

IV.A.1d Development of Metal Hydrides at Sandia National Laboratories

Lennie Klebanoff (Primary Contact), Jay Keller
Sandia National Laboratories (SNL)
7011 East Ave., MS 9161
Livermore, CA 94551
Phone: (925) 294-3471
E-mail: lekleba@sandia.gov

DOE Technology Development Manager:
Ned Stetson

Phone: (202) 586-9995
E-mail: Ned.Stetson@ee.doe.gov

DOE Project Officer: Paul Bakke

Phone: (303)275-4916
E-mail: Paul.Bakke@go.doe.gov

Subcontractor:

University of Missouri, St. Louis, St. Louis, MO

Project Start Date: January 2005

Project End Date: October 2010

Objectives

- Discover and develop new materials with potential to meet the DOE 2010 targets for system weight percent and charge/discharge rates.
- Theoretically predict and synthesize new materials that release hydrogen with favorable thermodynamics.
- Screen catalysts and additives for their efficacy in improving the kinetic performance of metal hydrides.
- Provide theoretical understanding on metal hydride kinetic and regeneration problems.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charge/Discharging Rates
- (J) Thermal Management

Technical Targets

Work is progressing on improving the reversibility of metal hydrides, predicting and synthesizing new materials with high hydrogen capacity and promising thermodynamics and kinetics properties, and understanding metal hydride regeneration issues. The targets being addressed include:

- System Gravimetric Capacity: 0.06 kgH₂/kg system
- System Volumetric Capacity: 0.045 kgH₂/L system
- Fill Time (for 5 kg): 3 minutes

Accomplishments

Our major accomplishments in Fiscal Year (FY) 2010 are summarized below:

- Performed multi-phase equilibrium theoretical studies on LiBH₄, Mg(BH₄)₂ and 2LiBH₄ + MgH₂. Found that Li₂B₁₂H₁₂ and MgB₁₂H₁₂ species play important roles during decomposition. Revealed a pressure-dependent mechanism governing the reaction pathways of 2LiBH₄ + MgH₂.
- Predicted that the decomposition of LiBH₄, Mg(BH₄)₂ and 2LiBH₄ + MgH₂ is accompanied by low levels of gas-phase impurities. In contrast, 2LiNH₂ + C, LiBH₄ + C, and Mg(BH₄)₂ + C are associated with large levels of impurities because of the strong thermodynamic stability of CH₄ and other hydrocarbons.
- Completed comprehensive prototype electrostatic ground state (PEGS) predictions of Ti(BH₄)₃, M[PB₂H₈]_x for M = Li, Na, K, Mg, Ca; x=1, 2.
- Confirmed remarkable catalysis of 2LiNH₂/MgH₂ by KH and KNH₂. Demonstrated that in the presence of catalysts, the absorption is >90% complete within minutes at 200°C.
- Improved the desorption kinetics of Mg(BH₄)₂ using various additives. Found that in the presence of 4 mol% TiF₃/ScCl₃ 9.6 % H₂ is released at 300°C in several hours.
- Observed low-temperature (<100°C) hydrogen evolution from Ti(BH₄)₃. However, the material was down-selected (removed from further study) due to irreversible hydrogen release.
- Developed a destabilization approach for releasing H₂ from [B₁₂H₁₂]²⁻ compounds at lower temperatures, confirming prior Metal Hydride Center of Excellence (MHCoe) theory.
- Experimentally demonstrated almost complete conversion of Li₂B₁₂H₁₂ and Na₂B₁₂H₁₂ to LiBH₄ and NaBH₄ in the presence of corresponding hydrides at high H₂ pressures.

- Successfully synthesized and studied hydrogen storage characteristics of several alkali and alkaline-earth bis(borano)hypophosphites of general formula $M[PB_2H_8]_x$. $Na[PH_2(BH_3)_2]$ was removed from further study due to formation of PH_3 and B_2H_6 , along with H_2 .
- Using simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) detected significant amounts of ammonia during the decomposition of $M'M''(BH_4)_x \cdot yNH_3$ and $M'M''(BH_4)_x(NH_2)_y$ (M' and $M'' = Li, Na, Ca$ and/or Mg). Found that small amounts of added LiH and MgH_2 significantly decrease the amounts of ammonia released.



Introduction

There are currently no materials that fully meet the DOE hydrogen storage performance targets. In order to address this problem, we at SNL have undertaken the prediction, synthesis and characterization of new high-hydrogen content complex metal hydrides for use as reversible hydrogen sorption materials. Also, we have further modified these hydrides through catalyst doping and cation substitution in order to improve their reversibility and sorption properties. Computational modeling has assisted in guiding these efforts, as well as understanding kinetic and regeneration issues for metal hydrides. In addition, we provide technical leadership and collaborate extensively with our partners in the MHCoe.

Approach

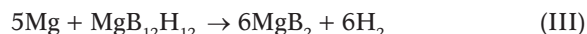
We are using an integrated theory/experiment approach to tackle the most challenging aspects of hydrogen storage in metal hydrides. Theoretical calculations are used to guide the search for better materials by (i) identifying promising metal hydrides, (ii) predicting their stability and crystal structure and (iii) estimating the thermodynamics of hydrogen release. We use both solid-state and solution techniques to make promising metal hydrides predicted by theory. The new materials are characterized by various traditional spectroscopic and diffraction techniques, including Fourier transform infrared (FTIR), Raman, nuclear magnetic resonance (NMR), mass-spectrometry, X-ray and neutron diffraction. The kinetics of hydrogen release are investigated using residual gas analysis (RGA), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), Sieverts and pressure-concentration-temperature measurements.

Results

Borohydrides

During the current fiscal year our major focus has been on exploring the hydrogen sorption properties of magnesium borohydride and several transition metal borohydrides. We isolated the low-temperature $Mg(BH_4)_2$ phase and found that upon desorption in vacuum up to 7.8 wt% H_2 is released. In the presence of a complex $TiF_3/ScCl_3$ additive, the amount of H_2 released increases to 9.6 wt%. The doped $Mg(BH_4)_2$ sample also shows dramatic enhancement in the kinetics of hydrogen release compared to milled $Mg(BH_4)_2$, as shown in Figure 1.

The decomposition of $Mg(BH_4)_2$ to MgH_2 can be represented as the first step (I) of the multi-step process (I–III):



With $TiF_3/ScCl_3$ additives, there is X-ray diffraction (XRD) evidence for the presence of Mg and MgF_2 in addition to MgH_2 . The presence of MgH_2 and Mg indicates that both reactions (I) and (II) are occurring to some extent. MgF_2 implies partial reaction of TiF_3 with $Mg(BH_4)_2$, possibly forming Ti-containing borohydride species which can then readily decompose to release hydrogen. However, the TiB_2 species were not observed in our study. We confirmed significant conversion of MgB_2 to fully hydrogenated $Mg(BH_4)_2$ for samples with and without additives.

We continued our efforts towards the understanding the role of dodecahydro-*closo*-dodecaborates in dehydrogenating/rehydrogenating reactions of metal borohydrides. In collaboration with our colleagues at the National Institute of Standards and Technology, we reported the structural aspects of the $M_2B_{12}H_{12}$ series

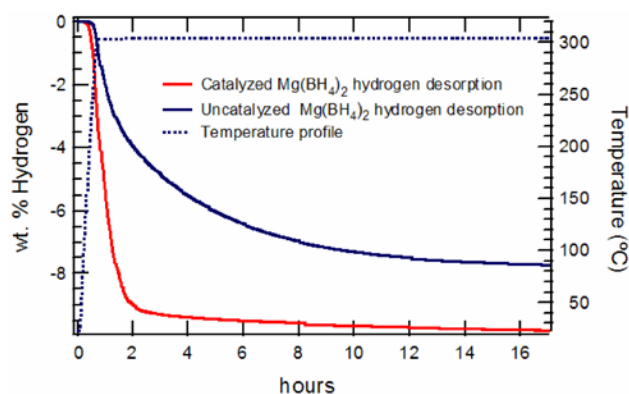


FIGURE 1. Hydrogen Desorption from Doped and Undoped $Mg(BH_4)_2$

(M=alkali metal). We also confirmed the MHCoe Theory Group prediction that $MB_{12}H_{12}$ compounds (M=Mg, Ca) can be destabilized in the presence of the corresponding metal hydrides. However, attempts to hydrogenate mixtures of $CaB_{12}H_{12}$ and CaH_2 into $Ca(BH_4)_2$ at 350-500°C and hydrogen pressures up to 900 bar were unsuccessful. Interestingly, under the same conditions both $LiB_{12}H_{12}$ and $Na_2B_{12}H_{12}$ react with the corresponding metal hydrides to form $LiBH_4$ and $NaBH_4$.

Stabilization of transition metal borohydrides through addition of alkali metal atoms has been explored both computationally and experimentally. Theory results for $LiTi(BH_4)_4$ and $NaTi(BH_4)_4$ indicate the compounds are unstable with respect to decomposition into $LiBH_4$, or $NaBH_4$, respectively. Although decomposition of pure titanium borohydride is calculated to occur spontaneously, in agreement with the observation of rapid decomposition at room temperature, it may be possible to stabilize the compound by incorporation within high surface area nano-frameworks.

Zak Fang in the MHCoe (University of Utah) recently reported up to 5 wt% H capacity at 90°C in the $3LiBH_4 \cdot TiF_3$ system. We explored various molar ratios in the $LiBH_4 \cdot TiF_3$ and $NaBH_4 \cdot TiF_3$ systems. However, we found no indication that mixed Li-Ti-BH₄ or Na-Ti-BH₄ phases form, which is in agreement with theoretical predictions. We used various ball-milling techniques and found that high-energy milling at room temperature is not appropriate as a synthetic technique for mixed borohydride species in these systems, presumably due to facile decomposition of the in situ-formed $Ti(BH_4)_3$. Temperature-programmed desorption (TPD) studies of the $LiBH_4 \cdot TiF_3$ and $NaBH_4 \cdot TiF_3$ composites show that most of the H_2 is released at temperatures between 20 and 175°C. However, at 175°C the hydrogen uptake of the dehydrogenated $LiBH_4 \cdot TiF_3$ and $NaBH_4 \cdot TiF_3$ materials is below 1 wt%. Thus, neither of the two is suitable for reversible hydrogen storage applications.

An alternative approach to decrease the desorption temperatures of main group metal borohydrides and is through “hydridic-protic” interactions in the presence of ammonia or metal amides. This FY we explored several mixed borohydride-ammonia and borohydride-amide compounds, $M'M''(BH_4)_x \cdot yNH_3$ and $M'M''(BH_4)_x(NH_2)_y$ (where M' and M''= Li, Na, Ca and/or Mg). We isolated $Mg(BH_4)_2(NH_3)_2$ and confirmed prior MHCoe results that the major gaseous product of the reaction is hydrogen. Rehydrogenation attempts on the products of desorption of $Mg(BH_4)_2(NH_3)_2$ and $MgCa(BH_4)_4(NH_3)_2$ were performed at 90 MPa H_2 pressure and 350°C. The XRD investigation of the samples after rehydrogenation showed that the starting materials do not form under these conditions. However, our TPD measurements indicate that the rehydrogenated products release 3.5 (Mg-system) and 2.8 wt% H (Mg-Ca system) upon

heating from room temperature to 350°C, suggesting partial reversibility in both systems. Another problem with the ammonia adducts is the contamination of hydrogen with impurity NH_3 gas. In an attempt to decrease the amount of ammonia released from the initial borohydride-ammonia materials, we isolated $Mn(BH_4)_2$ and reacted the material with gaseous NH_3 . Transition metals are known to display high affinity towards amine ligands. We found that the as-synthesized $Mn(BH_4)_2$ sample can absorb two or more moles of ammonia at room temperature; however most of the NH_3 is released upon heating the adduct above 120°C.

In the area of mixed borohydride-amide materials we investigated several compositions in the $M'M''(BH_4)_x(NH_2)_y$ systems (where M' and M''= Li, Na, Ca or Mg). We focused only on the systems where new phases are formed during the ball-milling process. We explored various molar ratios of the binaries in several lightweight borohydride-amide materials. Powder XRD data revealed that the ball-milling of these binary and ternary precursors resulted in the formation of a series of related M'-B-N-H (M'= Li, Na and/or Ca) phases. All tested binary borohydride-amide phases release a significant amount of ammonia upon heating, typically starting at temperatures <100°C. Significant mass losses were found by TGA/differential scanning calorimetry (DSC) in the $LiBH_4 \cdot Mg(NH_2)_2$ and $Mg(BH_4)_2 \cdot LiNH_2$ systems, which indicates to significant impurity gas formation. In contrast, $Ca(BH_4)_2 \cdot LiNH_2$ and $Ca(BH_4)_2 \cdot NaNH_2$ decompose to produce H_2 as the major product of the reaction. $Ca(BH_4)_2 \cdot LiNH_2$ system is more promising of the two materials and shows the first peak of H_2 release between 80 and 210°C in the STMBMS data of Figure 2. Ammonia is released in several steps between 40 and 310°C. RGA and STMBMS investigations of several ternary $Ca(BH_4)_2 \cdot LiNH_2 \cdot LiH$ and $Ca(BH_4)_2 \cdot LiNH_2 \cdot MgH_2$ compositions showed that the amount of ammonia can be significantly reduced when the corresponding metal hydrides are added before the ball-milling step.

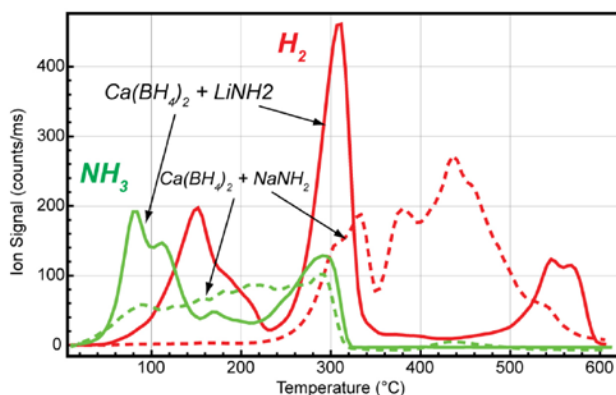


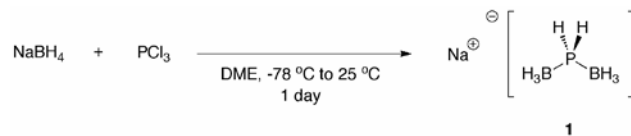
FIGURE 2. STMBMS Data for $Ca(BH_4)_2 \cdot LiNH_2$ and $Ca(BH_4)_2 \cdot NaNH_2$

RGA of the milled $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$ sample revealed that ammonia is the major product at relatively low temperatures (up to 140°C). Upon heating to 180°C , both H_2 and NH_3 are released, while at 290°C and above hydrogen is the major product. Small amounts of boron hydrides were also detected. The presence of significant amounts of ammonia at relatively low temperatures suggests this process is energetically favorable. Interesting enough, after the first dehydriding/rehydriding cycle, the amount of NH_3 released decreases dramatically. This is associated with a significant loss in capacity ($>50\%$). We also studied the effect of small amounts of MgH_2 and LiH on the impurity gas formation from the $\text{Mg}(\text{BH}_4)_2\text{-4LiNH}_2$ system. Our tests on the ball-milled $\text{Mg}(\text{BH}_4)_2\text{-4LiNH}_2\text{-0.1MgH}_2$ and $\text{Mg}(\text{BH}_4)_2\text{-4LiNH}_2\text{-0.1LiH}$ composites indicate to a decrease in the amount of NH_3 formed, presumably through formation of reactive amide species. As far as the reversibility is concerned, none of the borohydride-amide materials we studied so far display full reversibility, even at high temperatures (up to 500°C) and H_2 pressures (up to 100 MPa).

Phosphorous Materials

Syntheses of the various salts of $[\text{PH}_2(\text{BH}_3)_2]^-$ are known. However, most methods use phosphine, ammonia, and diborane, are performed at temperatures as low as -196°C , and take upwards of seven days

to complete. To avoid these hazards, a new method was developed from commercially available starting materials:



Differential scanning calorimetry of the sodium salt **1** was carried out in order to determine the heat of decomposition. A multi-step process between 150 and 200°C for $\text{Na}[\text{PH}_2(\text{BH}_3)_2]$ yields a ΔH of approximately $+1$ kcal/mol at $10^\circ\text{C}/\text{min}$ (Figure 3, left). Interestingly, this process appears to be heating rate-dependent. With fast heating rates ($>5^\circ\text{C}/\text{min}$), a sharp endothermic event is observed before a large, and long-lived, exothermic event occurs yielding the aforementioned value for ΔH . If the heating rate is slowed to $1^\circ\text{C}/\text{min}$, the sharp endothermic event becomes much less pronounced, and the exothermic signal intensifies (Figure 3, right). The multi-step process in the same temperature range ($150\text{-}200^\circ\text{C}$) becomes overall exothermic with a measured ΔH of roughly -10 kcal/mol. We hypothesize that fast heating rates allow the sample to melt before decomposing, whereas, a slow heating rate causes sample decomposition before undergoing the endothermic melting process. TGA shows a weight loss of approximately 6% over the same temperature range. No additional mass loss was observed up to 500°C .

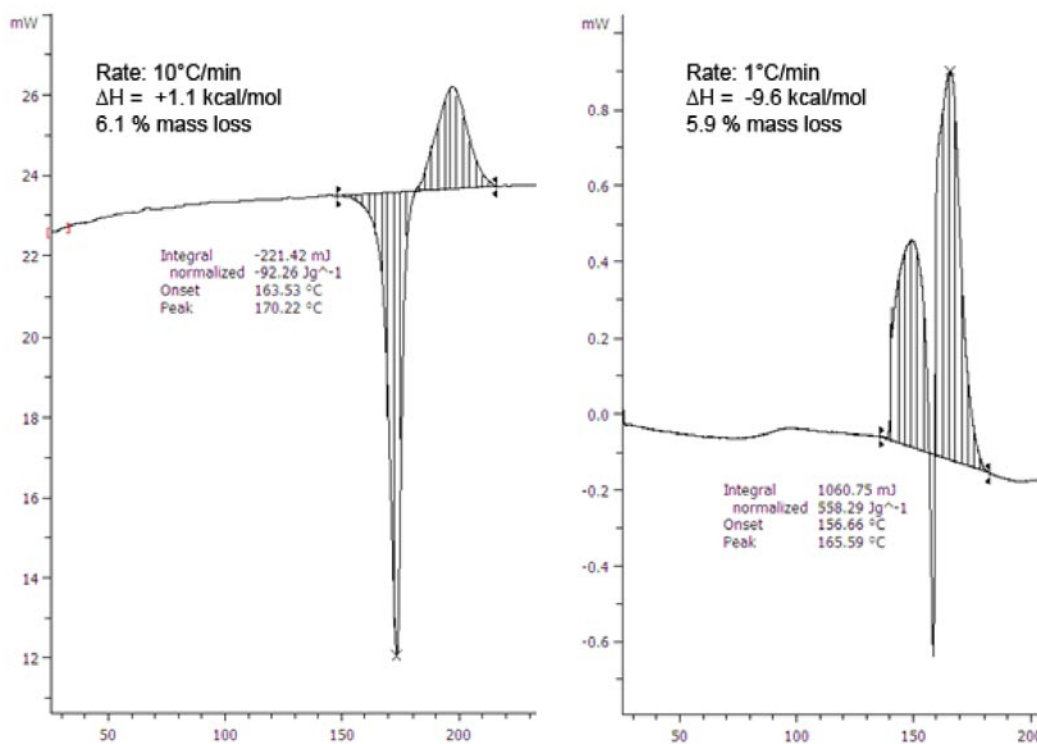


FIGURE 3. DSC of $\text{Na}[\text{PB}]$ Decomposition Showing Dependence on Heating Rate

The 6% mass loss observed during the thermal decomposition of $\text{Na}[\text{PH}_2(\text{BH}_3)_2]$ was initially attributed to H_2 loss. To confirm this assessment, analysis of the volatile compounds released from the solid material was performed using STMBMS. Large amounts of H_2 were detected as the sample was heated through the temperature range of 150-200°C along with PH_3 and B_2H_6 . The signal for hydrogen was qualitatively larger compared to other volatile species but the amount of phosphine and diborane were not negligible. Clearly, the loss of phosphorus and boron from the solid material is detrimental to achieving a reversible material.

To identify additional products formed during thermal decomposition, samples of the sodium salt were heated under vacuum to 150°C for fixed time intervals and then analyzed by attenuated total reflection-FTIR spectroscopy, NMR spectroscopy, XRD, DSC, and TGA. Regardless of the time interval (1h, 2h, 3h, 6h, and 18h) at 150°C, each reaction gave the same product, identified as sodium borohydride (NaBH_4):



The sodium salt crystallizes in the orthorhombic space group Ama2, with lattice parameters $a = 13.77\text{\AA}$, $b = 7.91\text{\AA}$, and $c = 4.50\text{\AA}$. The structure was predicted using the PEGS method that combines a simplified electrostatic Hamiltonian and Monte Carlo simulated annealing to find prototype structures that are further refined using state-of-the-art first-principles techniques. The Rietveld-refined XRD spectrum is shown in Figure 4, and indicates excellent agreement with the measured powder diffraction spectra.

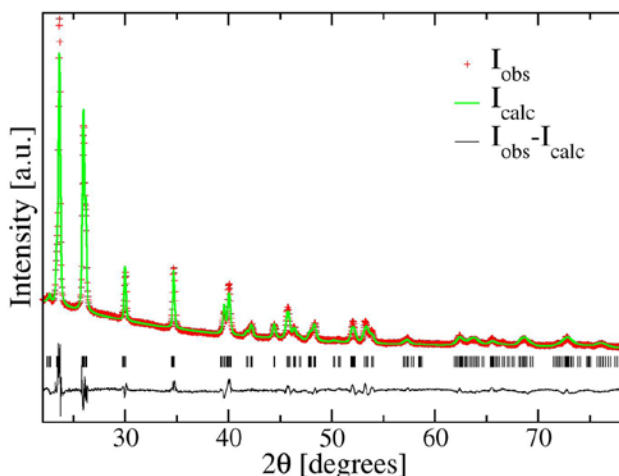


FIGURE 4. Rietveld refined powder XRD spectrum of **1** in space group Ama2. The difference curve (black trace) is below the observed data (red +), and spectra of the predicted structure (green trace).

Amide Materials

The $(2\text{LiNH}_2 + \text{MgH}_2)$ system has been selected as a near-term candidate for further development in the Engineering Center of Excellence. This material has convenient characteristics (i.e. pressure and temperature) for an operational storage system, with extensive cycle life of ~220 cycles. While the promising thermodynamic features and the high desorption rate of this material are attractive, its absorption rate is poor. The goal of this project is to search for adequate method to improve the sorption kinetics of this material. Previously we tested the traditional catalysts for hydrogen sorption, such as Pd, Pt, TiCl_3 , Nd_2O_5 , and found that none of them made significant improvements in the sorption behavior of the material. Up to now there has been no theory that can guide the discovery of effective catalysts for the amide materials. It is common that new catalysts are discovered unexpectedly. Recently, Dr. Ping Chen (DaLian Institute of Chemical Physics, Chinese Academy of Science) discovered a non-traditional catalyst, KH, that led to performance improvements. This motivated our investigation of potassium compounds, such as KH and KNH_2 , as candidate catalysts for $(2\text{LiNH}_2 + \text{MgH}_2)$.

Figure 5 shows the comparison of the absorption profiles of $(2\text{LiNH}_2 + \text{MgH}_2)$, with or without KH addition (at ~4 mole %), at 180, 200 and 220°C and

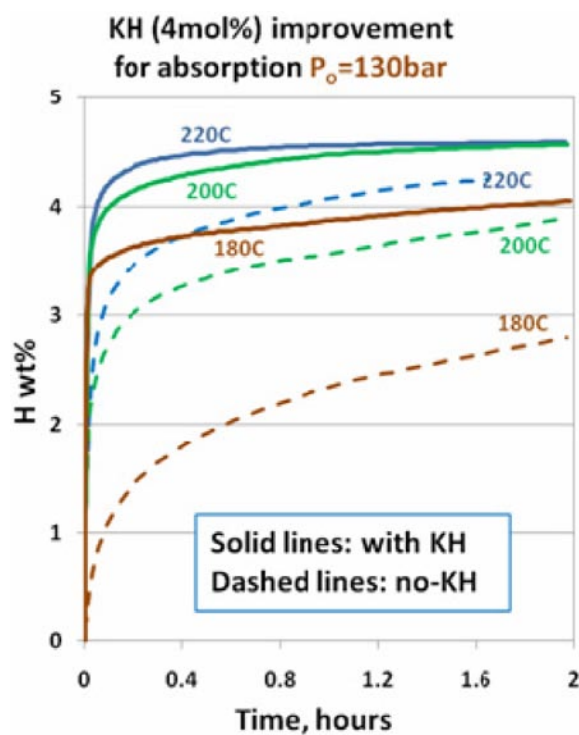


FIGURE 5. Absorption profiles for $(2\text{LiNH}_2 + \text{MgH}_2 + 0.04\text{KH})$ at 180, 200 and 220°C for initial H_2 pressure of 130 bar. The dashed lines for the absorption of the material without KH-addition are included for comparison.

initial H_2 pressure of 130 bar. The solid lines are for those with KH added and the dashed lines are for those without KH. It can be seen that with the addition of KH, the absorption rapidly achieves >90% completion at 200°C and above and more than 70% at 180°C. The van't Hoff plot for this material is shown in Figure 6. The formation enthalpy was measured to be 40 kJ/mol, very close to the previously reported value, 39.4 kJ/mol, indicating that the KH additive does not change the sorption thermodynamics. So far, we have been unable to detect any improvement on desorption of $2LiNH_2 + MgH_2$ in the presence of KH.

Theory Group Coordination

The Theory Group (TG) of the MHCoE makes use of first-principles methods to conduct materials discovery, provide thermodynamic and kinetic data for use by engineering and modeling efforts, and suggest new directions for experimentalists and interpretation of their results. The TG consists of researchers at the following institutions:

- Sandia National Laboratories (Mark Allendorf, TG Coordinator)
- Georgia Institute of Technology (Prof. David Sholl)
- National Institute of Standards and Technology (Dr. Ursula Kattner).
- University of Illinois/Champaign-Urbana (Prof. Duane Johnson)
- University of Missouri, St. Louis (Prof. Eric Majzoub)
- University of Pittsburgh (Prof. Karl Johnson)

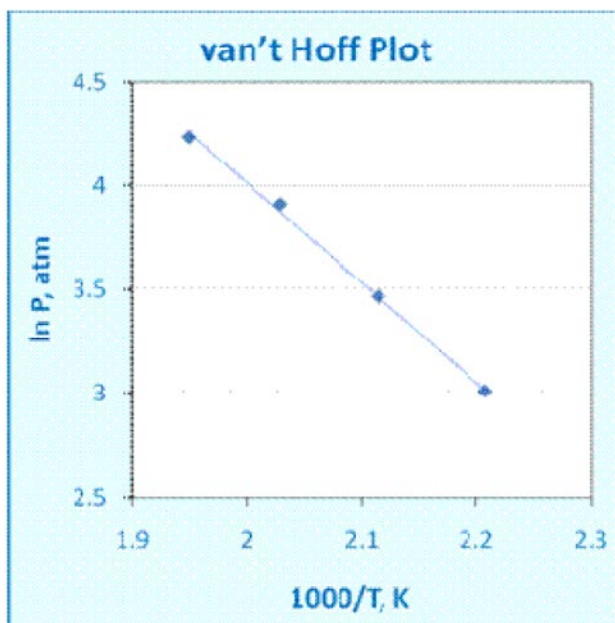


FIGURE 6. van't Hoff Plot for $(2LiNH_2 + MgH_2 + 0.04KH)$

To make maximum use of the different areas of expertise, joint TG efforts are guided by SNL not only in terms of technical direction, but also to ensure that TG efforts are complementary and have an effective synergy with experimentalists. The TG communicates through regular monthly conference calls involving all members of the team. This format has worked quite well and is followed up with a set of minutes and action items emailed to all participants. Depending on the topics under discussion, the TG also involves experimentalists from the various projects to provide insights into verification of theoretical predictions and suggestions for additional work by the TG.

Multiphase Equilibrium Modeling to Predict Impurity Gases and Phases

We computed the thermodynamic equilibrium including the possible evolution of gases other than H_2 in hydride systems based on $LiNH_2$, $LiBH_4$, $Mg(BH_4)_2$ and their mixtures with LiH , MgH_2 , or C . Although the majority of research on materials for reversible storage of H_2 has focused on issues associated with hydrogen capacity, the generation or absence of gaseous impurities from any storage system could be decisive in the value of such a system for practical applications. The extensive literature that has applied first-principles calculations to searching for metal hydrides and their mixtures with attractive properties for reversible storage has typically assumed that H_2 is the only gas phase product. The approach we introduced here couples first-principles (density functional theory) methods, which are used to obtain the thermodynamic properties of solid phases of interest, and free energy minimization incorporating a broad range of gaseous and liquid species to obtain a comprehensive thermodynamic picture of the metal hydride decomposition chemistry. This concept will be a valuable addition to computational efforts designed to aid development of reversible storage applications by screening large numbers of materials.

One useful way to categorize the systems we studied is to assess the purity of H_2 that is available at equilibrium in each case. To this end, we define R to be the fraction of H_2 that is observed at equilibrium relative to the amount of H_2 that would be predicted in the gas phase if H_2 was the only gaseous species considered in a thermodynamic calculation. The variation in R as a function of temperature at 1 atm pressure is shown for each system we considered in Figure 7. Interesting enough, the decomposition of $2LiBH_4 + MgH_2$ is pressure dependent. For $LiNH_2$, $LiBH_4$, and $2LiBH_4 + MgH_2$, R is very close to 1; that is, these examples are associated with very low levels of gas-phase impurities. The mixture $LiNH_2 + LiH$, in contrast, generates an appreciable level of N_2 and NH_3 when $LiNH_2$ decomposes, especially at temperatures above 700 K. All three of the mixtures we considered that included

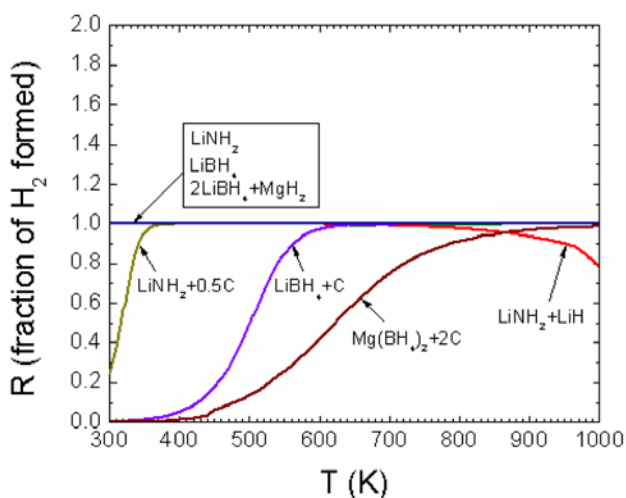


FIGURE 7. Mole fraction of H_2 predicted by our equilibrium calculations normalized with the H_2 available from the nominal for seven systems.

C, namely $2LiNH_2 + C$, $LiBH_4 + C$, and $Mg(BH_4)_2 + C$, are associated with very impure H_2 except at high temperatures because of the strong thermodynamic stability of CH_4 .

Conclusions

- Performed multi-phase equilibrium theoretical studies on $LiBH_4$, $Mg(BH_4)_2$ and $2LiBH_4 + MgH_2$. Found that $Li_2B_{12}H_{12}$ and $MgB_{12}H_{12}$ species play important roles during decomposition. Revealed a pressure-dependent mechanism governing the reaction pathways of $2LiBH_4 + MgH_2$.
- Predicted that the decomposition of $LiBH_4$, $Mg(BH_4)_2$ and $2LiBH_4 + MgH_2$ is associated with low levels of gas-phase impurities. In contrast, $2LiNH_2 + C$, $LiBH_4 + C$, and $Mg(BH_4)_2 + C$, are associated with very impure H_2 because of the strong thermodynamic stability of CH_4 .
- Completed comprehensive PEGS predictions of $Ti(BH_4)_3$, $M[PB_2H_8]_x$ for $M = Li, Na, K, Mg, Ca$; $x=1, 2$.
- Confirmed remarkable catalysis of $2LiNH_2/MgH_2$ by KH and KNH_2 . Demonstrated that in the presence of catalysts the absorption is $>90\%$ complete within minutes at $200^\circ C$.
- Improved the desorption kinetics of $Mg(BH_4)_2$ using various additives. Found that in the presence of 4 mol% $TiF_3/ScCl_3$ 9.6 % H_2 is released at $300^\circ C$.
- Observed low-temperature ($<100^\circ C$) hydrogen evolution from $Ti(BH_4)_5$. However, the material was down-selected (removed from further study) due to irreversible hydrogen release.
- Developed a destabilization approach for releasing H_2 from $[B_{12}H_{12}]^{2-}$ compounds at lower temperatures, confirming prior MHCoe theory.

- Experimentally demonstrated almost full conversion of $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ into $LiBH_4$ and $NaBH_4$ in the presence of corresponding hydrides at high H_2 pressures.
- Successfully synthesized and studied storage characteristics of several alkali and alkaline-earth bis(borano)hypophosphites of general formula $M[PB_2H_8]_x$. $Na[PH_2(BH_3)_2]$ was removed from further study due to formation of PH_3 and B_2H_6 , along with H_2 .
- Using STMBMS, detected significant amounts of ammonia during the decomposition of $M'M''(BH_4)_x \cdot yNH_3$ and $M'M''(BH_4)_x(NH_2)_y$ (where M' and $M'' = Li, Na, Ca$ and/or Mg). Found that small amounts of metal hydrides significantly decrease the amounts of ammonia released.

Special Recognitions & Awards/Patents Issued

- Director Klebanoff accepted a DOE Hydrogen Program 2010 “Special Recognition Award,” made to the entire MHCoe, “In Recognition of Outstanding Contributions to the Department of Energy.” This award was made June 8, 2010.
- The following paper was cited as a “Top Paper” by the Journal of Alloys and Compounds 2009: W. Luo and S. Sickafoose, J. Alloys and Compounds, 407 (2006) 274-281.
- Patent: Cordaro, J. G. “A Method for Synthesizing Metal Bis (Borano) Hypophosphite Complexes” United States patent application number 12/829,592. Filed July 2, 2010.

FY 2010 Publications/Presentations

- W. Luo, V. Stavila and L. Klebanoff, “Improvement of the Kinetics of H_2 Absorption of the $MgH_2+2LiNH_2$ System”, *International Symposium on Metal Hydrogen Systems*, Moscow Russia, July, 2010.
- R. Newhouse, V. Stavila, S. Hwang, L.E. Klebanoff, J. Zhang. “Reversibility and Improved Hydrogen Release of Magnesium Borohydride”, *Journal of Physical Chemistry, C* 2010, 114, 5224-5232.
- V. Stavila, J.-H. Her, W. Zhou, S.-J. Hwang, Ch. Kim, L.-A. M. Ottley, T.J. Udovic. “Calcium dodecahydro-closo-dodecaborate: synthesis, structure and relevance to hydrogen storage”, *Journal of Solid State Chemistry*, 2010, 183, 1133-1140.
- K.C. Kim, M.D. Allendorf, V. Stavila, D.S. Sholl. “Predicting Impurity Gases and Phases During Hydrogen Evolution from Complex Metal Hydrides using Free Energy Minimization Enabled by First-principles Calculations”, *Physical Chemistry Chemical Physics*, 2010, DOI:10.1039/C001657H.
- J.-H. Her, W. Zhou, V. Stavila, C.M. Brown, T.J. Udovic. “The crystal structure of $Na_2B_{12}H_{12}$ and the role of cation size on the structural behavior of the alkali-metal

dodecahydro-closo-dodecaborates”, *Journal of Physical Chemistry, C*, **2009**, *113*, 11187-11189.

6. “Boron and nitrogen-containing materials for hydrogen storage”, V. Stavila, W. Luo, M. Ulutagay-Kartin, S.-J. Hwang, A.M. Highley, R. Behrens. *18th World Hydrogen Energy Conference*, Essen, Germany, **2010**.
7. “Complex metal hydrides for hydrogen storage applications”, V. Stavila, (Invited talk). *Energy Storage and Intermittent Renewable Energy*, Santa Clara, CA, USA, **2010**.
8. “Hydrogen storage in alkali and alkaline earth borohydrides: Probing the role of intermediate species”, V. Stavila, R.J. Newhouse, S.-J. Hwang, M. Ulutagay-Kartin, J.-H. Her, L.E. Klebanoff, T.J. Udovic (Invited talk). *239th American Chemical Society National Meeting*, San Francisco, CA, USA, **2010**.
9. “Factors Affecting Hydrogen Release from Metal Borohydrides” V. Stavila, E.H. Majzoub, S.-J. Hwang, R.J. Newhouse, M. Ulutagay-Kartin, W. Luo, J.G. Cordaro, T.J. Udovic. Oral Presentation. *Materials Challenges in Alternative and Renewable Energy*, Cocoa Beach, Florida, USA, **2010**.
10. “Hydrogen multinuclear high resolution NMR Studies of dodecaborane intermediate of borohydride-based hydrogen storage systems”, S.-J. Hwang, C. Ahn, J. W. Reiter, J. A. Zan, V. Stavila, J. J. Vajo. Oral Presentation. *Materials Challenges in Alternative and Renewable Energy*, Cocoa Beach, Florida, USA, **2010**.
11. “Alkali and Alkaline-Earth Metal Dodecahydro-Closo-Dodecaborates: Probing Structural Variations via Vibrational Spectroscopy,” N. Verdal, W. Zhou, V. Stavila, J. H.- Her, M. Yousufuddin, T. Yildirim, J. J. Rush, and T.J. Udovic. *MH2010 - International Symposium on Metal-Hydrogen Systems*, Moscow, Russia, **2010**.
12. “Combining first principles and thermodynamic calculations to predict evolution of impurity gases from metal hydrides”, M. Allendorf, V. Stavila, K.C. Kim, D.S. Sholl (Invited talk). *239th American Chemical Society National Meeting*, San Francisco, CA, USA, **2010**.
13. Anstey, Mitchell R.; Corbett, Michael T.; Majzoub, Eric H.; Cordaro, Joseph G.; “Improved Synthesis of Bis(borano)hypophosphite Salts” *Inorg. Chem.* Submitted **2010**.