Introduction

This project is devoted to significantly extending the limits of hydrogen storage technology for practical transportation applications. To meet the capacity goals set forth by the DOE for hydrogen storage systems, solid-state materials consisting of light elements are being developed. Many light element compounds are known that have high hydrogen capacities. However, most of these materials are too thermodynamically stable, and they release and store hydrogen much too slowly for practical use. In this project we are developing new light element chemical systems that have high hydrogen capacities while also having suitable thermodynamic properties. In addition we are developing methods for increasing the rates of hydrogen exchange in these new light element systems.

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 coordinating a sub-team comprised of 10 organizations within the MHCoE that focuses specifically on the development of thermodynamically tuned destabilized materials for reversible storage.

Approach

The approach we have adopted in this project 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 these new light element systems.

The first component, hydride destabilization, is built upon the idea that if an alloy is stable with respect to its constituent elements then the hydride will be effectively destabilized. Destabilization occurs because the modified system can cycle between the hydride and the stable alloy instead of the pure metal. Formation of the alloy lowers the overall enthalpy for dehydrogenation, thereby increasing the equilibrium hydrogen pressure for the sorption reaction (i.e., destabilization results in a decrease in the temperature for hydrogen exchange). In contrast with other methods involving additives or alloy formation, these destabilized chemical systems can be thermodynamically tuned without forming new hydride phases; i.e., alloy formation occurs only in the dehydrogenated state. 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 to hydrogen exchange reactions in light metal hydrides. We are using catalysts as well as nanoscale reactants to improve the overall reaction kinetics. Catalysts have previously been shown to greatly increase the reaction rates in complex hydrides [1], and we are studying the effects of catalysts on reaction rates in destabilized hydride systems. Likewise, net sorption rates that are much faster than in bulk materials can be achieved by reducing the diffusion distance by using nanoscale reactants. In addition, the surface/volume ratio is increased and catalytic activity can be improved as particle size decreases. We are also investigating the use of nanoporous “scaffolds” as structure-directing agents for forming nanoscale metal hydride reactants. In addition to facilitating the formation of nanoscale material within the scaffold, the porous structure confines the hydride reactants, thereby mitigating potential problems that can arise from agglomeration and sintering of the nanostructured material during hydrogen cycling.

Results

There were two major objectives for this project in 2005/2006:

1. To identify and test new high capacity Li- and Mg-based destabilized hydrides. Specifically, we identified candidate LiBH₄ + MgX destabilized...
systems and evaluated energetics and kinetics in those systems.

2. To apply nano-engineering methods to address kinetics limitations in light metal hydrides. Specifically, we developed solid-state approaches for efficient synthesis of nanoscale reactants, assessed hydrogen exchange rates in nanoscale MgH2/Si and evaluated sorption kinetics of reversible metal hydrides in nanoporous scaffold hosts.

Results in these areas are described in greater detail in the following:

In 2005/2006 we performed equilibrium calculations using a thermodynamics calculation program (HSC), for several candidate LiBH4 + MgX (X= F, Cl, OH, O, S, Se, Si, Ge, and Ni) destabilized systems, and we find gravimetric capacities ranging from 5 to 10 wt% with T(1 bar) = 0 to 400°C. Partial reversibility was demonstrated in three of these:

- 2LiBH4 + MgF2 ↔ 2LiF + MgB2 + 4H2 (7.6 wt%, T1 bar = 150°C) (H2 uptake ~6.5% at 325°C; dehydrogenation 5.3%)
- 2LiBH4 + MgS ↔ Li2S + MgB2 + 4H2 (8.0 wt%, T1 bar = 170°C) (H2 uptake ~6% at 350°C; dehydrogenation ~4%; 2nd cycle uptake <4%)
- 2LiBH4 + MgSe ↔ Li2Se + MgB2 + 4H2 (5.4 wt%, T1 bar = 70°C) (H2 uptake ~4.5% at 350°C; dehydrogenation ~3.3%)

Although the thermodynamics calculations are encouraging, we find that experimentally measured sorption temperatures are much higher than HSC predictions of T(1 bar) in virtually all of these systems (see Table 1). This discrepancy is due to kinetic limitations that make it impractical to conduct meaningful sorption measurements at the calculated 1 bar equilibrium temperatures. Proposed methods for mitigating slow kinetics in low-Z destabilized hydrides are discussed later in this report.

TABLE 1. Comparison of measured and calculated reaction temperatures for the LiBH4/MgX destabilized reaction systems for different X substituents.

<table>
<thead>
<tr>
<th>X</th>
<th>Measured Hydrogenation Temperature (°C)*</th>
<th>Measured Dehydrogenation Temperature (°C)*</th>
<th>Calculated T(1 bar)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>300</td>
<td>280-400</td>
<td>170</td>
</tr>
<tr>
<td>F2</td>
<td>325</td>
<td>300-450</td>
<td>150</td>
</tr>
<tr>
<td>S</td>
<td>350</td>
<td>300-450</td>
<td>175</td>
</tr>
<tr>
<td>Se</td>
<td>350</td>
<td>350-450</td>
<td>70</td>
</tr>
</tbody>
</table>

* Hydrogenation at 100 bar H2 during heating at 2°C/min
* Dehydrogenation during heating at 2°C/minute
* Calculated using HSC Chemistry for Windows

An example illustrating hydrogenation and dehydrogenation in a specific LiBH4/MgX system is shown in Figure 1. In this case, H2 uptake and release vs. temperature are shown together with accompanying composition changes for the LiBH4/MgF2 destabilized system. Hydrogen sorption measurements were obtained using a custom pressure-volume-temperature system (Sieverts apparatus), and composition changes before and after the sorption cycles were obtained from x-ray diffraction (XRD) measurements. Both hydrogenation and dehydrogenation are clearly evident from these data. The accompanying XRD results show the emergence of new phases and changes in composition that occur during the sorption cycles in the destabilized system.

As mentioned previously, an important aspect of this research and development effort is the development and implementation of new approaches for improving the sorption kinetics in light-metal systems. In particular, we devoted considerable effort in 2005/2006 to exploring methods for enhancing kinetics in the MgH2/Si system. Thermodynamic calculations (HSC) predict a dramatic decrease (>250°C) in T(1 bar) when MgH2 is destabilized by the addition of Si. This result, coupled with the fact that the MgH2/Si system is amenable to nano-engineering by a variety of approaches, suggests this may be a particularly interesting prototype system for study. The chemical reaction that describes destabilization of MgH2/Si by the addition of Si is given as:

\[ 2\text{MgH}_2 + \text{Si} \leftrightarrow \text{Mg}_2\text{Si} + 2\text{H}_2 \]

In this case Mg2Si forms as a stable alloy upon dehydrogenation, and the Mg2Si phase must be converted back to the constituent components when the system is rehydrogenated. We have found that the kinetics in the forward direction (dehydrogenation) can be significantly enhanced by nano-engineering. For example, Figure 2 shows how the temperature for the onset of dehydrogenation can be decreased by the addition of nanoscale Ni as a catalyst and by the use of widely dispersed, small particles generated by energetic ball-milling of MgH2 in an excess of Si ("dilution milling"). Compared with a reference (stoichiometric) sample that was formed by milling without Ni, we find that the onset temperature decreases by more than 100°C when the sample is prepared by dilution milling in the presence of 5% nano-Ni.

Although dehydrogenation temperatures can be decreased using nano-engineering approaches, we have been unsuccessful in "reversing" the reaction; i.e., we have been unable to hydrogenate nanoscale Mg2Si. Numerous approaches were investigated, including attempts to hydrogenate Mg2Si in a H2 overpressure during milling and use of novel methods for synthesizing nanoscale Mg2Si with different structure and morphology. However, in all cases, hydrogenation was not observed, and demonstration of reversibility in the
MgH₂/Si remains an unanswered challenge. Future work in the remainder of FY 2006 will focus on the use of even smaller Mg₂Si particles (20–40 nm) produced by chemical vapor synthesis (U. Utah) and reactions involving Mg₂Si nanoparticles synthesized using Si precursors that contain a minimal surface oxide layer (oxide may seriously inhibit hydrogen dissociation and diffusion kinetics). A “go/no-go” decision for the MgH₂/Si system is currently planned for the end of FY 2006.

We have been exploring another approach for nanoparticle synthesis and confinement that utilizes nanoporous carbon aerogels as structure-directing agents. In addition to facilitating the formation of nanostructured light element hydrides, the aerogel scaffold inhibits sintering and agglomeration of the nanostructured hydride during hydrogen cycling – effects that could seriously compromise the sorption kinetics. Previously, Gutowska, and co-workers showed that silica aerogels could be used effectively as hosts for ammonia borane, H₃NBH₃, a high capacity chemical hydride [2]. Significant increases in the dehydrogenation rate as well as improvements in thermodynamics relative to pure ammonia borane were observed in that work. Also, Schüth and co-workers showed that NaAlH₄ exhibits improved kinetics when contained in carbon aerogels [3]. In 2005/2006 we studied the kinetics of hydrogen exchange in LiBH₄ incorporated into carbon aerogels and other nanoporous scaffolds. In addition to providing insight into the kinetic behavior of a high capacity complex hydride in a nanoporous scaffold, this work forms the foundation for studies of multi-component (destabilized) hydrides confined in scaffold hosts.

Thermo-gravimetric analysis data for hydrogen release from LiBH₄ contained in two aerogels with
pore sizes of 13 and 26 nm, activated carbon with a pore size of <2 nm, and a non-porous graphite control sample are shown in Figure 3. Release of hydrogen from the LiBH₄/graphite control sample occurs at a temperature comparable to that of neat LiBH₄. In contrast, the dehydrogenation temperature of LiBH₄ in the aerogels is reduced by up to 100°C. The magnitude of the temperature decrease varies inversely with pore size. The total mass loss varies with the loading, which is ~25 wt% for the 13 nm, activated carbon, and control samples, and ~45 wt% for the 26 nm sample. Thus, incorporation into the aerogel significantly accelerates the dehydrogenation of LiBH₄. This most likely originates from the reduced diffusion distances and increased surface areas for LiBH₄ in the aerogel.

The cycling behavior of LiBH₄ in the aerogel is shown in Figure 4, where the hydrogen loss from the first dehydrogenation is normalized to one for each sample, and the fraction of original capacity is shown for three cycles. Although there is a decrease in capacity for all samples, the samples containing LiBH₄ in the aerogels show a significantly reduced decrease in capacity compared to the LiBH₄/graphite control. Although, this work is ongoing, we feel that the improved cycling is related to the limited particle sizes for the LiH and B dehydrogenation products imposed by the aerogel host. With limited volume for particle growth, there is likely to be increased interfacial contact between the LiH and B phases, and this contact facilitates rehydrogenation.

The results presented in Figures 3 and 4 indicate that the hydrogen exchange reactions of complex hydrides can be significantly improved by incorporation into a nanoporous host. However, for the results shown, the maximum loadings were only 25-45 wt%, which are too low for practical use. An important issue is whether the gravimetric and volumetric penalties associated with using scaffolds can be sufficiently minimized for practical use. Loading of 45 wt% was obtained for an aerogel with a pore volume of 1.4 cm³/g filled with LiBH₄. If the pore volume can be increased to 4 cm³/g, then a 70 wt% loading can be achieved. Moreover, higher density hydrides will yield higher loadings. Aerogels with pore volumes of 3–4 cm³/g exist, although it is not known if these materials will provide the same kinetics improvements as those shown in Figures 3 and 4. We are collaborating with T. Baumann (LLNL), a partner in the DOE Carbon Center, on synthesis and characterization of carbon aerogels with larger pore volumes.

Future prospects for nanoporous hosts include further enhancement of reaction kinetics by incorporating catalysts and, eventually, incorporating complete destabilized systems such as LiBH₄/MgH₂. Aerogels containing Ni have been synthesized, although the catalytic activity for hydrogen exchange has not yet been assessed.

Conclusions and Future Directions

As mentioned in the previous sections, our effort in FY 2006 focused on development of new destabilized systems, implementation of new nanoparticle synthesis routes for improving kinetics in the MgH₂/Si system, and exploration of nanoporous scaffolds as structure-directing agents and confinement media for light-metal hydrides. A summary of this work, principal conclusions, and future plans are briefly delineated in the following.
Summary and Conclusions

**New Destabilized Systems**

1. Destabilization is a practical and versatile method for overcoming thermodynamic limitations.
2. The LiBH$_4$/MgX (X= F$_2$, S, Se) destabilized systems are partially reversible. However, currently, reaction temperatures and reversible capacities do not meet goals.
3. New systems identified by theory group should be evaluated experimentally.

**Nanoparticles/MgH$_2$-Si**

1. Synthesized nano-Mg$_2$Si using nanoscale Si precursors and self-propagating reactions.
2. Conducted systematic milling study – varied milling conditions, sample dilution, composition, H$_2$ overpressure, Ni and Pd catalyst incorporation.
3. Dilution milling and nano-catalyst dramatically improve dehydrogenation kinetics.
4. No reversibility (hydrogenation) observed – Reversibility also not seen by other MHCoE partners (Stanford, Sandia, Hawaii, Intematix).

Based upon results obtained thus far, we conclude that hydrogenation of Mg$_2$Si may not be possible under practical conditions.

**Nanoporous Scaffolds**

1. LiBH$_4$ incorporated into carbon aerogel has faster sorption kinetics and smaller pores yield lower reaction temperatures.
2. Small length scales may prevent large LiH and B particles from forming, which improves cycling capacity.

Future Work

**New Destabilized Systems**

1. Explore additional LiBH$_4$+MgX reactions.
2. Investigate new Li-Si-N systems.

**Nanoparticles/MgH$_2$-Si**

1. Use smaller particles with narrow size distribution.
2. Reduce surface oxide.
3. Test improved catalysts and other alloying agents.

**Nanoporous Scaffolds**

1. Incorporate destabilizing agents and catalysts.
2. Increase pore volume (to increase capacity).
3. Explore other nanoporous materials.

**Special Recognitions & Awards/Patents Issued**


**FY 2006 Publications/Presentations**

FY 2006 Presentations


Upcoming Presentations (2006):


Publications (planned for 2006)

References

