Center for Hydrogen Storage Research at Delaware State University

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Project ID #
STP 24

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Overview

Timeline
• Start – June 1, 2006
• Finish – May 30, 2009
• 66% complete

Budget
• Total project funding
  – DOE $990 K
  – DSU $247.5 K
• Funding received in FY 06
  – $875.6 K
• Funding for FY08
  – $361.9 K

Barriers
• Barriers addressed
  – Weight and Volume
  – Durability
  – Refueling Time
  – Hydrogen Capacity and Reversibility

Partners
• Interactions/collaborations
  – Georgia Tech
  – University of Pittsburgh
  – University of Delaware
  – Air Liquide
## Objectives

<table>
<thead>
<tr>
<th>Year</th>
<th>Objective</th>
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<tr>
<td><strong>Overall</strong></td>
<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><strong>2006</strong></td>
<td>Develop methods for the synthesis, characterization, and modeling of complex hydrides using LiBH$_4$/MgH$_2$ as a model system.</td>
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<td><strong>2007</strong></td>
<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><strong>2008</strong></td>
<td>Extend the studies to include other complex hydrides, that have greater hydrogen storage potential than the destabilized hydrides such as ternary borohydride systems. Perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures.</td>
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<tr>
<td>Year</td>
<td>Milestone: The methods and procedures to be used for testing and characterizing complex hydrides using NaAlH$_4$ as a model system were completed.</td>
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<td>2006</td>
<td>Go/No-Go decision: It was decided that most of the effort should be expended on studying the borohydride systems for hydrogen storage instead of the alanates.</td>
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<td>2008</td>
<td>Milestone: It was discovered that the CaH$_2$/LiBH$_4$ system could reversibly absorb and release approximately 9 weight percent hydrogen. It was also found that certain ternary mixtures could release hydrogen at significantly lower temperatures.</td>
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Approach

• Task 1 – Preparation and characterization of the LiBH$_4$/CaH$_4$ 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
  – Study ternary systems such as the LiBH$_4$/CaH$_4$/LiNH$_2$ system to determine if reaction temperatures can be lowered.
Technical Accomplishments/ Progress/Results

• Have completed the analyses on the LiBH$_4$/CaH$_2$ system using TGA, TPD and PCI analyses. Have found that this system can reversible store 9 weight percent hydrogen.

• Have done some kinetic modeling studies on the NaAlH$_4$ and LiBH$_4$/CaH$_2$ systems. Have identified the likely rate-controlling process.

• Have identified a ternary hydride system, CaH$_2$/LiBH$_4$/LiNH$_2$, that releases hydrogen at a significantly lower temperature than the binary CaH$_2$/LiBH$_4$ mixture.
Accomplishments
Thermal Analysis of the CaH$_2$/LiBH$_4$ System

- A comparison was made of the desorption temperatures with 4 different additives. The graphs show that the desorption temperatures are in the order TiF$_3$ < TiO$_2$ ≤ TiCl$_3$ < V$_2$O$_5$.
- None of these additives produce a lower temperature than 400 C.
Accomplishments

PCI Analysis of the LiBH$_4$/CaH$_2$ System

- Hydrogen is released from the LiBH$_4$/CaH$_2$ system via the reaction:
  \[ 6 \text{LiBH}_4 + \text{CaH}_2 \rightarrow 6 \text{LiH} + \text{CaB}_6 + 10 \text{H}_2 \]
- The isotherms show that a single plateau is present and that about 9 weight percent hydrogen can be reversibly absorbed and released in the 400 – 450 C range. The enthalpy of desorption is about 67 kJ/mole H$_2$. 
Accomplishments
Kinetic Modeling Studies on the LiBH$_4$/CaH$_2$ system

- An N-value was defined as the ratio of the plateau pressure to the applied pressure.
- The plots of reacted fraction versus time show that the rates increase with increasing N-values. Kinetic modeling was attempted with nucleation and growth, moving boundary and diffusion models. The best fit was obtained with the diffusion model according to the equation:

\[(1 - f)^{1/3} = 1 - \left(\frac{\sqrt{kt}}{R}\right)\]
Accomplishments
Hydrogen Storage in the LiBH$_4$/CaNi$_5$H$_4$ System

- TGA analyses were done on CaH$_2$/LiBH$_4$ with TiCl$_3$; CaH$_2$/LiBH$_4$ without TiCl$_3$; and a CaNi$_5$H$_4$/LiBH$_4$ mixture.
- The results show that all three mixtures release hydrogen at about the same temperature. Thus CaNi$_5$H$_4$ is not an effective dopant.
- The CaH$_2$/LiBH$_4$ mixture releases a lower weight percentage hydrogen due to the added weight of the nickel.
Accomplishments

Hydrogen Storage in the LiBH$_4$/CaH$_2$/LiNH$_2$ system

- TGA shows that the LiBH$_4$/CaH$_2$/LiNH$_2$ system releases hydrogen at about 100°C lower than the LiBH$_4$/CaH$_2$ system. However, the amount of hydrogen released from the ternary system is lower than the amount released from the binary system.
- TPD analysis shows that the ternary system does not absorb and release hydrogen reversibly. It initially releases about 7 weight percent hydrogen but subsequent attempts to re-hydride and release hydrogen were unsuccessful.
Accomplishments

Residual gas analysis of the LiBH$_4$/CaH$_2$/LiNH$_2$ System

- The analysis shows that about 0.06% of the gas released from the ternary mixture is B$_2$H$_6$. There was no detectable amount of NH$_3$ released.
Accomplishments
Kinetic Modeling Studies on the NaAlH$_4$ system

- Absorption and desorption experiments were done at 160 C for the lower plateau and at various N-values. The results show that a moving phase boundary model is a better fit for the data at various N-values.
- The moving boundary model is described according to the equation:

$$ (1 - f)^{1/3} = 1 - \left(\frac{k_2}{R}\right)t $$
Future Work

• In the FY 08-09, 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 FTIR and NMR to further characterize and understand complex hydrides
  – Improve kinetics and lower reaction temperatures by optimizing hydrogenation catalysts
Project Summary

Relevance: The materials under consideration in this study have the potential to provide the solution to the on board hydrogen storage goals established by the DOE.

Approach: Methods such as ball milling, TGA, TPD, XRD, PCI measurements, kinetics measurements and residual gas analyses were used to synthesize and characterize hydrides.

Technical Accomplishments: Have demonstrated that LiBH₄/CaH₂ may be a suitable hydrogen storage material. Have developed a ternary system that has significantly lower reaction temperature. Identified a possible rate controlling process via kinetic modeling.

Proposed Future Research: Studies will be done on a variety of destabilized hydrides including ternary systems, to determine those that meet DOE’s hydrogen storage goal and which have suitable kinetics and thermodynamic stability.