

IV.B.2 Fluid Phase Chemical Hydrogen Storage Materials

Benjamin L. Davis (Primary Contact),
Tessui Nakagawa, Ruiqin Zhong,
Troy A. Semelsberger, and Gerie Purdy
Materials Physics and Applications, Materials Chemistry
Los Alamos National Laboratory (LANL), MS J514
P.O. Box 1663
Los Alamos, NM 87545
Phone: (505) 500-2463
E-mail: bldavis@lanl.gov

DOE Manager
HQ: Grace Ordaz
Phone: (202) 586-8350
E-mail: Grace.Ordaz@hq.doe.gov

Partner:
Professor Larry Sneddon, University of Pennsylvania,
Philadelphia, PA

Project Start Date: October 1, 2010
Project End Date: Project continuation and
direction determined annually by DOE

other compositions of AB/ionic liquid (IL) systems; the original concept was developed by the Center's partner, Professor Larry Sneddon of the University of Pennsylvania. This work showed great promise with gravimetric and volumetric capacities as well as charging/discharging rates. Subsequent work at LANL has shown that these IL-based fuels could also be regenerated off board without separating the spent fuel from the IL. Successful development of fluid systems should meet the following DOE 2015 targets:

- Gravimetric Capacity (3 kWh/kg)
- Volumetric Capacity (2.7 kWh/L)
- H₂ Discharge Rate (minimum full flow rate 0.02 H₂ g/s kW)
- H₂ Purity (99.99 % H₂)
- Start-Up Time to Full Flow (5 s @ 20°C, 15 s @ -20°C)
- Shelf life: Loss of Usable H₂ (0.05 g/hr-kg H₂ stored)

FY 2011 Accomplishments

- Thermal stability of the ILs is dominated by choice of the cations/anions that comprise the IL.
- Pt and Rh on alumina were screened for their ability to improve H₂ release and minimize impurities over the base AB/IL systems. No improvement was observed.
- Hydrazine regeneration method was determined compatible with a spent fuel/IL composition
- H₂ release in the presence of dipentylamine or trimethylborazine did not prevent a phase change in the spent fuel.



Fiscal Year (FY) 2011 Objectives

- Develop liquid, pumpable ammonia-borane (AB) fuels with high H₂ content.
- Catalyst development for fluid phase storage materials that increases rate and extent of H₂ release while minimizing impurities.

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
- (B) System Cost
- (C) Efficiency
- (E) Charging/Discharging Rates
- (R) Regeneration Processes

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 liquid fuel that remains liquid through dehydrogenation to the spent fuel form is desired for more readily engineered fueling concepts. This project is exploring

Introduction

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

Researchers at LANL and the University of Pennsylvania are focused on the development of liquid AB fuels that integrate with the Hydrogen Storage Engineering Center of Excellence (HSECoE). We are currently studying the formation and stability of these liquid AB materials, as well as catalytic release of hydrogen. Candidate materials can be readily evaluated using resources developed by the HSECoE, including a validation test bed.

Approach

The large number of available ILs necessitates screening criteria. Using thermoanalytical methods (differential scanning calorimetry, thermogravimetric analysis [TGA]), properties of ILs were measured to gauge suitability for HSECoE's systems. To address the issue of H₂ release kinetics and impurity formation, commercially available heterogeneous catalysts were evaluated against the control (uncatalyzed) system. Research at the University of Pennsylvania addressed the phase change issue by dehydrocoupling AB in the presence of dipentylamine, a species known to make a form of spent AB fuel (polyborazylene) soluble in benzene.

Results

Thermal stability is an essential characteristic of any IL used to generate a liquid phase with AB. Using TGA, we have identified trends in cation/anionic choice which govern thermal stability (Figure 1). Further testing of ILs should yield greater confidence in compositional requirements.

To further reduce gaseous impurities and accelerate H₂ release, a selection of commercially available heterogeneous catalysts (Pt, Rh) were evaluated. As can be observed (Figure 2), no substantial change in the rate or extent of H₂ release was observed with these catalysts (only Pt data shown). There was a qualitative reduction in borazine as seen in a flow-through experiment (results not shown), thus achieving one of our two stated goals. We are confident that further catalyst evaluation will result in accelerated H₂ release.

Lastly we endeavored to maintain the liquid phase of AB/IL throughout the dehydrogenation process by using additives. Work at the University of Pennsylvania

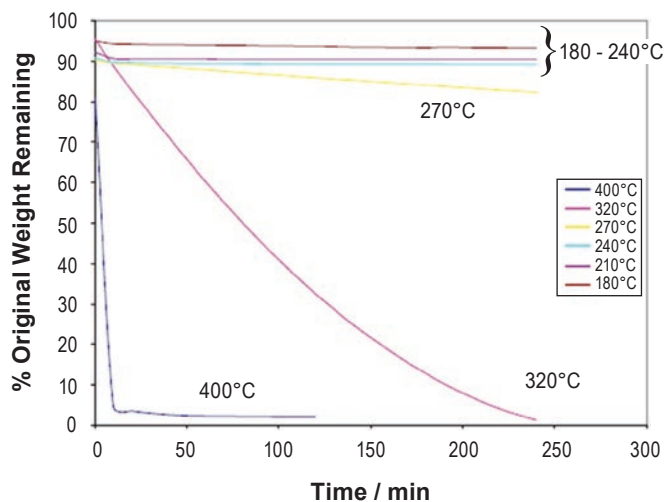


FIGURE 1. Decomposition of an IL assessed by isothermal TGA experiments. This IL shows a wide stability range (starts to decompose at 270°C) and will be used for the HSECoE validation test bed.

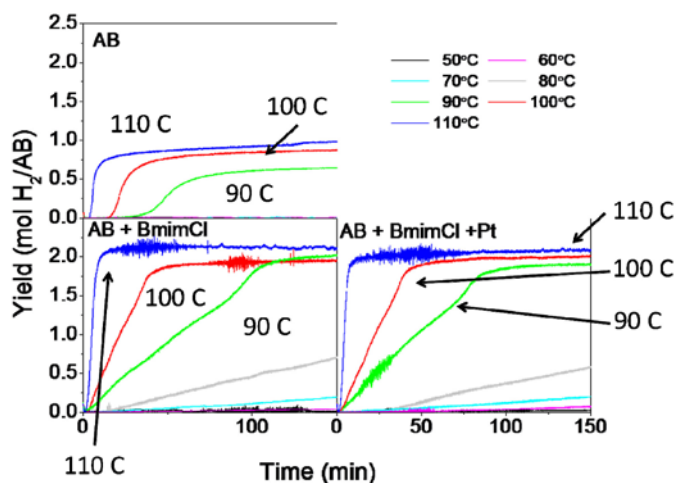


FIGURE 2. Dehydrogenation of AB, AB/IL (BmimCl), and AB/IL + Pt catalyst using an automated buret. The IL has a marked effect on H₂ release and extent relative to pure AB. The addition of the heterogeneous catalyst, however, does not dramatically alter H₂ performance.

had previously identified a reagent, dipentylamine, which could transform polyborazylene (a form of spent AB fuel) into a benzene soluble species [1]. With this knowledge, AB/IL dehydrocoupling was performed in the presence of dipentylamine and alkylated borazines with goal of making the spent fuel more soluble and preventing a phase change. As can be seen (Table 1), neither reagent prevented a phase change.

TABLE 1. Additives used with AB/IL Systems (Bmim – butyl, methylimidazolium, Bmmim – butyl, dimethylimidazolium, Pmim – propyl, methylimidazolium). Neither dipentylamine nor trimethylborazine at a 5% loading altered the state of the final spent fuel (solid in all cases).

IL	Temperature	Additives	Final Physical State
Bmim Cl	85°C	5% Dipentylamine	Solid
Bmmim Cl	85°C	5% Dipentylamine	Solid
Bmim Cl	85°C	5% trimethylborazine	Solid
Pmim I	85°C	5% trimethylborazine	Solid

Conclusions and Future Directions

- Cation/anion selection rules for IL performance (thermal degradation) have been partially identified. Further screening is required to be confident in these generalities. In the future, quantitative solubility of AB and spent fuel will be performed to further guide ionic liquid selection.
- A select group of commercially available noble metal catalysts were evaluated for their ability to accelerate H₂ release and reduce impurity formation. Qualitatively the impurity borazine was reduced in flow-through experiments using heterogeneous platinum catalysts.

Continued catalyst evaluation is planned to meet the DOE targets.

- Regeneration of spent fuel/IL was performed and was generally a success. Characteristics of the IL to yield a more robust process were identified.
- A preliminary survey of additives that were postulated to maintain the liquid phase of AB/IL throughout H₂ release was completed. At the AB loading of 50 wt%, a solid product was obtained after >2 equivalent of H₂ was released indicating that more work is necessary on the spent fuel composition to maintain a fluid, pumpable state for off-boarding of spent fuel. Future work will focus on different alkylborazines and fuel blends which should impart additional solubility on the spent fuel.

References

1. Sneddon *et. al.*, *Chem. Mater.*, **1998**, *10*, 412-421.