After Being Heated with Mg at 900°C for 60 Hours (b) Aerogel Loaded with ~1.5% of Ni Which Was Introduced by Ni(NO$_3$)$_2$ Followed by Reduction at 500°C for Six Hours (c) Aerogel with Mg and Ni after the Ni Loaded Aerogel Was Heated with Mg at 900°C for 60 Hours.
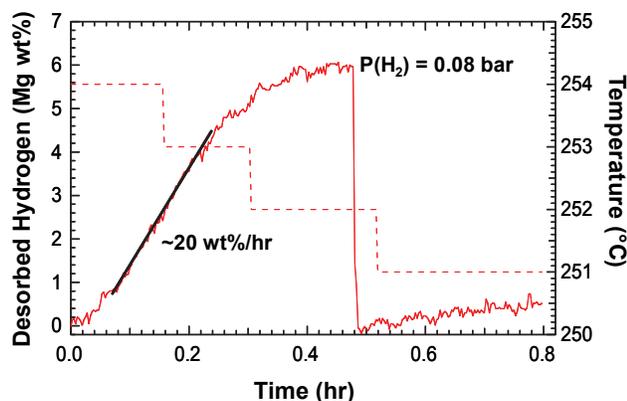
FIGURE 4. Dehydrogenation of Mg in Carbon Aerogel at 250°C (The sample was first hydrogenated at 250°C in 100 bar of H_2. The chamber was quickly evacuated and the isotherm desorption recorded. This experiment yields a desorption rate of ~ 20 wt%/hr, as compared to 26.4 wt%/hr from Liang et. al. [1] who used Ti as a catalyst and 30.0 wt%/hr from Aguey-Zinsou et. al. [2] who used MgO as a catalyst.)

Future prospects for nanoporous hosts include the use of materials with higher pore volume and small pore size to assess the practicality of this approach. Incorporating complete destabilized systems such as $LiBH_4/MgH_2$ remains the ultimate goal of this approach. Further enhancement in reaction kinetics is also possible with the inclusion of catalysts as well as other nanoporous hosts.

Conclusions and Future Directions

In summary, our effort in FY 2007 focused on continued search for new destabilized systems, implementation of nanoengineering approaches for improving kinetics of the MgH_2/Si system, and exploration of the effect of nanoconfinment by carbon aerogel on reaction kinetics of $LiBH_4$ and MgH_2. The highlight of this year's work is the vastly improved reaction rates enabled by the nanoconfinement approach, which holds great promise for solving one of the biggest challenges facing complex metal hydride hydrogen storage materials. A summary of this work, principal conclusions, and future plans are briefly delineated in the following:

Summary and Conclusions

- Two $LiBH_4/MgX$ systems where X= Cl and Cu were tested for reversible hydrogen exchange. Neither of them was found to be reversible. The chloride system most likely suffered from slow kinetics.
- Work on the MgH_2/Si system was completed. Numerous approaches of nanoengineering involving nanoparticles, reactive ball milling, and catalyst screening yielded much improved dehydrogenation

rates but rehydrogenation was never realized. A no-go decision was made at the end of FY 2006.

- Nanoconfinement of $LiBH_4$ in carbon aerogel had a profound impact on the kinetics and thermodyanics of the hydrogen exchange reaction. It greatly improves reaction kinetics with dehydrogenation rate increased by at least 50 times, dehydrogenation temperature lowered by 70°C, and reaction activation energy reduced. Nanoconfinement also appears to have changed the thermodynamics of the reaction.

Future Work

New destabilized systems

- Explore additional $LiBH_4/MgX$ reactions.

Nanoconfinement

- Complete characterization of Mg in carbon aerogels.
- Incorporate the destabilized system with catalysts.
- Further increase pore volume.
- Explore other nanoporous materials.

FY 2007 Publications/Presentations

1. J. J. Vajo and G. L. Olson, "Hydrogen Storage in Destabilized Chemical Systems," (invited "Viewpoint Set" article) *Scripta Materialia*, 56 829-834 (2007).

2. J. J. Vajo, T.T. Salguero, A.F. Gross, S.L. Skeith, and G. L. Olson "Destabilization Strategies and Kinetics Challenges in Light Metal Hydride Systems," in press, *J. Alloys and Compounds* – special proceedings issue for MH2006 Conference, Oct. 1-6, 2006.

3. A.F. Gross, J. J. Vajo, S.L. Skeith, and G.L Olson, "Enhanced Hydrogen Storage Kinetics of $LiBH_4$ in Nanoporous Carbon Scaffolds," in preparation.

4. J. J. Vajo, T.T. Salguero, A.F. Gross, S.L. Skeith, and G. L. Olson, "Destabilization Strategies and Kinetics Challenges in Light Metal Hydride Systems," invited presentation at MH2006 Conference, Lahaina, Hawaii, Oct. 1–6, 2006.

5. A. F. Gross, "Synthesis and Characterization of Nanoscale $LiBH_4$ for Hydrogen Storage Applications," Invited presentation, California State University Northridge, March 2007.

References

1. T. Ozawa, *J. Therm. Anal. 2*, 301 (1970).

2. G. Liang, J. Huot, S. Boily, A. Van Neste, and R. Schulz, *J. Alloys and Compds.*, 292, 247 (1999).

3. K.-F. Aguey-Zinsou, J.R. Ares Fernandez, T. Klassen, and R. Bormann, *Mater. Res. Bull.*, 41, 1118 (2006).