

IV.A.5 Center for Hydrogen Storage Research at Delaware State University*

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*Congressionally directed project

Objectives

- Identify complex hydrides that have the potential to meet DOE's goals for storage and demonstrate the optimum temperature and pressure ranges under a variety of conditions.
- Improve the sorption properties of systems that have been identified as good prospects for hydrogen storage.
- Determine the cyclic stability of new materials and develop strategies for improving reversibility.
- Perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures, thereby reducing refueling time.
- Extend the studies to include other complex hydrides, that have greater hydrogen storage potential.

Technical Barriers

This project addresses the following technical barriers taken 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
- (D) Durability/Operability
- (E) Charging/Discharging Rates

Technical Targets

This project is conducting fundamental studies of complex borohydride materials. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet DOE's 2010 goal of 6 wt% hydrogen storage for the system. Table 1 summarizes the targets.

TABLE 1. 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 (and fuel cost)	\$/kWh	6

Accomplishments

This project is conducting measurements on complex hydrogen storage systems to determine if they will meet DOE's targets for hydrogen storage.

- Have further characterized the LiBH₄/CaH₂ system. Cycling studies done at 450°C indicate that the absorption capacity decreases from 9 wt% hydrogen to less than 3 percent after 25 cycles.
- Have completed the analyses on a double cation borohydride system using thermal gravimetric analysis (TGA), thermally programmed desorption (TPD) and pressure-composition isotherm (PCI) analyses. The hydrogen sorption characteristics of systems of general composition MM'_{m-n}(BH₄)_m (M= Cu, Mn and Zr, M'= Li or Na) were studied. The Mn-containing material was found to release hydrogen at about 130°C but there was also some evidence of diborane release as well. These materials were stable solids under the conditions used.
- Have done kinetics studies on the MgH₂/LiBH₄ system, with varying amounts of LiBH₄, to determine desorption rates using constant pressure driving forces. The rates were found to decrease with increasing amounts of LiBH₄ in the system.



Introduction

Developing a safe, cost-effective, and practical means of hydrogen storage is essential for the advancement of hydrogen and fuel cell technologies. Materials such as sodium alanate were a vast improvement in storage capacity over most traditional hydrides. However, even the alanates fall short of meeting DOE's long-term hydrogen storage goals. Therefore interest has now focused on destabilized hydrides which have even greater potential for hydrogen storage.

The main goals of this project are (1) Establish a Center for Hydrogen Storage Research at Delaware State University for the preparation and characterization of selected complex metal hydrides and the determination their suitability for hydrogen storage. (2) Develop methods for the synthesis, characterization, and modeling of complex hydrides using $\text{LiBH}_4/\text{MgH}_2$ as a model system. (3) Identify the most promising types of complex hydrides destabilized hydrides and demonstrate the optimum temperature/pressure range and sorption kinetics of the hydrides under a variety of conditions. (4) Determine their cyclic stability and develop improved sorption catalysts. Extend the studies to include other complex hydrides that have greater hydrogen storage potential than the destabilized hydrides such as ternary borohydride systems. (5) Perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures.

Approach

To achieve the project objectives, new materials are being developed and characterized using a variety of techniques. Sample preparations prior to analysis were done in an argon-filled glove box (Vacuum Atmosphere Company). The hydrides were made by first ball milling the raw materials in a SPEX 8000 Mixer Miller and then directly combining them with hydrogen in a Sieverts apparatus. X-ray powder diffraction in a Panalytical X'pert Pro MPD Analytical X-Ray Diffractometer was used to confirm the formation of product and to determine phase purity.

TGA and TPD were used to determine the thermal stability and the hydrogen capacity of the mixtures. The TGAs were done in a Lab System-Diamond thermogravimetric/differential thermal analysis. This instrument was placed inside of an argon-filled glove box so that samples can be analyzed with virtually no exposure to air and moisture. The TPD analyses were carried out in a PCI unit. The instrument was supplied by Advanced Materials Corporation. Kinetic measurements were done to determine the overall reaction rates. Cycling measurements were done to determine the stability of the materials when subjected to repeated hydrogenation and dehydrogenation cycles. The B-H bond strength of the various synthesized double-cation borohydrides

were compared via Shimadzu Infrared Prestige-21 FTIR spectrophotometer. This instrument operates in a single-beam mode and is capable of data collection over a wave number range of $7,800\text{ cm}^{-1} \sim 350\text{ cm}^{-1}$. Residual gas analyses (RGA) were done in a RGA Pro 2000. The instrument was produced by Stanford Research Systems and distributed by Hy-Energy LLC in Newark, CA.

Results

In the previous year, the main focus of the research was the analyses of $\text{CaH}_2/\text{LiBH}_4$ mixtures. In those studies, the mixtures were found to reversibly absorb and release 9 wt% hydrogen. In the past year we did cycling studies to determine the stability of the materials when subjected to repeated hydrogenation and dehydrogenation cycles. Cycling studies done at 450°C indicate that the absorption capacity decreases from 9 wt% hydrogen to less than 3 wt% after 25 cycles. In addition, the $\text{CaH}_2/\text{LiBH}_4$ system absorbs and releases hydrogen at temperatures in the 400°C range, which is too high for fuel cell applications. Therefore an effort was made to develop other borohydride systems that had lower operating temperatures. One such system was the $\text{MM}'_{m-n}(\text{BH}_4)_m$ system ($M = \text{Cu, Mn and Zr, M}' = \text{Li or Na}$). The materials in this system were prepared by mechanically milling mixtures of $\text{CuCl}_2 + 3\text{LiBH}_4$, $\text{MnCl}_2 + 3\text{LiBH}_4$, and $\text{ZrCl}_4 + 6\text{LiBH}_4$.

Figure 1 shows the powder X-ray diffraction (XRD) profiles of the complex mixtures mechanically milled for 10 hours. The diffraction peaks measured at angles 30, 35, 50, 60 and 63 degrees are identified as LiCl, although slight peak shifts were observed, probably due to the partial substitution of M for Li in LiCl. There are no major diffraction peaks of the starting materials of MnCl_2 and LiBH_4 in the spectrum of $\text{MnLi}(\text{BH}_4)_3$, indicating that the reaction has progressed to completion. On the other hand, the diffraction peak of one of the starting material (LiBH_4) was present in the spectra of $\text{CuLi}(\text{BH}_4)_3$ and $\text{ZrLi}_2(\text{BH}_4)_6$ at angle 44

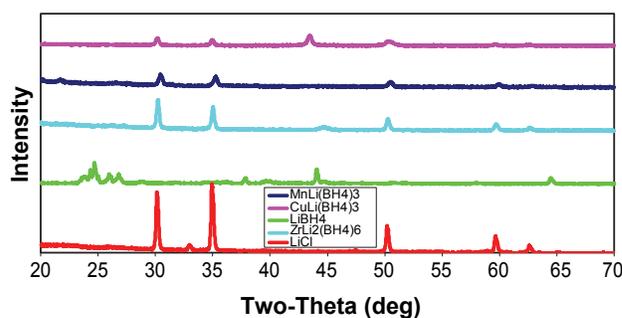


FIGURE 1. XRD spectra for the $\text{MLi}'_{m-n}(\text{BH}_4)_m$ system ($M = \text{Cu, Mn and Zr}$). There are no X-ray diffraction peaks of $\text{MM}'_{m-n}(\text{BH}_4)_m$ in the profiles of the samples due possibly to the absence of long range order in the structure of the synthesized samples.

degree. This indicates that the reaction did not proceed to completion under the milling conditions in this experiment. The formation of NaCl is an indication that complex borohydrides were formed. There are no XRD peaks of $MM'_{m-n}(BH_4)_m$ in the profiles of the samples prepared by mechanical ball milling, this might be due to the absence of long range order in the structure of the synthesized samples.

Fourier transform infrared spectroscopy (FTIR) was used to determine if the boron–hydrogen bonds had been affected by the presence of the cations (Cu, Mn or Zr). Figure 2 shows the composite FTIR spectrum of the synthesized double-cation borohydrides. For $M\text{Li}(\text{BH}_4)_n$ ($M=\text{Cu}$, Mn and Zr) complexes synthesized earlier, various peaks were observed from the infrared spectra. All of the spectra display similar characteristics. However, in the region of $1,400\text{--}1,200\text{ cm}^{-1}$, one of these materials display a significant difference from the others. The FTIR spectrum of all the materials except $\text{MnLi}(\text{BH}_4)_3$ have a single peak in this region. This indicates that the $\text{MnLi}(\text{BH}_4)_3$ material might have a different desorption behavior than the others.

TPD was used to determine the thermal stability and the hydrogen capacity of the mixtures. The composite TPD of the borohydride complexes prepared is shown in Figure 3. It can be seen that the partial substitution of Cu, Mn and Zr in LiBH_4 truly lowers the desorption temperature when compared with the desorption temperature of LiBH_4 . The $\text{MnLi}(\text{BH}_4)_3$ complex appears to be the best of the group. The Mn-containing material was found to release hydrogen at about 130°C . This is a big improvement over the 400°C temperature observed for the $\text{CaH}_2/\text{LiBH}_4$ system. However, when RGAs were done the presence of diborane was observed in all the synthesized complex borohydrides except $\text{CuLi}(\text{BH}_4)_3$. The loss of diborane from the complex borohydrides destroys the reversibility of the complex borohydrides.

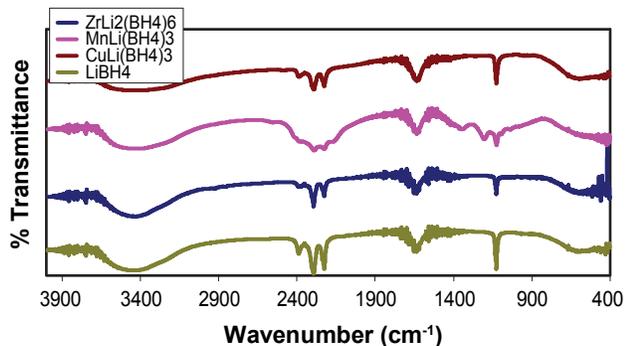


FIGURE 2. FTIR spectra of LiBH_4 , $\text{CuLi}(\text{BH}_4)_3$, $\text{MnLi}(\text{BH}_4)_3$ and $\text{ZrLi}_2(\text{BH}_4)_6$. The spectra are all similar but the Mn-containing complex displays two peaks in the $1,200\text{--}1,400\text{ cm}^{-1}$ region that are absent in the others.

A kinetics study was also done on the $\text{MgH}_2/\text{LiBH}_4$ system, with varying amounts of LiBH_4 , to determine the effect of LiBH_4 content on the desorption rates. The ratios of LiBH_4 to MgH_2 used in these studies were 2, 4 and 7. It was found that when the ratio of the plateau pressure/applied hydrogen pressure (N-value) was kept constant, the reaction rates decreased as the amount of LiBH_4 increased. The N-value is directly proportional to the thermodynamic driving force. As an example of these studies, the rate curves for the desorption kinetics at 450°C and $N = 3, 4$, and 5 are shown in Figure 4. It was found that when the N-value was increased, the reaction rates increased. This demonstrates the importance of keeping the N-value constant when comparing reaction kinetics of different materials.

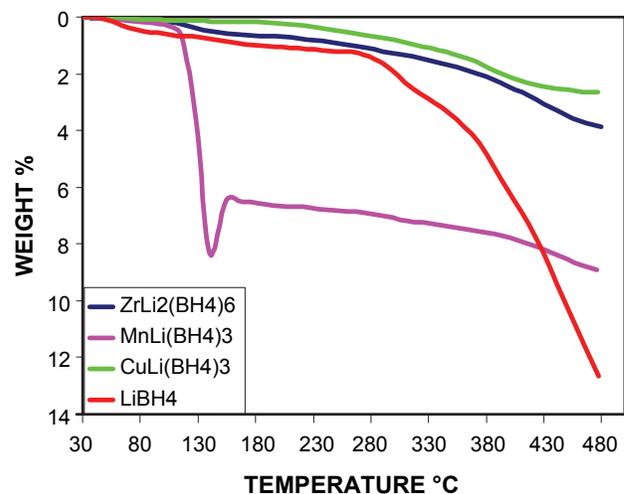


FIGURE 3. TPD of double-cation borohydrides. The desorption of gases by $\text{MnLi}(\text{BH}_4)_3$ starts around 116°C . $\text{CuLi}(\text{BH}_4)_3$ starts around 199°C , and $\text{ZrLi}_2(\text{BH}_4)_3$ starts around 81°C .

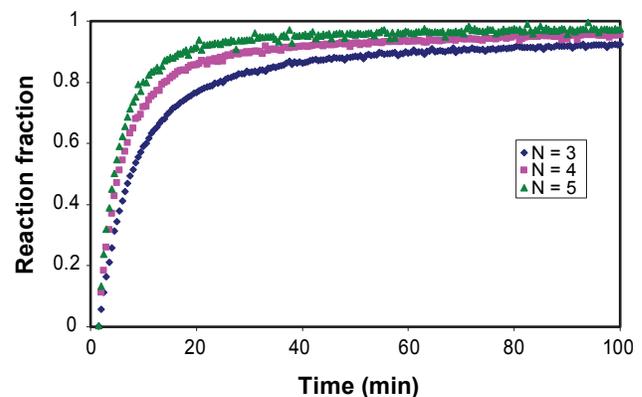


FIGURE 4. Desorption kinetics of the $\text{MgH}_2/\text{LiBH}_4$ system at 450°C and $N = 3, 4$, and 5 . The N-value is defined as the ratio of the dissociation plateau pressure to the applied hydrogen pressure.

Conclusions and Future Directions

- Cycling studies done at 450°C on the $\text{LiBH}_4/\text{CaH}_2$ system indicate that the absorption capacity decreases from 9 wt% hydrogen to less than 3 wt% after 25 cycles. Thus, this material is not suitable for hydrogen storage applications in its present form.
- Analyses on double cation borohydride systems of general composition $\text{MM}'_{m-n}(\text{BH}_4)_m$ (M= Cu, Mn and Zr, M'= Li or Na) show that the Mn-containing material begins to release hydrogen at about 130°C. This temperature is low enough for fuel cell applications. However, the release of diborane leads to irreversibility and thus a way to eliminate this need to be found.
- Kinetics studies were done on the $\text{MgH}_2/\text{LiBH}_4$ system, with varying amounts of LiBH_4 , to determine desorption rates using constant pressure driving forces show that the rates decrease with increasing amounts of LiBH_4 in the system. Thus, it is desirable to find complex systems with more metal and less complex anion.

In the next fiscal year we propose to perform 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. Nanotechnology will be used to reduce or eliminate the release of any diborane.

FY 2009 Publications/Presentations

1. A. Ibikunle, A.J. Goudy, and H. Yang Hydrogen Storage in a $\text{CaH}_2 / \text{LiBH}_4$ Destabilized Metal Hydride System, *J. Alloys and Compds.*, 475 (2009) 110-115.
2. H. Yang, A. Ojo, P. Ogaro and A.J. Goudy, "Hydriding and Dehydriding Kinetics of Sodium Alanate at Constant Pressure Driving Forces" *J. Phys Chem.*, (2009) In press.
3. O. Fagbami and A.J. Goudy, "Thermodynamic and Kinetics Measurements on Magnesium Hydride", 11th Undergraduate Research Symposium in the Chemical and Biological Sciences, UMBC, Baltimore, MD, October 11, 2008.
4. O. Fagbami and A.J. Goudy, "Thermodynamic and Kinetics Measurements MgH_2 for Hydrogen Storage", Posters on the Hill, Capitol Building, Washington, D.C., May 5, 2009.