DOE Hydrogen Program

Center for Hydrogen Storage Research at Delaware State University

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May 16, 2007

Project ID #

STP23

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Overview

Timeline

- Start – June 1, 2006
- Finish – May 30, 2009
- 33% complete

Budget

- Total project funding
  - DOE $990 K
  - DSU $247.5 K
- Funding received in FY 06
  - $492.8 K
- Funding for FY07
  - $382.8 K

Barriers

- Barriers addressed
  - Weight and Volume
  - Durability
  - Refueling Time
  - Hydrogen Capacity and Reversibility

Partners

- Interactions/ collaborations
  - Carnegie Mellon University
  - University of Pittsburgh

Objectives

Overall	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.
2006	Develop methods for the synthesis, characterization, and modeling of complex hydrides using $LiBH_4/MgH_2$ as a model system.
2007	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.
2008	Extend the studies to include other complex hydrides, that have greater hydrogen storage potential than the destabilized hydrides. Develop methods for improving kinetics.

Approach

- Task 1 – Design suitable methods using $LiBH_4/MgH_4$ as a model system
  - Synthesis of new materials by mechanical alloying using ball milling
  - Determine thermal stability using thermal gravimetric analyses (TGA)
  - Use XRD to determine phase purity and crystal structure
  - Use PCI analyses to determine thermodynamic stability

- Task 2 – Find catalysts for making the hydriding faster and reversible

- Task 3 - Kinetic modeling study
  - Determine kinetic rate curves
  - Perform modeling to gain understanding of the mechanism

- Task 4 – Study other classes of promising hydrogen storage materials
  - Investigations will focus on destabilized hydride systems

Technical Accomplishments/ Progress/Results

- Have developed methods for the synthesis and characterization of complex hydrides using $LiBH_4/MgH_2$ as a model system
- Ball milling techniques were successfully used to prepare hydrogen storage materials
- XRD analyses were done on destabilized hydrides to determine crystal structure and phase purity
- The TGA apparatus, when enclosed in an argon-filled glove box, provided satisfactory thermal analysis data
- Have completed some preliminary analyses on the $LiBH_4/CaH_2$ system using TGA and PCI analyses

Accomplishments

Preparation of MgH_2

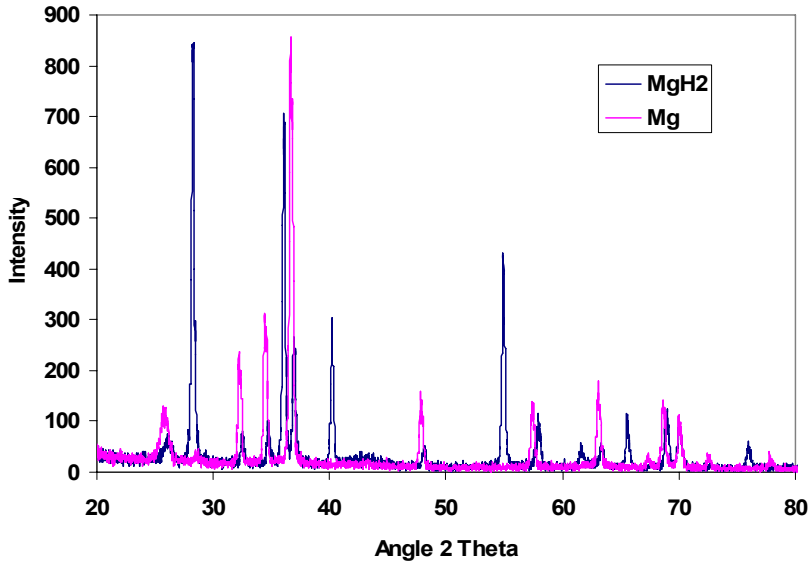

Figure 1. X-ray diffraction analysis of Mg before and after hydrogenation.

- MgH_2 was not commercially available. It was prepared by direct combination of Mg with hydrogen. A comparison of the x-ray spectra in Figure 1 reveals the formation of the product.

Accomplishments

Preparation and thermal analysis of $LiBH_4/MgH_2$

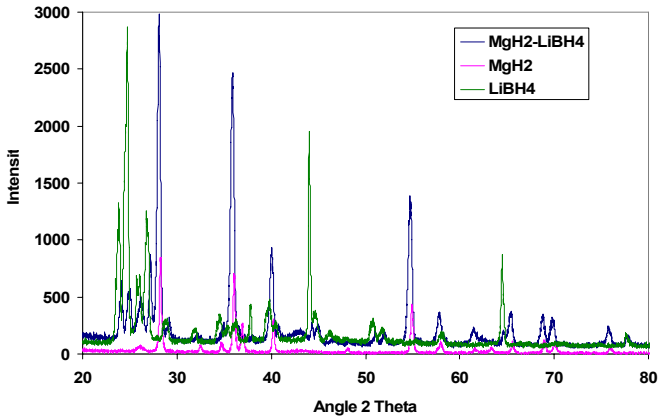

Figure 2. X-ray diffraction analysis of the $LiBH_4/MgH_2$ system.

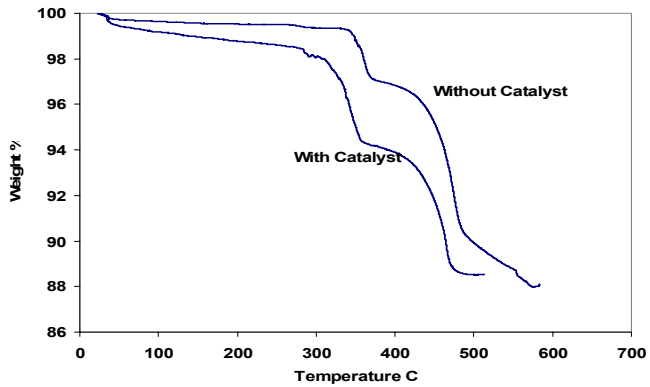

Figure 3. TGA scans of the $LiBH_4/MgH_2$ system with and without a $TiCl_3$ catalyst.

- $LiBH_4$ can be destabilized by ball milling it with MgH_2 via the reaction:
- $MgH_2 + 2LiBH_4 \rightarrow 2LiH + MgB_2 + 4H_2$
- The x-ray spectra in Figure 2 show that a reaction occurred
- The thermal analysis curves in Figure 3 show that about 11% hydrogen can be released. The $TiCl_3$ reduces the desorption temperature

Accomplishments

Absorption of hydrogen by the $LiBH_4/MgH_2$ system

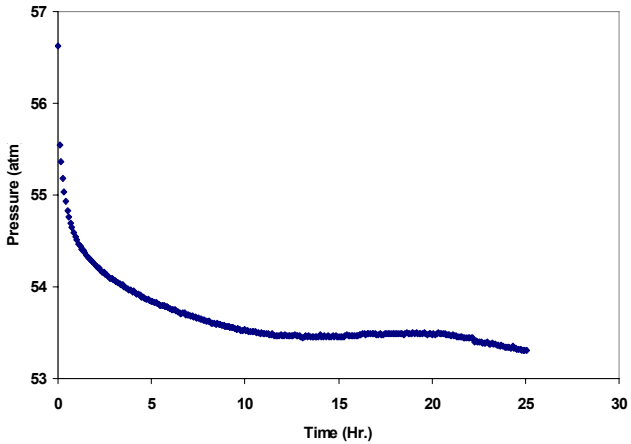

Figure 4. Shows the rate of absorption of hydrogen by the $LiBH_4/MgH_2$ system at 400 C.

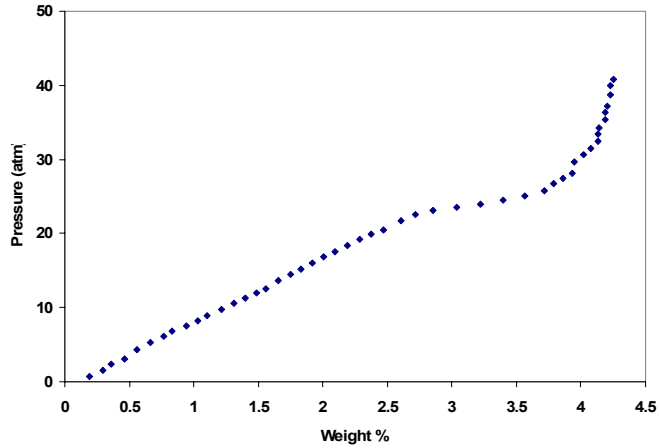

Figure 5. An absorption isotherm for the $LiBH_4/MgH_2$ system at 400 C.

- Hydrogen is absorbed by the $LiBH_4/MgH_2$ system via the reaction:
- $2LiH + MgB_2 + 4H_2 \rightarrow MgH_2 + 2LiBH_4$
- Figure 4 shows that the reaction is complete in about 12 hours at 400 C.
- The isotherm in Figure 5 shows that at 400 C, a single plateau is present at 25 atm. The amount of hydrogen is less than expected and re-calibrations of the equipment will be done to ascertain the cause of this.

Accomplishments

Desorption of hydrogen by the $LiBH_4/MgH_2$ system

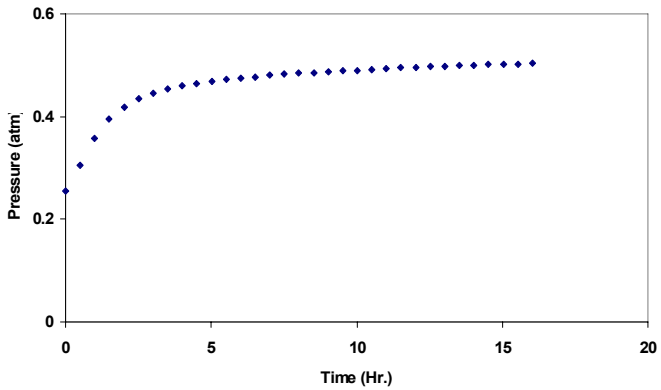

Figure 6. Shows the rate of desorption of hydrogen from the $LiBH_4/MgH_2$ system at 400 C.

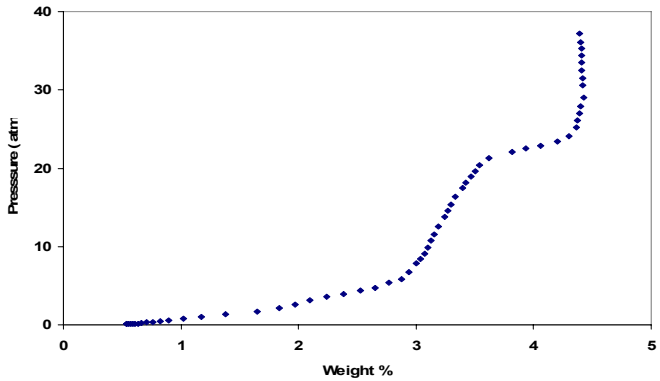

Figure 7. An desorption isotherm for the $LiBH_4/MgH_2$ system at 400.

- Desorption of hydrogen in the $LiBH_4/MgH_2$ system occurs via the reaction:
- $MgH_2 + 2LiBH_4 \rightarrow 2LiH + MgB_2 + 4H_2$
- The desorption profile in Figure 6 shows that H_2 is fully released at 400 C in about 2 hours
- The PCI curve in Figure 7 displays the presence of two plateau regions

Accomplishments

Preparation and thermal analysis of $LiBH_4/CaH_2$

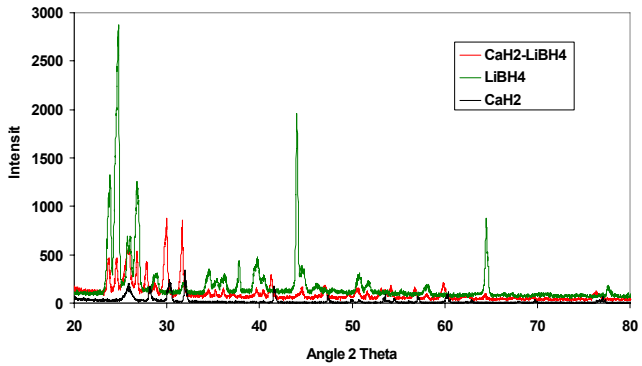

Figure 8. X-ray diffraction analysis of the $LiBH_4/CaH_2$ system.

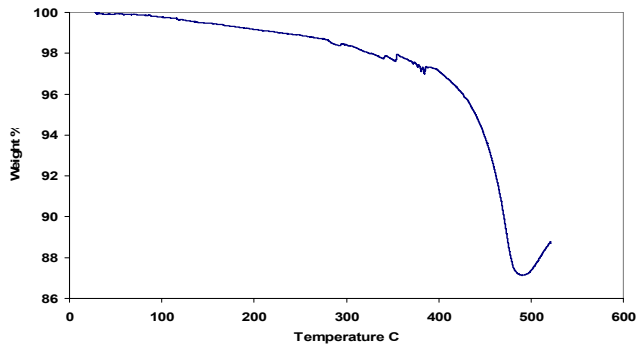

Figure 9. TGA scans of the $LiBH_4/CaH_2$ system with a $TiCl_3$ catalyst.

- $LiBH_4$ can be destabilized by ball milling it with CaH_2 via the reaction:
- $CaH_2 + 6LiBH_4 \rightarrow 6LiH + CaB_6 + 10H_2$
- The x-ray spectra in Figure 8 confirms that a reaction occurred
- This system releases close to 11.69 theoretical wt. % hydrogen according to the TGA curves in Figure 9. The $TiCl_3$ catalyst reduces the desorption temperature

Accomplishments

PCI Analysis of the $LiBH_4/CaH_2$ System

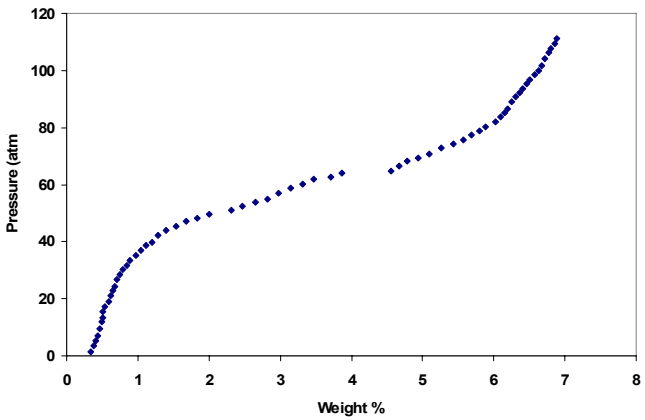

Figure 10. Absorption isotherm for the $LiBH_4/CaH_2$ system at 400 C.

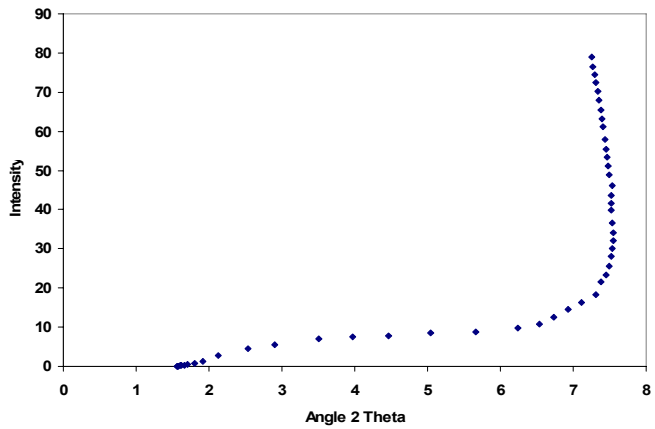

Figure 11. Desorption isotherm for the $LiBH_4/CaH_2$ system at 400 C.

- The isotherms in Figures 10 and 11 reveal the presence of a single plateau region at 400 C. According to the isotherms, the reversible storage capacity is about 7 weight percent. This is significantly below the amount predicted from TGA analyses.

Accomplishments

Preparation and thermal analysis of $LiBH_4/LiNH_2$ system

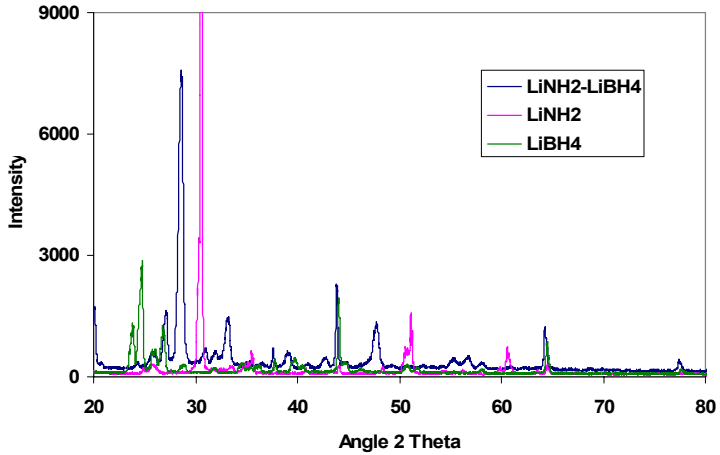

Figure 12. X-ray diffraction analysis of the $LiBH_4/LiNH_2$ system.

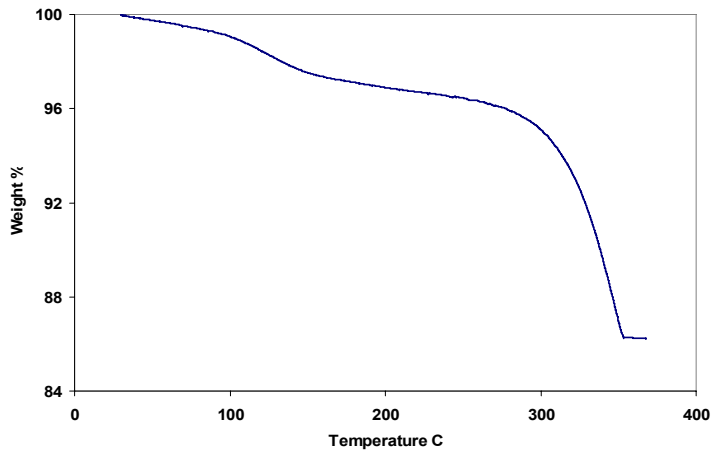

Figure 13. TGA scan of the $LiBH_4/LiNH_2$ with a $TiCl_3$ catalyst

- $LiBH_4$ was destabilized by ball milling it with CaH_2 via the reaction:
- $LiBH_4 + 2LiNH_2 \rightarrow Li_3BN_2 + 4H_2$
- The x-ray spectra in Figure 12 confirms that a reaction occurred
- Based on the TGA curves in Figure 13, it appears that this system releases in excess 14% of hydrogen. However further analysis revealed that NH_3 was produced during the hydriding process.

Future Work

- In the FY 07-08, the following are planned
  - Perform analyses on destabilized hydrides consisting of lithium borohydride destabilized with materials such as C, Sc, and CaH_2.
  - Perform XRD measurements as a function of temperature
  - Determine the cyclic stability of the hydrides
  - Perform detailed kinetic studies on selected materials
  - Improve kinetics by optimizing hydrogenation catalysts

Project Summary

Relevance:	The materials under consideration in this study may provide the solution to the on board hydrogen storage goals established by the DOE.
Approach:	Methods such as ball milling, TGA, XRD, and PCI measurements were used to synthesize and characterize hydrides.
Technical Accomplishments:	Have demonstrated that $LiBH_4/CaH_2$ may be a suitable hydrogen storage material. Suitable catalysts must be found to lower to desorption temperature.
Proposed Future Research:	Studies will be done on a variety of destabilized hydrides to determine those that meet DOE's hydrogen storage goal and which have suitable kinetics and thermodynamic stability.