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Hydrogen Storage Materials for Fuel Cell Powered Vehicles

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Project ID # ST048

Overview

Timeline

- Start – July 1, 2006
  - Renewed – June 1, 2009
- Finish – May 30, 2013
- 75% complete

Budget

- Total project funding
  - DOE $2,417 K
  - DSU $609 K
- Funding for FY 11 & FY12
  - $0 K
- Congressionally Directed Project, total project funds appropriated in FY06 and FY09.

Barriers

- Barriers addressed
  - Weight and Volume
  - Durability
  - Refueling Time
  - Hydrogen Capacity and Reversibility

Partners

- Interactions/ collaborations
  - Cal Tech
  - Georgia Tech
  - University of Pittsburgh
  - University of Delaware

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 $LiNH_2/MgH_2$ 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.

Destabilized Materials Involving $Mg(BH_4)_2$, $Ca(BH_4)_2$ $LiBH_4$ and $LiNH_2$

$Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2$

$3Ca(BH_4)_2 \rightarrow 2CaH_2 + CaB_6 + 10H_2$

$5Mg(BH_4)_2 + Ca(BH_4)_2 \rightarrow CaB_{12}H_{12} + 5MgH_2 + 13\ H_2$

$3Mg(BH_4)_2 + CaH_2 + 3NaH \rightarrow 3NaMgH_3 + CaB_6 + 10H_2$

$3Mg(BH_4)_2 + CaH_2 \rightarrow 3MgH_2 + CaB_6 + 10H_2$

$6\ LiBH_4 + CaH_2 \rightarrow 6\ LiH + CaB_6 + 10\ H_2$

$2\ LiBH_4 + MgH_2 \rightarrow 2\ LiH + MgB_2 + 4\ H_2$

$2LiNH_2 + MgH_2 \rightarrow MgLi_2(NH)_2 + 2H_2$

Approach

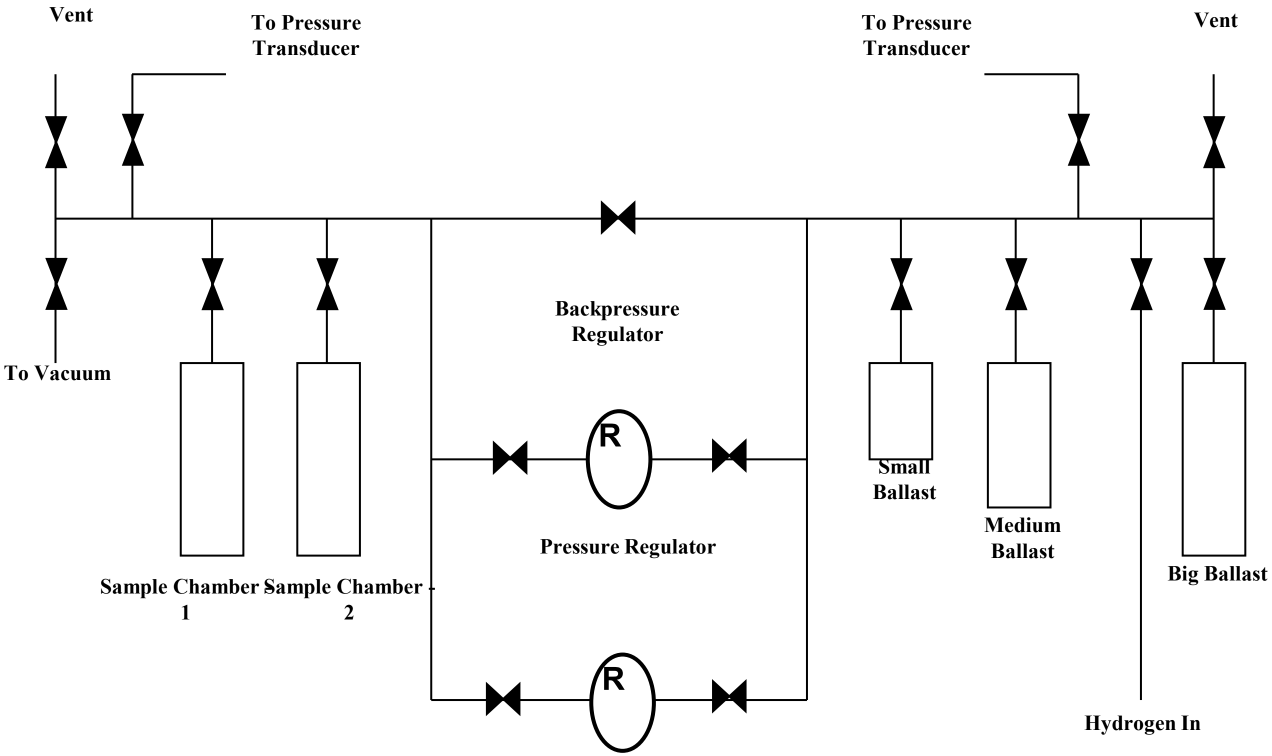
- Task 1 – Design suitable methods using MgH_2 as a model system
  - Synthesis of new materials by mechanical alloying using ball milling
  - Determine thermal stability using TGA or TPD.
  - Use XRD to determine phase purity and crystal structure
  - Use PCI analyses to determine thermodynamic stability

- 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 $MgH_2/LiNH_2$.

Schematic diagram of the apparatus used for performing kinetics measurements



Experimental Technique for Establishing Constant Pressure Thermodynamic Driving Forces

Use the same *pressure ratio*
for all samples

$N = P_m/P_{appl}$

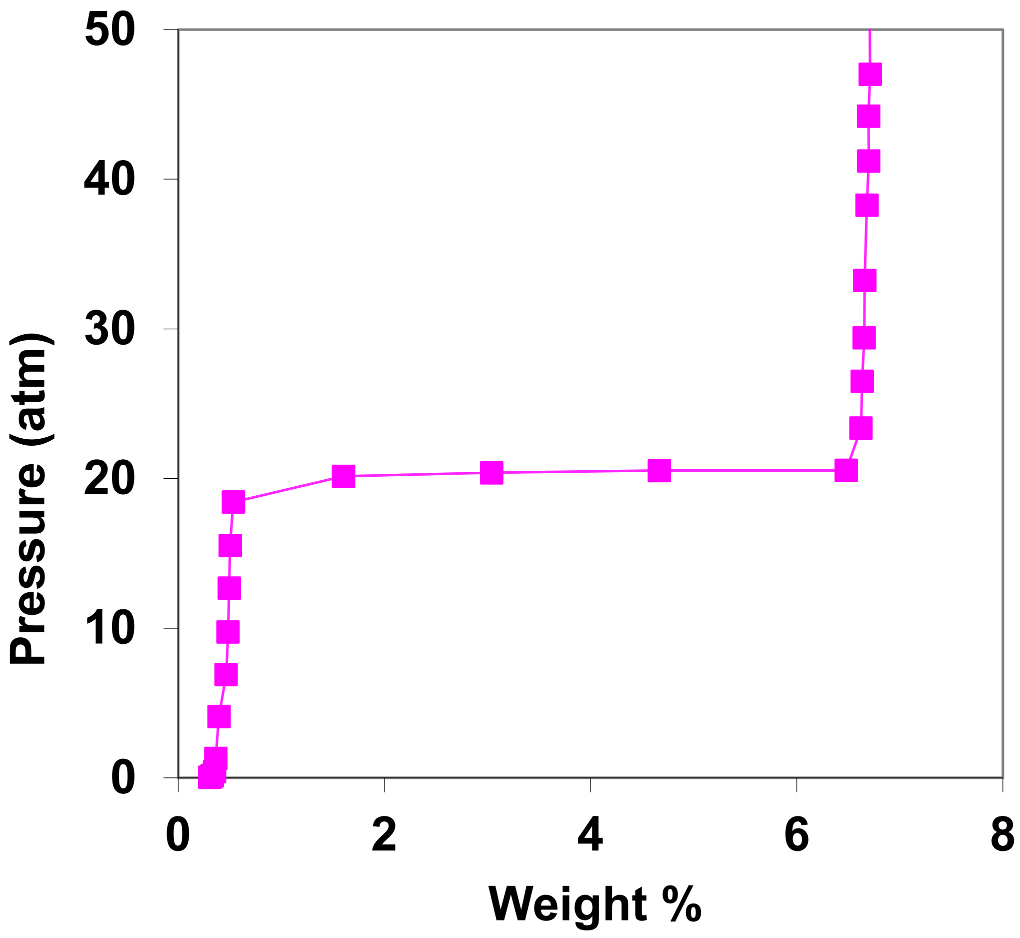
If we want N = 5;

For $P_m = 20$ and $P_{appl} = 4$
$N = 20/4 = 5$

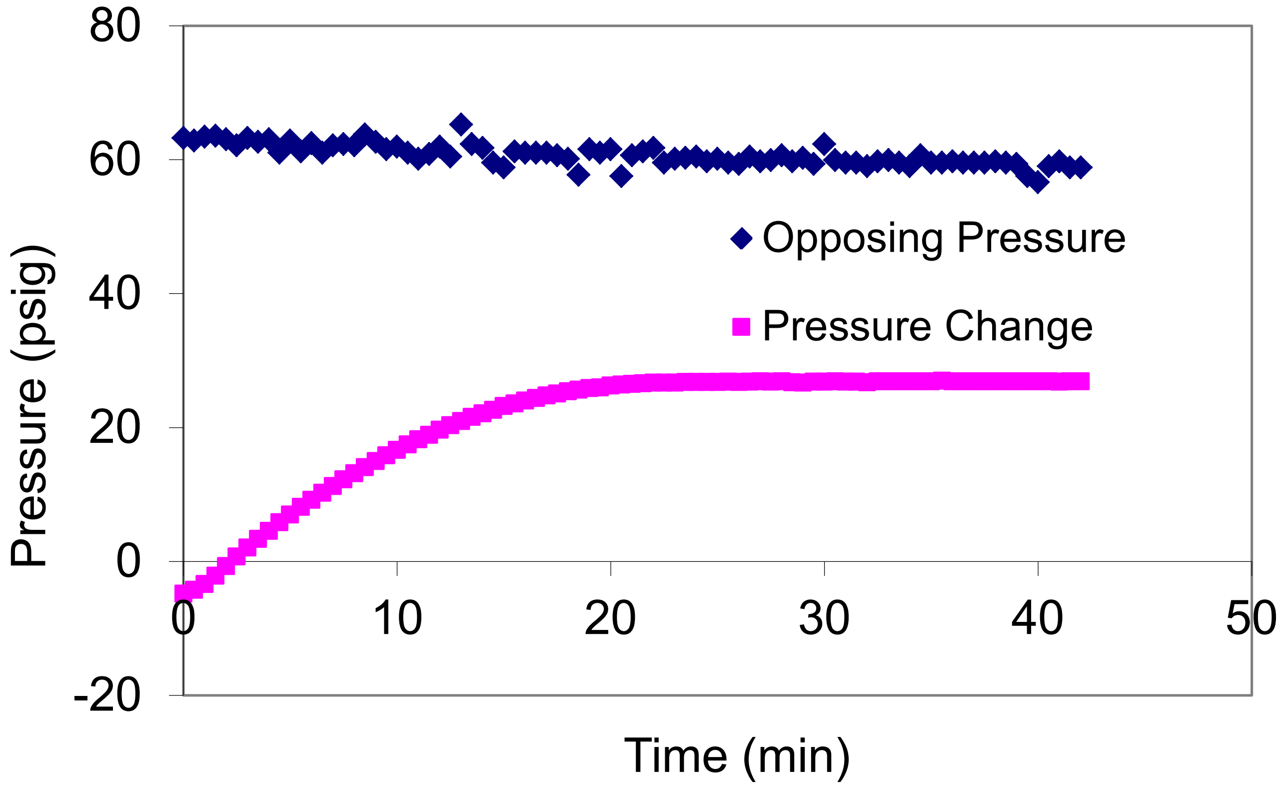
For Pm = 30 and $P_{appl} = 6$
$N = 30/6 = 5$

$\Delta G = RT\ Ln(P_m/P_{appl})$

Desorption PCI for MgH_2+TiH_2 at 400 °C

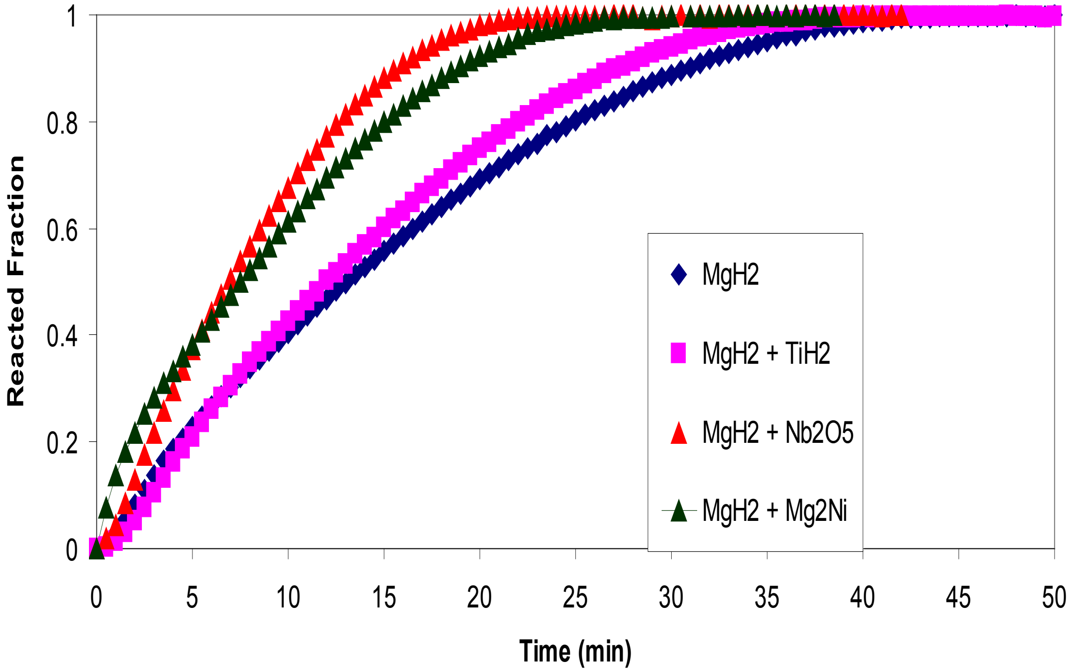


Transducer Plot



Kinetic data is obtained from the rate of pressure change in the reservoir. The opposing pressure applied to the sample is constant.

Kinetics Plots for Some MgH_2-Based Systems



- The curves show that pure MgH_2 releases hydrogen the slowest whereas the MgH_2 + 10 mol% Nb_2O_5 have the fastest rates at 400 °C and N = 5.

Modeling curves for pure MgH_2

Phase boundary controlled

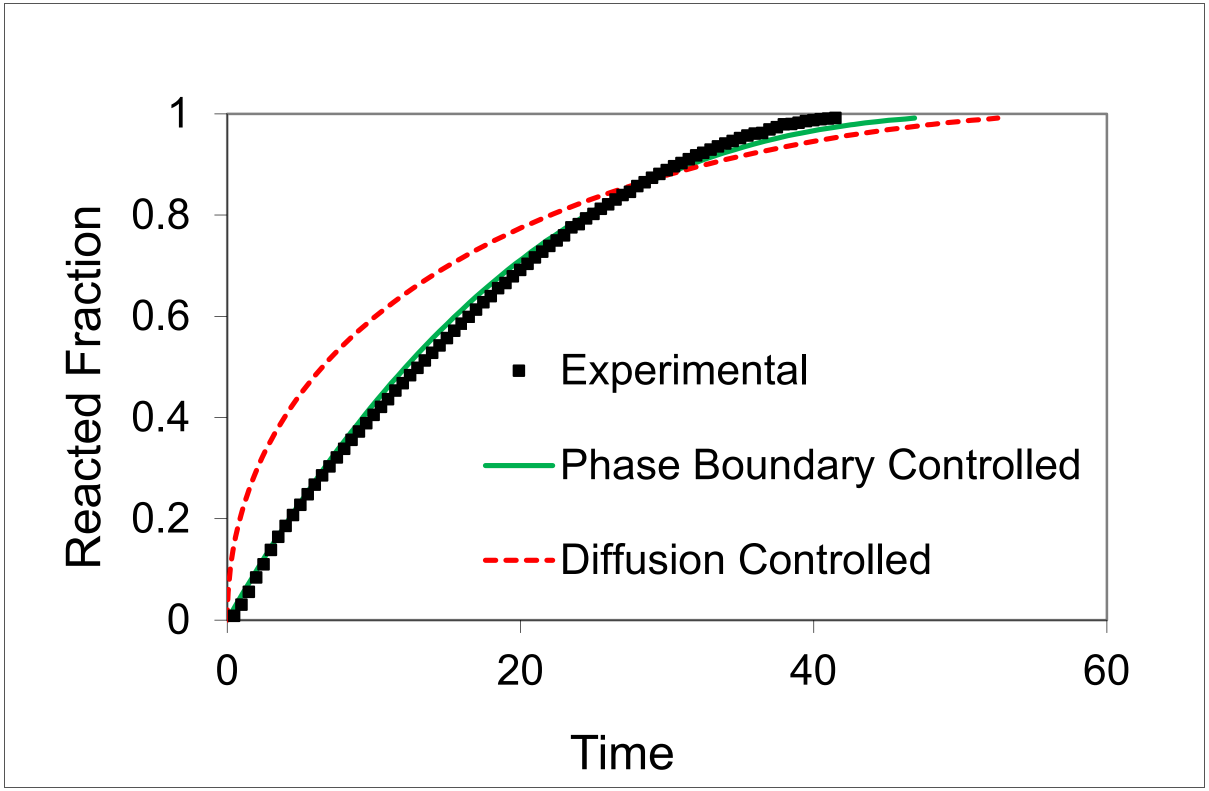
$$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$$

$$\tau = \frac{\rho_B R}{b k_s C_{Ag}}$$

Diffusion controlled

$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$$

$$\tau = \frac{\rho_B R^2}{6 b D_e C_{Ag}}$$



- The phase boundary model fits the experimental data better than the diffusion controlled model

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 $CaH_2/LiBH_4$ 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

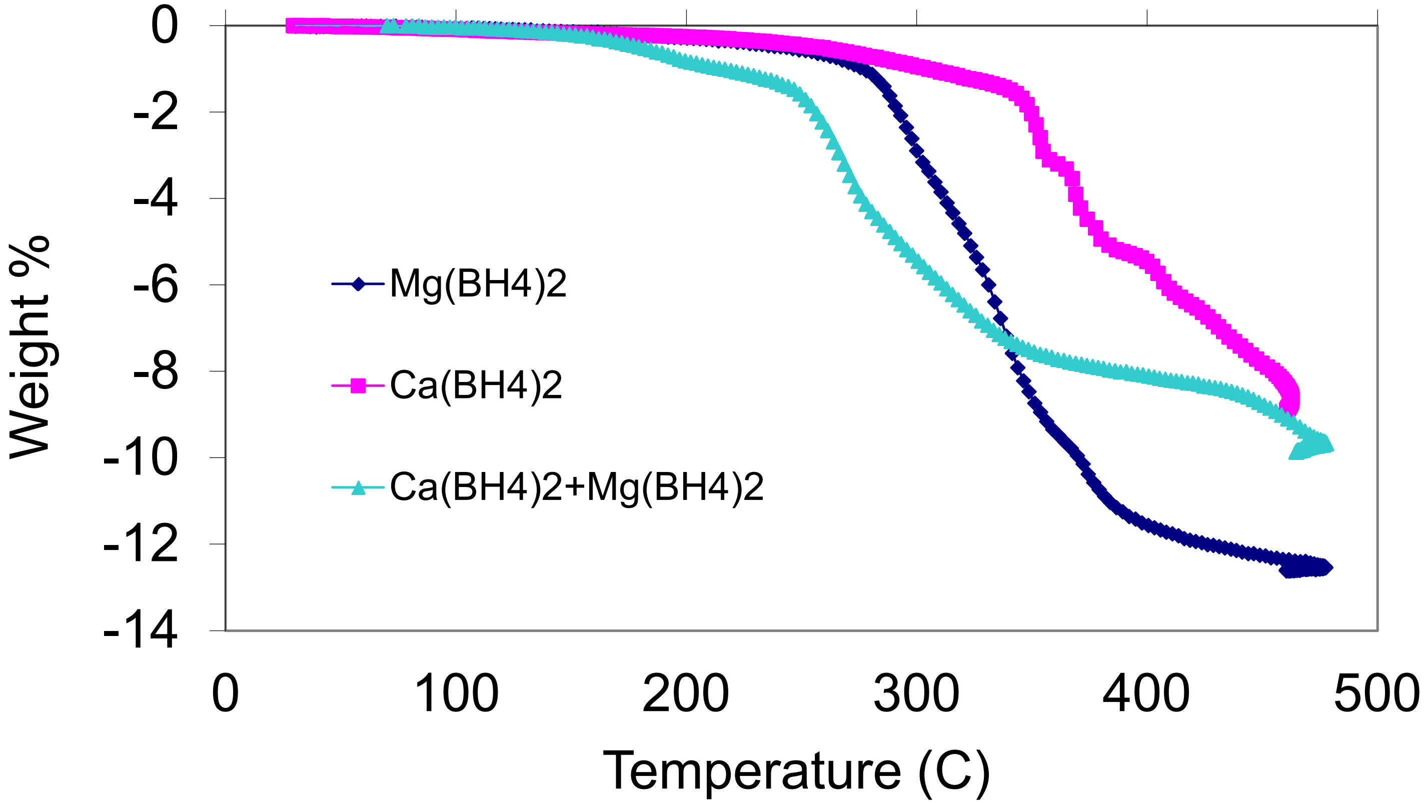
Year	Milestone or Go/No-Go Decision
2009	Go/No-Go Decision: We decided not to continue studies on ternary borohydride systems that contain amides. We will continue to focus on other borohydride systems with reaction enthalpies predicted to be less than 50 kJ/mol H_2.
2010	Milestone: It was discovered that some destabilized $Mg(BH_4)_2$-based systems could absorb and release hydrogen reversibly starting at less than 200 ^oC. 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.
2012	Milestone: It was demonstrated that a NbF_5 catalyst could dramatically improve the kinetics of a MgH_2-$LiBH_4$ system.

Technical Accomplishments/ Progress/Results

Hydrogen storage in $Mg(BH_4)_2/Ca(BH_4)_2$ systems

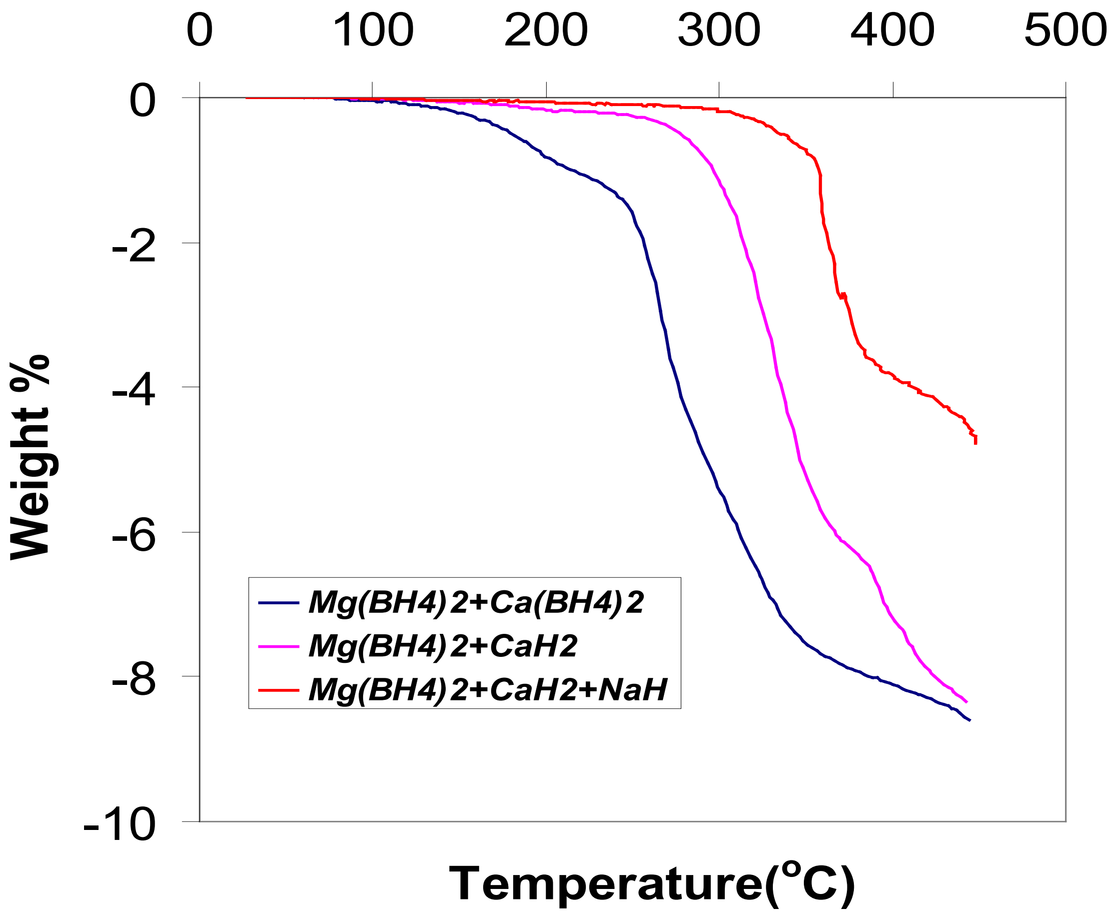
- Have compared the dehydriding kinetics of several borohydride systems at constant pressure driving forces and found that a mixture of $Mg(BH_4)_2/Ca(BH_4)_2$ releases hydrogen faster than either individual borohydride.
- Several borohydride systems have been kinetically modeled and the rate controlling process has been identified.
- Results are given in the following two slides.

TPD profiles for $Mg(BH_4)_2$, $Ca(BH_4)_2$ and a mixture of the two compounds

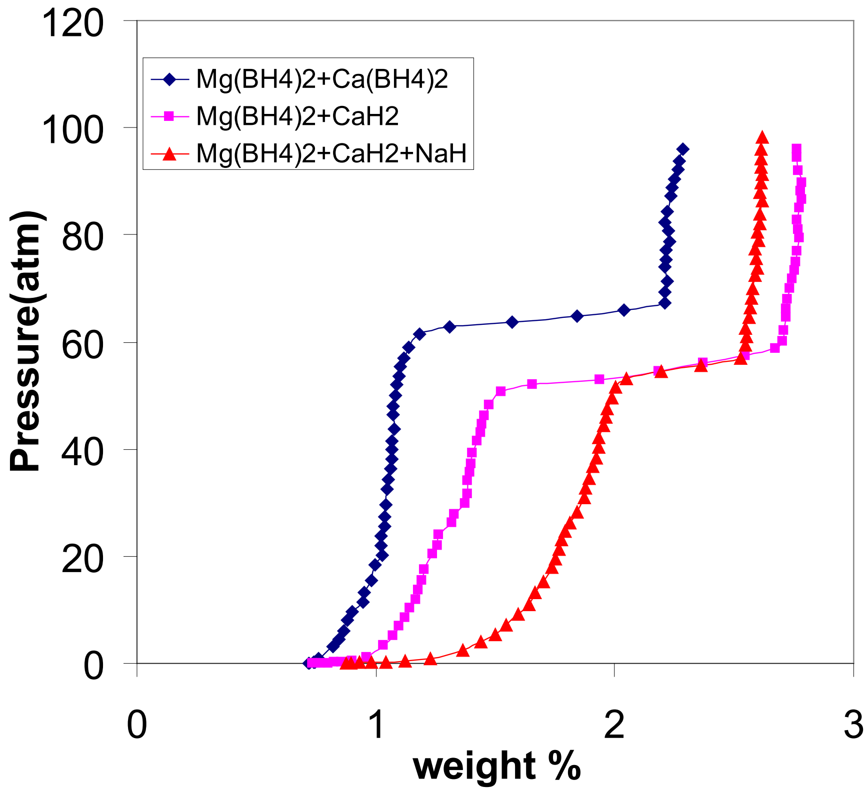


- A mixture of $Mg(BH_4)_2$/$Ca(BH_4)_2$ releases hydrogen at a lower temperature than either individual borohydride

TPD Profiles of some $Mg(BH_4)_2$ Destabilized Materials

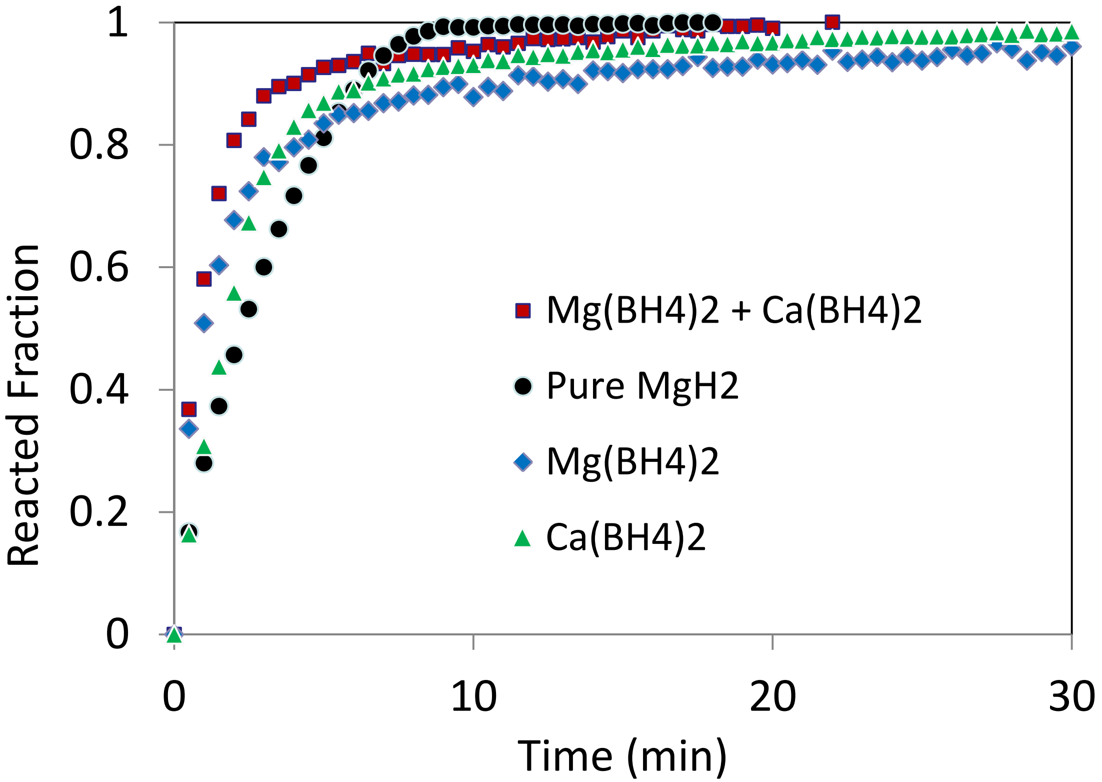


Desorption Isotherms for some $Mg(BH_4)_2$ based system



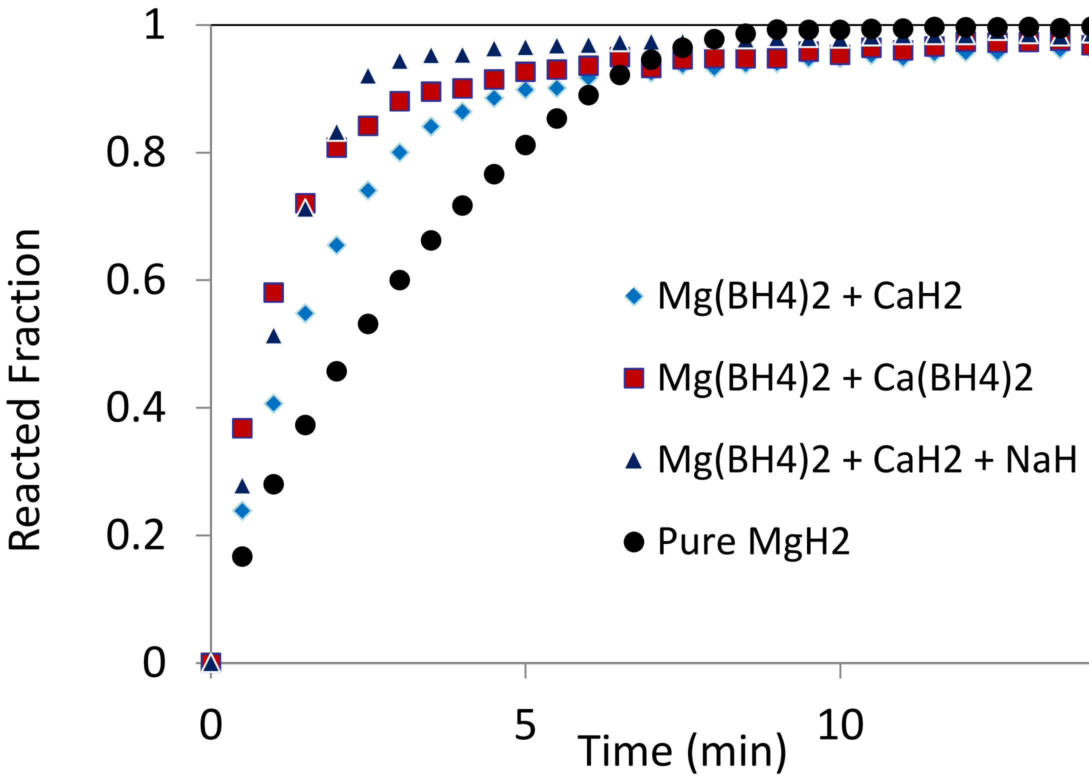
- The isotherms were done at 450 °C. The van't Hoff isochores were obtained from isotherms done at 350, 400, and 450 °C

Kinetics of $Ca(BH_4)_2$, $Mg(BH_4)_2$ and the Mixture



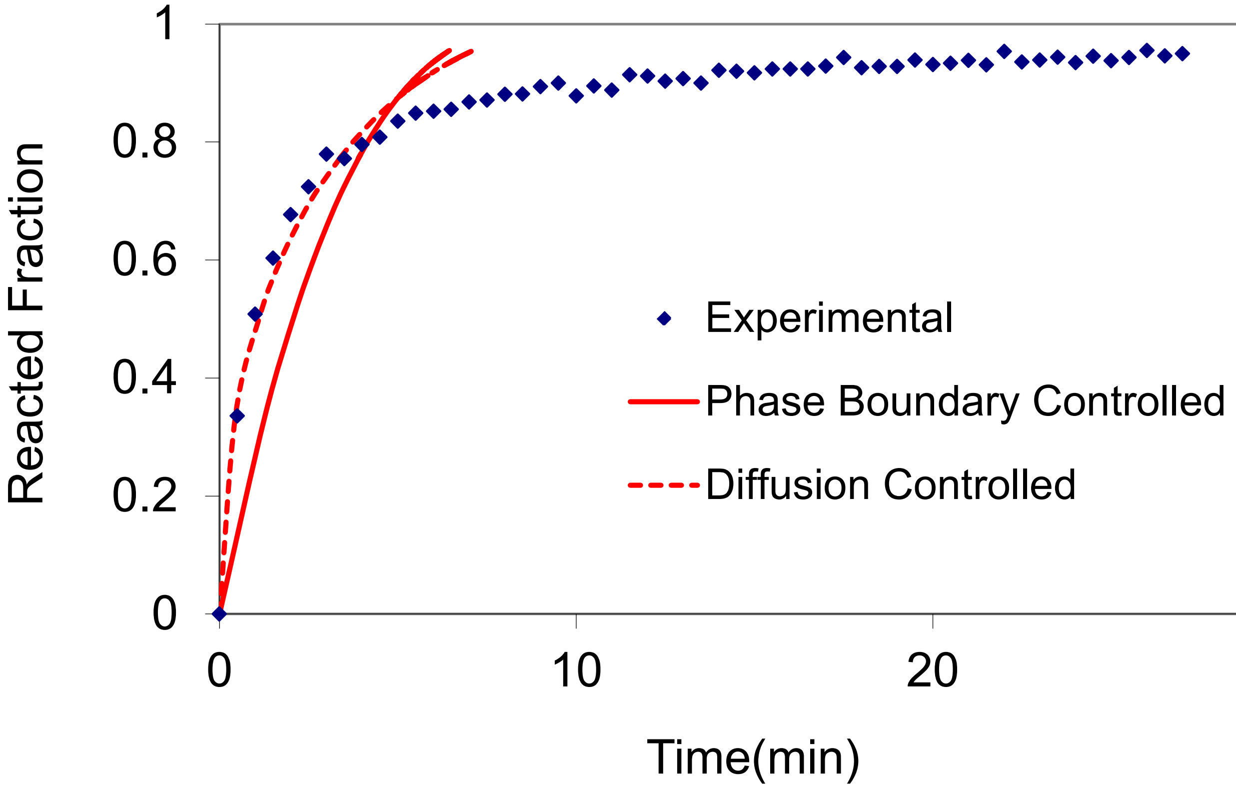
- Desorption kinetics at 450 °C and N = 10. The mixture reacts fastest.

Kinetics of Destabilized $Mg(BH_4)_2$



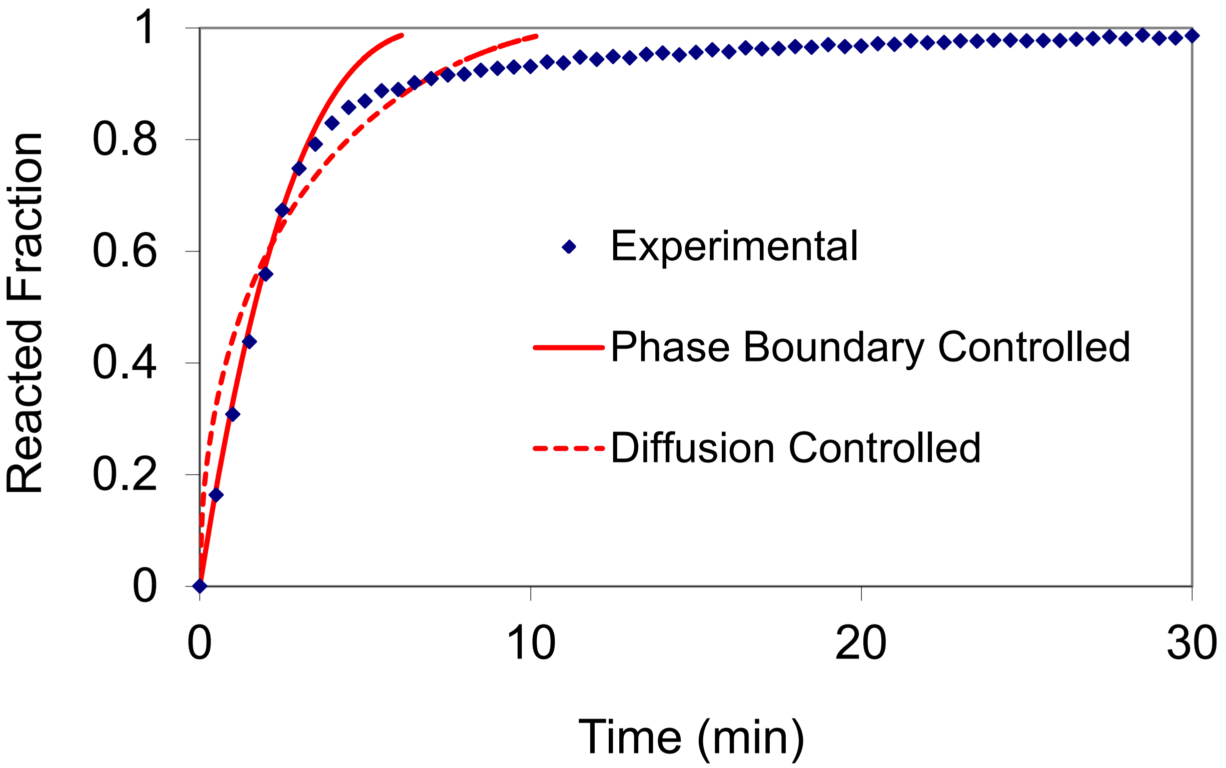
- Desorption kinetics at 450 ^{o}C and N = 10. All materials react faster than MgH_2

Modeling of $Mg(BH_4)_2$



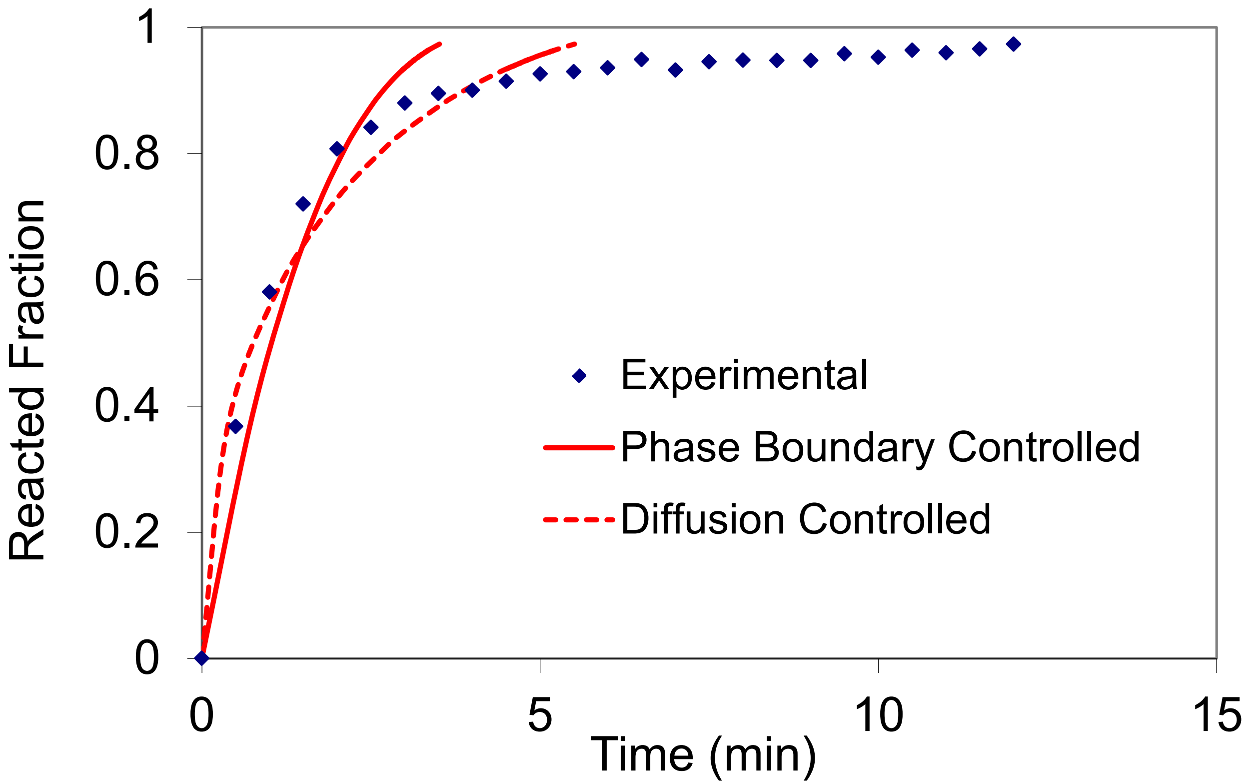
- Diffusion controls the reaction during the first 80%.

Modeling of $Ca(BH_4)_2$



- Reaction at the phase boundary controls the rate during the first 80%.

Modeling of $Mg(BH_4)_2$+$Ca(BH_4)_2$



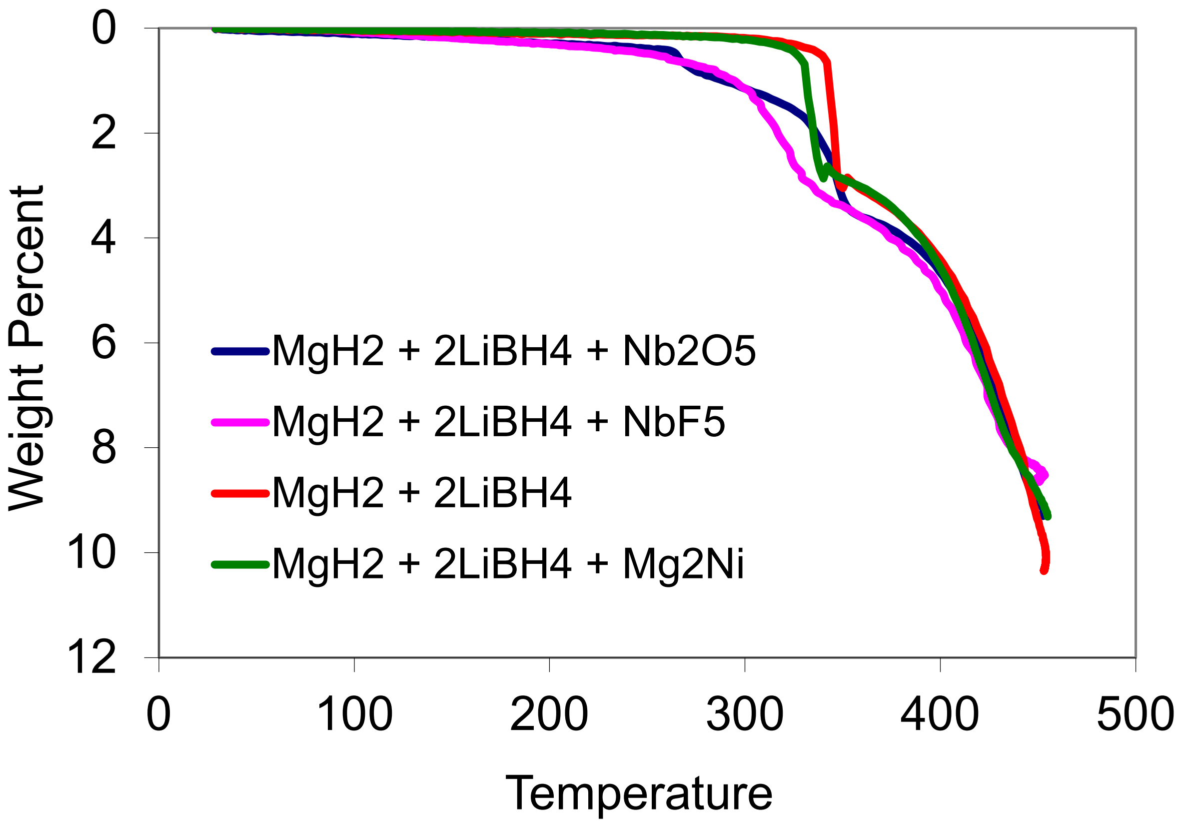
- Neither model fits the experimental data. The reaction may be under the mixed control of both processes.

Technical Accomplishments/ Progress/Results

Hydrogen desorption from a $MgH_2/LiBH_4$ system

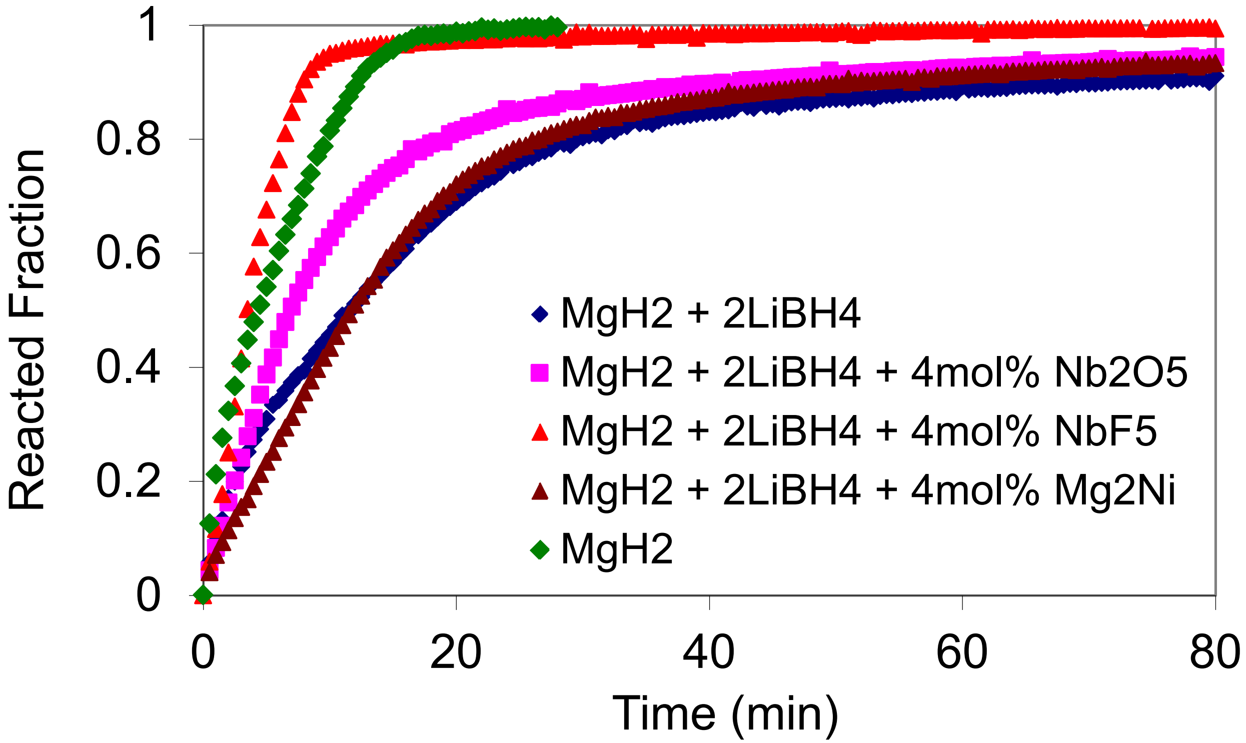
- The desorption properties of a $MgH_2/LiBH_4$ system have been determined.
- TPD results show that NbF_5 and Nb_2O_5 catalysts are more effective in lowering desorption temperatures than $MgNi_2$.
- Kinetics measurements show that NbF_5 is vastly superior to the other catalysts in improving reaction rates and that desorption is faster than that from MgH_2.
- Results of these studies are presented in the following two slides.

Combined TPD for $MgH_2/2LiBH_4$ systems



- The onset temperatures for the NbF_5 and Nb_2O_5 catalyzed $MgH_2/2LiBH_4$ systems are lowest.

Combined desorption kinetics for MgH2/LiBH4



- Kinetics measurements done at N = 3 and 450 °C show that NbF_5 is vastly superior to the other catalysts in improving reaction rates

Technical Accomplishments/ Progress/Results

Hydrogen desorption from a MgH_2/$LiNH_2$ system

- Mixtures with initial molar compositions of ($LiNH_2$ + MgH_2) and ($2LiNH_2$ + MgH_2) were studied with and without the presence of 3.3 mol% potassium hydride dopant. TPD analyses showed that the potassium hydride doped samples had lower onset temperatures than their corresponding pristine samples.
- The dehydrogenation kinetics of the doped and pristine mixtures was compared at 210^{o}C. In each case a constant pressure thermodynamic driving force was applied in which the ratio of the plateau pressure to the applied hydrogen pressure was set at 10. Under these conditions, the ($LiNH_2$ + MgH_2) mixture desorbed hydrogen about 4 times faster than the ($2LiNH_2$ + MgH_2) mixture.
- The addition of potassium hydride dopant was found to have a 25-fold increase on the desorption rates of the ($2LiNH_2$ + MgH_2) mixture, however it had almost no effect on the desorption rates of the ($LiNH_2$ + MgH_2) mixture. The catalyzed ($2LiNH_2$ + MgH_2) mixture reacted faster than the catalyzed ($LiNH_2$ + MgH_2) mixture.
- Results of these studies are presented in the following two slides.

The $LiNH_2/MgH_2$ System

The Effect of KH Catalyst

Desorption reaction in the $2LiNH_2/MgH_2$ system:

$MgH_2 + 2LiNH_2 \rightarrow Mg(NH)_2 + 2LiH$

$Mg(NH)_2 + 2LiH \leftrightarrow MgLi_2(NH)_2 + 2H_2$

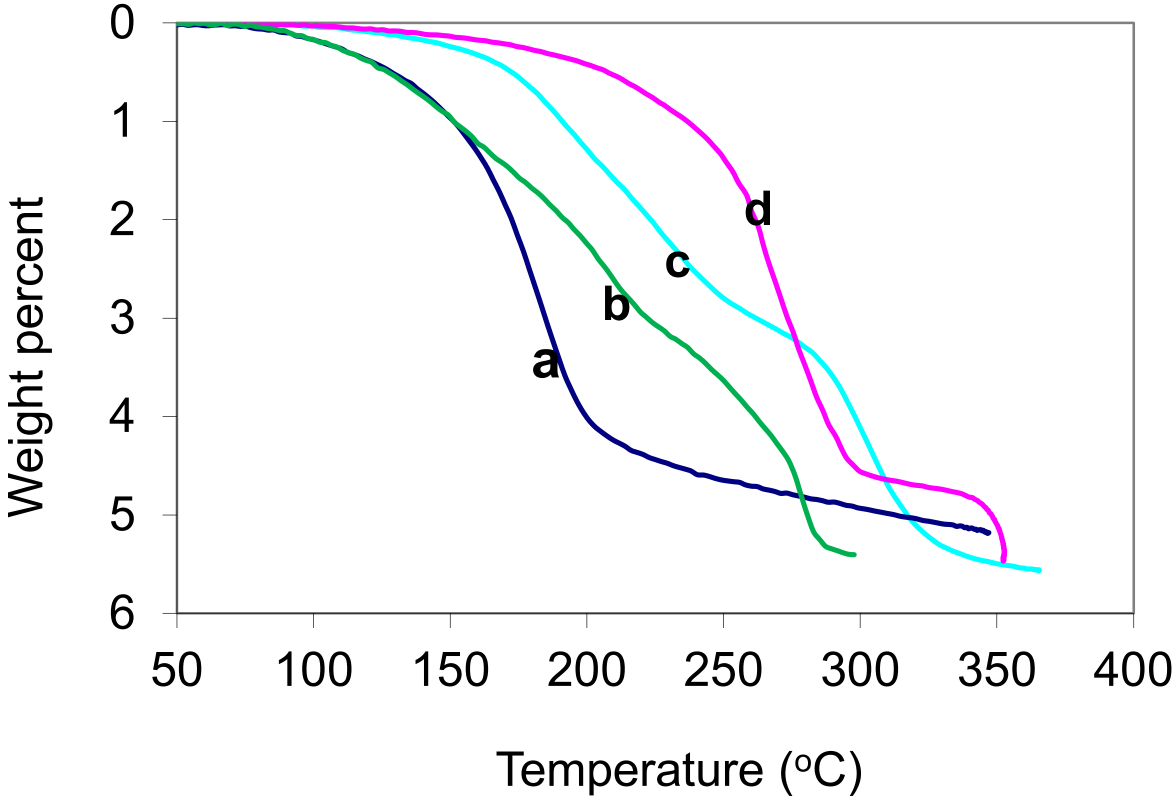
Desorption reactions in the $LiNH_2/MgH_2$ system:

$LiNH_2 + MgH_2 \rightarrow LiH + \frac{1}{2}Mg(NH_2)_2 + \frac{1}{2}MgH_2$

$LiH + \frac{1}{2}Mg(NH_2)_2 + \frac{1}{2}MgH_2 \leftrightarrow \frac{1}{2}Li_2Mg(NH)_2 + \frac{1}{2}MgH_2 + H_2$

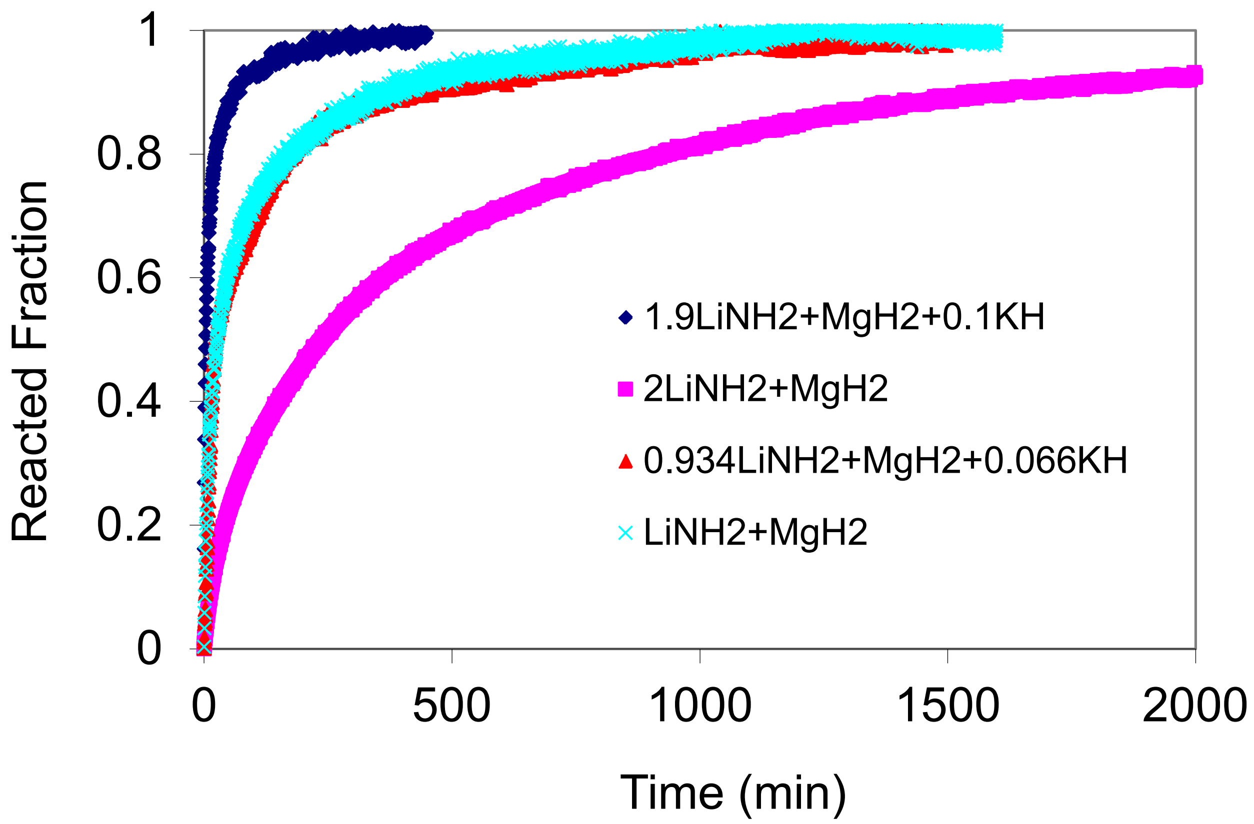
$\frac{1}{2}Li_2Mg(NH)_2 + \frac{1}{2}MgH_2 \leftrightarrow LiMgN + H_2$

Hydrogen Storage in the $MgH_2/LiNH_2$ System



- TPD curves for (a) $1.9LiNH_2+MgH_2+0.1KH$, (b) 0.934 $LiNH_2+MgH_2+0.066$ KH, (c) $LiNH_2+MgH_2$, and (d) $2LiNH_2+MgH_2$ samples

Kinetics of the $LiNH_2/MgH_2$ System



- Desorption kinetics were done at 210 °C and N = 10. There is a dramatic improvement in the desorption rates in the $2LiNH_2 + MgH_2$ system but virtually no improvement in the $LiNH_2 + MgH_2$ system.

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.
  - Son-Jong Hwang, at Cal Tech, is performing solid state NMR measurements on several borohydride materials to determine the composition of the products and the nature of any reaction intermediates.
  - The University of Delaware: Suresh Advani’s and Ajay Prasad are working with us in an effort to determine the feasibility of testing some hydrogen storage materials in an actual hydrogen storage containment system.

Future Work

- In the FY 12-13, the following work is planned:
  - Continue to perform absorption and desorption kinetics and modeling studies on several catalyzed MgH_2/Amide and MgH_2/$LiBH_4$ based destabilized systems using constant pressure driving forces.
  - Continue the cycling studies on amide and borohydride reactions.
  - Use techniques such as RGA to determine if dehydrogenation is accompanied by the release of other gaseous byproducts such as ammonia and diborane.
  - Continue to collaborate with Sonjong Hwang at Cal Tech in solid state NMR analyses of reaction intermediates in hydriding/de-hydriding reactions.
  - 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 $Mg(BH_4)_2$/$Ca(BH_4)_2$, MgH_2/$LiNH_2$ and MgH_2/$LiBH_4$ 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 NbF_5 catalyst can dramatically improve the desorption kinetics of a destabilized MgH_2/$LiBH_4$ based system. We have also demonstrated that the rate-controlling process for hydrogen desorption from $Mg(BH_4)_2$ differs from that for $Ca(BH_4)_2$.
Proposed Future Research:	Perform absorption/desorption kinetics and modeling studies on several MgH_2/Amide and MgH_2/Borohydride based destabilized systems. Continue with the design, fabrication and demonstration of a Hydride-Based Hydrogen Storage System.