

IV.E.1 Fluid Phase Chemical Hydrogen Storage Materials

Benjamin L. Davis (Primary Contact),
Brian D. Rekken, and Troy A. Semelsberger
Materials Physics and Applications, Materials Synthesis and
Integrated Devices
Los Alamos National Laboratory (LANL), MS J514
P.O. Box 1663
Los Alamos, NM 87545
Phone: (505) 500-2463
Email: bldavis@lanl.gov

DOE Managers

Grace Ordaz
Phone: (202) 586-8350
Email: Grace.Ordaz@hq.doe.gov
Ned Stetson
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov

Partner

Tom Baker, University of Ottawa, Ontario, Canada

Project Start Date: October 1, 2010
Project End Date: January 1, 2014

Technical Targets

A significant barrier to the application of off-board regenerable hydrogen storage materials is on- and off-boarding of the fuel and spent fuel, respectively. A fluid, pumpable fuel that remains liquid through dehydrogenation to the spent fuel form is desired for readily engineered fueling concepts. This project is exploring other compositions of AB/room temperature ionic liquid (RTIL) systems; the original concept was developed within Center of Excellence in Chemical Hydrogen Storage by Professor Larry Sneddon of the University of Pennsylvania. This work showed great promise with excellent gravimetric and volumetric capacities as well as discharging rates. Subsequent work at LANL has shown that these RTIL-based fuels could also be regenerated off-board without separating the spent fuel from the RTIL. Successful development of fluid systems should meet the following DOE 2017 and HSECoE targets:

- Gravimetric capacity (1.8 kWh/kg)
- Volumetric capacity (1.3 kWh/L)
- H₂ discharge rate (minimum full flow rate 1.5 kg H₂/min)
- H₂ purity (99.97% H₂)
- Start-up time to full flow (5 s @ 20°C, 5 s @ -20°C)
- Shelf life: loss of usable H₂ (0.05 g/hr-kg H₂ stored)
- HSECoE: 40 wt% AB dissolved or slurried

Overall Objective

Develop fluid, pumpable ammonia-borane (AB)-based fuels using ionic liquids that have sufficient H₂ content, release kinetics, and stability for use by the Hydrogen Storage Engineering Center of Excellence (HSECoE) for vehicular applications.

Fiscal Year (FY) 2013 Objectives

Further refine additives that incorporate neutral and ionic functionalities, that react with AB to yield fluid phase pumpable products.

Technical Barriers

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

- (A) System Weight and Volume
- (D) Durability/Operability
- (E) Charging/Discharging Rates

FY 2013 Accomplishments

- Designed and synthesized ionic liquids tethered to amineboranes (ILTA).
- Demonstrated several examples of ILTA that remain a liquid after H₂ release and cooling to room temperature (RT).
- Initial examples of ILTA/AB mixtures yield liquid products after H₂ release and cooling to RT.
- A survey of neutral functionalities tethered to aminoboranes was completed, with an additional candidate (benzylamineborane) evaluated. Currently none of the surveyed additives incorporating neutral functionalities are able to form slurries with AB that exceed the stored H₂ wt% demonstrated by hexylAB/AB described last year.
- Quantitatively observed that H₂ impurities are a function of AB particle size. A method for generating very small AB particles is detailed.



INTRODUCTION

Chemical hydrogen storage (CHS) involves storing H₂ in molecular chemical bonds where an onboard chemical reaction is used to release H₂. Currently the resulting spent fuel may be regenerated off-board using chemical processing. CHS provides a diversity of options to enable H₂ for transportation as well as other niche and stationary applications. Especially attractive, CHS offers the potential for no direct H₂ handling by the consumer, as well as low pressure storage concepts.

Researchers at LANL and the University of Ottawa are focused on the development of liquid AB fuels that integrate with the HSECoE. We are currently studying the formation, stability, and catalytic release of H₂ from these materials.

APPROACH

A serious drawback of AB-based pumpable fuels is product precipitation during H₂ removal. To address this concern, we are developing functionalized amineborane additives which react with AB to generate fluid products. The functionalities have the additional benefit of preventing the formation of gaseous impurities such as ammonia or borazine. Two classes of functionalities are being explored— inexpensive, off-the-shelf, neutral organic components and ionic liquid moieties that covalently attached to an amine. Currently fuel mixtures are heated for an extended period and their final phase assessed at the end of the experiment. Future experimental apparatus will assess the point in which the fuel's viscosity sharply increases, allowing us to identify which functionalities have the greatest impact on phase properties.

RESULTS

Building on FY 2012's results with functionalized amineborane additives, Ottawa surveyed available amines that are inexpensive yet may generate fluid phase properties in the AB slurry. A group of hydrophobic amines incorporating a phenyl functional group were chosen because of the possible pi-pi interactions with imidazolium-based ionic liquids. A list of the amineboranes synthesized along with their initial/final states after heating to 130°C is shown (Table 1).

TABLE 1. Amineboranes Synthesized along with their Initial/Final States after Heating to 130°C

Amine-Borane	H ₂ Charged State at RT	H ₂ spent State at RT
benylamine-borane	Solid (m.p. 57°C)	Solid
o-methylbenzylamine-borane	Solid (m.p. 110°C)	Solid
3-phenylpropylamine-borane (3-PPAB)	Liquid	Liquid

m.p. – melting point

Previous experience with AB and ionic liquids has shown that two solids may deliquesce, and as such mixtures of the above amineboranes with AB were examined. Only the liquid 3-PPAB formed a slurry with AB (1:1 molar), which became a homogenous liquid after H₂ release like hexylamineborane [1]. Although we did not determine the upper bound of AB that could be slurried with 3-PPAB, the 4.8 wt% of stored H₂ does not meet the HSECoE target for a slurry and thus this avenue of pursuit was suspended.

In conjunction with our HSECoE partners, an amineborane described last year was up scaled to use in reactor evaluations. Although 3-methoxypropylamineborane (3-MPAB) only stores 3.9 wt% H₂ neat, this amineborane readily forms slurries with AB (for instance a 1:1 molar slurry is 6.5 wt% H₂), and thus could meet the HSECoE target of 40 wt% AB or 6 wt% H₂ stored overall. H₂ measurements indicated 3-MPAB only released a portion of its stored H₂ [2] and ¹¹B NMR of the spent fuel indicated the presence of 3-MPAB and intermediate borazanes (Figure 1). One reason for the incomplete H₂ release from 3-MPAB could be the volatility of the 3-methoxypropyl functional group which allows the fuel and its intermediates to leave the reactor (parent amine boiling point ~120°C).

To avoid issues of volatility and possibly avoid the use of a pure ionic liquid entirely, amineboranes were covalently attached to an ionic liquid. Using a four step synthetic pathway multiple derivatives were formed (Figure 2), only a couple of which are liquid at room temperature (F, G).

Although the ILTAs made to date are insufficient to meet DOE targets in pure form, blends with AB were evaluated to increase stored H₂ density. ILTA “G” can be slurried with 2 equivalent of AB, yielding a material with 2.8 wt% H₂ that still remains liquid after H₂ release. Unfortunately the stored H₂ density can't be increased further; somewhere between 2 and 5 equivalent of AB, the products of H₂ release become solid.

The HSECoE has previously noted that the size of their AB particles was critical to forming slurries with silicon oil [3]; while releasing H₂ from the AB/ILTA fuel blends, it became evident that the size of AB may also affect the amount of impurities with the H₂ stream as well. By dissolving AB in dry tetrahydrofuran and rapidly adding hexanes, very small AB particles were produced (Figure 3). Evaluating the impurities in the H₂ release stream, not surprisingly, showed fewer impurities associated with AB using the smaller particles. We attribute this to the better mixing of the ILTA and AB, where there is a better chance to co-oligomerize/polymerize.

CONCLUSIONS AND FUTURE DIRECTIONS

- A survey of neutral functionalities tethered to AB is complete; 3-phenylpropyl was found to perform in

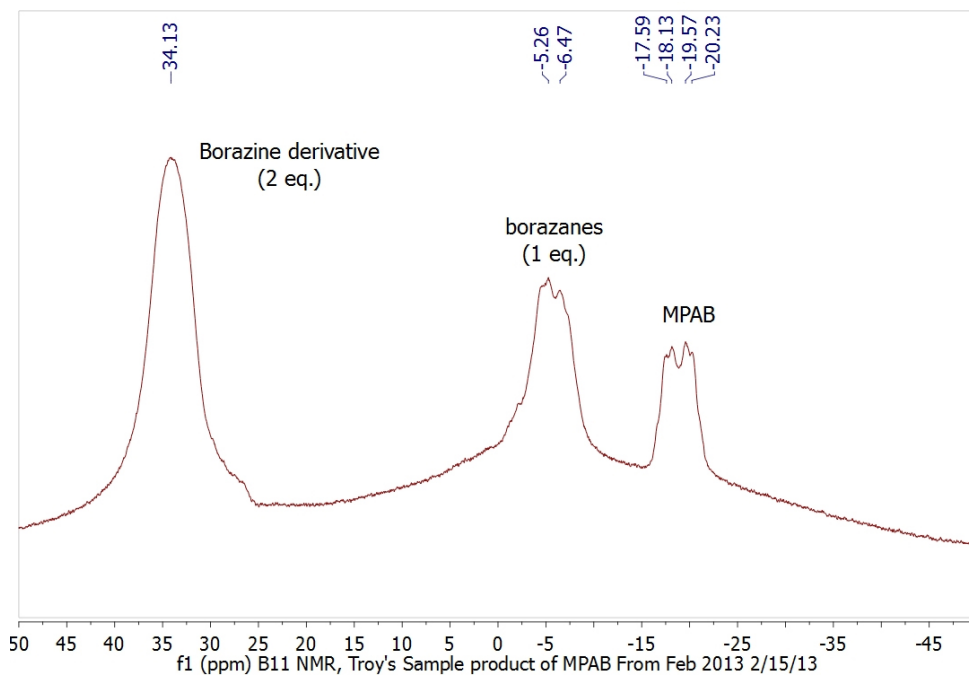


FIGURE 1. ¹¹B NMR of Spent 3-MPAB Fuel after Flowing thru the HSECoE Reactor

Additive	Identifier	Initial State (20 °C)	Spent State (20 °C)	Wt. % H ₂
	A	Solid	Solid	2.5
	B	Solid	Solid	1.5
	C	Solid	Solid	2.3
	D	Oily Wax	Solid	1.4
	E	Solid	Solid	2.1
	F	Liquid	Viscous liquid	1.4
	G	Liquid	Liquid	1.0

FIGURE 2. List of ILTA Synthesized, wt% H₂, and Room Temperature State before and after H₂ Release

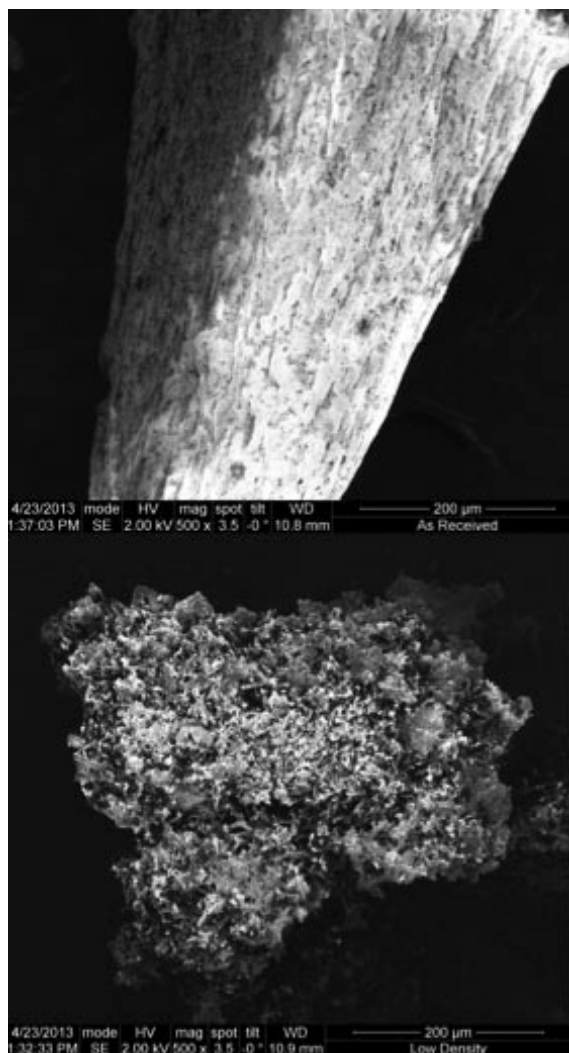


FIGURE 3. Scanning Electron Microscope Images of AB, as Received from JSC Aviohor (top), and Precipitated AB (bottom)

fashion similar to the hexyl moiety described last year. None of the neutral additives appear able to dissolve AB.

- Up scale and evaluation of 3-methoxypropylamineborane for HSECoE reactor testing suggests that neutral functionalities require higher boiling points than 120°C for the parent amine.
- Ionic liquids tethered to amineboranes were successfully synthesized and evaluated. Current derivatives store H₂ insufficiently and have limited ability to form slurries with AB that form fluid phase products and meet HSECoE material targets.
- Fine particle AB was produced that yields less impurities from AB/additive blends.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Nonprovisional patent application submitted for functionalized amineborane/AB fuel blends (13850959).

FY 2013 PUBLICATIONS/PRESENTATIONS

1. “Possible Gasoline Substitute: Storing H₂ Chemically for Automotive Applications” Bowdoin College, Sept 2012.
2. Benjamin L. Davis, Brian Rekken, Ryszard Michalczyk, Edward B. Garner, III, David A. Dixon, Hassan Kalviri, R. Tom Baker, and David L. Thorn. “Lewis Base Assisted B-H Bond Redistribution in Borazine and Polyborazylene” *Chem. Comm.*, **2013**, DOI:10.1039/C3CC44748K.

REFERENCES

1. IV.B.2 Fluid Phase Chemical Hydrogen Storage Materials, FY 2012 Annual Progress Report, DOE Hydrogen and Fuel Cells Program.
2. IV.B.4 Hydrogen Storage Engineering Center of Excellence: Chemical Hydrogen Rate Modeling, Validation, and System Demonstration, FY2013 Annual Progress Report, DOE Hydrogen and Fuel Cells Program.
3. Materials Operating Requirements, Chemical Hydrogen Storage. FY2013 Hydrogen Storage Engineering Technical Team Review, Ronnebro, E.; Westman, M.; Chun J.; Karkamkar, A. March 20–21, 2013, Southfield MI.