IV.G.3 Hydrogen Storage Materials for Fuel Cell-Powered Vehicles*

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Fiscal Year (FY) 2011 Objectives

The objectives of this project are to:

- Identify complex hydrides that have the potential to meet DOE's goals for storage and demonstrate the optimum temperature and pressure ranges under a variety of conditions. Develop new catalysts and engineering techniques for increasing reaction rates and lowering reaction temperatures.
- Perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures, thereby reducing refueling time.
- Extend the studies to include other complex hydrides, such as the $LiNH_2/MgH_2$ system, that have greater hydrogen storage potential.
- 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.
- Design, fabricate and test a hydride-based hydrogen storage system for fuel cell applications in collaboration with our partners at the University of Delaware. Improve the rate at which the hydrogen gas can be charged into a hydride-based hydrogen storage tank, and to improve the hydrogen storage density.

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 5.5 weight percent hydrogen storage for the system. The following Table summarizes the targets.

TABLE 1. Technical 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 (and fuel cost)	$/kWh	6

FY 2011 Accomplishments

- The desorption properties for a series of $MgH_2/LiBH_4$ systems of compositions MgH_2-$2LiBH_4$, MgH_2-$4LiBH_4$, and MgH_2-$7LiBH_4$ have been determined. Temperature programmed desorption (TPD) results show that desorption temperatures increase with increasing amounts of $LiBH_4$. Pressure-composition isotherm (PCI) results show that plateau pressures decrease with increasing amounts of $LiBH_4$ and the amount of hydrogen released increases with increasing amounts of MgH_2.
- This work has shown that KH is a very effective catalyst for the desorption of hydrogen from the MgH_2-$2LiNH_2$ system.
- We have determined activation energies for the MgH_2-$2LiNH_2$ system with and without a KH catalyst using Kissinger analysis. Results show that the KH lowers the activation energy.
- The design, fabrication and demonstration of a hydride-based hydrogen storage system for fuel cells is underway. Results show that the heat removal rate can be increased by increasing the effective thermal conductivity by mixing the metal hydride with conductivity-enhanced materials such as aluminum foam or graphite.

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Introduction

There has been considerable interest in complex hydrides such as borohydrides and amides because they have been determined to have great potential to meet DOE's goals for hydrogen storage. Current efforts in our research lab are focused on performing 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. We will also extend these studies to include carbon materials, MOFs and possibly other nanostructured and porous materials as potential hydrogen storage materials. 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. Efforts are currently underway with a partner institution to design a hydrogen storage system and test it using a suitable material. 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 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 thermo-gravimetric/differential thermal analyzer. 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 PCI unit. The instrument was supplied by Advanced Materials Corporation. Kinetic measurements were done to determine the overall reaction rates.

Results

Previous studies have indicated that the $MgH_2/LiBH_4$ system has the potential to meet DOE's hydrogen storage goals. Therefore the desorption properties of a series of $MgH_2/LiBH_4$ systems were studied to determine how

suitable these materials were for hydrogen storage. The systems studied had compositions of MgH_2-$2LiBH_4$, MgH_2-$4LiBH_4$, and MgH_2-$7LiBH_4$. TGA measurements were done on each of the three systems to see if there was any correlation between temperature and composition. The results in Figure 1 show that desorption temperatures increase with increasing amounts of $LiBH_4$. It was also of interest to determine the reversibility of these systems. To accomplish this, pressure-composition-isotherms were constructed for each system at several temperatures. The PCI results shown in Figure 2 demonstrate that plateau pressures decrease with increasing amounts of $LiBH_4$ and the amount of hydrogen released increases with increasing amounts of MgH_2. Kinetics and modeling studies are presently underway to determine the rates of hydrogen release from these materials at constant pressure thermodynamic forces. We have already determined that the rate decreases with increasing amounts of $LiBH_4$. It will
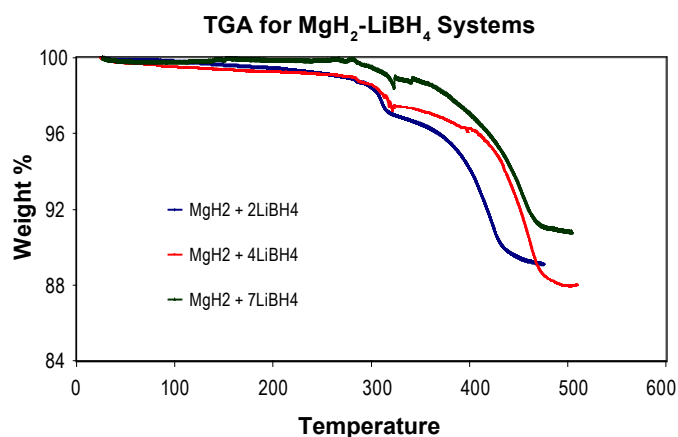

FIGURE 1. Thermal Gravimetric Analyses for Several MgH_2-$LiBH_4$ Systems. Desorption temperatures increase with increasing amounts of $LiBH_4$.
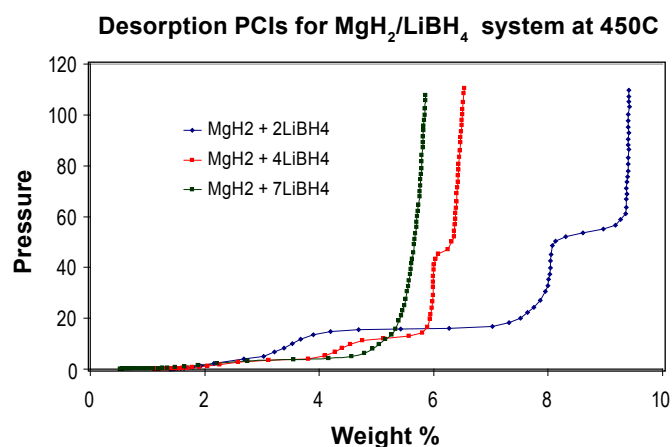

FIGURE 2. Desorption PCIs for $MgH_2/LiBH_4$ System at 450ºC. Plateau pressures decrease with increasing amounts of $LiBH_4$ and the amount of hydrogen released increases with increasing amounts of MgH_2.

also be useful to determine if the same or similar processes controls the reaction rates in all three systems.

There have been reports that systems based on $MgH_2/LiNH_2$ may also have the potential to meet DOE's goals for hydrogen storage. Therefore the desorption properties of a $MgH_2/2LiNH_2$ system were determined. PCIs were determined, with and without a KH catalyst, at several temperatures. The results show a well defined plateau region. Van't Hoff plots were used to determine the enthalpies of formation. Kinetics studies were done at constant pressure thermodynamic forces such that the ratio of the plateau pressure to the applied hydrogen pressure was held approximately constant at 10 in all cases. Results shown in Figure 3 indicate that the catalyzed system reacted much faster than the un-catalyzed system. Activation energies were determined by doing differential thermal analyses (DTA). Desorption temperatures were determined at several scan rates. DTA curves showed that the desorption temperatures increase with increasing scan rates. These results were used to construct Kissinger plots. The activation energies for the catalyzed and uncatalyzed systems were 106 and 116 kJ/mol respectively. As expected, the catalyzed system had lower activation energy than the catalyzed one.

Another project is underway entitled "Design, Fabrication and Demonstration of a Hydride-Based Hydrogen Storage System for Fuel Cell Applications". The overall objective is to improve the rate at which the hydrogen gas can be charged into a hydride-based hydrogen storage tank, and to improve the hydrogen storage density. A mathematical model is being used to predict the temperature at selected locations within the storage tank. A series of experimen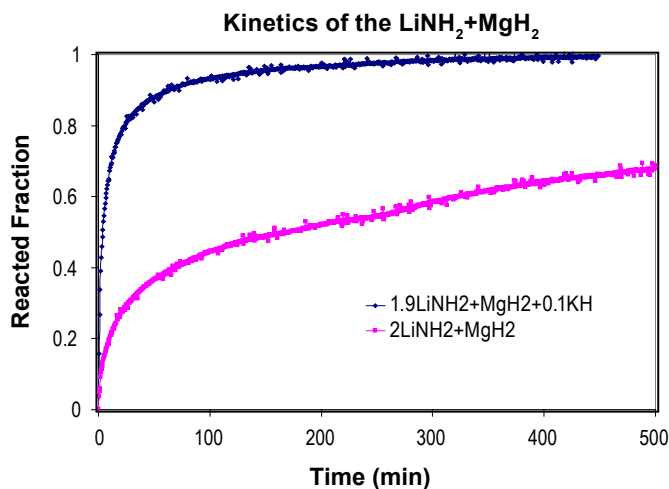ts have been performed to compare the temperature at these locations with the numerically predicted value. Three experiments in Figure 4 were done to compare the temperature in the storage tank to that predicted by a numerical model. The results for experiment agreed to within ±5 degrees. It has been determined that the heat removal rate can be increased by (i) increasing the effective thermal conductivity by mixing the metal hydride with conductivity-enhanced materials such as aluminum foam or graphite, (ii) optimizing the shape of the tank, and (iii) introducing an active cooling environment instead of relying on natural convection. All of this work is being done by our partners at the University of Delaware.

Conclusions and Future Directions

- This work has shown that several destabilized borohydride systems based on $Li(BH_4)_2/MgH_2$ can absorb hydrogen reversibly but the desorption temperatures increase and hydrogen holding capacities decrease as the relative amount of $LiBH_4$ increases. We have also determined that KH is a very effective catalyst for the desorption of hydrogen from the MgH_2-$2LiNH_2$ system.

- In the FY 2011-2012, the following work is planned:
  - Continue the desorption studies on several MgH_2/ Amide based destabilized systems using techniques such as ball milling, PCI measurements, XRD, TPD, TGA, kinetics and modeling.
  - Perform kinetics and modeling studies on the $MgH_2/LiBH_4$ systems at constant pressure driving forces in order to establish the rate-controlling process.

FIGURE 3. Kinetics of the MgH_2-$2LiNH_2$ System. Measurements were done at 210°C and the ratio of the plateau pressure to the applied hydrogen pressure was set at 10. The system containing 3.3 mol% KH catalyst reacts about 10 times faster than the un-catalyzed system. The un-catalyzed system required more than 3,000 min to reach completion.
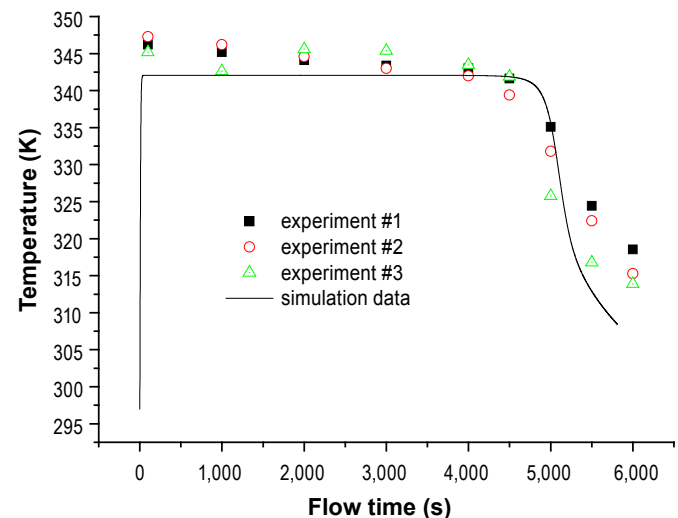

FIGURE 4. A mathematical model was used to predict the temperature at selected locations within the storage tank. Three experiments were done to compare the temperature in the storage tank to that predicted by a numerical model. The results for experiment agreed with the predicted values to within ±5 degrees.

– Use techniques such as residual gas analysis to determine if dehydrogenation is accompanied by the release of other gaseous byproducts.

– Continue with the design, fabrication and demonstration of a hydride-based hydrogen storage system that is on-going with our collaborators at the University of Delaware.

FY 2011 Publications/Presentations

1. Hongwei Yang, Samuel Orefuwa and Andrew Goudy, "Study of Mechanochemical Synthesis in the Formation of the Metal-Organic Framework $Cu_3(BTC)_2$ for Hydrogen Storage", Micropor. Mesopor. Mater., (2011) DOI: 10.1016/j.micromeso.2011.02.003.

2. T. Durojaiye, A. Ibikunle and A.J. Goudy, "Hydrogen Storage in Destabilized Borohydride Materials" Int. J. Hyd. Energy, (2010) DOI: 10.1016/j.ijhydene.2010.08.006

3. S.T. Sabitu, O. Fagbami, A.J. Goudy, "Kinetics and Modeling Study of Magnesium Hydride with Various Additives at Constant Pressure Thermodynamic Driving Forces," J. Alloys Compds, (2010), doi:10.1016/j.jallcom.2010.11.174.

4. Hongwei Yang, Adeola Ibikunle and Andrew J. Goudy, "Effects of Ti-based additives on the hydrogen storage properties of a $LiBH_4/CaH_2$ destabilized system" Advances in Materials Science and Engineering, vol. 2010, Article ID 138642, 7 pages, 2010. doi:10.1155/2010/138642.

5. A.J. Goudy; A. Ibikunle; and T. Durojaiye, "Hydrogen Storage in Destabilized Borohydride Materials", Symposium FB "Materials and Process Innovations in Hydrogen Production and Storage" of the 5th Forum on New Materials of CIMTEC 2010, June 13–18, 2010.

6. S.T. Sabitu, O. Fagbami and A.J. Goudy, "Kinetics and Modeling Study of Magnesium Hydride with Various Additives at Constant Pressure Thermodynamic Driving Forces", International Symposium on Metal-Hydrogen Systems – Fundamentals and Applications, Moscow, Russia, July 19–23, 2010.

7. A. Benson and A.J. Goudy, "Synthesis and Desorption Properties of Mixed Alkali Hexahydride Alanates", Intercollegiate Student Chemists Convention, West Chester, PA, 2011.