IV.A.7 Hydrogen Storage Materials for Fuel Cell-Powered Vehicles*

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*Congressionally directed project

Fiscal Year (FY) 2012 Objectives

The objectives of this project are to:

- Identify complex hydrides, such as the $LiNH_2/MgH_2$ system and the $LiBH_4/MgH_2$ system, that have great hydrogen storage potential.
- Develop new catalysts and engineering techniques for increasing reaction rates and lowering reaction temperatures.
- Perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures using MgH_2 as a model system.

Technical Barriers

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

(A) System Weight and Volume
(D) Durability/Operability
(E) Charging/Discharging Rates

Technical Targets

This project is conducting fundamental studies of complex borohydride materials and other promising hydrogen storage materials. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet DOE's 2015 goal of 5.5 weight percent hydrogen storage for the system. Table 1 summarizes the targets.

TABLE 1. Technical Targets

Storage Parameter	Units	Target
System Gravimetric Capacity: Usable, specific-energy from H_2 (net useful energy/max system mass)	kW.h/kg	1.5
System Volumetric Capacity: Usable energy density from H_2 (net useful energy/max system volume)	kW.h/L	1.2
Storage System Cost	$/kWh	6

FY 2012 Accomplishments

- Several borohydride systems have been kinetically modeled and the rate controlling process has been identified.
- The desorption properties of a $MgH_2/LiBH_4$ system have been determined. Temperature-programmed desorption (TPD) results show that NbF_5 and Nb_2O_5 catalysts are more effective in lowering desorption temperatures than $MgNi_2$. Kinetics measurements show that NbF_5 is vastly superior to the other catalysts in improving reaction rates and that desorption is faster than that from MgH_2.
- We have compared the dehydriding kinetics of several borohydride systems at constant pressure driving forces and found that a mixture of $Mg(BH_4)_2/Ca(BH_4)_2$ releases hydrogen faster than either individual borohydride. Modeling results indicate that the rate of hydrogen release from $Mg(BH_4)_2$, during the first 80% of the reaction, is diffusion controlled while in $Ca(BH_4)_2$ the reaction rate is phase boundary controlled. In the mixture the rate appears to be under the mixed control of both processes.
- Mixtures with initial molar compositions of ($LiNH_2 + MgH_2$) and ($2LiNH_2 + MgH_2$) were studied with and without the presence of 3.3 mol% potassium hydride dopant. TPD analyses showed that the potassium hydride doped samples had lower onset temperatures than their corresponding pristine samples.
- The addition of potassium hydride dopant was found to have a 25-fold increase on the desorption rates of the ($2LiNH_2 + MgH_2$) mixture, however it had almost no effect on the desorption rates of the ($LiNH_2 + MgH_2$) mixture. The catalyzed ($2LiNH_2 + MgH_2$) mixture reacted faster than the catalyzed ($LiNH_2 + MgH_2$) mixture.

- The design, fabrication and demonstration of a hydride-based hydrogen storage system for fuel cell is underway. Results show that the heat removal rate can be increased by increasing the effective thermal conductivity by mixing the metal hydride with conductivity-enhanced materials such as aluminum foam or graphite.

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Introduction

There has been considerable interest in complex hydrides such as borohydrides and amides because they have been determined to have great potential to meet DOE's goals for hydrogen storage. Current efforts in our research lab are focused on performing hydrogen storage studies on some new destabilized complex hydrides that have been predicted by first principles calculations to be suitable hydrogen storage materials. We will develop methods for the synthesis, characterization, and modeling of these new complex hydrides as well as developing new catalysts and engineering techniques for increasing reaction rates and lowering reaction temperatures. We will also extend these studies to include carbon materials, metal organic frameworks (MOFs) and possibly other nanostructured and porous materials as potential hydrogen storage materials. Once a suitable material has been identified for hydrogen storage it will be necessary to design, fabricate and test a hydride-based hydrogen storage system for fuel cell applications. Efforts are currently underway with a partner institution to design a hydrogen storage system and test it using a suitable material. This phase of the research will include using flow, reaction kinetics and thermal modeling, followed by system design, fabrication and performance evaluation.
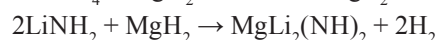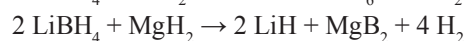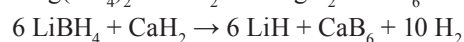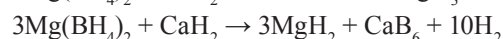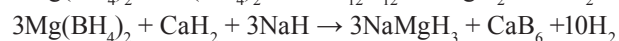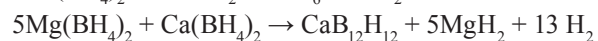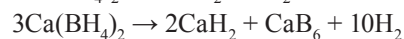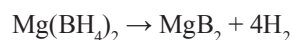
Approach

To achieve the project objectives, it was first necessary to design suitable methods using MgH_2 as a model system. These methods included:

- Synthesis of new materials by mechanical alloying using ball milling.
- Determining thermal stability using thermogravimetric analysis or TPD.
- Using X-ray diffraction to determine phase purity and crystal structure.
- Using pressure-composition isotherm analyses to determine thermodynamic stability.
- Finding catalysts for making the hydriding faster and reversible.
- Determining kinetic rate curves using constant pressure driving forces.

- Performing modeling to gain understanding of the mechanism.
- Studying other classes of promising hydrogen storage materials.

Results

First principles calculations have predicted that the following systems may be thermodynamically suitable for hydrogen storage.

$$Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2$$
$$3Ca(BH_4)_2 \rightarrow 2CaH_2 + CaB_6 + 10H_2$$
$$5Mg(BH_4)_2 + Ca(BH_4)_2 \rightarrow CaB_{12}H_{12} + 5MgH_2 + 13\ H_2$$
$$3Mg(BH_4)_2 + CaH_2 + 3NaH \rightarrow 3NaMgH_3 + CaB_6 + 10H_2$$
$$3Mg(BH_4)_2 + CaH_2 \rightarrow 3MgH_2 + CaB_6 + 10H_2$$
$$6\ LiBH_4 + CaH_2 \rightarrow 6\ LiH + CaB_6 + 10\ H_2$$
$$2\ LiBH_4 + MgH_2 \rightarrow 2\ LiH + MgB_2 + 4\ H_2$$
$$2LiNH_2 + MgH_2 \rightarrow MgLi_2(NH)_2 + 2H_2$$

Therefore several of these systems were studied thermodynamically and kinetically to confirm the theoretical predictions. A system of particular interest was the $Mg(BH_4)_2/Ca(BH_4)_2$ system. Calculations showed that a mixture of the two components would have better thermodynamic properties than those of either constituent. TPD curves were constructed for the $Mg(BH_4)_2/Ca(BH_4)_2$ mixture in the stoichiometric ratio of 5:1, along with those for pure $Mg(BH_4)_2$ and pure $Ca(BH_4)_2$. The curves shown in Figure 1 indicate that the mixture releases hydrogen at a lower temperature than $Mg(BH_4)_2$ or $Ca(BH_4)_2$. The kinetics of the $Mg(BH_4)_2/Ca(BH_4)_2$ mixture as well as those of the pure $Mg(BH_4)_2$ and $Ca(BH_4)_2$ components were also performed. Figure 2a contains plots in which the kinetics of the borohydrides are compared. It can be seen that the $Mg(BH_4)_2/Ca(BH_4)_2$ mixture has faster kinetics than either $Mg(BH_4)_2$ or $Ca(BH_4)_2$.
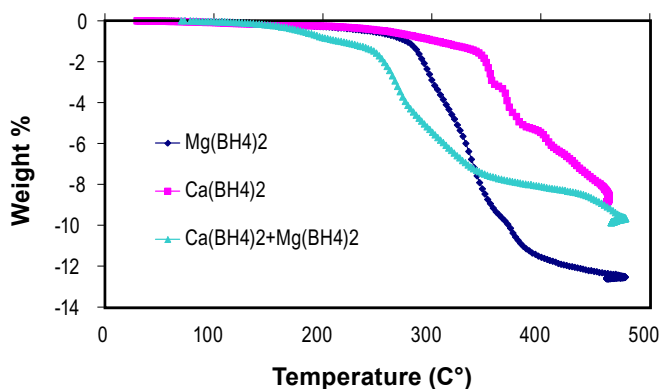
FIGURE 1. TPD profiles for $Mg(BH_4)_2$, $Ca(BH_4)_2$ and a mixture of the two compounds. A mixture of $Mg(BH_4)_2/Ca(BH_4)_2$ releases hydrogen at a lower temperature than either individual borohydride.
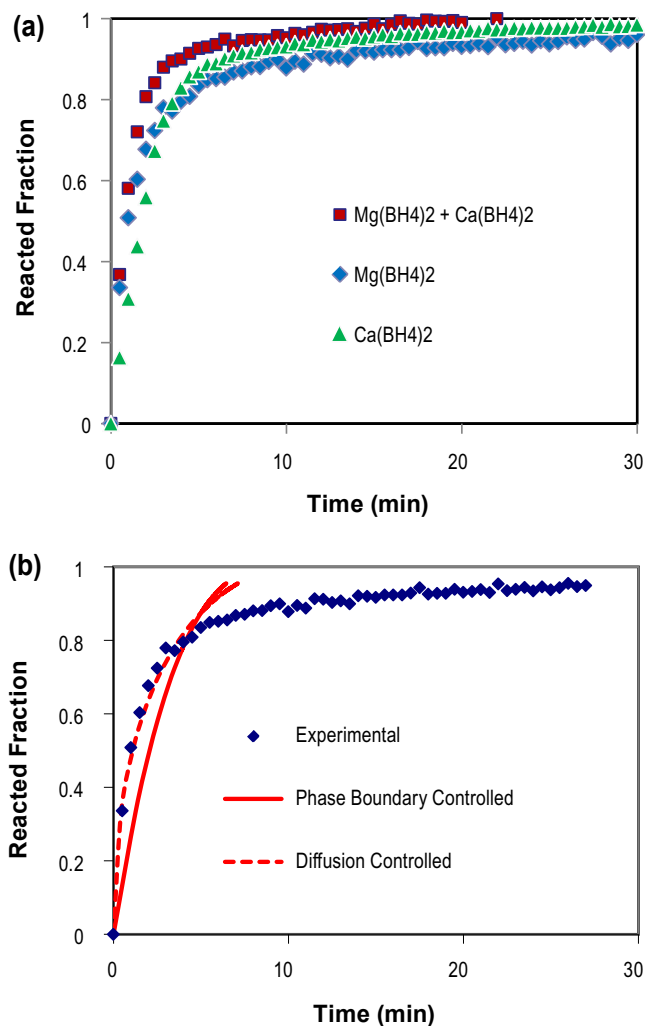
FIGURE 2. Figure 2a shows that the mixture desorbs hydrogen faster than either pure component. Figure 2b shows that the rate-controlling process for hydrogen desorption from $Mg(BH_4)_2$ is diffusion. Different processes controlled the kinetics for desorption from $Ca(BH_4)_2$ and the $Mg(BH_4)_2/Ca(BH_4)_2$ mixture.

An attempt was also made to determine the rate-controlling process in these samples by doing kinetic modeling. The theoretical equations that were used are shown below:

$$\frac{t}{\tau} = 1 - \left(1 - X_B\right)^{1/3} \tag{1}$$

$$\text{Where } \tau = \frac{\rho_B R}{b k_s C_{Ag}}$$

$$\frac{t}{\tau} = 1 - 3\left(1 - X_B\right)^{2/3} + 2\left(1 - X_B\right) \tag{2}$$

$$\text{Where } \tau = \frac{\rho_B R^2}{6 b D_e C_{Ag}}$$

Where t is the time at a specific point in the reaction, X_B is the fraction of the metal reacted. R is the initial radius of

the hydride particles, 'b' is a stoichiometric coefficient of the metal, C_{Ag} is the gas phase concentration of reactant, D_e is the effective diffusivity of hydrogen atoms in the hydride, r_B is the density of the metal hydride and k_s is a rate constant.

The model based on Eq. (1) will have chemical reaction at the phase boundary controlling the reaction rate whereas a model based on Eq. (2) is one in which diffusion controls the overall reaction rate. Both equations were fitted to the kinetic data for $Mg(BH_4)_2$, $Ca(BH_4)_2$ and $Mg(BH_4)_2+Ca(BH_4)_2$. Figure 2b contains modeling plots for $Mg(BH_4)_2$, based on the kinetics data in Figure 2a. In the graph, one curve is an experimental curve, a second curve is based on the overall rate being controlled by diffusion, and a third curve is calculated based on chemical reaction controlling the rate. The plots in Figure 2b show a good fit for a diffusion controlled model up to 80% of the reaction but not beyond. This means that the process controlling hydrogen desorption of this reaction at the later stage of the reaction is different from that at the beginning. Kinetic modeling was also done on $Ca(BH_4)_2$ and $Mg(BH_4)_2+Ca(BH_4)_2$ mixture. The results indicate that the rate of hydrogen release from $Mg(BH_4)_2$, during the first 80% of the reaction, is diffusion controlled while in $Ca(BH_4)_2$ the reaction rate is phase boundary controlled. In the mixture the rate appears to be under the mixed control of both processes.

Another system that was studied was $LiBH_4$-MgH_2. This system shows excellent hydrogen storage capacity but it still has the problem of sluggish kinetics. In order to improve the hydrogen desorption kinetics, mixtures of $LiBH_4$-MgH_2 (2:1) were doped with 4 mol% NbF_5, Nb_2O_5, and Mg_2Ni. The hydrogen desorption kinetics of these mixtures were compared using constant pressure thermodynamic forces in which the ratio of the equilibrium plateau pressure to the opposing plateau was the same for all the reactions studied. Figure 3 contains plots of reacted fraction versus time for hydrogen desorption from the samples. It can be seen from the plots that the un-catalyzed borohydride sample mixture has the slowest hydrogen desorption rate. The addition of
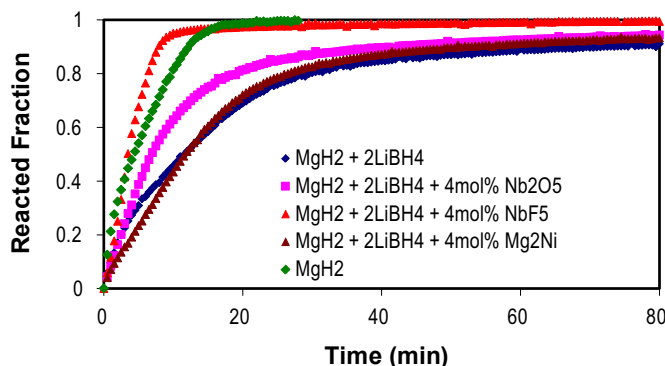

FIGURE 3. Kinetics measurements done at N = 3 and 450°C show that NbF_5 is vastly superior to the other catalysts in improving reaction rates.

4 mol% Mg_2Ni to the $2LiBH_4$-MgH_2 mixture does not have any significant effect on the reaction kinetics. However, the niobium-based catalysts are very effective in improving the kinetics of the mixture. The sample mixture doped with 4 mol% NbF_5 in particular has exceptionally fast desorption reaction kinetics. Under the conditions used, the NbF_5-catalyzed mixture releases approximately 80% of its hydrogen in 6.5 minutes, whereas the Nb_2O_5-catalyzed mixture takes 20 minutes and the un-catalyzed borohydride sample takes 30 minutes to release the same percentage of hydrogen. It is interesting to note that the NbF_5-catalyzed borohydride mixture is the only one to release hydrogen faster than pure MgH_2. These results showed NbF_5 to be vastly superior to the other catalysts for improving the kinetics of the composite mixture with the hydrogen desorption rates being in the order: $NbF_5 \gg Nb_2O_5 > Mg_2Ni$. Desorption enthalpies that were obtained from van't Hoff plots indicated that the thermodynamic stabilities of the catalyzed mixtures were in the order: $NbF_5 < Nb_2O_5 < Mg_2Ni$. Modeling studies indicated that chemical reaction at the phase boundary was the most likely process controlling the reaction rates for the catalyzed mixtures.

Another system that was studied was $LiNH_2$-MgH_2. Lithium amide and magnesium hydride are lightweight materials with high hydrogen-holding capacities and thus they are of interest for hydrogen storage. Mixtures with initial molar compositions of ($LiNH_2$ + MgH_2) and ($2LiNH_2$ + MgH_2) were ball milled with and without the presence of 3.3 mol% potassium hydride dopant. TPD analyses of the mixtures showed that the potassium hydride doped samples had lower onset temperatures than their corresponding pristine samples. The dehydrogenation kinetics of the doped and pristine mixtures was compared at 210°C. In each case a constant pressure thermodynamic driving force was applied in which the ratio of the plateau pressure to the

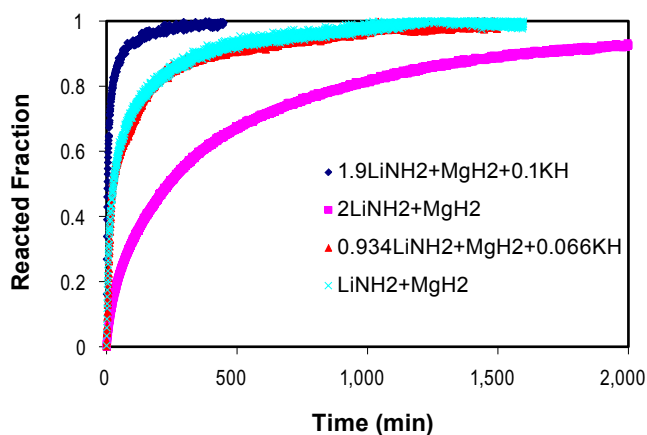applied hydrogen pressure was set at 10. It can be seen from Figure 4 that the doped ($1.9LiNH_2$+MgH_2+$0.1KH$) sample has the fastest desorption reaction kinetics while its pristine ($2LiNH_2$+MgH_2) sample has the slowest desorption reaction kinetics. The KH seems to have no effect on the desorption kinetics of ($0.934LiNH_2$+MgH_2+$0.066KH$) when compared with its pristine sample, ($LiNH_2$+MgH_2). The doped and pristine samples both take approximately the same time for hydrogen desorption. Activation energies were determined by the Kissinger method. Results showed the potassium hydride doped mixtures to have lower activation energies than the pristine mixtures.

Another project has been ongoing entitled "Design, Fabrication and Demonstration of a Hydride-Based Hydrogen Storage System for Fuel Cell Applications." The overall objective is to improve the rate at which the hydrogen gas can be charged into a hydride-based hydrogen storage tank, and to improve the hydrogen storage density. A mathematical model is being used to predict the temperature at selected locations within the storage tank. A series of experiments have been performed to compare the temperature at these locations with the numerically predicted value. All of this work is being done by our partners at the University of Delaware.

Conclusions and Future Directions

- The results of this study show that the rate of hydrogen desorption from $Mg(BH_4)_2$ can be increased by mechanically alloying it with $Ca(BH_4)_2$. Modeling studies indicate that the rate of hydrogen release from $Mg(BH_4)_2$, during the first 80% of the reaction, is diffusion controlled while in $Ca(BH_4)_2$ the reaction rate is phase boundary controlled. In the mixture the rate appears to be under the mixed control of both processes.

- Kinetics and modeling studies on a $2LiBH_4$/MgH_2 system show that the hydrogen desorption rates are in the order: $Mg_2Ni < Nb_2O_5 \ll NbF_5$. All of these findings indicate that NbF_5 is vastly superior to the other materials for catalyzing the $2LiBH_4$/MgH_2 system. The modeling studies indicate that chemical reaction at the phase boundary is the likely rate-controlling process in all of the catalyzed mixtures.

- Kinetics studies on a $LiNH_2$/MgH_2 system have shown that KH is a very effective catalyst for the desorption of hydrogen from the MgH_2-$2LiNH_2$ system but not so effective for MgH_2-$LiNH_2$ system.

In FY 2013, the following work is planned:

- Continue to perform absorption and desorption kinetics and modeling studies on several catalyzed MgH_2/Amide and MgH_2/$LiBH_4$ based destabilized systems using constant pressure driving forces.

FIGURE 4. Desorption kinetics were done at 210°C and N = 10. There is a dramatic improvement in the desorption rates in the $2LiNH_2$ + MgH_2 system but virtually no improvement in the $LiNH_2$ + MgH_2 system.

- Continue the cycling studies on amide and borohydride reactions.
- Use techniques such as residual gas analysis to determine if dehydrogenation is accompanied by the release of other gaseous byproducts such as ammonia and diborane.
- Extend the studies to include carbon materials and MOFs.
- Continue to collaborate with Sonjong Hwang at Cal Tech in solid state nuclear magnetic resonance analyses of reaction intermediates in hydriding/de-hydriding reactions.
- Continue with the design, fabrication and demonstration of a hydride-based hydrogen storage system that is on-going with our collaborators at the University of Delaware.

FY 2012 Publications/Presentations

1. Samuel A. Orefuwa, Hongwei Yang, and Andrew J. Goudy, "Rapid Solvothermal Synthesis of an Isoreticular Metal Organic Framework with Permanent Porosity for Hydrogen Storage", Micropor. Mesopor. Mater., 153 (2012) 88–93.

2. Durojaiye T, Goudy A, "Desorption kinetics of lithium amide/magnesium hydride systems at constant pressure thermodynamic driving forces", Int. J. Hyd. Energy, 37 (2012) 3298-3304.

3. Andrew Goudy, Adeola Ibikunle, Saidi Sabitu and Tolulope Durojaiye, "Thermodynamics and Kinetics of Complex Borohydride and Amide Hydrogen Storage Materials" Proceedings of the MCARE Conference, 2012.

4. Andrew Goudy, "Thermodynamics, Kinetics and Modeling Studies on Hydrogen Storage Materials", Low Carbon Earth Summit, Dalian, China, October 2011.

5. Synthesis of New Naphthalene Linkers for the Incorporation in Hydrogen Storing Metal Organic Frameworks Bryan Wakefield, Andrew Goudy, Samuel Orefuwa, Lewis Q. Lott, Dante Alexander, Andre Kerr, ACS Meeting, Washington, D.C., 2011.

6. Andrew Goudy, "Thermodynamics and Kinetics of Complex Borohydride and Amide Hydrogen Storage Materials", Materials Challenges in Alternative & Renewable Energy, Clearwater Beach, FL, 2012.

7. Hongwei Yang, Samuel Orefuwa and Andrew Goudy, "Solvent-Assisted Mechanochemical Synthesis of Metal-Organic Framework $Cu_3(BTC)_2$ for Hydrogen Storage" MRS Fall meeting, April 9 – April 13, 2012, San Francisco, CA.