

IV.C.8 Boron-Based Hydrogen Storage: Ternary Borides and Beyond

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Subcontractors

- Sandia National Laboratories, Livermore, CA
- University of Missouri, St. Louis, MO

Project Start Date: August 1, 2014

Project End Date: January 31, 2016

Overall Objectives

Improve the hydrogen cycling kinetics of high capacity boron-based hydrogen storage materials

- Eliminating multiple-phase reaction barriers using ternary borides and mixed-metal borohydrides that maintain single phases during cycling
- Minimizing boron atom rearrangement using borane substrates that cycle hydrogen by reacting with lithium hydride while preserving the boron-boron bond framework

Fiscal Year (FY) 2015 Objectives

- Synthesize single-phase Mg/transition metal ternary boride and mixed-metal borohydride with potential hydrogen content of 11 wt%
- Demonstrate example of reversible borane/lithium hydride reaction with measureable (>0.1 wt%) hydrogen release
- Calculate stability of Mg-based ternary borides and mixed-metal borohydride with potential hydrogen contents of >10 wt%
- Calculate energetics of Li/H exchange reactions with model borane substrates

Technical Barriers

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

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charging and Discharging Rates

Technical Targets

This project is conducting initial studies of hydrogen storage in ternary borides/mixed-metal borohydrides and lithiated boranes. Results of these studies will be applied toward developing hydrogen storage materials that meet the following DOE hydrogen storage system targets.

- Specific energy: 5.5 wt% H₂
- Energy density: 40 g-H₂ /L

FY 2015 Accomplishments

- Calculation of stable Mg-based ternary borides with Mn, Fe, and Co
- Synthesis of single-phase Mg/Mn (1:1, 3:1, and 9:1) ternary borides
- Demonstration of ~1 wt% H₂ cycling in Mg-Mn ternary boride
- Common scheme synthesis of Mg and Mn borohydrides
- Calculation of Li/H exchange energies and influence of heteroatom dopants
- Formation of polymerized borane BH_x from B₁₀H₁₄
- Demonstration of hydrogen evolution from reaction of BH_x with LiH



INTRODUCTION

Many boron based hydrogen storage materials have been identified with high capacities and thermodynamics that can be tailored. However, the kinetics of hydrogen exchange in these materials are too slow for practical applications. In part, the kinetic limitations originate from the multiple phases that are typically involved and/or from the extensive rearrangement of the boron atom framework over the dehydrogenation/rehydrogenation cycle. To address these

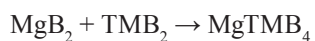
issues, this project is exploring two classes of boron-based hydrogen storage materials. The first is ternary (or possibly higher order) metal borides that reversibly hydrogenate to single-phase mixed-metal borohydrides. By reducing the number of phases to a single dehydrogenated phase (the ternary boride) and a single hydrogenated phase (the mixed-metal borohydride), the kinetic barriers associated with phase nucleation and diffusion of heavy atoms should be minimized thus improving the kinetics. In addition, use of multiple metals of varying electronegativity permits tuning of the exchange thermodynamics. The second class of materials termed “lithiated boranes” reversibly release hydrogen from boranes (B_nH_x) by reaction with LiH to form B_nLi_x while preserving the underlying boron atom framework (B_n). By preserving this framework, the kinetic barriers associated with boron atom rearrangement are avoided. If possible, this reaction would constitute a new class of hydrogen storage materials.

APPROACH

Work in this project involves parallel experimental efforts for both classes of materials approached from the hydrogenated and the dehydrogenated states. Thus, ternary borides will be synthesized from the elements or the corresponding binary borides. After characterization to determine that the desired ternary boride is single-phase and stable, the hydrogenation behavior will be studied. Similarly, from the hydrogenated state, mixed-metal borohydrides will be synthesized directly or from the pure metal borohydrides. Dehydrogenation of these materials will then be studied. For reaction of boranes with lithium hydride, a variety of possible borane substrates will initially be screened. These range from molecular to polymeric and nanoparticle, and extended Li-B alloys representing the dehydrogenated state. Selected boranes will then be mixed with lithium hydride and their hydrogen cycling behavior studied. Together with this experimental effort, a computational effort will guide material choices. Computations will be used to screen the stability of possible ternary borides and mixed-metal borohydrides. Calculations will also be performed to access the energetics of Li/H exchange in reaction of LiH with model borane compounds.

RESULTS

Initial work on the ternary borides began by considering ternary borides of Mg with the first row transition metals (TM). Figure 1 shows predicted reaction energies (ΔE) for the formation of Mg/TM ternary borides with the compositions of $MgTMB_4$ and Mg_2TMB_6 , according to the reactions



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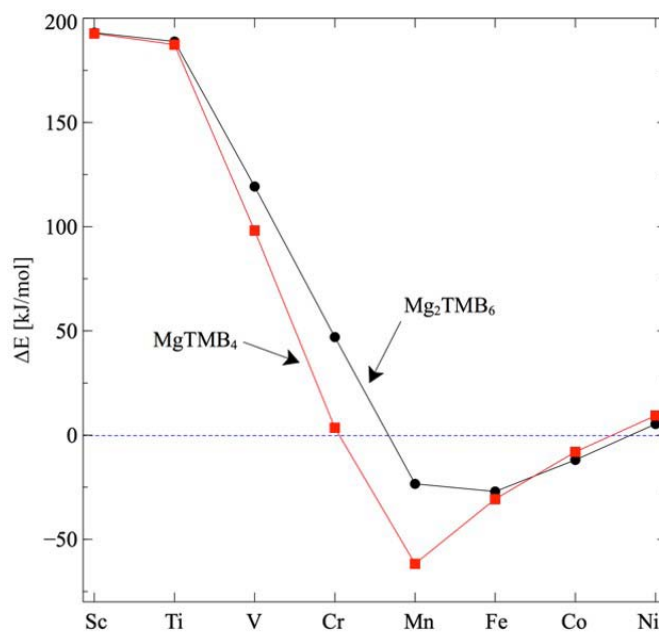


FIGURE 1. Predicted stability of ternary borides. Reaction energies for the formation of $MgTMB_4$ and Mg_2TMB_6 from the binary borides calculated using density functional theory at 0 K including zero point energies (ZPE) with known experimental structures, such as Pb_{am} , as prototypes.

The binary borides TMB_2 do not form for $TM = Fe, Co,$ and Ni . Thus, for these reactions $B + TMB$ was substituted for TMB_2 . If fully hydrogenated to the mixed-metal borohydrides, all of these compositions would have capacities of >11 wt% hydrogen enabling meeting the DOE system target. The reaction energy is predicted to be >0 kJ/mol for $TM = Sc, Ti, V$, indicating that these borides may be unstable and could phase separate into the binary borides during hydrogen cycling. In contrast, for $TM = Mn, Fe,$ and Co , the predicted energy is negative indicating that these compounds are stable. Compositions with Mg:TM ratios of 1:1 are predicted to be more stable than for ratios of 2:1. For $TM = Cr$ and Ni , the predicted energy is approximately thermo-neutral.

Based in part on the calculations described above, synthesis of $Mg_xMn_{1-x}B_2$ for $x = 0.5, 0.75,$ and 0.9 was performed by high-energy mechanical milling of the binary borides, MgB_2 and MnB_2 . The results for $x = 0.5$ (Mg:TM ratio of 1:1) are shown using X-ray diffraction in Figure 2. The diffraction pattern for the milled sample shows the same symmetry as MgB_2 suggesting a single phase was in fact synthesized, exclusive of small peaks associated with a Mn_3B_4 impurity in the MnB_2 starting material. The diffraction angles are intermediate between those for MgB_2 and MnB_2 . This also suggests a single phase with an intermediate unit cell size. In addition, energy dispersive X-ray analysis showed a uniform distribution of Mg and Mn.

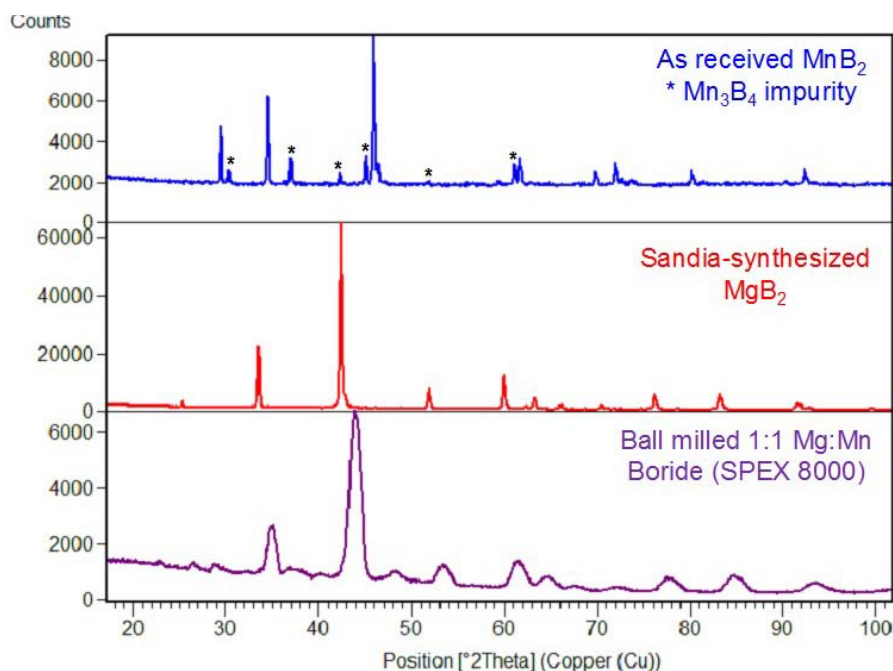


FIGURE 2. Synthesis of $Mg_{0.5}Mn_{0.5}B_2$ ternary boride. (top panel) X-ray diffraction patterns for commercial MnB_2 with Mn_3B_4 impurity; (middle panel) MgB_2 synthesized at Sandia National Laboratories; and (bottom panel) ternary boride from 1:1 mixture of MgB_2 and MnB_2 after mechanical milling (SPEX 8000) for 16 h.

Finally, the peaks are broadened indicating a nanocrystalline phase resulting from the milling.

For a similarly synthesized sample with a composition of $Mg_{0.75}Mn_{0.25}B_2$, the hydrogen cycling behavior was studied. After hydrogenation in 150 bar H_2 at $380^\circ C$ for 38 h, the uptake was estimated to be 1.2 wt% H_2 . Infrared spectroscopy indicated that borohydride anions $[BH_4]^-$ were formed, although the composition of the hydrogenated phase is still being investigated. Following hydrogenation, hydrogen desorption began upon heating to $225^\circ C$ with 0.8 wt% H_2 desorbed up to $400^\circ C$. While this capacity is small, under the same conditions little detectable hydrogen cycling (~ 0.07 wt%) and borohydride formation occurred for pure MgB_2 . This comparison illustrates a beneficial effect of using the ternary borides. In this case the Mn may have acted as a catalyst promoting dissociative hydrogen adsorption.

Reversible reaction of a borane substrate with lithium hydride to evolve hydrogen and form a lithiated borane has not, to our knowledge, been reported. Thus the energetics of such reactions are not known. To assess whether such reactions could have energies suitable for practical hydrogen storage, calculations were performed for Li/H exchange from LiH in a series of small molecular boranes. Initial calculations assumed gas phase boranes for simplicity. The results are shown in Figure 3. The predicted energies are highly endothermic, >100 kJ/mol- H_2 . However, the energies decrease drastically with framework size indicating more favorable energies for larger solid polymeric boranes.

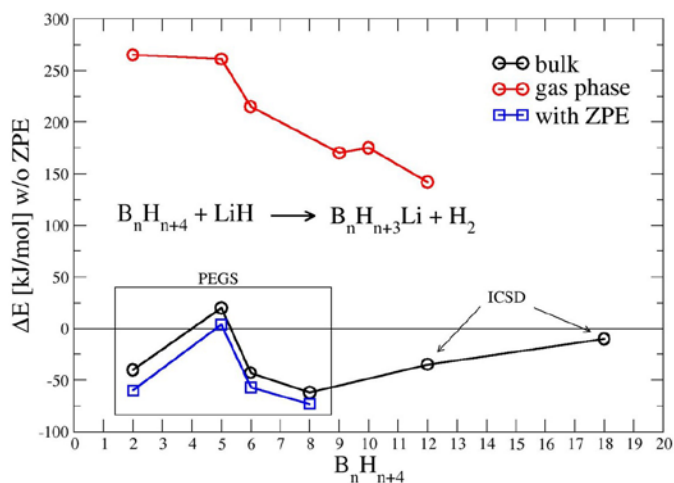


FIGURE 3. Energies for Li/H exchange reactions. Comparison of first principles gas-phase calculations (top circles, red) with bulk density functional theory calculations (bottom circles, black) including ZPE (squares, blue) all at $T = 0$ K. As indicated, bulk calculations using prototype electrostatic ground state structures for $n = 2, 5, 6$ and 8 and inorganic crystal structure database structures for $n = 12$ and 18 .

Subsequently, calculations for solid-state clusters of selected boranes were also performed. As also shown in Figure 3, these calculations give much lower predominately exothermic energies that may increase with framework size. As expected, solid-state energies differ significantly from gas-phase

energies for small frameworks. However, they appear to converge for larger frameworks, suggesting an exchange energy of ± 25 kJ/mol- H_2 for boranes B_nH_x with $n > 20$. While this current uncertainty is large, the results suggest that a reversible reaction is feasible. Additional calculations performed have focused on how heteroatom doping, for example with C, N, O, or Cl alters the exchange energy.

Initial experiment work to demonstrate a reversible lithiated borane hydrogen storage reaction utilized commercially available molecular substrates $B_{10}H_{14}$ and $C_2B_{10}H_{12}$. While reactions with LiH were seen, the volatile nature of these substrates made them impractical for hydrogen storage and lab-scale Sieverts apparatus measurements. To eliminate the issue of volatility, $B_{10}H_{14}$ was thermally polymerized by extended (days) heating at temperatures of 200°C to 300°C. The resulting borane was found to have a composition, by both weight loss measurements and neutron prompt gamma ray activation analysis (conducted at the National Institute of Standards and Technology), of BH_x with $x = \sim 0.6$ to 0.7. After polymerization the resulting BH_x material was milled with LiH at a B:Li ratio of 1:1. The first cycle dehydrogenation of a sample polymerized at 250°C for 2 days is shown in Figure 4. A small (~ 0.5 wt%) but significant hydrogen desorption occurs from $\sim 100^\circ\text{C}$ to 200°C. This dehydrogenation appears to be associated with reaction with LiH because a control sample similarly prepared but not milled with LiH showed desorption beginning at higher temperatures with much less hydrogen evolved (~ 0.1 wt%). Thus far, this hydrogen desorption has not been reversible and differential scanning calorimetry measurements indicated that the reaction is exothermic. At higher temperatures (350°C to 400°C) reversible cycling of ~ 1 wt% H_2 occurred; however, this hydrogen appeared to be associated with the formation of $LiBH_4$. Study of this reaction is continuing and modified polymerization routes that incorporate heteroatoms are being considered.

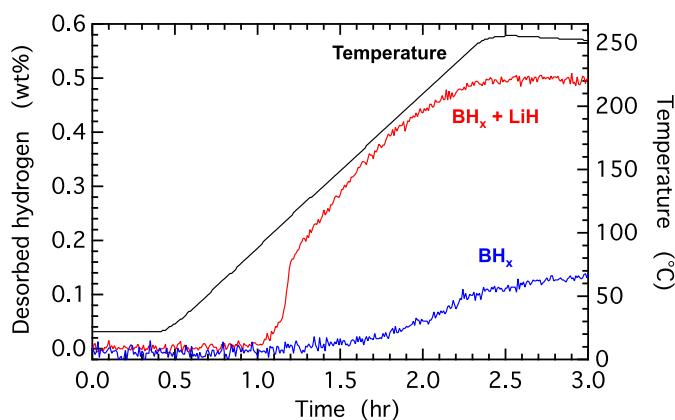


FIGURE 4. Dehydrogenation in polymerized borane/lithium hydride reaction. As labeled: temperature ramp (black) and desorbed hydrogen from polymerized borane $BH_x + LiH$ (red) and polymerized borane BH_x without LiH (blue).

SUMMARY AND FUTURE DIRECTIONS

Stable Mg/TM ternary borides were predicted computationally and a stable single-phase Mg/Mn material was achieved experimentally. The Mg/Mn boride showed significant enhancements for hydrogen uptake (~ 1 wt% for the conditions of the experiment) and borohydride formation when compared to pure MgB_2 . Polymerized $B_{10}H_{14}$ was identified as a nonvolatile substrate for Li/H reaction with LiH. Additives could be incorporated into the boron framework during polymerization enabling versatile modification by heteroatom doping. A low temperature (100°C to 200°C) Li/H exchange (hydrogen evolution) reaction of polymerized borane with LiH was identified, although thus far the reaction was not reversible. Calculations were performed to determine the energetics of exchange. An initial estimate, limited by the complexity of crystalline molecular boranes, of ± 25 kJ/mol- H_2 was found indicating that a practical reversible reaction may be possible.

Future work will include:

- Calculations of ternary borides with lower TM ratios in the solid solubility range in order to optimize potential hydrogen capacity.
- Synthesis and characterization of Mg/Fe and Mn/Co ternary borides with a wide range of compositions.
- Synthesis and hydrogen cycling behavior of mixed-metal borohydrides.
- Optimization of borane polymerization to achieve reversible hydrogen cycling with LiH.
- Evaluation of hydrogenated boron nanoparticles for Li/H exchange.
- Refinement of the predicted energies for Li/H exchange.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. "Boron-Based hydrogen Storage: Ternary Borides and Beyond," Presentation to the Hydrogen Storage Tech Team, Southfield, MI, January, 2015.
2. "Boron-Based hydrogen Storage: Ternary Borides and Beyond," Presentation at the Hydrogen Storage PI Meeting, Golden, CO, January, 2015.
3. "Boron-Based hydrogen Storage: Ternary Borides and Beyond," Presentation at the 2015 DOE Fuel Cell Technologies Program Annual Merit review, Crystal City, Virginia, June 2015.