

IV.A.4 Hydrogen Storage Materials for Fuel Cell-Powered Vehicles

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Contract Number: DE-FC36-06GO86046

Start Date: July 1, 2006
Projected End Date: May 30, 2013

Objectives

- Study new destabilized complex hydrides that have been predicted by first principles calculations to be suitable hydrogen storage materials.
- Develop methods for the synthesis, characterization, and modeling of new complex hydrides.
- Identify the most promising types of complex hydrides and develop new catalysts and engineering techniques for increasing reaction rates and lowering reaction temperatures.
- Extend studies to include carbon materials, metal organic frameworks (MOFs), and possibly other nanostructured and porous materials as potential hydrogen storage materials using hydrogen spillover.
- Perform cycling studies to test the durability of destabilized complex hydrides and MOFs.
- Design, fabricate and test a hydride-based hydrogen storage system for fuel cell applications.

Technical Barriers

This project addresses the following technical barriers taken from the Hydrogen Storage section of the Fuel Cell 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 complex borohydride materials and other promising hydrogen storage materials. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet DOE's 2015 goal of 4.5 weight percent hydrogen storage for the system. The following table summarizes the targets:

Storage Parameter	Units	Target
System Gravimetric Capacity: Usable, specific-energy from H ₂ (net useful energy/max system mass)	kWh/kg	1.5
System Volumetric Capacity: Usable energy density from H ₂ (net useful energy/max system volume)	kWh/L	1.2
Storage System Cost	\$/kWh	6

Accomplishments

- We have determined that several destabilized borohydride systems based on Mg(BH₄)₂ can absorb hydrogen reversibly starting at temperatures less than 200°C.
- We used thermodynamic measurements, based on van't Hoff plots to determine the reaction enthalpies of the destabilized systems.
- We have also determined that mixed catalysts are most effective in catalyzing the MgH₂ system and they may be effective for destabilized systems as well.
- We have determined the activation energies for the CaH₂/LiBH₄ system using the Kissinger analysis.



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.

During the next several years we propose to perform hydrogen storage studies on some new destabilized complex hydrides that have been predicted by first principles calculations to be suitable hydrogen storage

materials. We will develop methods for the synthesis, characterization, and modeling of these new complex hydrides as well as developing new catalysts and engineering techniques for increasing reaction rates and lowering reaction temperatures. Nanotechnology will be used to reduce or eliminate the release of any diborane. We will also extend these studies to include carbon materials, MOFs and possibly other nanostructured and porous materials as potential hydrogen storage materials. There have been recent reports that some MOFs had a hydrogen storage capacity of 7.5 wt% H₂ at 77 K and 70 bar. Unfortunately, the hydrogen adsorption capacities of most carbon materials at ambient temperature and pressure are quite low, generally being less than 1 wt%. Scientists are seeking materials that can absorb and release significant quantities of hydrogen near room temperature. Most recently it was found that IRMOF-8 could adsorb 4.0 wt% at room temperature and 100 bar using hydrogen spillover. This is significant because there is a good possibility that other MOFs could be made that might have even greater capacity at room temperature using the spillover technique. We will thus explore this possibility.

Once a suitable material has been identified for hydrogen storage it will be necessary to design, fabricate and test a hydride-based hydrogen storage system for fuel cell applications. A partner institution will be involved in this aspect of the research. This phase of the research will include using flow, reaction kinetics and thermal modeling, followed by system design, fabrication and performance evaluation.

Approach

To achieve the project objectives, new materials are being developed and characterized using a variety of techniques. Sample preparations prior to analysis were done in an argon-filled glove box (Vacuum Atmosphere Company). The hydrides were made by first ball milling the raw materials in a SPEX 8000 Mixer Miller and then directly combining them with hydrogen in a Sieverts apparatus. X-ray powder diffraction in a Panalytical X'pert Pro MPD Analytical X-Ray Diffractometer was used to confirm the formation of product and to determine phase purity.

Thermogravimetric analyses (TGA) and temperature programmed desorption (TPD) were used to determine the thermal stability and the hydrogen capacity of the mixtures. The TGA analyses were done in a Lab System-Diamond TG/DTA. This instrument was placed inside of an argon-filled glove box so that samples can be analyzed with virtually no exposure to air and moisture. The TPD analyses were carried out in a pressure composition isotherm (PCI) unit. The instrument was supplied by Advanced Materials Corporation. Kinetic measurements were done to determine the overall

reaction rates. Cycling measurements were done to determine the stability of the materials when subjected to repeated hydrogenation and dehydrogenation cycles. The B-H bond strength of the various synthesized double-cation borohydrides were compared via Shimadzu IR Prestige-21 Fourier transform infrared spectrophotometer. This instrument operates in a single-beam mode and is capable of data collection over a wave number range of 7,800 cm⁻¹ ~ 350 cm⁻¹. Residual gas analyses were done in a RGA Pro 2000. The instrument was produced by Stanford Research Systems and distributed by Hy-Energy LLC in Newark, CA.

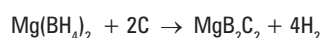
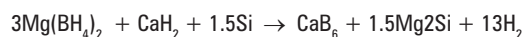
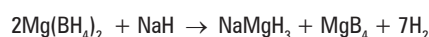
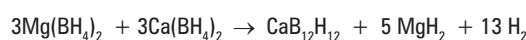
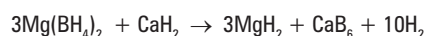
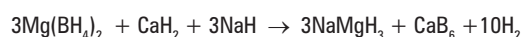
Results

Last year we reported that the destabilized borohydride system described by the equation



absorbed hydrogen in a reversible manner. Further studies have been done to determine the effect of various additives on the desorption temperatures and activation energy of this system. The additives studied were TiCl₃, TiF₃ and TiO₂. It was found that the TiCl₃ additive lowered the dehydrogenation temperature more than the other additives. Furthermore, higher amounts of TiCl₃ were more effective in reducing the desorption temperature than lesser amounts. Kissinger plots were used to determine the activation energies of the catalyzed systems. The activation energies for mixtures containing 4, 10 and 25 mol% of TiCl₃ were 141, 126 and 110 kJ/mol, respectively.

The following six systems based on Mg(BH₄)₂ have also been studied to determine their reversibility and thermodynamic behavior:



The systems described in the first three equations are reversible with some releasing as much as 8 wt% hydrogen at temperatures beginning at less than 200°C (see Figure 1). The last three reactions did not show any well defined plateau region. Therefore, thermodynamic measurements were done only on the systems described by the first three equations. Cycling studies showed that these systems are only partially reversible. The hydrogen-holding capacities diminished to about

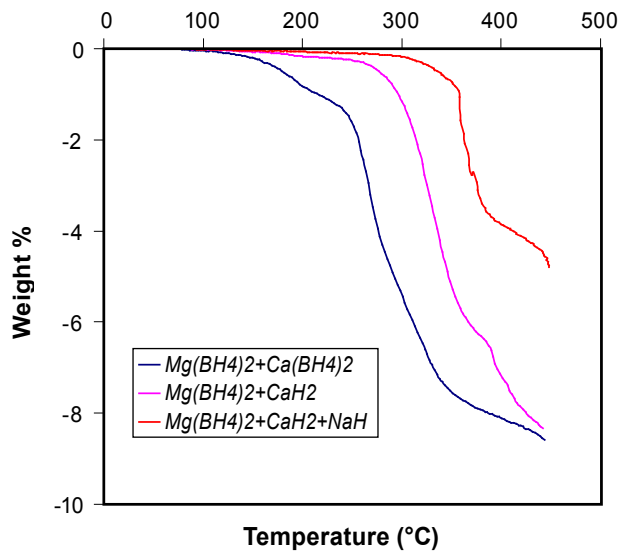


FIGURE 1. TPD Profiles of the $\text{Mg}(\text{BH}_4)_2$ Destabilized Systems (TPD profiles were performed in an automated system controlled by LabVIEW-based software.)

2 wt% upon continued cycling. Thermodynamic measurements, based on van't Hoff plots showed that the reaction enthalpies were in the 82-88 kJ/mol range. Results are given in Figure 2. Thermodynamics and kinetics measurements were done using MgH_2 as a model system. The goal was to determine what catalysts work best in lowering reaction temperatures and increasing reaction rates. It was found that a mixture of two catalysts was more effective than either catalyst alone. Larger amounts of catalysts were more effective in lowering reaction temperatures but the hydrogen-holding capacity was significantly diminished as the amount of catalyst increased. Results are shown in Figures 3-4.

Conclusions and Future Directions

This work has shown that several destabilized borohydride systems based on $\text{Mg}(\text{BH}_4)_2$ can absorb hydrogen reversibly starting at temperatures less than 200°C. We have also determined that mixed catalysts are most effective in catalyzing the MgH_2 system and they may be effective for destabilized systems as well. In Fiscal Years 2010-2011, the following are planned:

- Prepare and characterize several $\text{Mg}(\text{BH}_4)_2$ -based destabilized systems using ball milling, X-ray diffraction, TPD and TGA.
- Perform thermodynamic measurements, such as PCI analyses, on destabilized systems found to be reversible.

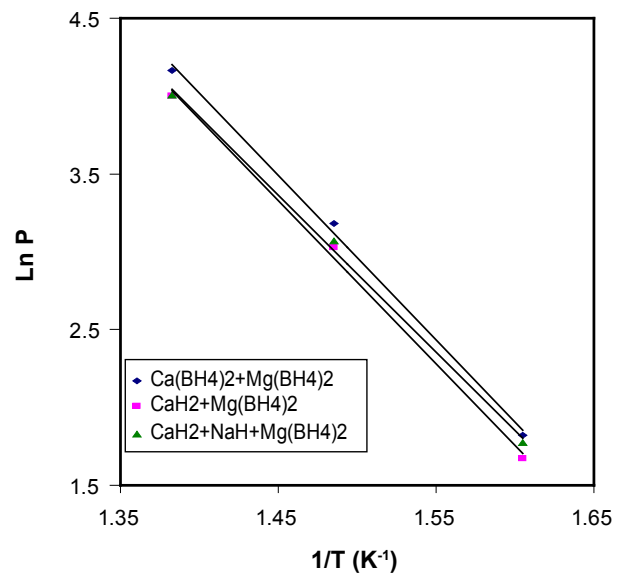
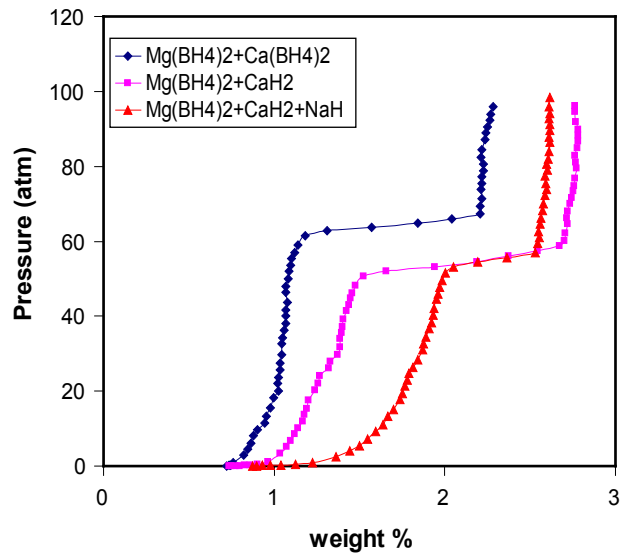


FIGURE 2. Desorption Isotherms and Van't Hoff Isochores for the $\text{Mg}(\text{BH}_4)_2$ System with Various Additives (The isotherms were done at 450°C. The van't Hoff isochores were obtained from isotherms done at 350, 400, and 450°C.)

- Perform kinetics and modeling studies on the destabilized systems at constant pressure driving forces in order to establish the rate-controlling process.
- Use techniques such as residual gas analysis to determine if dehydrogenation is accompanied by the release of other gaseous byproducts.
- Use various catalysts and combinations of catalysts to lower reaction temperatures and increase reaction rates. MgH_2 will be used as a model system in these efforts.

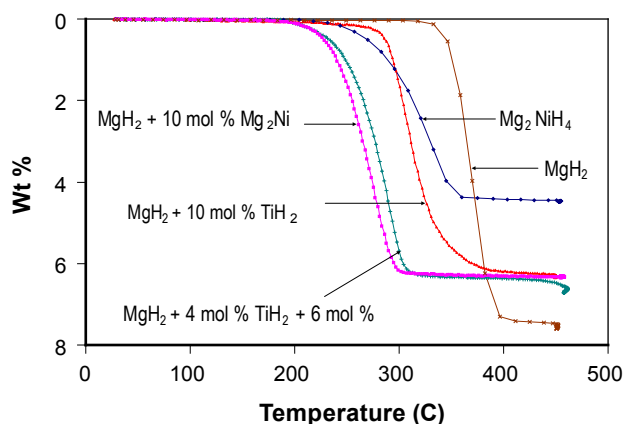


FIGURE 3. TPD Profiles for MgH_2 , Mg_2NiH_4 and Several Mixtures Containing Various Amounts of TiH_2 and/or Mg_2Ni (The curves show that pure MgH_2 has the highest desorption temperature whereas the $MgH_2 + 10 \text{ mol}\% Mg_2Ni$ has the lowest.)

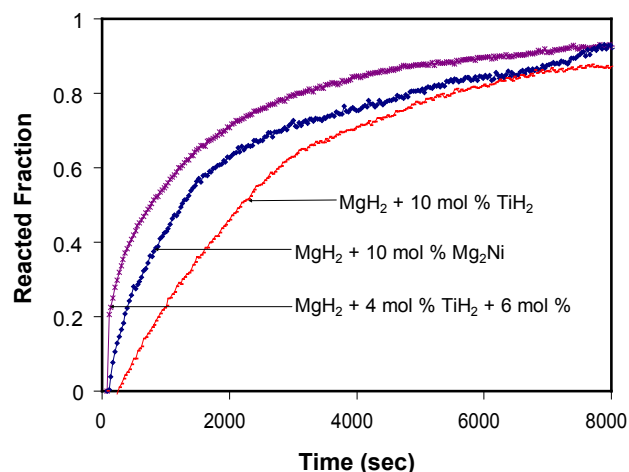


FIGURE 4. Reaction Rate Plots for Mixtures Containing 90 mol% MgH_2 and 10 mol% TiH_2 , Mg_2Ni or Both (The curves show that the mixture containing 10 mol% TiH_2 reacts the slowest whereas the one with the mixed catalyst reacts the fastest.)

FY 2010 Publications/Presentations

1. H. Yang, A. Ibikunle and A.J. Goudy, "Effects of Ti-based additives on the hydrogen storage properties of a $LiBH_4 / CaH_2$ destabilized system" *Adv in Materials Science and Eng.* (2010) Under review.
2. S.T. Sabitu, G. Gallo and A.J. Goudy, "Effect of TiH_2 and Mg_2Ni additives on the hydrogen storage properties of magnesium hydride" *J. Alloys and Compds.* 449 (2010) 35-38.
3. A. Ibikunle, A.J. Goudy, and H. Yang Hydrogen Storage in a $CaH_2 / LiBH_4$ Destabilized Metal Hydride System, *J. Alloys and Compds.* 475 (2009) 110-115.
4. H. Yang, A. Ojo, P. Ogaro and A.J. Goudy, "Hydriding and Dehydriding Kinetics of Sodium Alanate at Constant Pressure Driving Forces" *J. Phys Chem C*, 113 (2009) 14512-14517.
5. A.J. Goudy, A. Ibikunle and T. Durojaiye, "Hydrogen Storage in $LiBH_4$ Destabilized Metal Hydride Materials", Gordon Conference, Lucca, Italy, 2009.
6. Hongwei Yang and Andrew Goudy, "Kinetic and Modeling Study of Sodium Alanate at Constant Pressure Thermodynamic Driving Forces", MRS Fall meeting, November 30 - December 3, 2009, Boston, MA.
7. Adeola Ibikunle, Tolulope Durojaiye and Andrew Goudy, "Hydrogen Storage in Modified $LiBH_4$ Metal Hydride Materials" NOBCCChE Southeast Regional Meeting, University of Maryland, November 2009.
8. Saidi T. Sabitu, George Gallo and Andrew J. Goudy, "Thermodynamic studies on the interactions of TiH_2 and Mg_2Ni with MgH_2 for high capacity hydrogen storage" NOBCCChE Southeast Regional Meeting, University of Maryland, November 2009.
9. Andrew Goudy and Saidi Sabitu "Improved Hydrogen Storage in Magnesium Hydride Catalyzed by TiH_2 and Mg_2Ni ", NHA Hydrogen Conference and Expo, Long Beach, CA, May 3-6, 2010.