

Hydrogen Storage Materials for Fuel Cell Powered Vehicles

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Project ID # ST048

Overview

Timeline

- Start – July 1, 2006
- Finish – September 30, 2013
- 50% complete

Budget

- Total project funding
 - DOE \$2,417 K
 - DSU \$609 K
- Fed. funding received in FY10
 - \$0 K
- Fed. funding for FY11
 - \$0 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

Relevance

- 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.
- Improve the sorption properties of systems that have been identified as good prospects for hydrogen storage.
- Determine the cyclic stability of new materials and develop strategies for improving reversibility.
- 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 $\text{LiNH}_2/\text{MgH}_2$ system, that have greater hydrogen storage potential.
- 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. This is being done in collaboration with the University of Delaware.

Approach

- Task 1 – Design suitable methods using MgH_2 as a model system
 - Synthesis of new materials by mechanical alloying using ball milling
 - Determine thermal stability using TGA or TPD.
 - 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 using constant pressure driving forces
 - Perform modeling to gain understanding of the mechanism
- Task 4 – Study other classes of promising hydrogen storage materials
 - Focus on new classes of destabilized hydride materials such as those based on $\text{MgH}_2/\text{LiNH}_2$.

Approach/Milestones

Year	Milestone or Go/No-Go Decision
2006	Milestone: The methods and procedures to be used for testing and characterizing complex hydrides using NaAlH_4 as a model system were completed.
2007	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.
2008	Milestone: It was discovered that the $\text{CaH}_2/\text{LiBH}_4$ system could reversibly absorb and release approximately 9 weight percent hydrogen, with a desorption enthalpy of 63 kJ/mol H_2 . It was also found that certain ternary mixtures could release hydrogen at significantly lower temperatures but they were not reversible.

Approach/Milestones

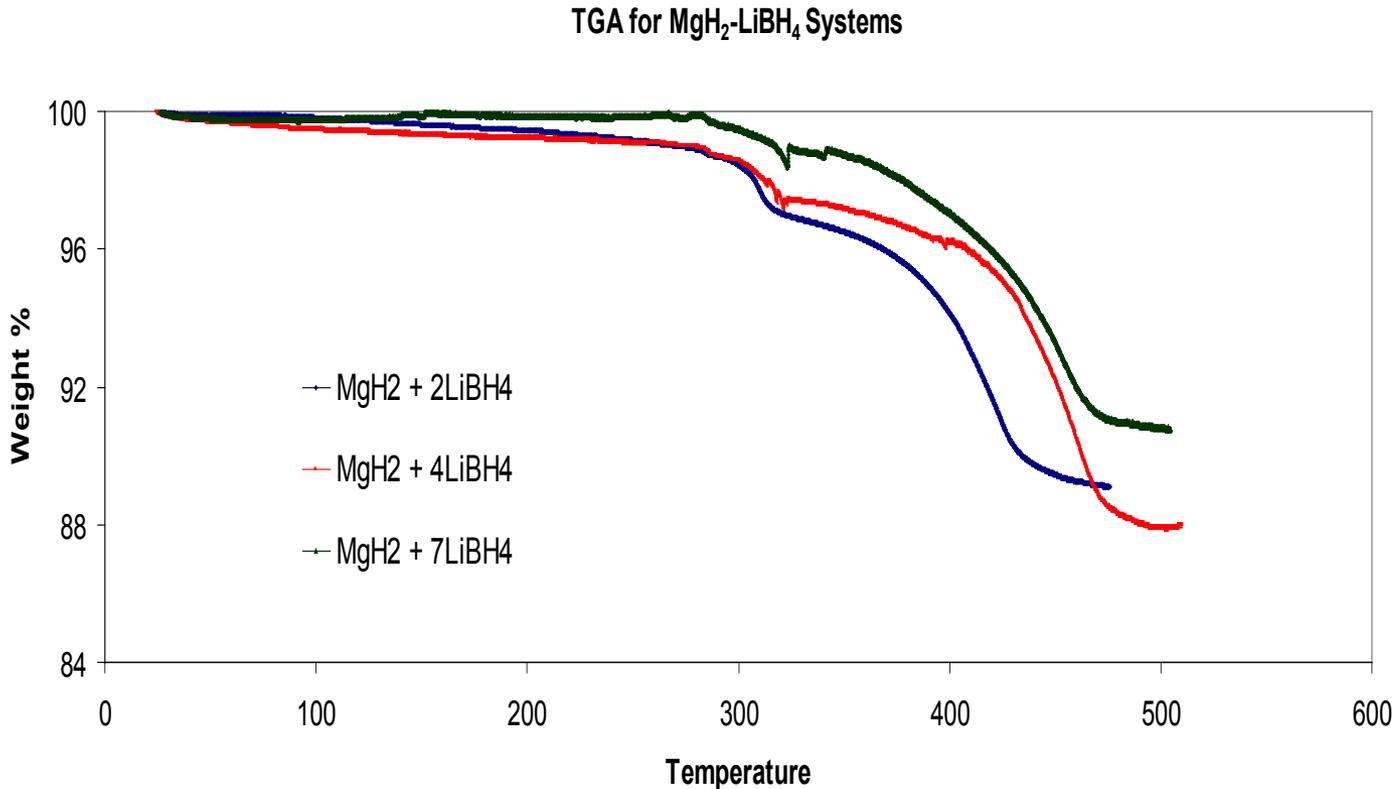
Year	Milestone or Go/No-Go Decision
2009	Go/No-Go Decision: We decided not to continue studies on ternary borohydride systems that contain amides. We will continue to focus on other borohydride systems with reaction enthalpies predicted to be less than 50 kJ/mol H ₂ .
2010	Milestone: It was discovered that some destabilized Mg(BH ₄) ₂ -based systems could absorb and release hydrogen reversibly starting at less than 200 °C. Studies on pure MgH ₂ showed that a mixture of catalysts may be the most effective way to lower temperatures and increase rates.
2011	Milestone: It was demonstrated that a KH catalyst could dramatically improve the kinetics of a MgH ₂ -LiNH ₂ system.

Technical Accomplishments/ Progress/Results

Hydrogen storage in $\text{MgH}_2/\text{LiBH}_4$ systems

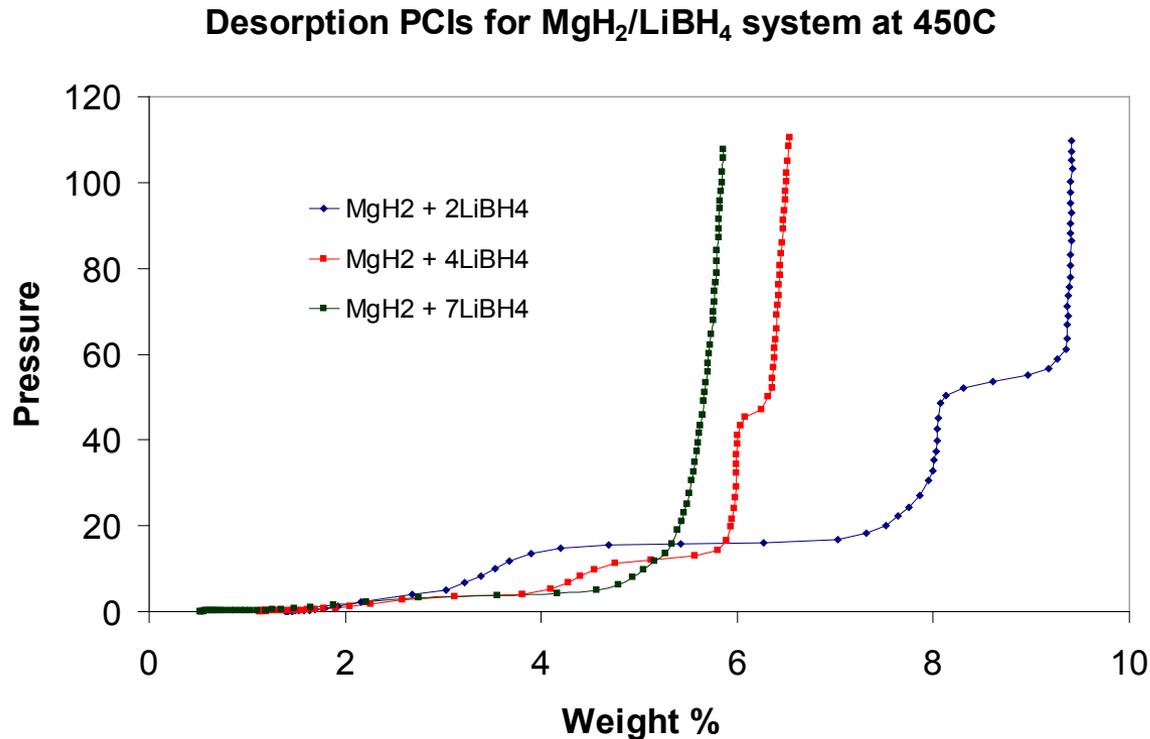
- The desorption properties for a series of $\text{MgH}_2/\text{LiBH}_4$ systems have been determined. The systems had compositions of $\text{MgH}_2\text{-}2\text{LiBH}_4$, $\text{MgH}_2\text{-}4\text{LiBH}_4$, and $\text{MgH}_2\text{-}7\text{LiBH}_4$.
- TPD results show that desorption temperatures increase with increasing amounts of LiBH_4 .
- 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 .
- Kinetics and modeling studies are presently underway.
- Results are given in the following two slides.

Thermal Gravimetric Analyses for the $\text{MgH}_2\text{-LiBH}_4$ System



- Desorption temperatures increase with increasing amounts of LiBH_4

Desorption PCIs for MgH₂/LiBH₄ System at 450 °C



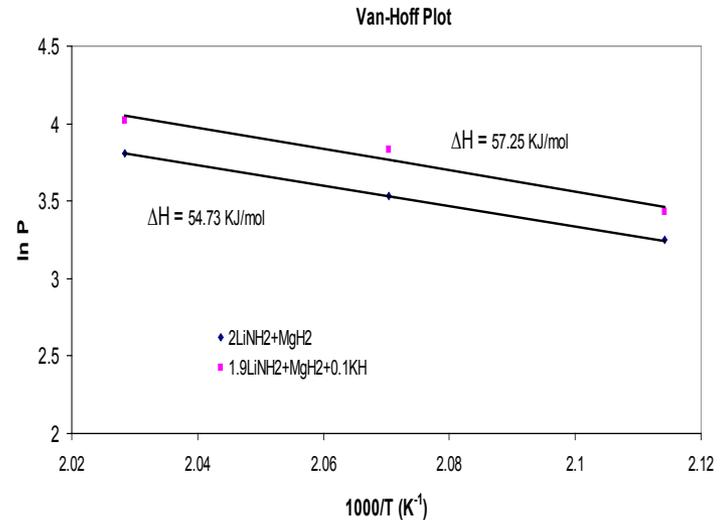
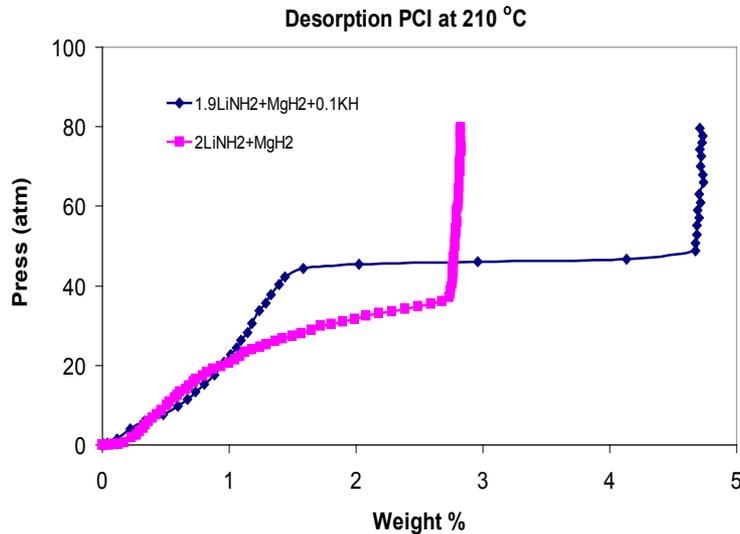
- Plateau pressures decrease with increasing amounts of LiBH₄ and the amount of hydrogen released increases with increasing amounts of MgH₂.

Technical Accomplishments/ Progress/Results

Hydrogen desorption from a $\text{MgH}_2/\text{LiNH}_2$ system

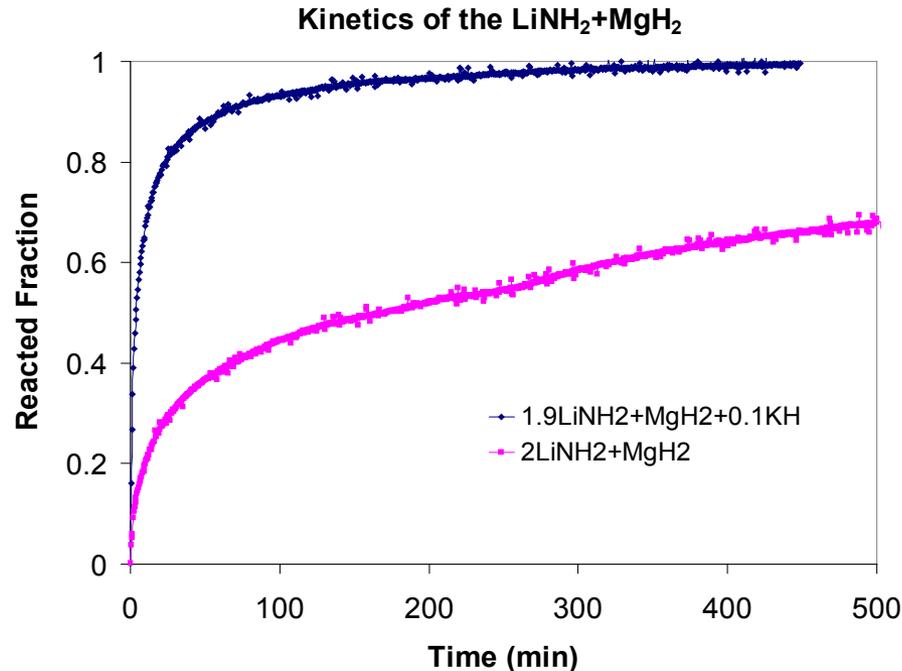
- The desorption properties of a $\text{MgH}_2/\text{LiNH}_2$ system have been determined. This is a system that has been identified by DOE as one with excellent potential for hydrogen storage. Pressure Composition Isotherms were determined, with and without a KH catalyst, at several temperatures. The 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. The catalyzed system reacted much faster than the un-catalyzed system.
- Activation energies were determined by constructing Kissinger plots. As expected, the catalyzed system had lower activation energy than the un-catalyzed one.
- Results of these studies are presented in the following three slides.

Thermodynamics of the $\text{MgH}_2\text{-}2\text{LiNH}_2$ System



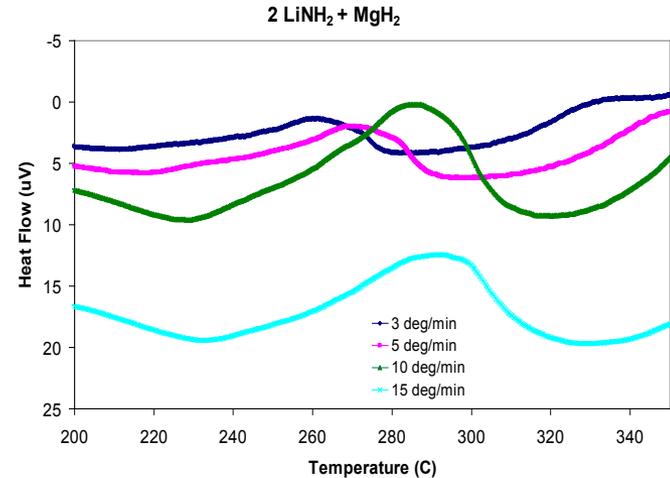
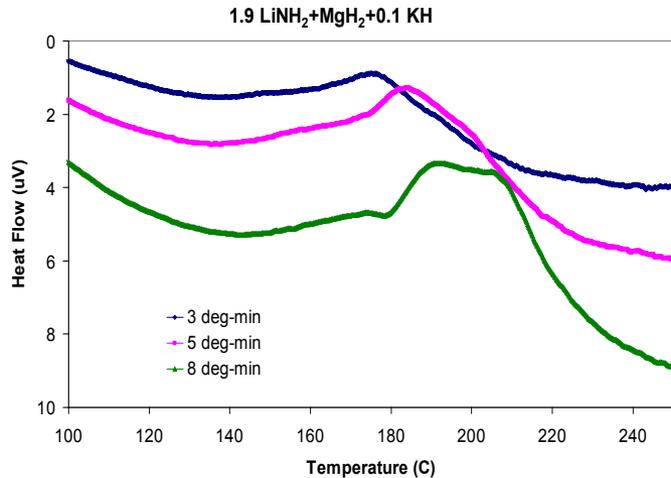
- PCIs show that KH addition causes the plateau pressure to increase and the plateau becomes more well defined. Van't Hoff plots were used to determine the enthalpies of formation.

Kinetics of the $\text{MgH}_2\text{-}2\text{LiNH}_2$ System

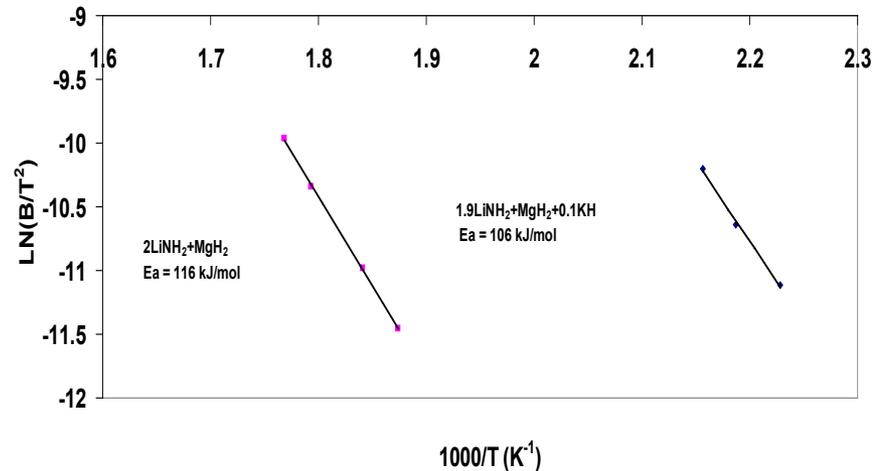


- Measurements were done at 210 °C and the ratio of the plateau pressure to the applied hydrogen pressure was set at 10. The system containing 3.3 mol% KH catalyst reacts about 10 times faster than the un-catalyzed system. The un-catalyzed system required more than 3000 min to reach completion.

DTA and Kissinger Plots for Some $\text{MgH}_2\text{-}2\text{LiNH}_2$ Systems



DTA curves show that the desorption temperatures increase with increasing scan rates. The system catalyzed with KH has a lower activation energy than the un-catalyzed system

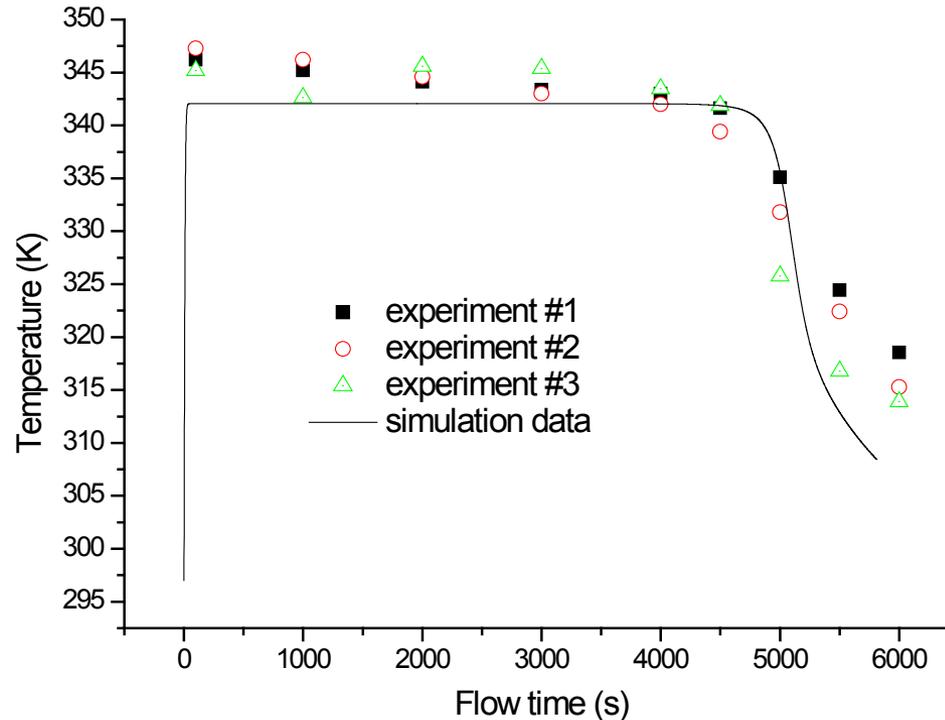


Technical Accomplishments/ Progress/Results

Design, Fabrication and Demonstration of a Hydride-Based Hydrogen Storage System for Fuel Cell Applications

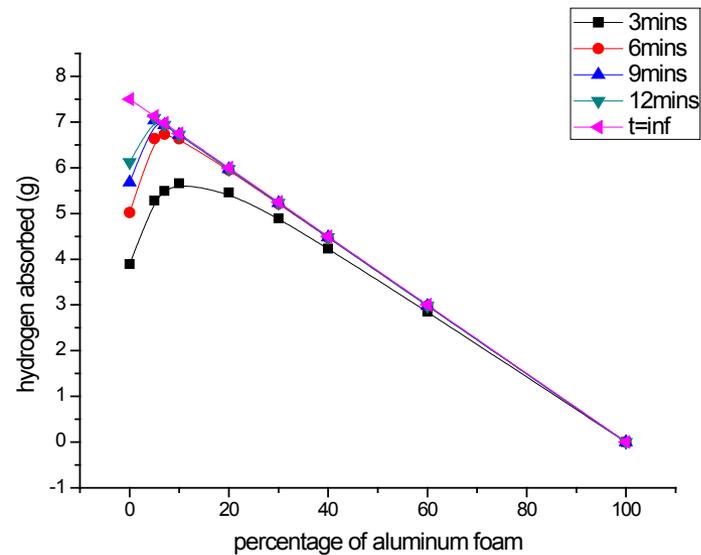
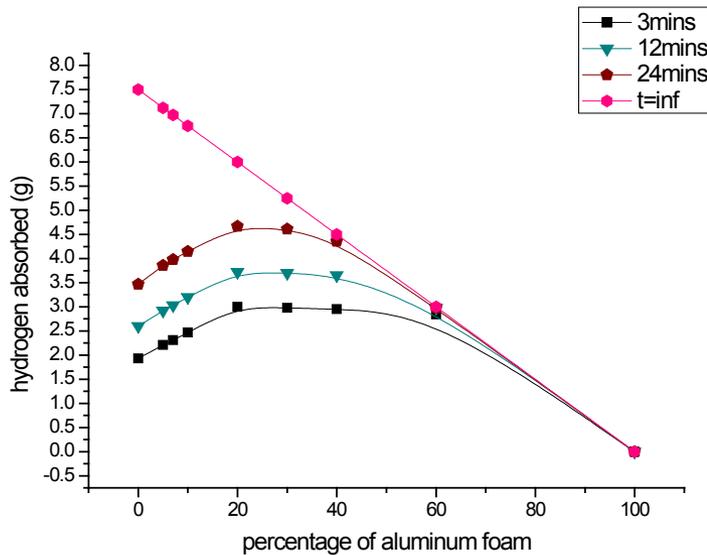
- The overall objective is to improve the rate at which the hydrogen gas can be charged into a hydride-based hydrogen storage tank, and to improve the hydrogen storage density.
- The heat removal rate can be increased by (i) increasing the effective thermal conductivity by mixing the metal hydride with 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.
- A study was done to explore quantitatively the influence of these parameters on hydrogen storage efficiency.
- A mathematical model was used to predict the temperature at selected locations within the storage tank. A series of experiments was performed to compare the temperature at these locations with the numerically predicted value. All of this work was done by our partners at the University of Delaware.
- Results are shown in the following two slides.

Model Validation



- Three experiments 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.

Effect of Al foam on hydrogen absorption



- The first figure shows the variation of hydrogen absorbed with percentage of Al foam at different filling times under natural convection ($h=25 \text{ W}/(\text{m}^2\text{-K})$) conditions. The second figure shows the variation of hydrogen absorbed with percentage of Al foam at different filling times under forced convection cooling conditions ($h=2500 \text{ W}/(\text{m}^2\text{-K})$).

Collaborations

- Collaborators
 - Theoreticians Karl Johnson and David Scholl, from the University of Pittsburgh and Georgia Tech, respectively have been very useful in helping us choose what destabilized systems to focus on.
 - The University of Delaware and Air Liquide: Suresh Advani's group is working with us in an effort to determine the feasibility of testing some hydrogen storage materials in an actual hydrogen powered vehicle.
 - At Delaware State University, Bryan Wakefield (an organic chemist) is helping to synthesize some of the hydrogen storage materials of interest.

Future Work

- In the FY 11-12, 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 $\text{MgH}_2/\text{LiBH}_4$ systems at constant pressure driving forces in order to establish the rate-controlling process.
 - Use techniques such as RGA 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

Project Summary

- Relevance:** The materials under consideration in this study have the potential to meet the on board hydrogen storage goals established by the DOE. Issues such as reaction temperatures, reaction rates and reversibility are being addressed since they are important in practical uses.
- Approach:** Destabilized $\text{MgH}_2/\text{LiNH}_2$ and $\text{MgH}_2/\text{LiBH}_4$ systems were prepared by mechanical alloying and characterized by XRD, TGA, TPD, PCI and kinetics analyses in order to compare their thermodynamics and kinetics and determine their suitability for hydrogen storage.
- Technical Accomplishments:** We have demonstrated that a KH catalyst can dramatically improve the desorption kinetics of a destabilized $\text{MgH}_2/\text{LiNH}_2$ based system. We have also demonstrated the composition of a $\text{MgH}_2/\text{LiBH}_4$ system has a major impact on desorption properties.
- Proposed Future Research:** Continue the desorption studies on several $\text{MgH}_2/\text{Amide}$ and $\text{MgH}_2/\text{Borohydride}$ based destabilized systems. Continue with the design, fabrication and demonstration of a Hydride-Based Hydrogen Storage System.