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

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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 Hydrogen, Fuel Cells and Infrastructure 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 metal hydrides with high hydrogen capacity and good thermodynamics, and understanding metal hydride kinetic and regeneration issues. The targets being addressed include:

- System Gravimetric Capacity: 0.06 kgH_2/kg system
- System Volumetric Capacity: 0.045 kgH_2/L system
- Fill Time (for 5 kg): 3 minutes

Accomplishments

- Completed a comprehensive prototype electrostatic ground state (PEGS) study of the polymorphs of $Ca(BH_4)_2$, validated with experimental findings.
- Measured the enthalpy of desorption of $Ca(BH_4)_2$, found it to be 60-100 kJ/mole H_2. This enthalpy is too large for $Ca(BH_4)_2$ to be considered a viable hydrogen storage material.
- Experimentally synthesized a variety of metal-$B_{12}H_{12}$ salts, thereby gaining understanding of their chemistry and role as intermediates in borohydride-based hydrogen storage.
- Found that $CaB_{12}H_{12}$ cannot be readily hydrogenated, explaining in part the poor cycling characteristics of $Ca(BH_4)_2$.
- Using simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS), found that $Ca(BH_4)_2$ releases substantial BH_3 along with H_2 when heated.
- "Downselected" $Ca(BH_4)_2$, removing it from further study as a viable hydrogen storage material.
- Completed theoretical studies of the reaction pathways and thermodynamics of hydrogen desorption from $Mg(BH_4)_2$ and $Ca(BH_4)_2$.
- Developed a method to dope MgB_2 with carbon, thereby opening up a study of the effects of C on $Mg(BH_4)_2$ hydrogen release.
- Initiated a study of the properties of $Ti(BH_4)_3$, opening up future studies of mixtures of borohydrides with $Ti(BH_4)_3$.
- Synthesized ammonia additives of mixed metal borohydrides, found them to behave very differently from the ammonia adduct of magnesium borohydride.
- Initiated studies of mixtures of borohydrides and amides, found reduced thermal requirements for some compounds.
- Initiated studies of P-based hydrogen storage materials. Found that $Na[PH_2(BH_3)_2]$ could be synthesized, and the compound releases hydrogen at ~150°C.
- Developed a route to incorporating $Ca(BH_4)_2$ into C-aerogel with 50% loading, completing our work on the nanoframeworks project with United Technologies Research Center (UTRC).
- Completed phase equilibrium theoretical studies of the $LiNH_2$, $LiNH_2$ + LiH and $LiBH_4$ + C systems.

Found that gas phase species other than H_2 are important for determining reaction pathways and thermodynamics.

- Quantum chemical calculations show that the AlH_3 complex with triethylamine is the least stable of the amines and thus most easily decomposed to release pure AlH_3. Of the ethers, $AlH_3O(C_2H_5)_2$ has the smallest complexation energy.

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Introduction

There are currently no materials that fully meet the DOE hydrogen storage performance targets. In order to address this problem, we at Sandia National Laboratories (SNL) have undertaken the prediction, synthesis and characterization of new high-hydrogen content complex metal hydrides for use as reversible hydrogen sorption materials. In addition, 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 directing these efforts, as well as understanding kinetic and regeneration issues for metal hydrides. We provide technical leadership and collaborate extensively with our partners in the Metal Hydride Center of Excellence (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.

This past year, a truly unique analytical capability has been added to the SNL research and development effort, called STMBMS. The essential features of STMBMS are illustrated in Figure 1, where a sample is placed within the reaction cell, the reaction cell is heated in a controlled manner and the identities and number densities of all gaseous species within the reaction cell are determined as a function of time. This basic information allows the rates of formation of all species to be determined as a function of time.

As part of our Center lead activities, we continued to provide technical leadership (setting directions, evaluating results) for the MHCoE Theory Group (TG) that makes use of first-principles methods to conduct materials discovery, provide thermodynamic and kinetic data for use by engineering and modeling
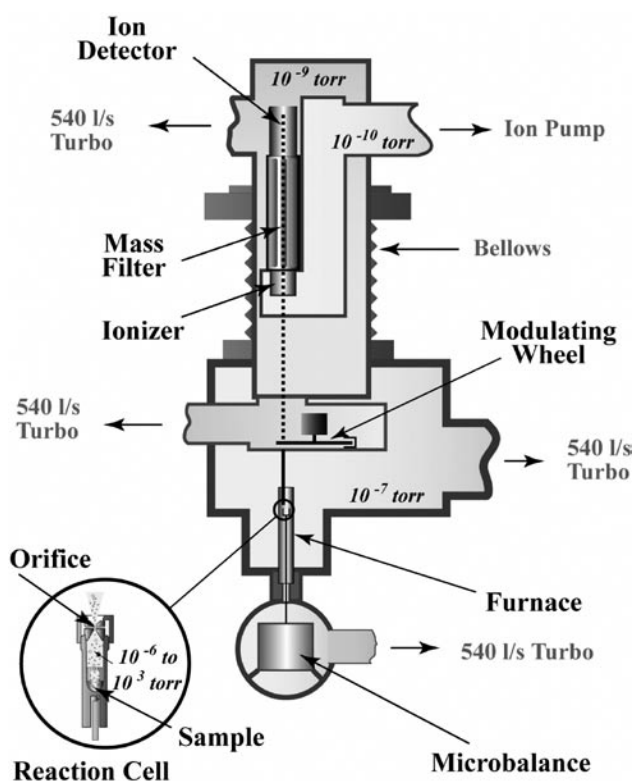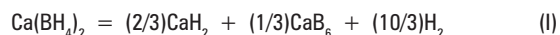

FIGURE 1. Layout of Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry Apparatus

efforts, and suggest new directions for experimentalists and interpretation of their results. The TG consists of researchers at five institutions, comprising effectively four groups: SNL; Carnegie Mellon University and the University of Pittsburgh; University of Illinois at Urbana-Champagne; and the National Institute of Standards and Technology (NIST).

Results

Borohydrides and Related Materials

During Fiscal Year 2009 we completed extensive experimental and theoretical studies on borohydrides and related materials, particularly calcium borohydride $Ca(BH_4)_2$. The PEGS method was used to predict the enthalpies for the following two decomposition pathways for $Ca(BH_4)_2$:

$$Ca(BH_4)_2 \;=\; (2/3)CaH_2 \;+\; (1/3)CaB_6 \;+\; (10/3)H_2 \qquad (I)$$

$$Ca(BH_4)_2 \;=\; (5/6)CaH_2 \;+\; (1/6)CaB_{12}H_{12} \;+\; (13/6)H_2 \qquad (II)$$

Although the two reactions were predicted to have almost identical enthalpies, ~40 kJ/mol H_2 [1], the amounts of hydrogen released differ significantly in **I** and **II** and correspond respectively to 9.63% and 6.26% mass

fraction of hydrogen. A first-principles PEGS study and predictions of the structures of polymorphs of $Ca(BH_4)_2$ resulted in the correct identification of the beta-phase, observed in synthesis and cycling experiments. A PEGS and database search correctly found the ground state and several high-energy polymorphs which correspond to the high-temperature phases of $Ca(BH_4)_2$.

We conducted an experiment to estimate the enthalpy of desorption of $Ca(BH_4)_2$. Desorption isotherm measurements were carried out at two temperatures, 380°C and 354°C and desorption enthalpy was calculated using the van't Hoff formalism. The difficulty in achieving true equilibrium in this system may introduce uncertainty in the derived desorption enthalpy. Nonetheless, we estimate that desorption enthalpy to be in the range 60-100 kJ/mole H_2, significantly larger than the desired 20-40 kJ/mole H_2.

Our cycling measurements on pure and catalyzed $Ca(BH_4)_2$ revealed that the material suffers from a severe capacity loss on each subsequent cycle, as illustrated in Figure 2. We tested 30 different additives in order to decrease the desorption temperature and improve reversibility, but none were effective.

We speculated that formation of $CaB_{12}H_{12}$ might be the cause of the lack of reversibility for $Ca(BH_4)_2$. Using Sandia's high-pressure station, we showed that under the conditions known to promote partial reversibility in $Ca(BH_4)_2$, the mixture of CaH_2 and $CaB_{12}H_{12}$ cannot react to form $Ca(BH_4)_2$. This experiment shows that $CaB_{12}H_{12}$, if formed, would hinder reversibility.

Experiments in the MHCoE suggest that hydrogen desorption from borohydrides can lead to undesirable $B_{12}H_{12}$ intermediates that can act as hydrogen sinks. Using PEGS, we predicted the crystal structures for a number of alkali- and alkali-earth $B_{12}H_{12}$ compounds. The crystal structures are critical for the evaluation of the thermodynamic characteristics of the reactions involving these species [1]. To better understand the
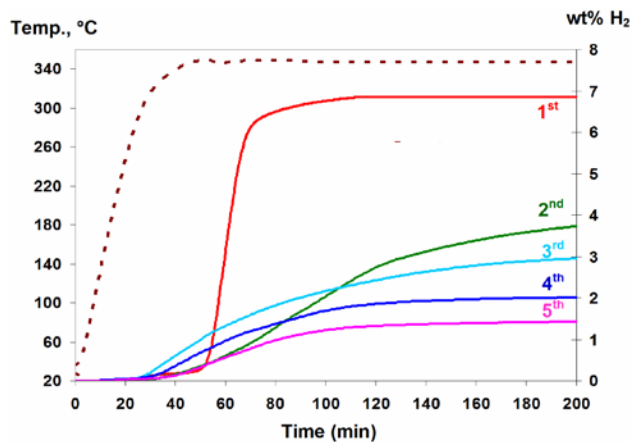
experimental reactivity of $B_{12}H_{12}$ species, we synthesized a number of alkalai and alkaline earth $B_{12}H_{12}$ salts. In collaboration with NIST, we validated the previously predicted structures. The crystal structures of monoclinic $Na_2B_{12}H_{12}$ is $P2_1/n$ and that for $CaB_{12}H_{12}$ is $C2/c$. We also demonstrated experimentally that the *closo*-dodecaborate salts are highly stable and cannot be dehydrogenated or hydrogenated under practical conditions.

Using STMBMS, we characterized the evolution of H_2 and other minor species as $Ca(BH_4)_2$ was heated from 20 to 1,000°C. Data from one series of these experiments is shown in Figure 3, which displays the rates of H_2 and BH_3 evolution as samples of uncatalyzed and $PdCl_2/TiCl_3$ catalyzed $Ca(BH_4)_2$ are heated through a series of isothermal steps between 120 and 500°C. It is clear that hydrogen is evolved in two distinct steps as the sample is ramped in temperature from 100-305°C. It is also clear that BH_3 is released along with H_2 in the desorption process. A detailed investigation of these effects is in progress.

During FY 2009, we made a decision to "down-select" $Ca(BH_4)_2$ as a potential bulk hydrogen storage material, removing it from further study. This decision was made after considering its poor reversibility, very high desorption temperature, and poor thermodynamics. Our attention then shifted to other borohydride materials, with a focus on $Mg(BH_4)_2$.

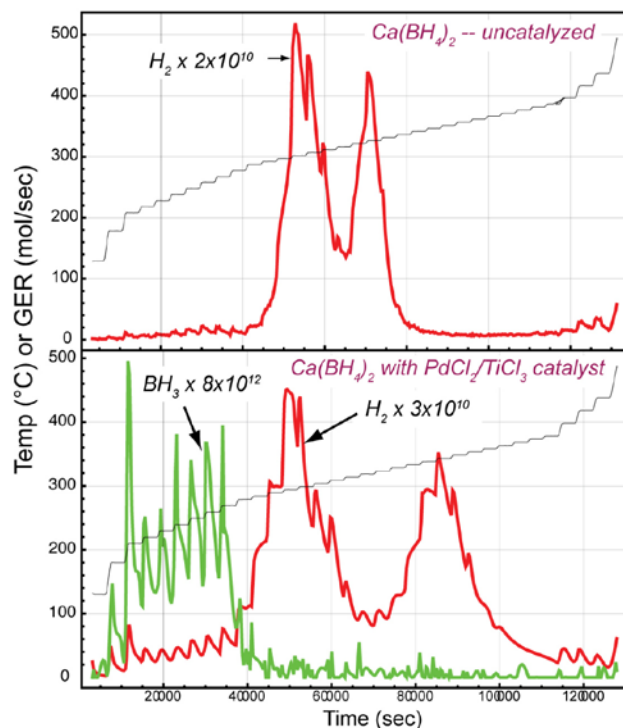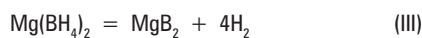Magnesium borohydride is known to release ~14 weight percent hydrogen when decomposed to MgB_2:

FIGURE 2. Cycling Behavior of $Ca(BH_4)_2$ in the Presence of $PdCl_2$

FIGURE 3. STMBMS Analysis of Desorption from Catalyzed $Ca(BH_4)_2$

$$Mg(BH_4)_2 = MgB_2 + 4H_2 \qquad (III)$$

In collaboration with University of Hawaii we demonstrated that reverse reaction of **III** occurs in good yield when MgB_2 is heated at 440°C and 70 MPa hydrogen pressure [4]. The importance of this result is that it sets a record for the highest hydrogen weight percent (~14 wt%) for a fully reversing metal hydride material. Work will be ongoing to reduce the pressure and temperature demands for this material.

In the past year we also examined the effects of carbon dopants on $Mg(BH_4)_2$. First, dopant levels of carbon were incorporated into the MgB_2 precursor by heating mixed powders of magnesium, boron and carbon. Thereafter, the as-made $MgB_{2-x}C_x$ pellets were reacted at 1,034 bar (15,000 psi) H_2 pressure while heating to synthesize C-doped $Mg(BH_4)_2$. Future work will focus on improving the yield of the doped borohydride fabricated in this way as well as incorporating transition metal dopants as potential ways to improve the thermodynamic and kinetic properties of $Mg(BH_4)_2$ for hydrogen storage.

A first-principles study of the thermodynamics of reactions in the Li-Mg-Ca-B-H system indicated several new reaction pathways involving $[B_{12}H_{12}]$ closo-borate. Structures of the closo-borate salts were predicted using the PEGS method and several were verified experimentally via diffraction and Rietveld refinement. The formation of these salts is shown to significantly impact the storage properties of $Mg(BH_4)_2$ and $Ca(BH_4)_2$, while several new 'destabilized' reactions involving the salts were identified. $LiSc(BH_4)_4$ formation and decomposition pathway were also investigated in collaboration with Caltech/Jet Propulsion Laboratory and SNL. Thermodynamic pathways were calculated using prototype structures generated using the PEGS method and are in agreement with experimentally observed decomposition products.

In collaboration with UTRC, we initiated a collaborative effort on mixed main-group – transition metal borohydride materials. The calculations predicted several stable compounds in the $Li-Ti-BH_4$ and $Na-Ti-BH_4$ systems. The synthesis of these compounds is challenging, however we made significant progress in isolating the unstable $Ti(BH_4)_3$, which serves as a starting material in these reactions. We also tested the effect of several Ti(III) precursors on the hydrogen desorption from $LiBH_4$, $Mg(BH_4)_2$ and $Ca(BH_4)_2$ and showed that up to 3 wt% H_2 can be released at temperatures as low as 175°C.

Another approach we used to decrease the desorption temperatures of main group metal borohydrides is through complexation with ammonia. We explored $Ca(BH_4)_2-NH_3$ and several mixed-heterometallic $M'M''(BH_4)_{x \cdot y}NH_z$ systems (where M' and M''= Li, Na, Ca and/or Mg;). Soloveichik *et al.* [5] have recently demonstrated that the magnesium borohydride ammonia complex, $Mg(BH_4)_2(NH_3)_2$, exhibits improved hydrogen desorption properties compared to pure $Mg(BH_4)_2$, decreasing the dehydrogenation temperature by about 100°C. In our work, $Ca(BH_4)_2-NH_3$, $LiCa(BH_4)_3-NH_3$, and $MgCa(BH_4)_4-NH_3$ were synthesized and displayed increased stability compared to the initial borohydrides. However, we found that significant amounts of ammonia was released upon heating. This finding indicates that the metal-ammonia bond in these complexes is more labile compared to $Mg(BH_4)_2(NH_3)_2$. In the case of $Ca(BH_4)_2-NH_3$ the ammonia release is quantitative and pure β-$Ca(BH_4)_2$ was recovered after heating the adduct in vacuum at 195°C for 2 hours.

Interest in P compounds as hydrogen storage species has not been developed despite literature reports of compounds containing >9 wt% hydrogen. For example, $Na[PH_2(BH_3)_2]$ was reported to release hydrogen upon heating but the amount of hydrogen and the products of this thermal reaction were not explored [6]. We have developed novel methods for synthesizing phosphino-borane adducts and begun investigating the thermal decomposition chemistry.

A new family of inorganic hydrogen storage materials has been identified based of phosphino-borane salts. Depending on the nature of the alkali and alkaline earth metal salts, the hydrogen wt% can vary from 8.08 to 11.99. The sodium compound $Na[PH_2(BH_3)_2]$ **(1)** was initially synthesized at low temperature following eq **IV** [7].

$$NaBH_4 + H_3P \bullet BH_3 \rightarrow Na[PH_2(BH_3)_2] + H_2 \qquad IV$$

Conversely, **1** was synthesized by the action of excess $NaBH_4$ on PH_4I. However, neither $H_3P \bullet BH_3$ or PH_4I are readily available starting materials and require the use of the extremely hazardous gas PH_3. Therefore, an alternative route was devised using commercially available PCl_3. The theoretical stoichiometry for the balanced reaction between phosphorus trichloride and sodium borohydride is given in eq **V**. Generation of boron trichloride and other side products are only speculative.

$$2PCl_3 + 5NaBH_4 \rightarrow 2Na[PH_2(BH_3)_2] + 3NaCl + BCl_3 + 2H_2 \quad V$$
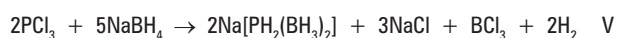
After varying solvent, reaction temperature, and the order of addition, the sodium phoshinoborane salt **1** was isolated and identified by ^1H and ^{31}P NMR spectroscopy.

Efforts to fully characterize **1** are ongoing. Hydrogen release measurements on **1** have been performed using thermal gravimetric analysis and our coupled thermogravimetric analysis-mass spectrometer instrument. Preliminary results show that hydrogen release occurs near 150°C with some other additional species evolved in the process. The approximate mass

loss for **1** is near 6%. More efforts to identify the nature of the products and volatile species are underway.

Nanostructured Materials

We completed our collaboration with UTRC exploring methods to incorporate metal hydrides into nanostructured frameworks, with a focus on $Ca(BH_4)_2$ and C-aerogel. Precursor $Ca(BH_4)_2(THF)_2$ was modified with alternative Lewis basic solvents such as pyridine, NH_3, dimethoxyethane, and Et_2O. The products were characterized by beryllium dome X-ray diffraction and infra-red spectroscopy. If crystals were obtained, single crystal X-ray diffraction structural studies were undertaken to assist in identification. We attempted to "dip-coat" load the tetrahydrofuran (THF) adduct into yttria-stabilized zirconia (YSZ) and C-aerogel. However, it was unclear if any loading took place. We therefore turned to "incipient wetness loading" of $Ca(BH_4)_2(THF)_2$ in a THF solution onto both YSZ and carbon aerogel (CA). This approach was more successful, loadings of up to 14% were observed.

Although incipient wetness yielded higher loadings, the calculated pore volume of the substrate indicated that the ceramic should be able to absorb more adduct. We exposed a CA sample to a concentrated solution of $Ca(BH_4)_2(THF)_2$ in THF. After the aerogel was soaked in the solution, it was dried under vacuum at $100^{\circ}C$ for 2 hours to remove the solvent. The results from this coated aerogel suggest that the amount of $Ca(BH_4)_2$ incorporated was over 50%. The desorption capacity was found to be low and significant improvement is necessary.

Gas-Phase Equilibria Modeling

We initiated the first theoretical studies of the effects of gaseous species (other than H_2) on the equilibrium of hydrogen desorption reactions. The composition of the gas-phase above a metal hydride was computed using a Gibbs free energy minimization method incorporated into a commercial thermodynamic modeling package known as FactSage. In this method, thermodynamic data taken from published thermodynamic data bases, such as the *JANAF Thermochemical Tables*, is combined with data for condensed-phase products available from similar public sources. Data for metal hydrides and some of their decomposition products, however, are often not available. To fill this gap we partnered with the research groups of Prof. David Sholl (Georgia Tech) and Prof. Karl Johnson (University of Pittsburgh), who developed computational methods based on density functional theory (DFT) to predict the thermochemistry of these materials.

Phase-equilibrium calculations were performed for several relatively well-understood hydride systems to assess the potential for the approach. These systems

include: $LiNH_2$, $LiNH_2 + LiH$, and $LiBH_4 + MgH_2$. In addition, several destabilized reactions identified by Profs. Sholl and Johnson were examined, including $LiBH_4 + C$ and $MgBH_4 + C$, to determine whether these decompose to produce pure H_2 or significant concentrations of impurities are produced.

Some illustrative results are presented in Figure 4 for $LiNH_2 + LiH$ (left) and $LiBH_4 + C$ (right). The nominal reactions in the absence of LiH are: $2LiNH_2 \leftrightarrow Li_2NH + NH_3$ as well as $2LiNH_2 \leftrightarrow Li_2NH + 0.5N_2 + 1.5H_2$. However, when LiH is added, a new channel is possible: $LiNH_2 + LiH \leftrightarrow Li_2NH + H_2$ The results show that the NH_3 concentration is ~30 ppm for $LiNH_2$ alone, but that addition of LiH reduces NH_3 by nearly two orders of magnitude (~0.5 ppm) at temperatures desired for on-board regeneration with a fuel cell power train (~375 K).
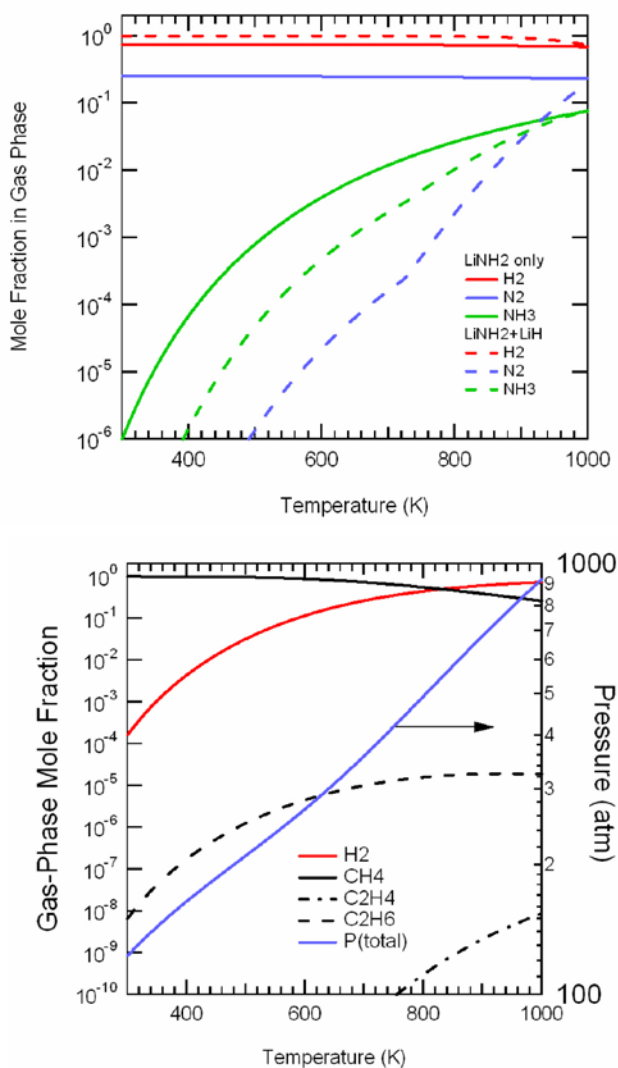

FIGURE 4. Gas-Phase Composition at Equilibrium as a Function of Temperature for top: $LiNH_2$ (+ LiH); and bottom: $LiBH_4 + C$

In contrast, $LiBH_4$ destabilized by adding carbon does not produce fuel cell poisons like NH_3. However, the formation of gas-phase hydrocarbons is possible. The nominal reaction is: $LiBH_4 + C \leftrightarrow LiBC + 2H_2$. However other possible reactions include:

$LiBH_4 + 2C \leftrightarrow LiBC + CH_4$ in addition to $LiBH_4 + 0.75C \leftrightarrow LiH + B + 0.75CH_4$.
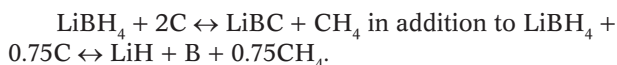
The latter two reactions are thermodynamically favorable and redirect the hydrogen to form methane. Hydrogen does not become the thermodynamically favored gas-phase product until temperatures exceed 800 K.

Thermochemistry of Alane Complexes

We also performed calculations of the stability of AlH_3 with amines and ethers to help guide AlH_3 regeneration efforts of our partner Brookhaven National Laboratory. High-level computations using quantum-chemistry methods were used to obtain electronic energies, geometries, and vibrational frequencies for alane complexes. In particular, we employed the Bond Additivity Correction (BAC) suite of methods, developed by Sandia for the purpose of computing accurate heats of formation for small molecules. Other approaches, including the Gaussian-3 Method, DFT/B3LYP, and coupled-cluster methods, were also employed to calibrate the BAC methods and test for systematic errors.

Preliminary heats of formation and complexation energies reported last year were finalized this year by applying high-level methods described above to identify and compensate for systematic errors present in the lower-level (e.g. BAC-second-order Moller-Plesset perturbation theory [BAC-MP2]) methods. Heats of formation and complexation energies were determined for several 1:1 and 1:2 complexes of alane with electron donors, AlH_3:L and AlH_3:L_2, where L represents an electron-donating ligand with a nitrogen or oxygen atom bound to Al. The nitrogen-containing ligands investigated include ammonia and several primary, secondary, and tertiary amines, while the oxygen-containing ligands comprise water, several alcohols, and a number of ethers. To determine thermochemical data for all complexes of interest, we applied the composite electronic structure method BAC-MP2.

Results for the heats of formation are shown in Figure 5. For the 1:1 complexes, Al:N bond strengths are found to range from 26–35 kcal/mol, while the Al:O bonds are significantly weaker, with bond strengths between 17 and 26 kcal/mol. In the 1:2 complexes, the Al:N and Al:O bonds are considerably weaker than in the 1:1 complexes, and total complexation energies for the 1:2 complexes are only about 40-50% higher than for their 1:1 counterparts. In the amine complexes, the complexation enthalpy tends to increase with the substitution level on the amine (primary < secondary
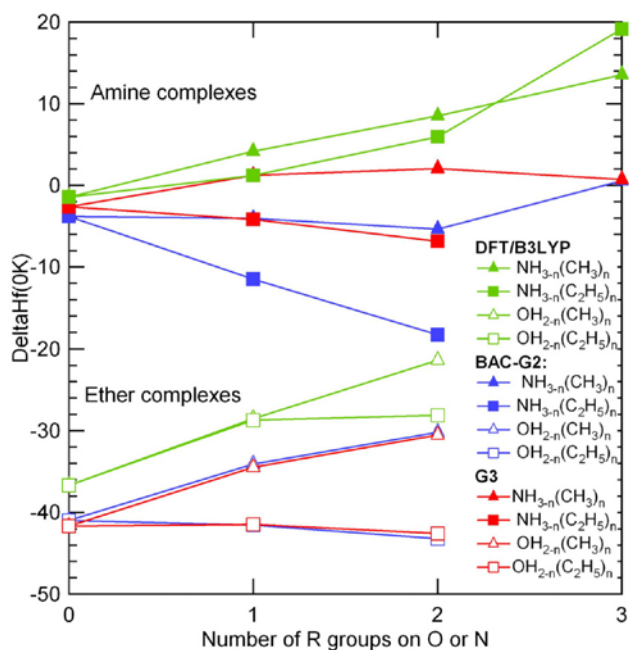

FIGURE 5. Trends in Heats of Formation (0 K) of Alane-Amine and Alane-Ether Complexes Predicted by DFT, BAC-G2, and the G3 Methods

< tertiary), with a similar trend observed for ether complexes, although steric effects destabilize some of the tertiary amine complexes. Based on these results, we conclude that the complex with triethylamine is the least stable of the amines and thus most easily decomposed to release AlH_3, while of the ethers $AlH_3O(C_2H_5)_2$ has the smallest complexation energy.

Conclusions

Our work in FY 2009 can be summarized as follows:

- Completed a comprehensive PEGS study of the polymorphs of $Ca(BH_4)_2$, validated with experimental findings.
- Measured the enthalpy of desorption of $Ca(BH_4)_2$, found it to be 60-100 kJ/mole H_2. This enthalpy is too large for $Ca(BH_4)_2$ to be considered a viable hydrogen storage material.
- Experimentally synthesized a variety of metal-$B_{12}H_{12}$ salts, thereby gaining understanding of their chemistry and role as intermediates in borohydride hydrogen storage.
- Found that $CaB_{12}H_{12}$ cannot be readily hydrogenated, explaining in part the poor cycling characteristics of $Ca(BH_4)_2$.
- Using STMBMS, found that $Ca(BH_4)_2$ releases substantial BH_3 along with H_2 when heated.
- "Down-selected" $Ca(BH_4)_2$, removing it from further study as a viable hydrogen storage material.

- Completed theoretical studies of the reaction pathways and thermodynamics of hydrogen desorption from $Mg(BH_4)_2$ and $Ca(BH_4)_2$.

- Developed a method to dope MgB_2 with carbon, thereby opening up a study of the effects of C on $Mg(BH_4)_2$ hydrogen release.

- Initiated a study of the properties of $Ti(BH_4)_3$, opening up future studies of mixtures of borohydrides with $Ti(BH_4)_3$.

- Synthesized ammonia additives of mixed metal borohydrides, found them to behave very differently from the ammonia adduct of magnesium borohydride.

- Initiated studies of mixtures of borohydrides and amides, found reduced thermal requirements for some compounds.

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The main focus of our future work will be improvement of existing materials and synthesis of new hydride materials with improved hydrogen storage characteristics. Future directions also will include extensive theoretical and experimental efforts towards gaining mechanistic understanding regarding the fundamental processes occurring during the cycling of metal hydrides.

Special Recognitions & Awards/Patents Issued

1. Rönnebro, E.; Severa, G.; Jensen, C. Patent application. 2009.

2. Jay Keller, the MHCoE Deputy Director and Sandia Hydrogen Program Manager, received the 2009 "DOE Hydrogen Program Special Recognition Award" for years of outstanding contributions to the DOE Hydrogen Program.

FY 2009 Publications/Presentations:

1. "Role of Cation Size on the Structural Behavior of the Alkali-Metal Dodecahydro-*closo*-Dodecaborates", J.-H. Her,

W. Zhou, V. Stavila, C.M. Brown and T.J. Udovic, *J. Physical Chemistry C*, **2009**, (in press) DOI: 10.1021/jp904980m.

2. "Probing the structure, stability and hydrogen storage properties of calcium dodecahydro-*closo*-dodecaborate", V. Stavila, J.-H. Her, W. Zhou, S. Hwang, Ch. Kim, L.A.M. Ottley, T.J. Udovic, submitted.

3. "Alkali and alkaline-earth dodecahydro-closo-dodecaborates and their relevance to hydrogen storage" V. Stavila, J.-H. Her, M. Kartin, W. Zhou, S. Hwang, Ch. Kim, T.J. Udovic, 238th American Chemical Society meeting, Washington, D.C., August 16–20, **2009**.

4. "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", J.-H. Her, W. Zhou, V. Stavila, C.M. Brown, T.J. Udovic, 238th American Chemical Society Meeting, Washington, D.C., August 16-20, **2009**.

5. "Crystal structures of $M_nB_{12}H_{12}$ (n=1,2) compounds – possible intermediate species in the decomposition of $M(BH_4)_n$", J.-H. Her, V. Stavila, M. Yousufuddin, W. Zhou, S.S. Jalisatgi, E. Rönnebro, T.J. Udovic, American Crystallographic Association Meeting, July 25–30, **2009**, Toronto, Canada.

6. "$LiSc(BH_4)_4$ as a Hydrogen Storage Material: Multinuclear High Resolution Solid State NMR and First-Principles Density Functional Theory Studies," S. Hwang, C. Kim, R. Bowman, J. Reiter, J. Zan, J. Kulleck, H. Kabbour, V. Ozolins, E.H. Majzoub, Journal of Physical Chemistry C **113**, 9956-9968 (2009).

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