

## IV.A.3 Efficient Discovery of Novel Multicomponent Mixtures for Hydrogen Storage: A Combined Computational/Experimental Approach

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### Objectives

The objective of this project is to discover novel mixed hydrides for hydrogen storage, which enable the DOE 2010 system-level goals. Our goal is to find a *material* that desorbs 8.5 wt% H<sub>2</sub> or more at temperatures below 85°C. The project will combine first-principles calculations of reaction thermodynamics and kinetics with material and catalyst synthesis, testing,

and characterization. We will combine materials from distinct categories (e.g., chemical and complex hydrides) to form novel multicomponent reactions. Systems to be studied include mixtures of complex hydrides and chemical hydrides (e.g. LiNH<sub>2</sub>+NH<sub>3</sub>BH<sub>3</sub>) and nitrogen-hydrogen based borohydrides (e.g. Al(BH<sub>4</sub>)<sub>3</sub>(NH<sub>3</sub>)<sub>3</sub>).

### 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:

- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (A) System Weight and Volume
- (E) Charging/Discharging Rates

### Technical Targets

This study is aimed at fundamental insights into new materials and the thermodynamic and kinetic aspects of hydrogen release and reabsorption from them. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L

### Accomplishments

- Used computational methods (density functional theory [DFT], prototype electrostatic ground state [PEGS], grand-canonical linear programming [GCLP]) to scan through and predict all possible reactions in Li-Mg-B-N-H system with reversible thermodynamics.
- New high-capacity reactions predicted, including those involving (NH<sub>4</sub>)<sub>2</sub>B<sub>12</sub>H<sub>12</sub> (preliminary experimental verification underway).
- Used PEGS method to predict amido-borane structures. Good agreement with experiment where available (e.g., LiAB and KAB) and good prediction of structure for many other cases.
- NHBHNHBH<sub>3</sub> dianion as ammonia-borane (AB) intermediate product supported by DFT calculations.
- Computational prediction and experimental observation of new mixed BH<sub>4</sub>/NH<sub>2</sub> compounds in Na and Ca systems.

- PEGS predictions for ammoniated borohydrides and mixed-metal borohydrides.
- Exploration of novel catalyst design - initial results for  $\text{Ca}(\text{BH}_4)_2$ .



## Introduction

The 2010 and 2015 FreedomCAR/DOE targets for hydrogen storage systems are very challenging, and cannot be met with existing materials. The vast majority of the work to date has delineated materials into various classes, e.g., complex and metal hydrides, chemical hydrides, and sorbents. However, very recent studies indicate that *mixtures* of storage materials, particularly mixtures *between various classes*, hold promise to achieve technological attributes that materials within an individual class cannot reach. Our project involves a systematic, rational approach to designing novel multicomponent mixtures of materials with fast hydrogenation/dehydrogenation kinetics and favorable thermodynamics using a combination of state-of-the-art scientific computing and experimentation. Specifically, we focus on combinations of materials from distinct categories (e.g., chemical and complex hydrides) to form novel multicomponent reactions.

## Approach

We use the accurate predictive power of first-principles modeling to understand the thermodynamic and microscopic kinetic processes involved in hydrogen release and uptake and to design new material/catalyst systems with improved properties. Detailed characterization and atomic-scale catalysis experiments elucidate the effect of dopants and nanoscale catalysts in achieving fast kinetics and reversibility. And, state-of-the-art storage experiments give key storage attributes of the investigated reactions, validate computational predictions, and help guide and improve computational methods. In sum, our approach involves a powerful blend of: 1) hydrogen storage measurements and characterization, 2) state-of-the-art computational modeling, 3) detailed catalysis experiments, and 4) in-depth automotive perspective.

## Results

### First-Principles Prediction Of Novel Storage Reactions in the Li-Mg-B-N-H System

Metal borohydrides and amides exhibit some of the highest hydrogen capacities among the known solid-state materials. Compounds with Li, Mg, B, N, and H are particularly interesting as they involve numerous

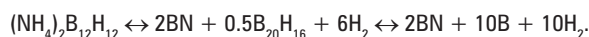
compounds of potentially high relevance for hydrogen storage:

1. Borohydrides:  $\text{LiBH}_4$ ,  $\text{MgBH}_4$ ,  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ ,  $\text{MgB}_{12}\text{H}_{12}$
2. Amides and imides:  $\text{LiNH}_2$ ,  $\text{Mg}(\text{NH}_2)_2$ ,  $\text{Li}_2\text{NH}$ ,  $\text{MgNH}$ ,  $\text{Li}_2\text{Mg}(\text{NH})_2$ , etc.
3. Borohydride-amide mixed compounds:  $\text{Li}_2\text{BNH}_6$ ,  $\text{Li}_4\text{BN}_3\text{H}_{10}$
4. Ammoniated borohydrides:  $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$
5. AB and derivatives:  $\text{BH}_3\text{NH}_3$ ,  $\text{BH}_2\text{NH}_2$ ,  $\text{LiBH}_2\text{NH}_3$ , etc.
6. B-N-H and B-H compounds:  $\text{B}_2\text{H}_6$ ,  $\text{B}_4\text{H}_{10}$ ,  $\text{B}_{16}\text{H}_{20}$ ,  $\text{B}_{20}\text{H}_{16}$ ,  $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ , etc.
7. Various reaction products: elements (Li, Mg, B,  $\text{N}_2$ ), metal hydrides ( $\text{LiH}$ ,  $\text{MgH}_2$ ), metal borides ( $\text{MgB}_2$ ,  $\text{MgB}_4$ ,  $\text{MgB}_7$ ), metal nitrides ( $\text{Mg}_2\text{N}_3$ ,  $\text{Li}_3\text{N}$ ,  $\text{LiMgN}$ ), boronitrides (BN,  $\text{Li}_3\text{BN}_2$ ,  $\text{LiMgBN}_2$ ), etc.

Using DFT methods, we have calculated the total crystal binding energies and vibrational free energies of all currently known compounds in the Li-Mg-B-N-H system (approximately 50 compounds). The structures of most of these compounds have been taken from the Inorganic Crystal Structure Database. To these, we have added the theoretically predicted compounds whose structures have been obtained using the PEGS search and other structure prediction methods. The calculated free energies have been used as inputs to the GCLP approach for determining reaction pathways in multinary systems [1]. Using the GCLP method, we have rigorously determined all the thermodynamically allowed reversible reactions in the Li-Mg-B-N-H system which involve the currently known (or predicted) compounds (some of these predictions may change with the discovery of new, currently unknown Li-Mg-B-N-H compounds). Our predictions for the DOE targeted range of temperatures and pressures are given in Table 1, and the corresponding van't Hoff plots are shown in Figure 1.

Three of the five reactions in Table 1 were found by us in an earlier paper [2]. Two of these reactions (#2 and #3 in Table 1) involve  $\text{Mg}(\text{BH}_4)_2$  and  $\text{LiBH}_4$  as reactants and  $\text{MgB}_{12}\text{H}_{12}$  and  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  as end products. In Ref. [2] we showed that both these reactions possess excellent thermodynamic properties that combine low reaction enthalpies with low entropies. They remain the two most-promising single-step reversible reactions in the Li-Mg-B-N-H system.

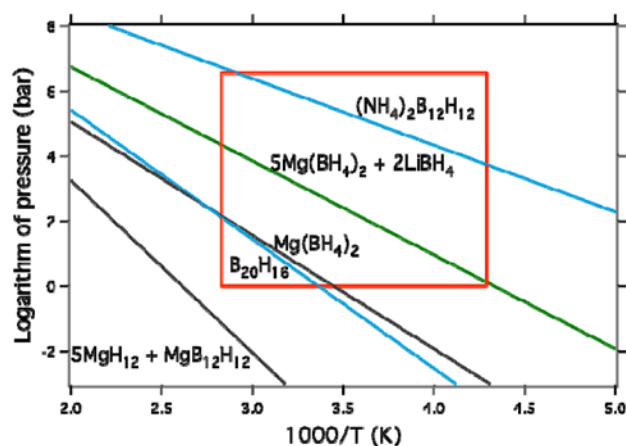
Interestingly, we now predict a novel two-step reaction involving ammonium dodecahydro-closo-dodekaborate as the starting material:



These reactions releases 11.3 wt%  $\text{H}_2$  over both steps. At  $p=1$  bar  $\text{H}_2$  pressure, the first step (decomposition of  $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$  into BN,  $\text{B}_{20}\text{H}_{16}$ ,

**TABLE 1.** Predicted thermodynamically reversible hydrogen storage reactions that fall in (or near) the targeted temperature and pressure window of -40 to 80°C and 1 to 700 bar, respectively.

Reactions	H <sub>2</sub> wt%	$\Delta H^{300K}$ (kJ/mol H <sub>2</sub> )	$\Delta S^{300K}$ (J/mol-K)
$2(\text{NH}_4)_2\text{B}_{12}\text{H}_{12} \leftrightarrow 4\text{BN} + \text{B}_{20}\text{H}_{16} + 12\text{H}_2$	6.81	17	104
$5\text{Mg}(\text{BH}_4)_2 + 2\text{LiBH}_4 \leftrightarrow 5\text{MgH}_2 + \text{Li}_2\text{B}_{12}\text{H}_{12} + 13\text{H}_2$	8.37	24	104
$6\text{Mg}(\text{BH}_4)_2 \leftrightarrow 5\text{MgH}_2 + \text{MgB}_{12}\text{H}_{12} + 13\text{H}_2$	8.10	29	100
$\text{B}_{20}\text{H}_{16} \leftrightarrow 20\text{B} + 8\text{H}_2$	6.95	33	111
$5\text{MgH}_2 + \text{MgB}_{12}\text{H}_{12} \leftrightarrow 6\text{MgB}_2 + 11\text{H}_2$	7.46	44	115



**FIGURE 1.** The calculated van't Hoff diagram for the thermodynamically reversible hydrogen storage reactions given in Table 1. Each line is labeled by the reactant or the combination of reactants. The red rectangle represents the targeted temperature-pressure window of -40 to 80°C and 1 to 700 bar, respectively.

and H<sub>2</sub>) occurs at -120°C, while the second step (decomposition of B<sub>20</sub>H<sub>16</sub> into B and H<sub>2</sub>) proceeds at 20°C. In contrast to the conventional complex hydrides that contain metal cations and complex anions, the above reaction represents a new paradigm where the storage material contains both anionic and cationic complexes.

### First-Principles Studies of Metal Amidoboranes

Metal amidoboranes, M(NH<sub>2</sub>BH<sub>3</sub>)<sub>n</sub> (M=metal atoms) or MAB, are interesting candidates for on-board hydrogen storage materials with promising properties, like high gravimetric capacity, low hydrogen release temperature, and the ability to suppress toxic borazine emission. But details about the intermediate products are largely unknown and these products are often categorized as amorphous. Armed with the PEGS+DFT methodology, we have searched for crystal structures of possible intermediate phases with [NHBH<sub>2</sub>], [NBH], [NBH<sub>6</sub>], polymer-[NHBH<sub>2</sub>] anion groups in the decomposition of LiAB and CaAB. All of these anion

groups were selected in analogy with the decomposition sequence and products for NH<sub>3</sub>BH<sub>3</sub>. However, all these reaction pathways produce high-endothermic hydrogen release enthalpies, which are far away from the experimental suggested nearly thermoneutral values, (-3~-5 kJ/mol H<sub>2</sub> in LiAB and 3.5 kJ/mol H<sub>2</sub> in CaAB).

Recently, proposals in the literature have pointed towards the possibility of a new dianion group [NHBHNHBH<sub>3</sub>], which might be formed in the decomposition of CaAB. For the cases of LiAB and CaAB, we used PEGS+DFT to predict crystal structures of this new metal-dianion intermediate compounds. For the static energies, these reaction pathways are much lower in energy than the above anion groups, lending credibility to the possible stability of the dianion group as an intermediate product. Hydrogen release enthalpies are calculated to be (static) 27.36 kJ/mol H<sub>2</sub> in LiAB and 27.33 kJ/mol H<sub>2</sub> in CaAB. Introducing the entropy effects from phonon calculations, the enthalpies are shifted down by a roughly constant amount, ~25 kJ/mol H<sub>2</sub> at 0 K and ~20 kJ/mol H<sub>2</sub> at 300 K. With these shifts due to vibrations, we successfully obtain calculated enthalpies that are in good agreement with the experimentally suggested nearly thermoneutral data at finite temperatures. This good agreement gives confidence in the ability of PEGS+DFT to determine MAB reaction products, and also provides strong evidence that the dianion phases are highly probable products in the decomposition of metal amidoboranes.

### Exploration of Catalyst for Improved Hydrogen Absorption/Desorption Kinetics

Hydrogen evolution from complex hydrides is dictated by an inter-related sequence of chemical reaction steps including decomposition of the hydride, diffusion of hydrogen atom/ion and counter ions in the solid lattice, surface diffusion of these atoms/ions, recombination of hydrogen atoms, transformation of lattice phases, and desorption of hydrogen molecules. Reversing these step would lead to formation of the hydride. Improving kinetics in these reaction steps allows complex hydrides to evolve hydrogen under milder operating conditions (i.e. temperature and

pressure). For this funding period, we explore the concept that the hydrogen evolution kinetics can be facilitated by a catalyst external to the complex hydride. Furthermore, the effectiveness of the catalyst depends on the contact area between the catalyst and the complex hydride. Our hypothesis is that a light-weight, effective catalyst could be constructed with a known transition metal hydrogenation catalyst, that dissociatively adsorb and associatively desorb hydrogen molecules readily, highly dispersed on a carbon support on which hydrogen atoms can diffuse rapidly. By dispersing such a composite catalyst in a mixture with complex hydride, we can attain a high contact area between the catalyst and the hydride with minimal weight penalty. The contact points would serve both for hydrogen transfer between the catalyst complex and the hydride and as potential nucleation points for phase transformation of the hydride.

To test our hypothesis, we used a well characterized hydride, calcium borohydride  $\text{Ca}(\text{BH}_4)_2$ , that decomposes at a high temperature (380-420°C). It was mixed with a series of composite catalysts comprising non-precious metal nanoparticles and multi-walled carbon nanotubes (MWCNTs). Non-precious metals were used for lower costs, and MWCNT was chosen because of their low density and their aromatic nature permits facile hydrogen diffusion. The hydrogen desorption behavior of these mixtures was characterized by their hydrogen pressure-temperature profiles. The metal-decorated MWCNTs catalytic matrix was prepared by sonication-assisted impregnation. The metal precursor containing Co, Ni, or Fe (usually metal nitrates) was dissolved in a solvent and sonicated with MWCNTs. The resulting solid mixture was thermally treated in a  $\text{H}_2$ -Ar stream, which converted (by decomposition and reduction) the loaded metal precursor to metal nanoparticles on the MWCNTs. The thermal treatment was carried out in a special sample holder that allows the reduced sample being transferred into a glove-box with no further surface oxidation.

Figure 2 shows the pressure change-temperature profiles for the pristine  $\text{Ca}(\text{BH}_4)_2$  and the catalyst- $\text{Ca}(\text{BH}_4)_2$  mixtures. It was found that the addition of either carbon nanotubes or metal-decorated carbon nanotubes lowered the decomposition temperature of  $\text{Ca}(\text{BH}_4)_2$  by 15-20°C. Among the Ni-, Fe-, and Co-MWCNT composites, Co-MWCNT was most effective and showed the lowest initial decomposition temperature.

The preliminary results show that the addition of the metal-decorated carbon nanotubes can lower the decomposition temperature of  $\text{Ca}(\text{BH}_4)_2$  complex hydride. At this moment cobalt is the most promising among Co, Fe, and Ni, metals that were investigated. Future work will include optimization of the preparation parameters for the Co-decorated MWCNT matrix, as

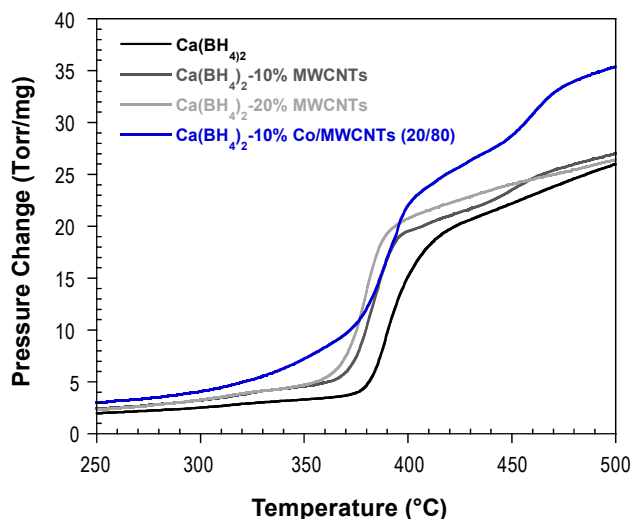


FIGURE 2. Pressure Change-Temperature Profiles

well as the parameters for operating the catalytic matrix for a more well-characterized complex hydride, for instance,  $\text{NaAlH}_4$ .

Several rate-controlling mechanisms have been proposed for the hydrogen desorption/recombination in complex hydrides. Overall, in order for hydrogen to desorb/recombine more efficiently, the hydride should have: (1) smaller particle size to obtain larger surface areas for gas phase exposure; (2) shorter diffusion length for its reaction species; (3) nucleation sites for the formation of the decomposition product phases.

The present catalyst composite can be further modified to better meet the above requirements. Our proposed reaction model involves complex hydrides in contact with the multi-functional catalytic matrix under development. The high surface area provided by the carbon nanotubes and the hydrogen spillover effect by the metal nanoparticles will increase the hydrogen gradient on the interfaces. The metal catalyst particles will serve as nucleation sites can enhance the kinetics of the subsequent reactions. Alternatively, product seeding could be attempted. For the complex hydrides with a low melting point, for example,  $\text{NaAlH}_4$ , a solid-liquid region can be retained between the interfaces of the hydride and the catalytic matrix by capillary action. Such region benefits the overall kinetics by facilitating the chemical bond breakage as well as the mass transfer of the product nuclei, which can be dispersed homogeneously via the liquid phase. In addition, carbon nanotubes, an excellent thermal conductor, can transfer heat effectively during the thermal decomposition of the hydrides. This working model cannot be realized if the hydride particles lose contact with the catalytic matrix, possibly due to the volume/morphology change in the hydride during its decomposition. Thus, to supplement the carbon nanotubes, two-dimensional graphene layers

will also be introduced into the catalytic matrix to help maintain the hydride/matrix interfaces.

### Conclusions and Future Directions

- Extend computational search for all possible promising reversible reactions in Li-Ca-B-N-H system.
- Experimentally characterize storage properties/ reactions of  $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$  and other predicted reactions.
- Extend experimental catalyst studies to  $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$  and other predicted promising materials.
- Continue computational exploration for: 1) novel  $\text{BH}_4/\text{NH}_2$  compounds and reversible reactions, 2) mixed metal borohydrides, and 3) AB reaction products.

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