

IV.E.3 Novel Carbon(C)-Boron(B)-Nitrogen(N)-Containing H₂ Storage Materials

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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/Discharging Rates

Technical Targets

This project is developing and characterizing new CBN materials for hydrogen storage. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2017 hydrogen storage system targets:

- Specific energy: 1.8 kWh/kg (5.5 wt%)
- Energy density: 1.3 kWh/L (4.0 vol%)

FY 2013 Accomplishments

- Synthesized 9 out of 12 proposed CBN materials
- Characterized all synthesized materials in terms of capacity, melting point, and density
- Characterized Compound **B** with regard to: viscosity, polarity, enthalpy of H₂ desorption, H₂ purity, thermal stability
- Characterized properties of fuel blends with **B** as the “solvent”
- Calculated important thermodynamic and kinetic parameters for select CBN compounds and developed a preliminary understanding of the desorption mechanism for CBN material **B**
- Demonstrated stable fuel cell operation with Compound **B**



INTRODUCTION

Approaches to store H₂ in chemical bonds provide a means for attaining high energy densities. Molecular complexes containing protic and hydridic hydrogen such as ammonia-borane (AB) provide between 8 to 16 wt% H₂ at acceptable temperatures in a kinetically controlled decomposition. AB shows promise to meet a number of

Overall Objective

Develop new CBN-based chemical hydrogen storage materials that have the potential to meet the DOE technical targets for automotive applications.

Fiscal Year (FY) 2013 Objectives

- Synthesize Compound **E** and its derivatives
- Develop catalysts that can achieve H₂ desorption from the carbon portions of the CBN compounds to achieve higher storage capacity of these materials
- Determine the thermodynamics and kinetics for the desorption of Compound **H**
- Characterize the viscosity of spent fuel of Compound **B** and its fuel blends
- Complete the potential energy surface calculations for the potential diverse pathways of H₂ desorption from Compound **B**

important technological targets such as high volumetric and gravimetric density of H₂, fast kinetics, thermal stability, facile synthesis at large scale, and safe handling under atmospheric conditions. Some of the challenges involving AB include: volatile impurities (e.g., ammonia, diborane, borazine), handling of solids, and the economics of spent fuel regeneration [1-4].

This project is developing hydrogen storage materials that contain the element carbon in addition to boron and nitrogen. The inclusion of carbon can be advantageous for developing chemical H₂ storage materials that are structurally well defined (thus have good potential to be liquid phase), exhibit thermodynamic properties conducive to reversibility, and demonstrate good storage capacities.

APPROACH

This project will develop new CBN H₂ storage materials that have the potential to meet the DOE targets for motive and non-motive applications. Specifically, we will be focusing on three basic systems: 1) liquid-phase systems that release H₂ in a well-defined and high-yield fashion, minimizing the formation of NH₃ and B₃N₃H₆; 2) reversible storage systems that could potentially be regenerated onboard; and 3) high H₂-content storage systems that can be used in slurries and regenerated off-board (see Figure 1). Computational chemistry studies will help direct our research. Finally, we will demonstrate the developed material with a fuel cell. These new materials will be prepared and characterized

by our interdisciplinary team comprised of the University of Oregon, The University of Alabama, Pacific Northwest National Laboratory, and Protonex Technology Corporation (Southborough, MA, a small business fuel cell manufacturer).

RESULTS

Characterization of the Liquid Carrier B and its Fuel Blends

In FY 2012, we synthesized a liquid carrier Compound **B** and developed catalytic conditions for the release of H₂ from this compound at 80°C. This year, we performed additional characterization studies of Compound **B** that are relevant to H₂ storage applications.

The thermal stability of liquid carrier **B** was investigated using thermal gravimetric analysis/mass spectrometry (TGA/MS). We did not detect any volatile materials (H₂, Et₂O, tetrahydrofuran [THF], pentane, etc.) in the mass spectrometer at 30°C. However, slight H₂ evolution can be observed starting at 50°C (Figure 2a, green trace; t = 360 min). Similarly, escape of residual diethyl ether (Figure 2a, black trace) and THF (Figure 2a, red trace) from the liquid carrier **B** can be observed starting at 50°C. Also, the thermal decomposition of Compound **B** was monitored using ¹¹B nuclear magnetic resonance spectroscopy, which corroborates the TGA/MS data and indicates that the liquid carrier **B** decomposes slowly at 50°C.

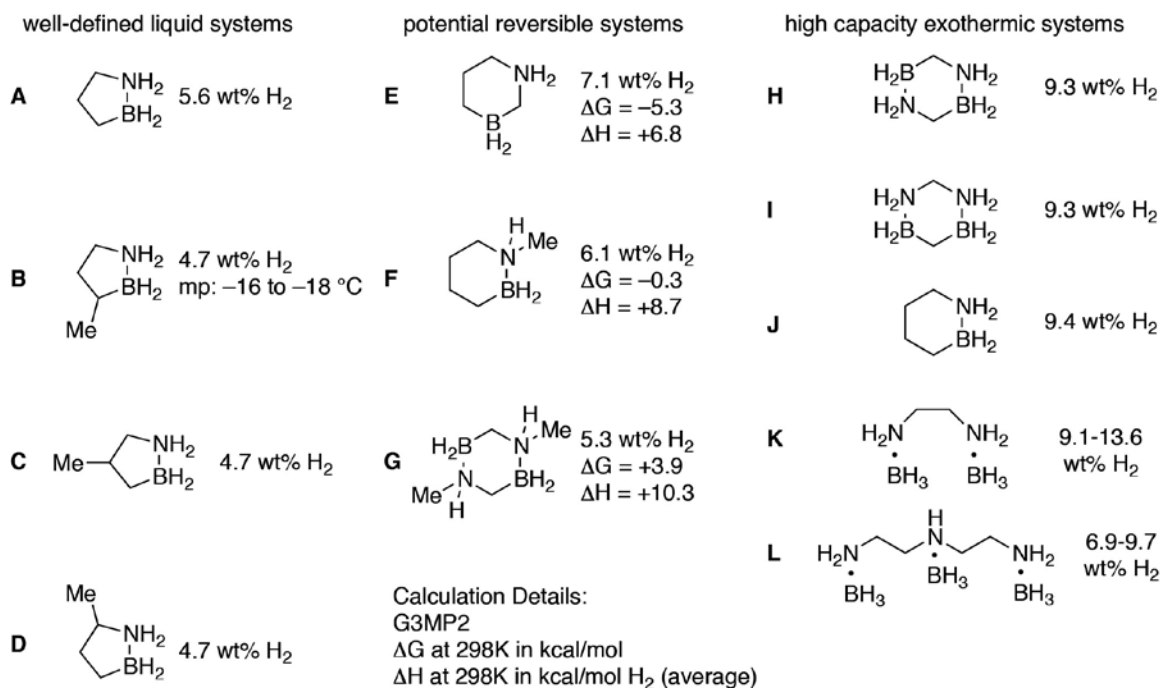


FIGURE 1. Selected synthetic targets and their potential storage capacities and predicted thermodynamic parameters.

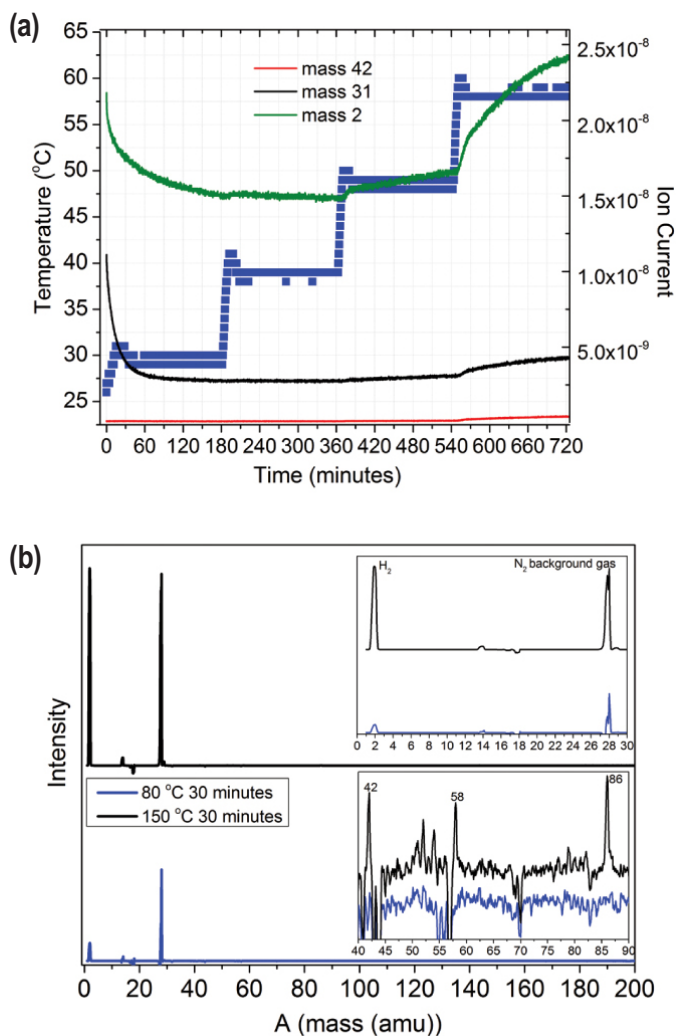


FIGURE 2. (a) MS coupled TGA: monitoring of volatile materials via mass spectrometry (green: hydrogen; black: diethyl ether; red: THF). (b) RGA data for liquid carrier **B** at 150°C (black trace) and at 80°C (blue trace). Top right inset: zoomed-in region below 30 amu. Bottom right inset: zoomed-in region from 40–90 amu.

The purity of generated H₂ gas is an important factor to evaluate the hydrogen storage material. We carried out residual gas analysis (RGA) of the volatile components when **B** was heated at 150°C, (Figure 2b, black trace) and at 80°C (Figure 2b, blue trace) to monitor the purity of H₂ generated from the desorption of **B**. As can be seen from the data, with the exception of some N₂ background gas, H₂ is the major detectable species both at 80 and 150°C. At 150°C, a trace amount of Compound **B** (amu = 86) can be detected in the gas stream (Figure 2b, bottom right inset). The data indicate that (1) both the starting material carrier **B** and its spent fuel trimer are not very volatile at an operating temperature of 80°C, and (2) the thermal hydrogen desorption from **B** does not lead to appreciable impurities in the H₂ gas stream. Some residual ether (THF, diethyl ether) from the synthesis was detected in some experiments, but notably no parent borazine B₃N₃H₆ was detected.

Another important characteristic of a liquid H₂ storage carrier is its viscosity. A viscosity value smaller than 500 cP is considered to be suitable for pumping [5]. We measured the viscosity of Compound **B** using a dynamic mechanical rheometer and found it to be 25 ± 5 cP at room temperature, which is comparable to that of ethylene glycol. Temperature dependent viscosity studies in the range of 15–50°C did not show significant changes.

We determined that AB is relatively soluble in the liquid Compound **B**. The resulting fuel blend (**B**: AB = 2:1 molar ratio) exhibits improved H₂ capacity (5.6 wt% H₂ vs. 4.7 wt% H₂ for pure **B**), faster kinetics (relative to thermal H₂ desorption for either pure **B** or AB), and produces a spent fuel that is a liquid at room temperature. RGA analysis of the volatiles that were released upon thermal decomposition shows no detection of borazine, ammonia, or diborane.

Synthesis and Characterization of New Targets D, G, and B-Methyl Substituted Amine-Boranes

With respect to new targets, we successfully synthesized targets **D**, **G**, and **H** and performed measurements of the dehydrogenation reaction of some of these compounds using the automated gas burette. At a concentration of 0.59 M in diglyme, we dehydrogenated Compound **D** using CoCl₂ and found that it took about 100 minutes to dehydrogenate two equivalents hydrogen at 80°C, which is much slower than any of the BN-cyclopentyl series, i.e., compounds **A**-**C**. As for Compound **G**, two equivalents of H₂ could also be released as expected at 0.17 M using Pd/C at 120°C.

In addition to the compounds listed in Figure 1, we synthesized *B*-methyl substituted amine-boranes for potential use in chemical hydrogen storage. Though many *N*-substituted amine-boranes have been studied, a relatively small number of *B*-substituted amine-boranes have been investigated. We synthesized *B*-methyl AB derivatives by mixing ammonium chloride or methylamine hydrochloride and lithium methylborohydride in ether solution to give NH₃BH₂Me and MeNH₂BH₂Me, respectively. We dehydrogenated both of these two compounds under Co(II) chloride catalysis at 80°C, the same as for Compound **B**. Two equivalents of hydrogen can be released from both *B*-methyl AB derivatives (Figure 3). The spent fuel product of MeNH₂BH₂Me can be regenerated to the charged form with formic acid and lithium aluminum hydride.

Investigation of CBN Systems with Computational Chemistry

We have predicted the boiling points and many thermodynamic parameters (heats of formation, heats of dehydrogenation, etc.) of the target CBN compounds using computational chemistry. We have also been investigating possible mechanisms for the dehydrogenation of **B**. We began our work first using density functional theory at the B3LYP/DZVP2 level and then refined the calculations using the

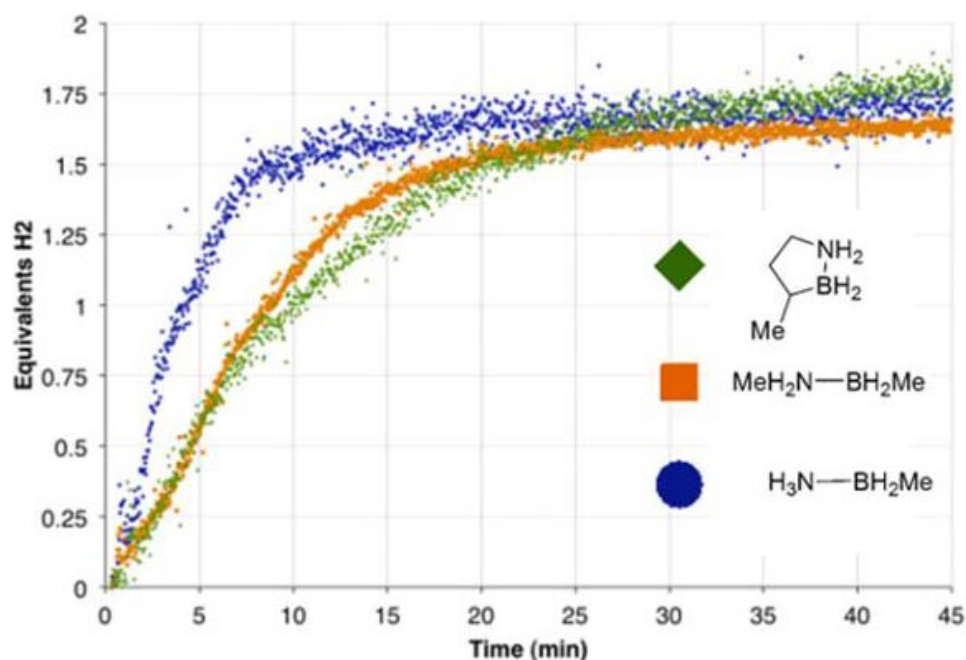


FIGURE 3. Synthesis and dehydrogenation of *B*-methyl AB derivatives

higher correlated molecular orbital theory G3MP2 level, all at 298 K. The potential energy surface for our current working mechanistic hypothesis for the dehydrogenation of **B** is shown in Figure 4. Compound **B** first forms a dehydromonomer with release of 2 equivalent of H₂ (Figure 4a). This dehydromonomer is in equilibrium with its dehydromonomer. This dehydromonomer of **B** can react with the dehydromonomer (Figure 4b) to generate a cyclotriborazane. The sequential release of hydrogen from the cyclotriborazane intermediate is exothermic by 24 kcal/mol to form the final spent fuel material (Figure 4c). The stepwise dehydrogenation reactions have barriers that decrease as each equivalent of hydrogen is released.

Scale-Up Synthesis and Fuel Cell Operation of Compound B

With preliminary RGA studies showing the purity of the hydrogen stream, we set out to test the hydrogen produced from **B** in a working fuel cell. However, this required the use of large quantities of material. In order to access larger quantities (~40 g), we had to modify the existing protocols to use techniques such as distillation and filtration that allow for greater scalability. Previously, we reported the isolation of less than 1 g at a time. Using the current system, we can isolate >10 g at a time. About 45 g of **B** have been produced in this manner. Additional compound **B** was obtained from recycling of its spent fuel according to our published procedures [6].

Initial fuel cell tests using Compound **B** showed the presence of some volatiles in the gas stream; the fuel cell stack performance decreased rapidly when its hydrogen

source was switched from Protonex facility hydrogen to the hydrogen generated by the dehydrogenation of **B** using an iron(II) chloride catalyst. Upon investigation, we found that the gas stream contained miniscule amounts of THF, which was used in the preparation of **B**. We used a cold trap (dry ice/methanol) to collect volatiles when we tested **B** on the largest scale to date (17.4 g) and were pleased to find virtually identical fuel cell stack operation for this test versus using facility hydrogen. We were able to operate the stack for 6.75 minutes with a load of 4 A and 8.5 V. After switching the stack back to facility hydrogen, we observed no decrease in stack performance.

CONCLUSIONS AND FUTURE DIRECTIONS

This year, we were able to synthesize all target compounds in Figure 1 with the exception of **E**, **I**, and **L**. Additionally, we synthesized new *B*-methyl AB derivatives and characterized their hydrogen release and recyclability. We investigated the hydrogen release characteristics of pure and blended CBN compounds. Mechanistic studies were initiated by the use of computational chemistry. Finally, we operated a fuel cell stack using the hydrogen generated from liquid carrier **B**. Next year, we will try to:

- Synthesize derivatives of **E** and investigate reversible H₂ activation.
- Develop catalysts to achieve H₂ desorption from the carbon portions of the CBN compounds.

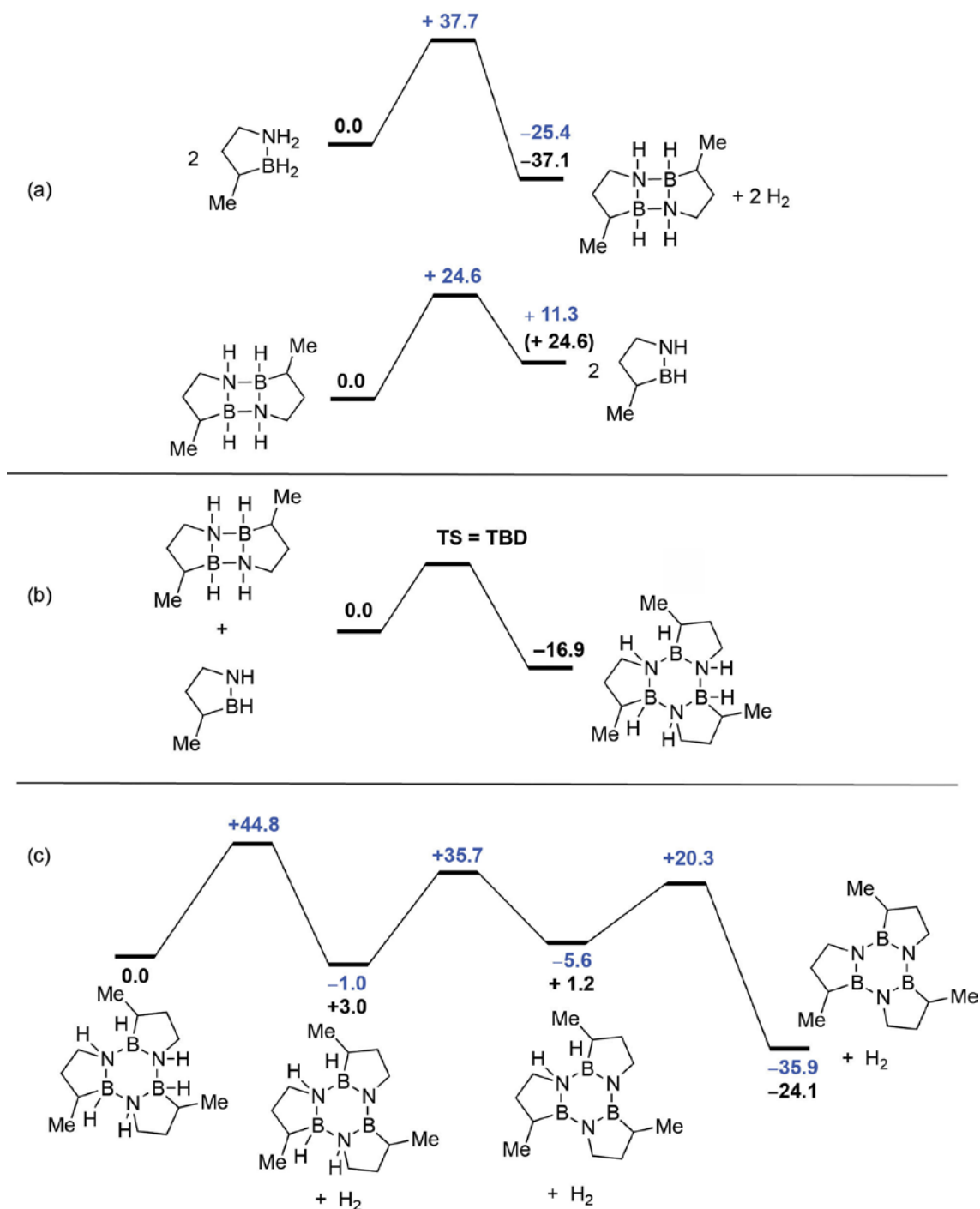


FIGURE 4. Potential energy surface in kcal/mol for the current working mechanistic hypothesis. a) dehydrogenation of **B** to form dehydromonomer and dissociation of the dehydrodimer to form the dehydromonomer. b) reaction of the dehydrodimer with the dehydromonomer to form a cyclotrimer. c) Sequential dehydrogenation of cyclotrimer to the final spent fuel material. Blue values are B3LYP/DZVP2 and black values are G3MP2.

- Achieve 4-5 equivalent of H₂ release for Compound **H** (9.3 wt% to 11.6 wt%).
- Determine the thermodynamics and kinetics for the desorption of Compound **H**.
- Characterize viscosity of spent fuel of Compound **B** and its fuel blends.
- Continue to optimize fuel blends with respect to capacity, melting point, stability.

- Continue computational investigation of dehydrogenation mechanisms. Complete the potential energy surface for direct comparison of different pathways for the H₂ desorption from **B**.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

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