IV.A.3 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 their suitability for hydrogen storage.
- Develop methods for the synthesis, characterization, and modeling of complex hydrides using $NaAlH_4$ as a model system.
- Identify the most promising types of complex 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 destabilized complex hydrides.

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

Technical Targets

This project is conducting fundamental studies of alanates and mixed alanates. 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 weight percent hydrogen storage for the system. The following table summarizes the targets.

Storage Parameter	Units	Target
System Gravimetric Capacity: Usable, specific-energy from hydrogen (net useful energy/max system mass)	kWh/kg	1.5
System Volumetric Capacity: Usable energy density from hydrogen (net useful energy/max system volume)	kWh/L	1.2
Storage System Cost (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 completed the analyses on the $LiBH_4/CaH_2$ system using thermal gravimetric analysis (TGA), thermally-programmed deposition (TPD) and pressure composition isotherm (PCI) analyses.
- PCI results show that this system reversibly absorbs and releases 9.0 weight percent hydrogen.
- TGA measurements show that additives have a small effect in lowering the reaction temperatures.
- Kinetic modeling studies on the $LiBH_4/CaH_2$ system indicate that diffusion may be the rate-controlling step.

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Introduction

Developing 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 $LiBH_4/MgH_2$ 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 as well as extend the studies to include other complex hydrides that have greater hydrogen storage potential than the destabilized hydrides such as ternary borohydride systems; and (5) perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures.

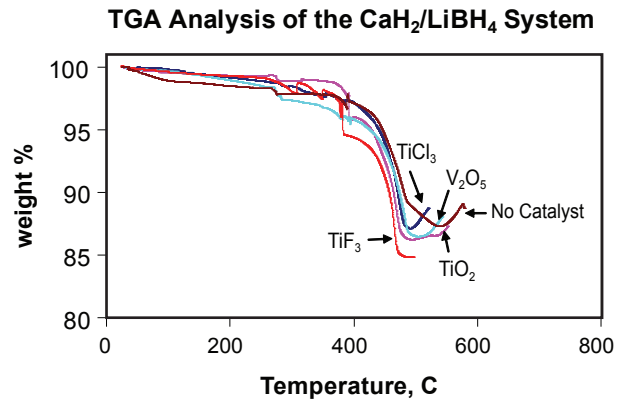

FIGURE 1. Thermal Analysis of the $CaH_2/LiBH_4$ System

Approach

The materials to be used for this research were prepared and characterized by several methods. The hydrides were made by first ball milling the raw materials and then directly combining them with hydrogen in a Sievrts apparatus. X-ray powder diffraction was used to confirm the formation of product and to determine phase purity. Each material was combined with a catalyst in order to improve the overall hydriding characteristics.

The hydriding characteristics of the materials were determined via TGA. This gave us quick estimates of the thermal desorption characteristics of each material. All analyses were done under an argon atmosphere to prevent them from reacting with air and moisture. Pressure-composition-temperature isotherms were constructed in order to determine the dependence of absorption capacity on pressure. Kinetic measurements were done to determine the overall reaction rates and reaction mechanism. Cycling measurements will be done to determine the stability of the materials when subjected to repeated hydrogenation and dehydrogenation cycles.

Results

In the past year, the main focus of the research was the analyses of $CaH_2/LiBH_4$ mixtures. In this study, five $CaH_2 + LiBH_4$ mixtures were prepared by ball milling stoichiometric amounts of the reactants with 4 mole percent of the additives: $TiCl_3$, TiF_3, TiO_2, and V_2O_5. It was desirable to know which additive would result in the lowest desorption temperature. Figure 1 contains TGA scans of weight loss versus temperature for each mixture. The results show that all of the mixtures release hydrogen the 400–500°C range. The presence of each additive had a small effect on the desorption temperature with the desorption temperatures of the mixtures being in the order: $TiF_3 < TiO_2 \leq TiCl_3 < V_2O_5 <$ no additive. It is evident that more effective additives are needed for lowering the desorption temperature below 400°C.

It was also desirable to determine if the desorption reaction was reversible. A series of PCI analyses were done on the $CaH_2/LiBH_4$ mixture containing $TiCl_3$ additive in order to see if reversibility was possible. Figure 2 contains absorption and desorption isotherms for the mixture containing 4 mole percent $TiCl_3$. The isotherms show that the mixture can absorb and release about 9 weight percent hydrogen reversibly in the temperature ranges chosen. The absorption isotherms are not well defined and have a significant slope whereas the desorption isotherms have a fairly well defined plateau region.

Desorption kinetics measurements were done to determine reaction rates and to do modeling studies. The experiments were done using constant pressure driving forces as first described by Goudy and co-workers [1,2]. In these experiments the ratio of the plateau pressure to the applied hydrogen pressure was held constant during the measurements. This ratio is referred to as the N-value. Figure 3 contains plots of reacted fraction versus time for experiments carried out at 450°C and at N-values of 2 and 3. It is clear that the reaction rate increases with increasing N-value. An attempt was also made to fit the data to kinetic models. The three models considered include: the nucleation and growth model, the phase boundary movement model, and the diffusion model. For the nucleation and growth model, the reaction fraction (f) can be expressed by a time-dependent kinetic equation:

$$f = 1 - \exp(-k_1 t^n) \quad (1)$$

in which k_1 is the kinetic constant, while n is usually an integer indicating the geometry of growth. For the phase boundary movement model, the equation will be:

$$(1-f)^{1/3} = 1 - (\frac{k_2}{R})t \quad (2)$$

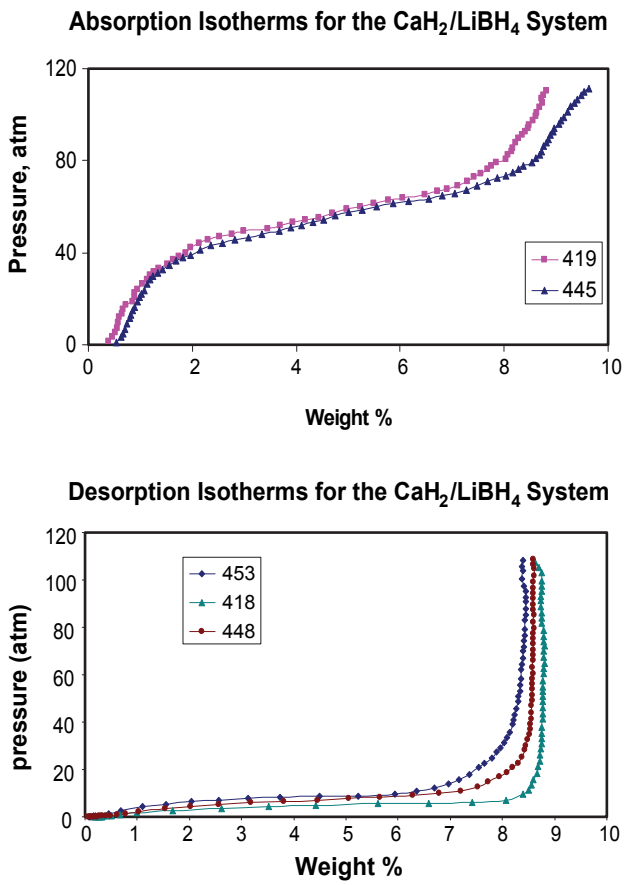

FIGURE 2. PCI Analysis of the $LiBH_4/CaH_2$ System

in which k_2 is the kinetic constant and R is the average particle size of samples. For the diffusion model, the equation will be:

$$(1-f)^{1/3} = 1-(\frac{\sqrt{k}}{R}) \quad (3)$$

The graphs in Figures 3 show that it is likely that hydrogen gas diffusion is the rate-controlling process. It is evident in the graphs of $(1\text{-}f)^{1/3}$ versus $t^{1/2}$ that a small change in slope occurs at a $(1\text{-}f)^{1/3}$ value of approximately 0.6. This indicates that the rate controlling process may change during the course of the reaction. Additional studies must be done to confirm that this is the case.

In a further attempt to lower the hydrogen desorption temperature of the $CaH_2/LiBH_4$ system, a ternary mixture was made by ball milling $LiNH_2$ with CaH_2 and $LiBH_4$. It was recently reported that a ternary mixture of $MgH_2/LiBH_4/LiNH_2$ released hydrogen at a temperature that was significantly lower than that from a binary mixture of $MgH_2/LiBH_4$ [3]. It was hoped that a similar effect would occur in the $CaH_2/LiBH_4$ system. In order to determine if this was the case, TGA analyses were performed on the $CaH_2/LiBH_4/LiNH_2$ ternary system. Figure 4 contains TGA graphs for the $CaH_2/LiBH_4/LiNH_2$ and $CaH_2/LiBH_4$ systems. A comparison

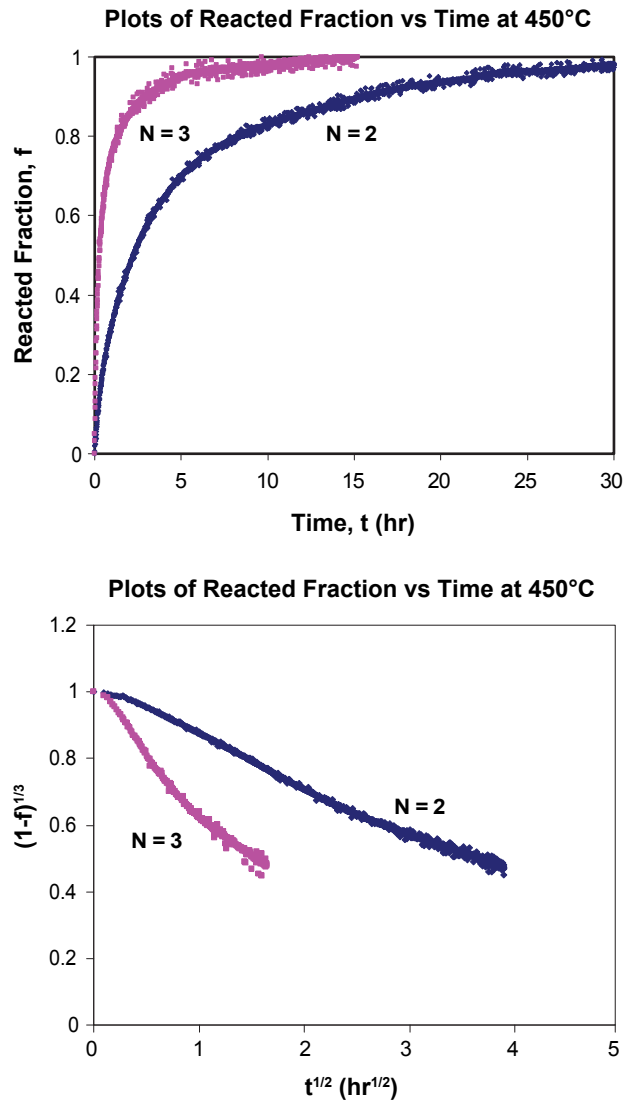

FIGURE 3. Kinetic Modeling Studies on the $LiBH_4/CaH_2$ System

of the curves reveals that the ternary mixture begins to release hydrogen at 130°C and continues to release hydrogen up to 340°C. The total amount of hydrogen released is 7.2 weight percent. The 130°C temperature for the initial release of hydrogen from the ternary mixture is 260°C lower than the initial temperature of release from the binary mixture. The 340°C temperature required for complete release of hydrogen is 140°C lower than the 480°C temperature required for full release from the binary mixture. PCI measurements were performed on the ternary system to determine if hydrogen could be absorbed and released reversibly from the mixture. These efforts were unsuccessful. Apparently the products formed are very stable and cannot be decomposed under the reaction conditions used.

To further confirm that these reactions were irreversible, TPD analyses were done in the gas reaction

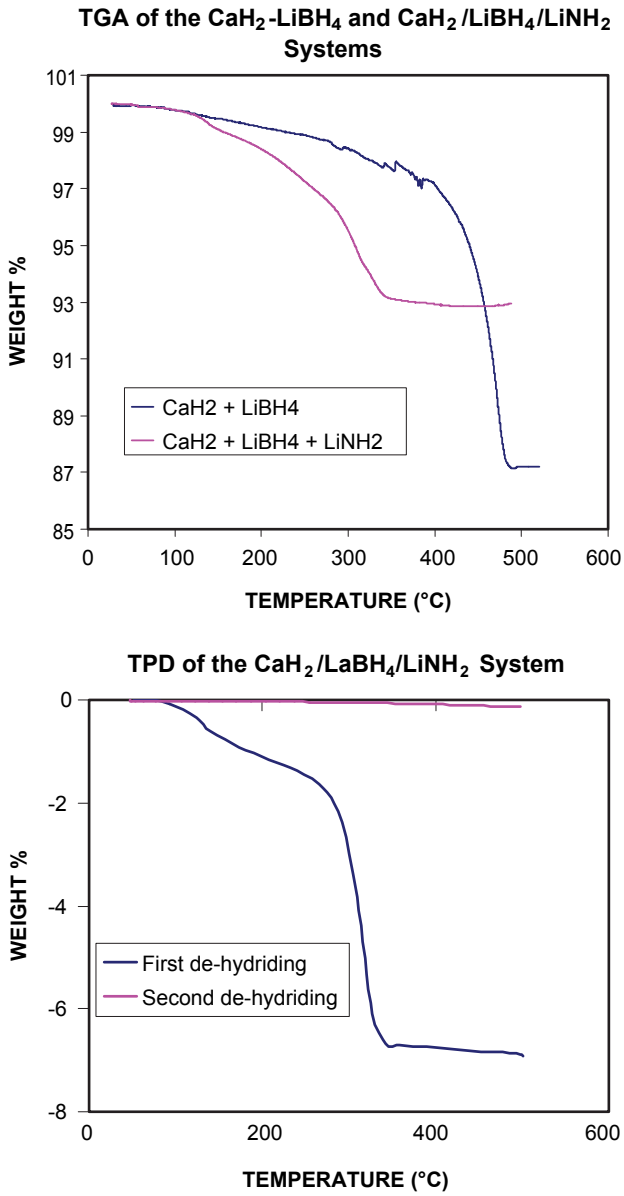

FIGURE 4. Hydrogen Storage in the $LiBH_4/CaH_2/LiNH_2$ System

controller. A fresh sample of the ternary mixture was placed into the gas reaction controller. The temperature was allowed to increase from 50 to 450°C and the weight percentage of hydrogen released was determined. The set of curves in Figure 4 show that 7.2 weight percent hydrogen is released in the 300°C range. This is in excellent agreement with the results obtained from TGA measurements. An attempt was made to re-hydride the sample by pressurizing the system to 150 atmospheres and maintaining it at 450°C for two days. Then the mixture was cooled to 50°C and kept under high pressure for another day. When the TPD was repeated the second curve showed that virtually no hydrogen is released. This confirms that the reaction is not reversible under the reaction conditions being used. Residual gas analysis was also done to determine if the non-reversibility was caused by the release of a gas such as NH_3. The results revealed that about 0.06% of the gas released was B_2H_6 but no NH_3 was detected. Thus the loss of volatile gas products was not the cause of non-reversibility. Another possibility is that a very stable compound may be formed during the course of the reaction. If this compound is too stable to react with hydrogen under the reaction conditions, it would explain the lack of reversibility. It will be necessary to study this system in more detail to develop a strategy for making it reversible.

Conclusions and Future Directions

- The results of this study show that the $CaH_2/LiBH_4$ system absorbs and releases about 9 weight percent of hydrogen reversibly. Thus it is a good prospect for hydrogen storage. However, the hydrogen is released at temperatures too high for fuel cell applications.
- Kinetic modeling studies suggest that desorption reaction rates are controlled by a diffusion model but the reaction rates are too slow for practical applications. Therefore, better catalysts and additives must be found to lower the reaction temperatures and increase reaction rates.
- The existing additives: $TiCl_3$, V_2O_5, TiF_3 and TiO_2 have a small effect in lowering reaction temperatures however better ones are needed. An attempt to lower the reaction temperature by using $CaNi_5H_4$ as a destabilizing agent instead of CaH_2 was unsuccessful. The presence of nickel apparently has no effect on weakening the boron-hydrogen bond and the added weight of the nickel reduced the overall weight percentage of hydrogen released from the system.
- An attempt to reduce the reaction temperature of the $CaH_2/LiBH_4$ mixture by adding $LiNH_2$ to form a ternary mixture was successful. TGA analyses showed that the desorption temperature could be reduced by 140°C however, attempts to do pressure composition isotherm analyses and temperature programmed desorption measurements showed that the release of hydrogen from the ternary mixture occurs irreversibly. It is likely that the reaction products are very stable and thus, they won't react with hydrogen in the reverse reaction.

In the Fiscal Year 2008-2009, the following are planned:

- Find a way to make the $LiBH_4/CaH_2/LiNH_2$ system absorb and release hydrogen reversibly.
- Preparation and thermal analysis of the other ternary systems similar to the $LiBH_4/CaH_2/LiNH_2$ system.

- Determine the cyclic stability of complex hydrides.
- Use techniques such as Fourier transform infrared and nuclear magnetic resonance to further characterize complex hydrides.
- Improve kinetics by optimizing hydrogenation catalysts.

FY 2008 Publications/Presentations

1. A. Goudy and A. Ibikunle, "Hydrogen Storage in a CaH_2 – $LiBH_4$ Destabilized Metal Hydride System", Gordon Conference, Waterville, Maine, 2007.

2. H. Yang and A. J. Goudy, "Absorption and Desorption Kinetics of Catalyzed $NaAlH_4$" Materials Research Society Meeting, Boston, MA, November 2007.

3. A. Ibikunle, A. J. Goudy, and H. Yang, "Hydrogen Storage in a CaH_2 / $LiBH_4$ Destabilized Metal Hydride System", J. Alloys and Compounds, (under review).

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2. R.M. Donohue and A.J. Goudy, Inorg. Chem., 30 (1991) 800-802.

3. J. Yang, A. Sudik, D. Siegel, D. Halliday, A. Drews, R. Carter, C. Wolverton, G. Lewis, J. Sachtler, J. Low, S. Faheem, D. Lesch and V. Ozolins, Angew. Chem. Int. Ed., 47 (2008) 882 – 887.