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

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*Congressionally directed project

Objectives

- Establish a Center for Hydrogen Storage Research at Delaware State University for the preparation and characterization of selected complex metal hydrides and the determination of their suitability for hydrogen storage.
- Develop methods for the synthesis, characterization, and modeling of complex hydrides using $NaAl_4$ and $LiBH_4/MgH_2$ as model systems.
- 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. 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. Develop methods for improving kinetics.

Technical Barriers

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

(A) Weight and Volume

(D) Durability/Operability

(E) Charging/Discharging Rates

Technical Targets

This project is conducting fundamental studies of destabilized metal hydrides. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: $4/kWh net
- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L

Accomplishments

- Have developed methods for the synthesis and characterization of complex hydrides using $NaAlH_4$ and $LiBH_4/MgH_2$ as model systems.
- Ball milling techniques were successfully used to prepare hydrogen storage materials.
- X-ray diffraction (XRD) analyses were done on destabilized hydrides to determine crystal structure and phase purity.
- Have demonstrated that when a thermal gravimetric analysis (TGA) apparatus was enclosed in an argon-filled glove box, satisfactory thermal analysis data could be obtained.
- Have completed some preliminary analyses on the $LiBH_4/CaH_2$ system using TGA and pressure composition isotherm (PCI) analyses.

Approach

The primary focus of the center is finding novel materials that can store and release large quantities of hydrogen gas at moderate temperatures and pressures. The center is involved in all aspects of hydrogen storage research including: fabricating and testing the hydrogen storage materials, determining the amount of hydrogen that can be absorbed and released from these materials, determine their thermodynamic stability, and measuring the kinetics of uptake and release. The techniques involved include: mechanical alloying by ball milling, TGA, thermodynamic analyses from PCI measurements, sample characterization by X-ray powder diffraction, and kinetics measurements on a Sieverts apparatus.

Results

Some scientists at Carnegie Mellon University and the University of Pittsburgh have determined that in order for materials to absorb and release hydrogen at appropriate temperatures they should have enthalpies of formation in the 30 to 60 kJ/mol H_2 range. They used first principles density functional theory calculations to identify reaction schemes that have the desired enthalpies and thus they may be useful for hydrogen storage. The following five reaction schemes have been proposed by scientists in Pittsburgh as promising for hydrogen storage. According to calculations, these reactions have enthalpies close to the desired range with the potential to absorb and release large quantities of hydrogen.

$$3LiNH_2 + 2LiH + Si \rightarrow Li_5N_3Si + 4H_2 \qquad \Delta H = 34 \text{ kJ/mole } H_2 \quad (1)$$

$$4LiBH_4 + MgH_2 \rightarrow 4LiH + MgB_4 + 7H_2 \qquad \Delta H = 60 \text{ kJ/mole } H_2 \quad (2)$$

$$7LiBH_4 + MgH_2 \rightarrow 7LiH + MgB_7 + 11.5H_2 \qquad \Delta H = 66 \text{ kJ/mole } H_2 \quad (3)$$

$$6LiBH_4 + CaH_2 \rightarrow \mathbf{6LiH + CaB_6} + 10H_2 \qquad \Delta H = 53 \text{ kJ/mole } H_2 \quad (4)$$

$$LiNH_2 + MgH_2 \rightarrow \mathbf{LiMgN + 2H_2} \qquad \Delta H = 32 \text{ kJ/mole } H_2 \quad (5)$$

We have already completed preliminary measurements on most of these reaction schemes. More detailed studies are planned in the next year. Studies on reactions (1) and (5) initially led us to believe that large amounts of hydrogen were involved. However, further analyses revealed the presence of ammonia. Apparently the $LiNH_2$ was reacting with hydrogen according to the reaction:

$$LiNH_2 + H_2 \rightarrow LiH + NH_3$$

The formation of ammonia makes these materials unsuitable for hydrogen storage applications. Therefore no further studies are planned on these systems.

Studies on the systems in equations (2), (3) and (4) have shown these systems to be very promising for hydrogen storage. TGA analyses on the $LiBH_4/MgH_2$ system depicted in Figure 1 show that this material releases over 10 weight percent hydrogen. The use of a $TiCl_3$ catalyst lowers the desorption temperature slightly. However, the temperature is still well above the 100°C temperature that is needed for most fuel cell applications. Therefore, over the next year more studies will be done to find better catalysts for this reaction. PCI analyses were also done on this system. The results of absorption and desorption analyses show that the system absorbs hydrogen reversibly.

A similar study was done on the $LiBH_4/CaH_2$ system. The graph in Figure 2 shows that this system releases over 10 weight percent hydrogen. However, the high temperature required means that better catalysts must be found before it can be of practical use. PCI analyses were also done on this system and the curves are shown in Figures 3 and 4. The fact that both absorption and desorption isotherms could be done shows that this system absorbs hydrogen reversibly.

The results on the $LiBH_4/CaH_2$ system are very encouraging because the reversible hydrogen capacity is sufficient to meet DOE's 2010 goal for hydrogen storage. As was the case for the $LiBH_4/MgH_2$ system, better catalysts than $TiCl_3$ must be found to lower the reaction temperature to values suitable for fuel cell usage.

Conclusions and Future Directions

In FY 2006-2007 we learned that the techniques and methods used to study traditional metal hydrides would have to be significantly modified. We now have the methodology in place that will be needed to perform basic studies on complex metal hydride systems. The results of studies this past year have shown that:

- The $LiBH_4/CaH_2$ system has the potential to meet DOE's 2010 target for hydrogen storage. However better catalysts must be found to lower the reaction temperature.

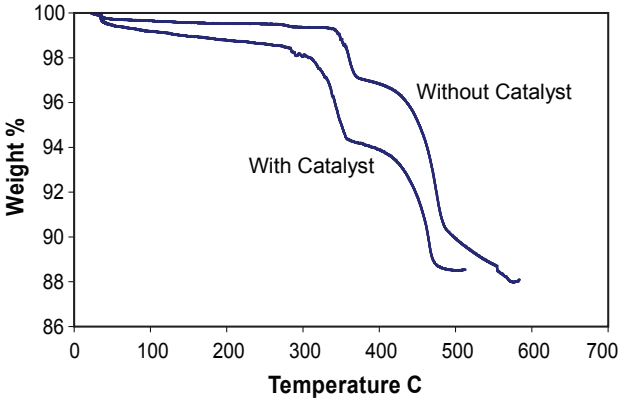

FIGURE 1. TGA Scans of the $LiBH_4/MgH_2$ System with and without a $TiCl_3$ Catalyst

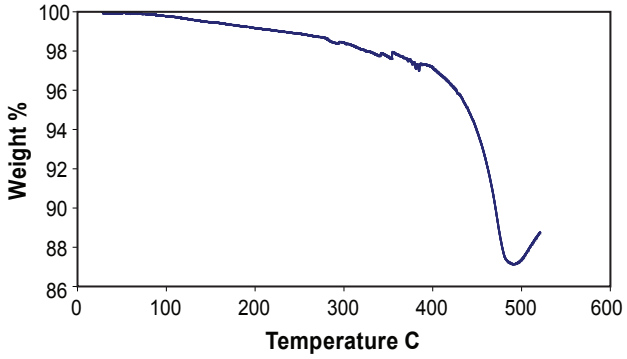

FIGURE 2. TGA Scans of the LiB H_4/Ca H_2 System with a $TiCl_3$ Catalyst

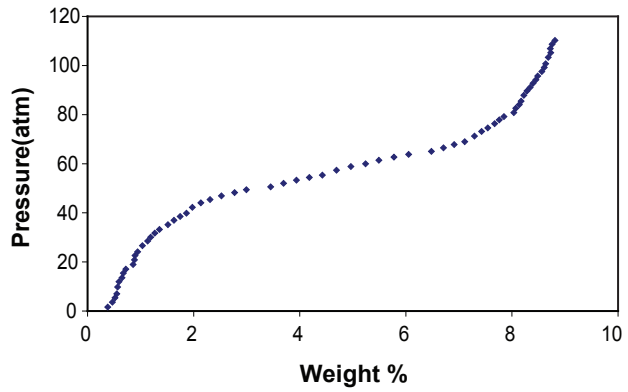

FIGURE 3. Absorption Isotherm for the LiB H_4/Ca H_2 System at 400°C

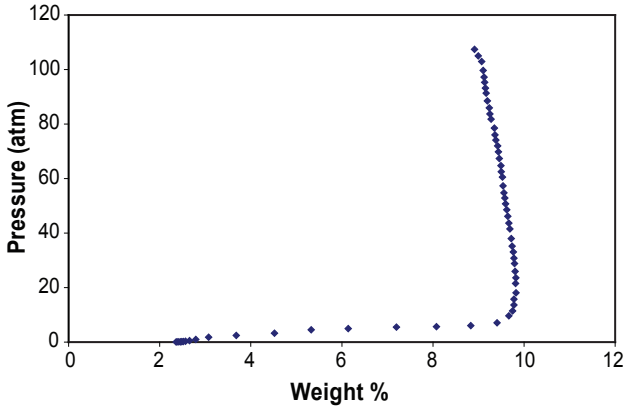

FIGURE 4. Desorption Isotherm for the LiB H_4/Ca H_2 System at 400°C

- Systems consisting of $LiBH_4/CaH_2$ are not suitable for hydrogen storage because of the ammonia that is released.

In the FY 2007-2008, the following are planned:

- Perform further analyses on destabilized hydrides consisting of lithium borohydride destabilized with CaH_2 to determine if different catalysts can lower the reaction temperature.
- Perform analyses on destabilized hydrides consisting of lithium borohydride destabilized with materials such as C and ScH_2. These materials have been predicted to have large hydrogen capacities and to react at temperatures below 100°C.
- Perform XRD measurements as a function of temperature.
- Determine the cyclic stability of the hydrides.
- Perform detailed kinetic studies on selected materials.

FY 2007 Publications/Presentations

1. P. Ogaro, A. Ojo and A. J. Goudy, "A Comparison of the De-Hydriding Behavior of Lithium Alanate, Sodium Alanate and Mixed Alanate Materials", International Symposium on Metal-Hydrogen Systems – Fundamentals and Applications, Lahaina, Maui, Hawaii, October 1–6, 2006.