

## IV.B.1j Chemical Hydrogen Storage using Ultra-High Surface Area Main Group Materials and the Development of Efficient Amine-Borane Regeneration Cycles

Philip P. Power (Primary Contact),  
Susan M. Kauzlarich  
University of California, Davis (UC Davis)  
Department of Chemistry  
One Shields Ave.  
Davis, CA 95616  
Phone: (530) 752-6913; Fax: (530) 752-8995  
E-mail: pppower@ucdavis.edu

DOE Technology Development Manager:  
Grace Ordaz  
Phone: (202) 586-8350; Fax: (202) 586-9811  
E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Jim Alkire  
Phone: (303) 275-4795; Fax: (303) 275-4753  
E-mail: James.Alkire@go.doe.gov

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### Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (R) Regeneration Processes

### Technical Targets

This project is conducting studies of light element nanoparticles and molecular compounds. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L

### Objectives

#### Regeneration

- Provide new materials, compounds and support for chemical regeneration of amine-boranes (AB) or boron amides from B-X (X= halide or oxide) compounds.
- To develop a method of regenerating AB or other chemical hydrides from spent fuel with use of a metal formate/hydride cyclable system.
- To develop light element hydride nanomaterials:
  - Test light element hydride nanomaterials ability to transfer hydrogen using different spent fuel forms.
  - Test light element hydride nanomaterials for spent chemical hydride regeneration such as “AB” regeneration.

#### Release

- Enhancement of hydrogen release for chemical hydrides such as AB with light element hydride nanoparticles.
  - Produce light element hydride nanoparticles in a low-cost, high-yield method.

### Accomplishments

#### Regeneration

- Further refined our generic route to tin monoformate synthesis; tin monoformates were identified as the most promising compounds for the metal formate/hydride cycle for regeneration.
- Synthesis and characterization of monomeric and one-dimensional tin formates to test the metal formate/hydride cycle; thermolysis reactions yielded non-CO<sub>2</sub> elimination or ambiguous reaction products.
- Tri-n-butyltin formate repeatedly yields tri-n-butyltin hydride under thermolysis conditions and can be easily prepared.
- NaSi and NH<sub>4</sub>Br for regeneration of AB from spent fuel: Quantification of the production of AB by simple one pot method.
- Si-H nanoparticles for regeneration of AB from spent fuel: Quantification of the production of AB by application of nanoparticles.

## Release

- Light element hydride nanomaterials to affect hydrogen release kinetics: nano-boron-nitrogen (BN) produced from mechanically activated hexagonal-BN mixed with AB show elimination of foam problem associated with release, lowering of the release temperature and a smaller enthalpy for the first release of H<sub>2</sub> from AB. Confirmed and quantified release and provided a hypothesis for the mechanism.
- Preliminary results on the synthesis of mesoporous BN.



## Introduction

UC Davis has two efforts in support of the Chemical Hydrogen Storage Center of Excellence: nanomaterials and molecule development for regeneration of molecular-based chemical hydrogen materials and enhancement of hydrogen release. In order to help support the Center, the UC Davis group is providing two approaches to the regeneration cycle, working closely with Los Alamos National Laboratory (LANL) and the Pacific Northwest National Laboratory (PNNL) on strategies. For regeneration the UC Davis group investigated main group formate small molecules or hydride nanomaterials as low-cost reagents to convert B–O or B–X in one step to B–H, as is proposed for the metal formate/hydride cycle as part of the overall LANL regeneration scheme. The formate work which demonstrated a completed cycle to regenerate B–H bonds was carried out at UC Davis by Bobby Ellis. A paper describing this work in collaboration with that of John Gordon at LANL will be submitted shortly. A postdoc from UC Davis has been working at PNNL for the past year to enable more effective collaboration on the use of nanomaterials for regeneration. We have quantified the amount of AB that is regenerated by the reaction of hydrogen terminated Si nanoparticles versus NaSi + NH<sub>4</sub>Br in a one pot reaction. We have also studied the affect of nanoscale hexagonal BN (nano-BN) as an additive for AB and have shown that it decreases the onset temperature for hydrogen release. Both the nano-BN and the AB:nano-BN samples were prepared by ball milling. The materials were characterized by X-ray powder diffraction, <sup>11</sup>B nuclear magnetic resonance (NMR), thermal gravimetric analysis/differential scanning calorimetry/mass spectrometry (TGA/DSC/MS), and the hydrogen release was measured by a volumetric gas burette system. Several beneficial effects of the mixtures of AB:nano-BN in comparison with neat AB were noted: these were the decrease of the dehydrogenation temperature, the decrease in NH<sub>3</sub> formation as well as the decrease of the exothermicity of hydrogen release with increasing the

nano-BN concentration. Mesoporous BN was prepared and characterized by scanning electron microscope (SEM) and Brunauer-Emmett-Teller.

## Approach

### Regeneration

#### Main Group Formate Compounds

- Synthesize main group formates. Investigate their interconversion with metal hydrides under mild reaction conditions with the object of creating a simple chemical cycle to regenerate B–H bonds in AB.

#### Light Element Hydride Nanomaterials

- Synthesize light element hydride nanomaterials such as hydrogen capped Si<sub>1-x</sub>P<sub>x</sub> and compared properties to hydrogen capped Si nanoparticles.

### Release

- Enhancement of release kinetics with additional of BN nanomaterial (elimination of foaming problem related to hydrogen release of AB and reduction of ammonia release).
- Initiated the synthesis of mesoporous BN in order to optimize hydrogen release capabilities of AB.

## Results

### Regeneration

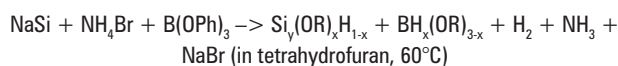
#### Main Group Formate Compounds

UC Davis is collaborating with LANL on the regeneration of B–X to B–H. The proposed cycle starts with a metal formate with the ejection of CO<sub>2</sub> to give the metal hydride. This is part of the overall regeneration scheme for AB, proposed by LANL. The goal of this research is to find a molecular compound that can be used in this cycle and then optimize the process. The tin monoformates with bulky substituents that we examined did not eliminate CO<sub>2</sub> under our thermolysis conditions. There was no indication of any gas evolution in the systems that formed 1-dimensional polymers in the solid state {C<sub>6</sub>H<sub>11</sub> (Cy), CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (Bn)} at elevated temperatures up to 200°C. The substituents with increased steric bulk that allowed for the isolation of monomeric tin formates {C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub> (Mes), C<sub>6</sub>H<sub>3</sub>-2,4,6-Me<sub>2</sub> (Dmp)} resulted in CO ejection to yield tin hydroxides when heated at elevated temperatures. We have had success, however, with the less bulky tri-n-butyltin formate {Bu<sub>3</sub>SnOC(O)H}, which results in the formation of a tin hydride under

thermolysis conditions.  $\text{Bu}_3\text{SnOC(O)H}$  is readily prepared by treatment of  $\text{Bu}_3\text{SnCl}$  with equimolar amounts of  $\text{HOC(O)H}$  and  $\text{NEt}_3$ . The reaction proceeds rapidly with the precipitation of  $(\text{HNEt}_3)\text{Cl}$  that is easily removed. This procedure eliminates the need to isolate the tin oxide, which would be used to generate the tin formates by treatment with formic acid. Distillation of the resulting tin formate under vacuum through a column packed with glass beads yields the tin hydride  $\text{Bu}_3\text{SnH}$ . We are currently optimizing the reaction conditions to maximize the yield of the tin hydride.

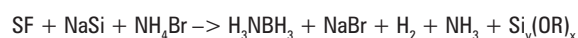
### Light Element Hydride Nanomaterials

We have explored the regeneration of B–H bonds from a B–O model system, by reacting nanoparticles of hydrogen terminated Si and  $\text{NaSi} + \text{NH}_4\text{Br}$  with  $\text{B(OPh)}_3$  in solution. The most promising reaction is provided:



This reaction provided new resonances in the  $^{11}\text{B}$  solution NMR consistent with the products indicated above, along with a small amount of AB. However, we were not able to optimize the reaction products further and have abandoned this approach.

We have also been exploring the regeneration of spent fuel with both hydrogen terminated Si nanoparticles and directly from  $\text{NaSi}$  and  $\text{NH}_4\text{Br}$ .  $^{11}\text{B}$  decoupled NMR indicates that AB can be generated at  $60^\circ\text{C}$  in 5 hours according to the reaction:



### Release

We fully characterized nano-BN prepared by mechanical alloying and quantified the hydrogen release of AB when nano-BN was used as an additive. The initial work demonstrating the reduction in hydrogen release temperature, reduction in enthalpy of hydrogen release has been published. We have also designed a low-cost approach to the synthesis of mesoporous BN as a possible “scaffold” for AB. SEM results suggest that the synthesis is successful.

### Conclusions and Future Directions

This project is relevant to the Center’s goals of recycling spent chemical hydride and AB regeneration. The approach provides novel nanomaterials and the synthesis of metal hydrides for efficient AB regeneration. We have made progress on two major areas that are part of the overall Center goals, collaborating with LANL and PNNL.

**Regeneration:** Demonstrated conversion of boron halide to boron hydride using a recyclable tin formate/tin hydride system. Demonstrated regeneration of AB from spent fuel via reaction with  $\text{NaSi} + \text{NH}_4\text{Br}$  in simple one pot method.

**Release:** Light element hydride nanomaterials to affect hydrogen kinetics: preliminary results show elimination of foam problem associated with release, lowering of the release temperature, smaller enthalpy for the first release of  $\text{H}_2$  from AB. The ratio of nano-BN:AB has been optimized. Delay in hydrogen release at temperature is eliminated. Preliminary understanding of the effect of nano-BN accomplished through high field NMR, high resolution transmission electron microscopy, TGA/DSC/MS, Fourier transform infrared, and Raman spectroscopy. Prepared mesoporous BN and verified via SEM characterization.

In terms of technology transfer/collaborations, we have active partnerships with LANL, PNNL, and University of Alabama and have provided the results to the wider scientific public by means of presentations, publications, and patent applications. We initiated collaboration with SigNa, a start-up company that has developed an inexpensive route to  $\text{NaSi}$ , which we have explored as a useful hydrogen generation agent during this time period.

Future directions include understanding the reaction of  $\text{NaSi} + \text{NH}_4\text{Br}$  for possible regeneration ability and the effect of catalysts and mesoporous BN on hydrogen release of AB.

### Regeneration

- Main group formate compounds.
  - Develop a method of M-H recycling via hydrogenolysis as an alternative to the metal formate/hydride approach.
- Light element hydride nanomaterials.
  - Gain a better understanding through NMR and other spectroscopies as to why spent fuel can be almost fully regenerated, but  $\text{B(OR)}_3$  cannot.
  - Quantify the reaction of spent fuel for production of AB. Optimize reaction parameters.

### Release

- Further optimization of light element nanoparticles (such as BN) to reduce foam and to affect the hydrogen release kinetics without adding contamination, additional weight, and regeneration issues.
- Addition of catalyst for AB release to the nano-BN.
- Preparation of meso-BN in order to further optimize the effect of nano-BN upon hydrogen release from AB. This will take advantage of higher surface area.

## FY 2009 Publications/Presentations

1. *Promotion of Hydrogen Release from Ammonia Borane with Mechanically Activated Hexagonal Boron Nitride*, D. Neiner, A. Karkamkar, J.C. Linehan, B. Arey, T. Autrey, and S.M. Kauzlarich, *J. Phys. Chem. C*, **2009**, *113*, 1098-1103.
2. *Nanomaterials as Additives for Hydrogen Release from Ammonia Borane*, S. M. Kauzlarich, oral presentation at the NEDO Hydrogen Storage Meeting, 8–10 September 2008.
3. *Promotion of hydrogen release from ammonia borane with nanostructured hexagonal boron nitride* S.M. Kauzlarich, invited oral presentation at the 237<sup>th</sup> ACS National Meeting, Division of Industrial & Engineering Chemistry, Nanotechnology and the Environment: Emphasis on Green Nanotechnology, Salt Lake City, UT, March 22-26, 2009, Paper number: 128.