

IV.E.1 Novel Carbon(C)-Boron(B)-Nitrogen(N)-Containing H₂ Storage Materials

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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 2014 Accomplishments

- Investigated liquid fuel blends of compound **B** and ammonia borane (AB) with different ratios to maximize hydrogen release while minimizing borazine formation
- Full characterization of compound **B** regarding thermal stability
- Synthesized a series of compound **E** derivatives
- Calculated important thermodynamic and kinetic parameters and molecular properties to help develop an understanding of the hydrogen desorption mechanism

Overall Objectives

Develop new carbon-boron-nitrogen (CBN)-based chemical hydrogen storage materials that have the potential to meet the DOE technical targets for vehicular and non-automotive applications

Fiscal Year (FY) 2014 Objectives

- Continue to optimize fuel blends with respect to capacity, melting point, and stability
- Synthesize compound **E** and its derivatives
- Continue the potential energy surface calculations of the various pathways of H₂ desorption from CBN compounds

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell



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 AB provide between 8 to 16 wt% H₂ at acceptable temperatures in a kinetically controlled decomposition. AB shows promise to meet a number of 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) 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 is developing new CBN H₂ storage materials that have the potential to meet the DOE targets for motive and non-motive applications. Specifically, we are focusing on 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 (Figure 1). Computational chemistry studies help direct our research. Finally, we will demonstrate the developed material as a fuel in a fuel cell device. These new materials are prepared and characterized by our interdisciplinary team comprised of Boston College, The University of Alabama, Pacific Northwest National Laboratory, and Protonex Technology Corporation (Southborough, MA, a small business fuel cell manufacturer). Note: This project has moved from the University of Oregon to Boston College at the end of FY 2013.

RESULTS

Characterization of the Liquid Carrier B and its Fuel Blends

In FY 2013, we performed additional characterization studies of compound **B** that are relevant to H₂ storage applications. This year, we investigated liquid fuel blends of compound **B** and AB to maximize hydrogen while minimizing borazine content. We determined that the solubility of AB in **B** is approximately 16 mol% (**B**:AB ~5:1). Consequently, a ratio of **B**:AB (2:1) is a suspension at room temperature that, however, has relatively low viscosity. Upon dehydrogenation, the product is a clear liquid at room temperature.

We have investigated different ratios of compound **B** and AB to determine how fuel composition affects borazine production. We measured borazine released at 110°C with blends of **B** and AB, ranging from 1:1 to 4:1 molar ratios. We synthesized pure borazine and calibrated its residual gas analysis traces by comparing the signal intensity with the reported vapor pressure at different temperatures. The concentration of borazine drops substantially with increasing fraction of **B**, as shown in Figure 2a. The results are compared to borazine formation of AB in tetraglyme solution. The 3:1 and 4:1 **B**:AB blends reduced the concentration of borazine by factors of 21 and 46, respectively. The presence of a catalyst allowed hydrogen release at a lower temperature and resulted in a dramatic

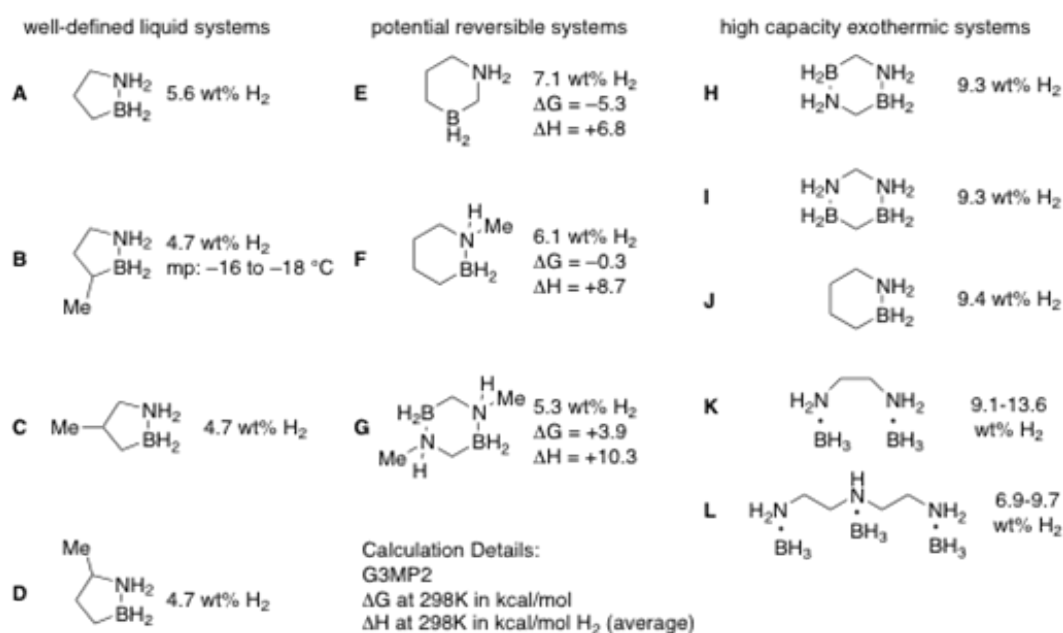


FIGURE 1. Selected Synthetic Targets and their Potential Storage Capacities and Predicted Thermodynamic Parameters

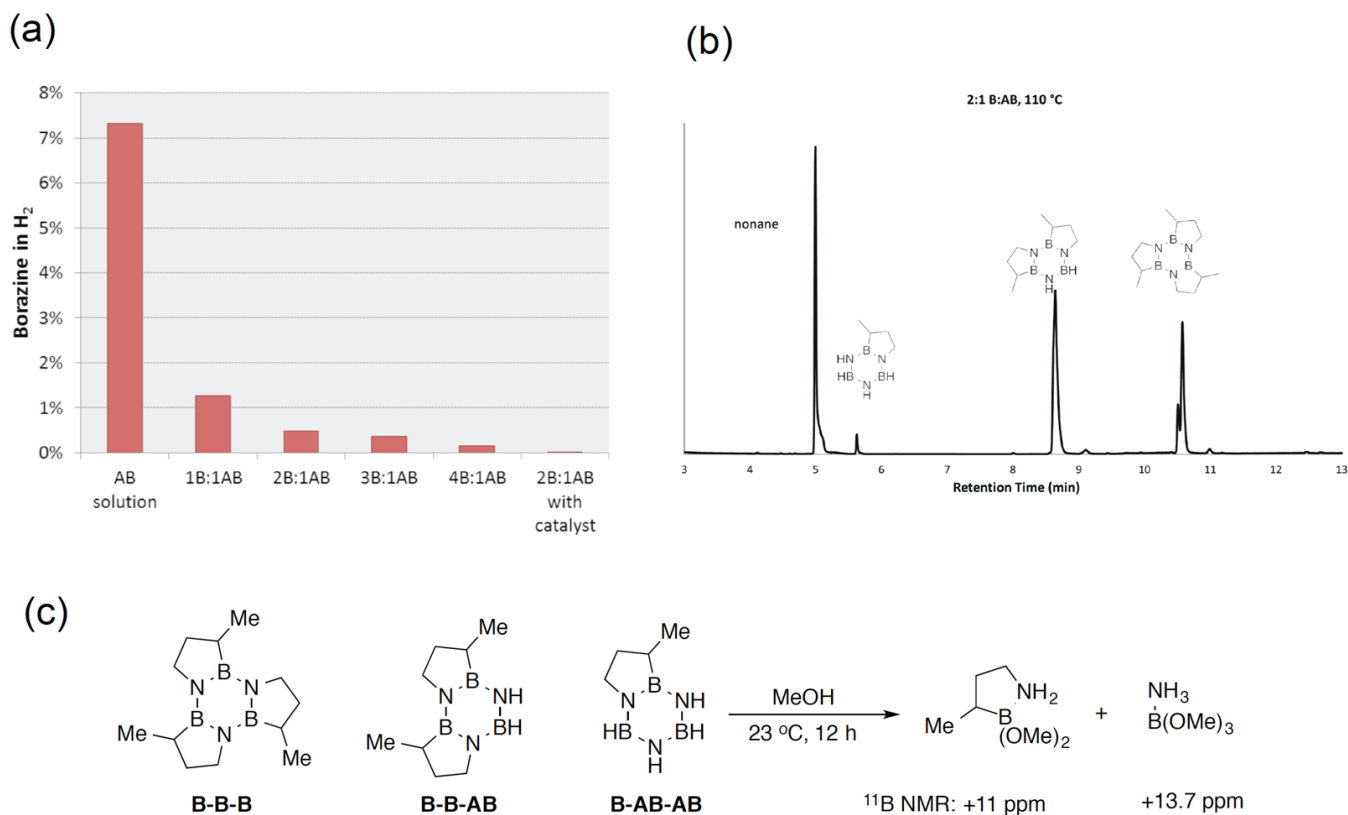


FIGURE 2. (a) Concentration of borazine in gas stream from B:AB blends measured by residual gas analysis, compared to a solution of AB in tetraglyme. Dehydrogenation was carried out at 110°C, except for the catalyzed (Pt/Ni on C) sample, which was conducted 80°C. (b) GC/MS trace of the dehydrogenation products at 110°C of a B:AB (2:1) blend. The two signals for the B trimer at ca. 10.6 minutes originate from the different diastereomers. (c) Methanolysis of the spent fuel mixture.

reduction in borazine concentration to 0.01%, 670 times lower than the corresponding AB in tetraglyme sample.

The ¹¹B nuclear magnetic resonance (NMR) spectra of the dehydrogenation products showed signals at +31 ppm and +41 ppm, consistent with the formation of 6-membered B-N rings. This could arise from a mixture of separate molecules of borazine and the trimeric product from dehydrogenation of B, or from individual molecules containing fragments of both of these compounds. Gas chromatography/mass spectrometry (GC/MS) results demonstrated that the spent fuel products contained mixed trimers. Figure 2b shows the GC/MS trace obtained after dehydrogenation of a B:AB (2:1) blend at 110°C. The largest signal, at a retention time of ca. 8.7 min, had a mass corresponding to a trimer containing B-B-AB fragments. The B-B-B and B-AB-AB trimers were also observed. The relative quantities of these trimers varied in the expected way with different starting compositions in the fuel blend, suggesting that the products were a statistical mixture of the possible trimeric compounds.

With respect to regeneration of spent fuel, we have shown previously that the B trimer can be digested in methanol to protonate the N atom and form a dimethoxy

borate ester [5]. The ester can be subsequently treated with metal hydrides to regenerate compound B. Our initial experiments suggest that this regeneration scheme would also work for the mixed trimeric dehydrogenation products identified above. ¹¹B NMR spectra shown that the spent fuel is completely reacted after methanolysis. The borate ester of compound B is identified by the resonance at +11 ppm, and the resonance at +13.7 ppm is believed to arise from NH₃B(OMe)₃ (Figure 2c). Reduction of this mixture is therefore likely to regenerate the mixture of B and AB.

Thermal Stability of Compound B and the Spent Fuel

We measured the thermal stability of compound B at 50°C using a gas burette. Figure 3a (red trace) shows that compound B evolves gas at this temperature, at an initial rate of ca. 0.3 equivalents H₂/day. The rate drops with time, reaching a plateau when 1 equivalent of H₂ was released after approximately one week. The second equivalent of hydrogen is not released at 50°C. We also recorded the ¹¹B NMR spectrum of the product after one week and found the formation of a species consistent with a cyclodiborazane dimer which has ca. 2.3 wt% H₂ capacity. We also measured

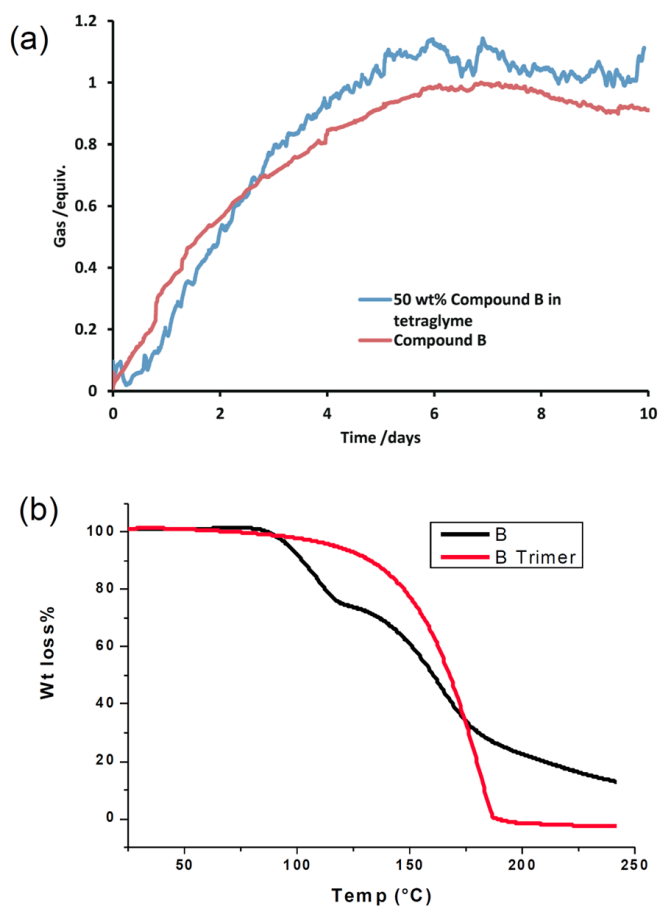


FIGURE 3. (a) Gas evolution from **B** with and without tetraglyme at 50°C, measured by gas burette. (b) TGA traces for compound **B** (black) and the spent fuel trimer of compound **B** (red).

the stability of compound **B** in tetraglyme solution (50 wt%). Despite the dilution, the rate of gas evolution (Figure 3a, blue trace) was not significantly changed indicating that tetraglyme is not effective at stabilizing compound **B**.

The thermal stability of compound **B** and its spent fuel was also measured by thermogravimetric analysis (TGA), at a heating rate of 1°C/min (Figure 3b, black trace). The loss of 4.7 wt% H₂ at ca. 100°C coincided with an additional weight loss of ca. 20 wt%, probably due to the high vapor pressure of compound **B**. Above 120°C, a more substantial weight loss took place such that nearly all the sample had volatilized by 180°C. The weight loss above 120°C is attributed to the vaporization of the spent fuel trimer, confirmed by TGA of an authentic trimer sample (Figure 3b, red trace).

We have made a No-Go decision on compound **B** blends due to the thermal stability issue. Current efforts are geared toward understanding the factors that improve thermal stability.

Compound E and its Derivatives

We attempted to synthesize compound **E** and its derivatives, which may activate and release H₂ reversibly via the frustrated Lewis pair-type reactivity. For the parent compound **E**, however, there is a potential for dimerization after dehydrogenation, which needs to be prevented (potentially by introducing bulky groups at boron and/or nitrogen positions). Thus, we designed compounds **3** and **6** (Figure 4) for that purpose. The synthesis of the key intermediate, compound **1**, is straightforward by using the protocol reported by our group in 2011 [6].

Replacement of the B-diisopropylamino group in compound **1** with the acetoxy group followed by treatment with lithium aluminum tetrahydride (LiAlH₄) yielded compound **2**. Hydrogenation of compound **2** in the presence of 10 mol% of Pd/C cleanly transformed **2** into **3**, which however, formed dimer **4** and unidentified oligomers instantly. Accordingly, compound **6**, which has a bulkier substituent at boron, was proposed as a better candidate. Following a similar synthetic route, compound **6** could potentially be obtained through hydrogenation of compound **5**. In fact, the reduction of compound **5** with H₂ (45 psi) was accomplished efficiently in the presence of 20 mol% of Pd/C as catalyst at 100°C for 14 h. However, both ¹¹B and ¹H NMR indicated the formation of dimer **7** instead of the expected product **6**, suggesting an even bulkier group is needed on either boron or nitrogen to prevent the dimerization. Consequently, we proposed compound **9**, which has the 2,4,6-triisopropylphenyl (Tip) group on boron. However, all attempts to place the Tip group on the boron center to prepare compound **8** through established protocols were unsuccessful, most likely due to the significant steric hindrance between the two reagents (Figure 4).

We have made a No-Go decision on compound **E** because we were only able to partially hydrogenate its spent fuel, and dimer formation prevents its full potential.

Investigation of CBN Systems with Computational Chemistry

We have continued to perform mechanistic studies of H₂ desorption from CBN materials using computational chemistry. A range of potential energy surfaces for H₂ release and dimer and trimer formation have been obtained at a reliable correlated molecular orbital theory G3MP2 level. In addition, we calculated molecular properties of various CBN materials. The ¹¹B NMR chemical shifts (Figure 5) for a range of compounds containing B-N bonds were calculated, and the results are being used to aid the experimental identification of intermediates in dehydrogenation processes. Thermodynamic properties of a broad range of compounds including spent fuel derivatives have been calculated in the gas phase and in the liquid phase together with boiling points.

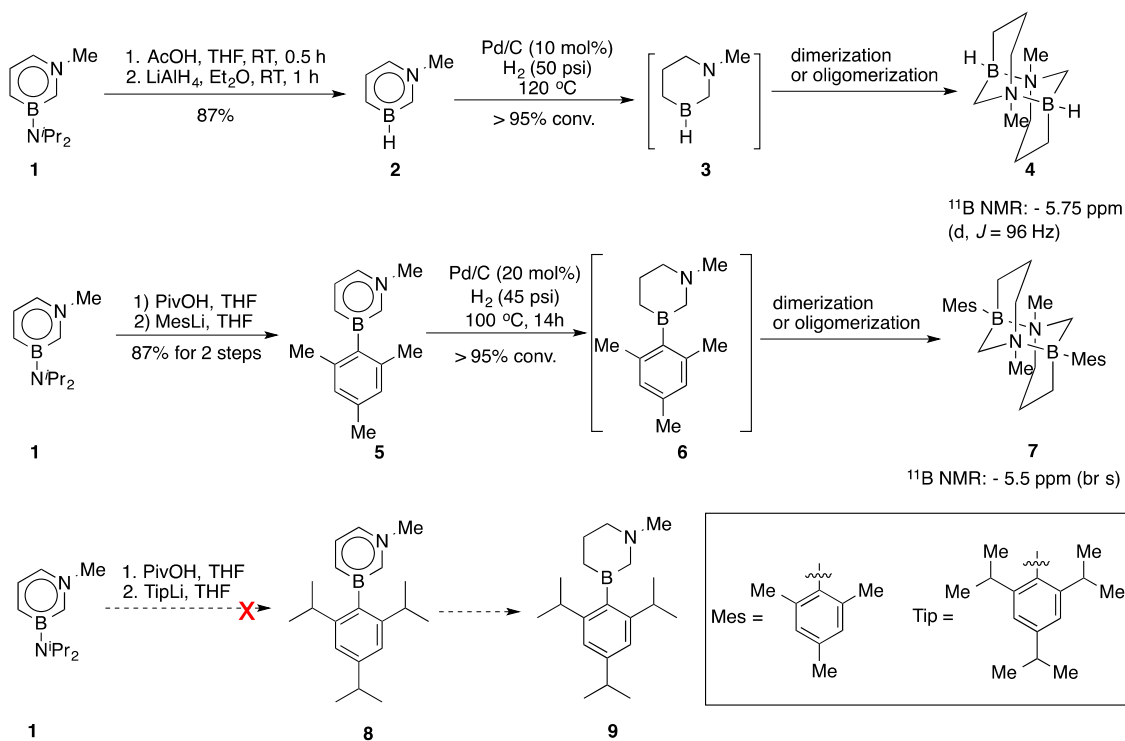


FIGURE 4. Attempts to Synthesize Compound E Derivatives as Reversible Hydrogen Storage Materials

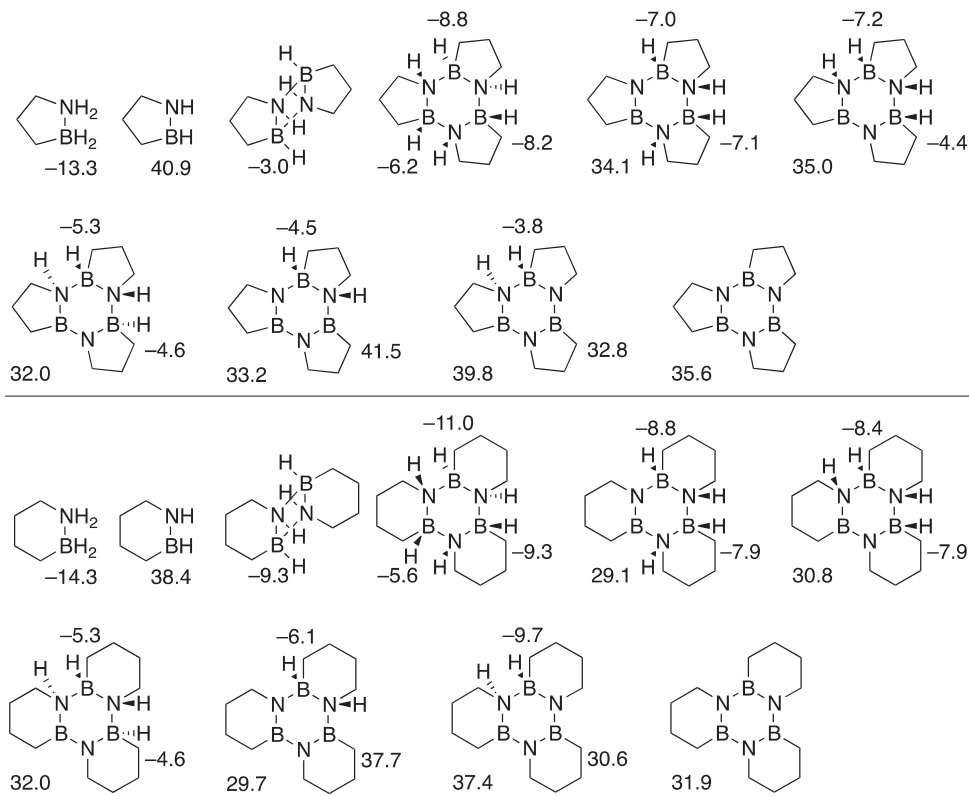


FIGURE 5. Predicted ^{11}B NMR Chemical Shifts for Select Compounds in PPM (against $\text{BH}_3 \cdot \text{THF}$ Standard)

CONCLUSIONS AND FUTURE DIRECTIONS

This year, we investigated liquid fuel blends of compound **B** and **AB** to maximize hydrogen release while minimizing borazine formation. Characterization of compound **B** with respect to thermal stability was also carried out. We were able to synthesize a series of compound **E** derivatives, however dimerization or oligomerization of the partially hydrogenated compounds prevented the full potential of this class of compounds. Additionally, we calculated molecular properties such as ^{11}B NMR chemical shifts which are helpful in aiding the experimental identification of intermediates in dehydrogenation processes. Our future goals are to:

- Achieve hydrogen desorption from the carbon portion of CBN
- Determine the mechanism for H_2 desorption for CBN materials by both experiment and computation
- Further characterize and determine thermodynamics and kinetics for the desorption of compound **H**
- Achieve 4-5 equivalent of H_2 release for compound **H** (9.3 wt% - 11.6 wt%)
- Develop thermally stable CBN compounds as H_2 storage material
- Continue theory support for property predictions including thermodynamics and spectroscopy, and finalize the desorption mechanism of CBN compounds

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. D.A. Dixon named in ACS Fellow at the 2013 Fall American Chemical Society National Meeting, Indianapolis, IN

FY 2013 PUBLICATIONS/PRESENTATIONS

1. “Development of a Single-Component Liquid-Phase Hydrogen Storage Material”; Singapore, 15th Asian Chemical Congress 2013, Asia America Chemical Symposium on “Advanced Materials, August 2013. (Presentation, Liu)
2. “An Extremely Stable Chemical Hydrogen Storage Material: Synthesis, Structure and Potential Application of 1,4-Diazonia-2,5-Diboratacyclohexanes”; Newark NJ, *Boron in the Americas XIV*, June 16, 2014. (poster presentation: Gang Chen, Lev Zakharov, Shih-Yuan Liu)

3. “Novel Carbon(C)-Boron(B)-Nitrogen(N)-Containing H_2 Storage Materials ”; Washington, DC, DOE Annual Merit Review, June 17, 2014. (Presentation, Tom Autrey)

4. “Exploring the use of carbon, nitrogen, and boron containing heterocycles in liquid hydrogen storage”; Dallas TX, 247th American Chemical Society National Meeting & Exposition, March 16, 2014. (Presentation, Sean Whittemore, PNNL)

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