Center for Hydrogen Storage Research
at Delaware State University

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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

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<th>Overall</th>
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<td>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.</td>
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<td>Develop methods for the synthesis, characterization, and modeling of complex hydrides using LiBH₄/MgH₂ as a model system.</td>
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<td>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.</td>
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<td>Extend the studies to include other complex hydrides, that have greater hydrogen storage potential than the destabilized hydrides. Develop methods for improving kinetics.</td>
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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$_2$

- 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.

Figure 1. X-ray diffraction analysis of Mg before and after hydrogenation.
Accomplishments
Preparation and thermal analysis of LiBH$_4$/MgH$_2$

- LiBH$_4$ can be destabilized by ball milling it with MgH$_2$ via the reaction:
  - MgH$_2$ + 2LiBH$_4$ → 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

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.
Accomplishments
Absorption of hydrogen by the LiBH$_4$/MgH$_2$ system

- Hydrogen is absorbed by the LiBH$_4$/MgH$_2$ system via the reaction:
  \[2\text{LiH} + \text{MgB}_2 + 4\text{H}_2 \rightarrow \text{MgH}_2 + 2\text{LiBH}_4\]
- 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

- Desorption of hydrogen in the LiBH$_4$/MgH$_2$ system occurs via the reaction:
  $$\text{MgH}_2 + 2\text{LiBH}_4 \rightarrow 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2$$
- 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 LiBH₄/CaH₂

- LiBH₄ can be destabilized by ball milling it with CaH₂ via the reaction:
  \[ \text{CaH}_2 + 6\text{LiBH}_4 \rightarrow 6\text{LiH} + \text{CaB}_6 + 10\text{H}_2 \]
- 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 TiCl₃ catalyst reduces the desorption temperature.
Accomplishments
PCI Analysis of the LiBH$_4$/CaH$_2$ System

- 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

- LiBH$_4$ was destabilized by ball milling it with CaH$_2$ via the reaction:
  - LiBH$_4$ + 2LiNH$_2$ → Li$_3$BN$_2$ + 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 CaH₂.
  – 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.