IV.B.2 Fluid Phase Chemical Hydrogen Storage Materials

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Fiscal Year (FY) 2012 Objectives

Develop fluid, pumpable ammonia-borane (AB)-based fuels with high-H_2 content.

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:

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

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 excellence 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 Hydrogen Storage Engineering Center of Excellence (HSECoE) targets:

- Gravimetric Capacity (1.8 kWh/kg)
- Volumetric Capacity (1.3 kWh/L)
- H_2 Discharge Rate (minimum full flow rate 1.5 kg H_2/min)
- H_2 Purity (99.97 % H_2)
- Start-Up Time to Full Flow (5 s @ 20°C, 5 s @ -20°C)
- Shelf Life: Loss of Usable H_2 (0.05 g/hr-kg H_2 stored)
- HSECoE: 40 wt% AB dissolved or slurried

FY 2012 Accomplishments

- Additive amine-boranes with 3-4 wt% usable H_2 and maintain fluid phase after H_2 release.
- 20 wt% AB in hexylamine-borane (6.0 wt% H_2 material) transforms from a slurry to a liquid upon H_2 release.
- Developed ^{11}B nuclear magnetic resonance (NMR) solubility quantification method and measured AB, polyborazylene (PB) solubility in a variety of RTILs.
- Identified, removed, and measured the impact of water on AB solubility and stability in RTILs.
- Developed a method for measuring the known impurities of AB dehydrogenation (borazine, diborane, and ammonia) and hydrogen in a single flow-thru apparatus. Evaluation of several fuel blends indicates the impurity profile is AB/RTIL composition dependent.

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Introduction

Chemical hydrogen storage (CHS) involves storing H_2 in molecular chemical bonds where an on-board chemical reaction is used to release H_2. Currently the resulting spent fuel may be regenerated off-board using chemical processing. CHS provides a diversity of options to enable H_2 for transportation as well as other niche and stationary applications. Especially attractive, CHS offers the potential for no direct H_2 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 H_2 from these materials.

Approach

A serious drawback of AB-based pumpable fuels is product precipitation during hydrogen removal. To address this concern, we developed a solubility quantification method based on ^{11}B NMR to screen RTIL for their ability to solubilize AB (to maximize capacity) and its dehydrogenation products (to avoid precipitation). In addition, we identified amineborane additives which can improve the solubility properties of the dehydrogenation products. To meet the other technical targets for fuel stability and H_2 purity, we identified/removed impurities in commercially available RTIL and developed a method to measure the known gaseous effluents from the decomposition of AB/RTIL fuel blends.

Results

One technique for mitigating product precipitation is to find a solvent or solvents that dissolve the reactant and product. To this end, we developed a method for quantifying the solubility of boron species using ^{11}B NMR which would allow us to correlate the reactant/product solubility with RTIL components (cations, anions). The solubility results for AB and PB (derived from borazine decomposition) indicate RTIL composition only affects AB dissolution (Figure 1).

At this time we have not performed extensive solubility evaluations to determine which RTIL would be optimal for AB/RTIL fuel blends. It is clear from this initial survey, however, that we will not be able to make a solution of AB in RTIL that meets the HSECoE's minimum target of 40 wt%. Slurries of AB in RTIL are being pursued as a consequence.

We hypothesized that the insolubility of PB, a material similar to the products previously characterized after the dehydrogenation of AB/RTIL fuels [1], was related to the extensive polymeric networks that are possible. To improve the solubility AB/RTIL dehydrogenation products, we designed functionalized amineborane additives that should react with AB given sufficient activation energy or a catalyst. The first generation additives are hexylamineborane, $H_3C(CH_2)_5NH_2BH_3$ (hexyl-AB), and 3-methoxypropylamineborane, $H_3CO(CH_2)_3NH_2BH_3$ (methoxy-AB), whose analogous synthetic preparation is described in the literature [2].

To assess whether hexyl-AB and methoxy-AB additives would impart greater solubility on AB dehydrogenation products, we first heated each in a closed vessel at 130°C for 12 hours. In each case a liquid product formed, even after cooling to room temperature. AB/BmimCl under the same conditions results in a solid product. When 1:1 molar mixtures of hexyl-AB or methoxy-AB with AB are heated under the same conditions, a liquid product also results (Figure 2). This is a significant result, as 1:1 mixtures of hexyl-AB:AB store 6 wt% H_2, which is equal to the HSECoE minimum requirement of 40 wt% AB dissolved/slurried.

The ultimate goal of amineborane additives is to broaden the liquid range of the AB/RTIL fuel, which we define as the amount of hydrogen released per gram of fuel before product precipitation. To assess the methoxy-AB additive, we prepared a 23 wt% AB/BmimCl solution where ~60 mg of RTIL was substituted for methoxy-AB and measured the release of hydrogen at 90ºC. A 23 wt% AB/BmimCl solution without additive was used as a control. Greater than 10 mM of H_2/gram of fuel was released when methoxy-AB additive was used, compared to ~7.5 mM for the control. This 30% greater H_2 release is consistent with the H_2 stored in methoxy-AB.

While formulating AB/RTIL fuel blends, we recognized that many RTIL are hygroscopic and this dissolved water might be an issue for H_2 capacity after cycling, accurate solubility measurements, and long-term storage. To reduce the influence water may have, we utilized Karl Fisher titrations to accurately measure water content in

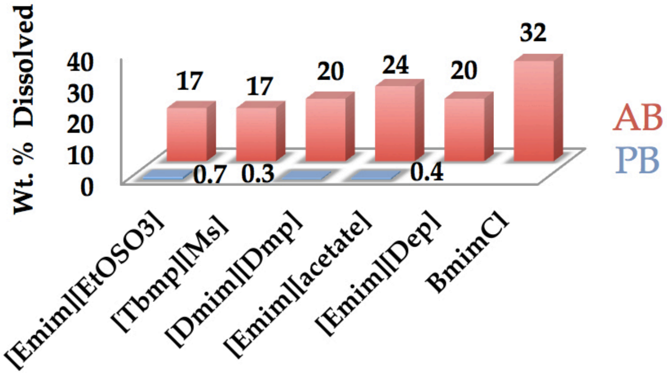

FIGURE 1. Solubility (wt%) of AB and PB in RTIL using ^{11}B NMR method. Emim = ethyl, methyl imidazolium, Bmim = butyl, methyl imidazolium, Tbmp = tributylmethylphosphonium, $EtOSO_3$ = ethylsulfonate, Ms = methylsulfonate, Dmp = dimethylphosphonate, Dep = diethylphosphonate.

FIGURE 2. 1:1 molar mixture of hexyl-AB, heated for 12 h @ 130°C. Picture was acquired at room temperature.

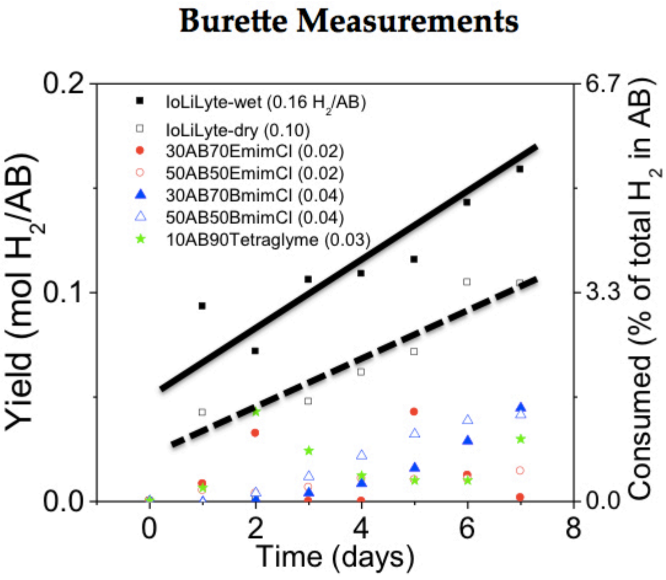

FIGURE 3. Short-term stability measurements of AB/RTIL fuel blends. Measurements of H_2 were made at room temperature. Note significant reduction in H_2 formation with the dried RTIL (dashed best fit line) as compared to the as-received 'wet' fuel (solid best fit line). IoLiLyte is a tradename by Iolitec (Tuscaloosa, AL) for Emim $EtOSO_3$.

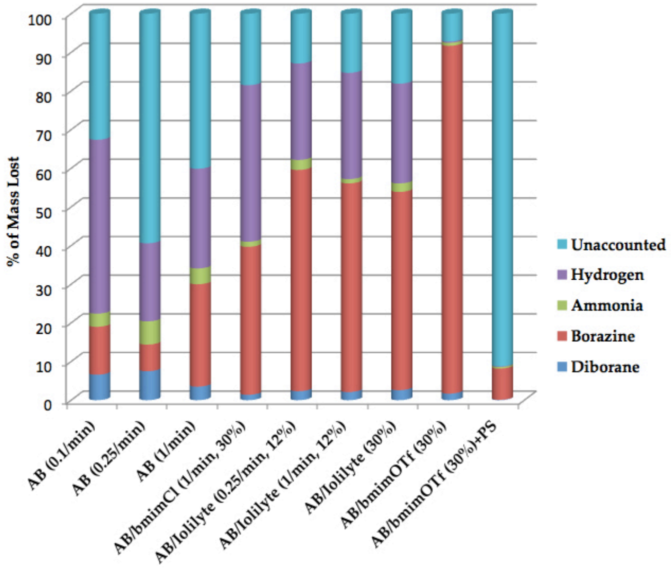

FIGURE 4. Gaseous measurements of borazine, diborane, ammonia, and hydrogen from decomposed samples of AB and AB/RTIL at different ramp rates, loadings, and compositions. Data was acquired on a calibration thermogravimetric analysis-infrared-mass spectrometry coupled system.

commercially sourced RTILs and then verify the extent of dryness after a water removal procedure was applied. With the dried RTILs, we then determined AB solubility and found improvements in almost all cases (Table 1). No dry RTIL, however, was able to dissolve 40 wt% AB, the HSECoE's minimum target. Water removal also impacted short term room temperature stability measurements (Figure 3).

TABLE 1. Water content in as-received and dried RTIL. Subsequent AB wt% solubility.

RTIL	As Received H_2O content (ppm)	Dried RTIL H_2O content (ppm)	AB wt% dissolved in dried RTIL
Emim$EtOSO_3$	1,600	80	27
DmimDmp	4,000	250	32
EmimAcetate	1,500	100	31
BmimCl	10,000	320	31
BmimOTf	450	<30	4.4

Lastly, to help the HSECoE select a AB/RTIL fuel blend that is compatible with their developing filtration technologies, we developed a method to measure the known impurities (ammonia, borazine, and diborane) in the H_2 effluent when AB/RTIL is decomposed. Using a calibrated thermogravimetric analysis-infrared-mass spectrometry system, several compositions of AB, AB/RTIL, and additives were decomposed (Figure 4). While mass balance indicates there are some unaccounted species, the variable distribution of products suggests that fuel composition may be used to tailor impurity profiles.

Conclusions and Future Directions

- Solubility measurements of AB and PB in RTIL indicate there is no clear path to >40 wt% AB/RTIL solutions or a solvent system for preventing PB precipitation; slurries of AB in RTIL will be required to meet gravimetric targets for H_2 stored.
- Amineborane additives show promise for altering the solubility of AB dehydrogenation products, yielding liquid products with AB after extensive heating in some cases. Future work will focus on non-volatile amineborane derivatives.
- Some quality control is required with commercially sourced RTILs, since impurities such as water have an impact on room temperature stability and maximum dissolved AB.
- A method for measuring known impurities (ammonia, borazine, diborane) and evolved H_2 from decomposed AB and AB/RTIL fuel blends was developed. This is a useful tool for the HSECoE to gauge which fuel blends will be compatible with their filtration systems.

References

1. Sneddon et al., *Inorg. Chem.*, **2009**, *48*, 9883.

2. Framery et al., *Heteroatom Chem.*, **2000**, *11*, 218.