



# Amineborane-Based Chemical Hydrogen Storage

Department of Chemistry  
University of Pennsylvania

DOE Chemical Hydrogen  
Storage Center of Excellence

2010 DOE Hydrogen Program Review

June 10, 2010

Project ID: ST039

This presentation does not contain any proprietary or confidential information

# Project Overview

## Timeline

Project Start: FY 2005  
Project End: March 2010  
Percent complete: 95%

## Budget

Total Project Funding: \$1,783,787  
DOE: \$1,417,353  
Penn: \$366,434

DOE Funding in 09: \$300,000  
DOE Funding in 10: \$300,000

## Barriers Addressed

### Barriers

- A. System Weight and Volume
- B. System Cost
- E. Charging/Discharging Rates
- R. Regeneration Processes

### Targets

DOE storage targets for kg-H<sub>2</sub>/kg, kWh/L and \$/kWh

## Collaborators on Amineborane Project



# *Relevance and Overall Objectives*

## **Project Relevance**

*The development of efficient hydrogen storage systems that can meet the DOE targets is key to enabling the use of hydrogen as an alternative energy carrier for transportation.*

## **Project Objectives**

- *Develop new chemical hydride based systems for on-demand, low temperature H<sub>2</sub>-release that can achieve the DOE targets for hydrogen storage*
- *Develop high conversion off-board methods for chemical hydride regeneration*

In collaboration with Center Partners, this project focused on new methods for H<sub>2</sub>-release and spent-fuel regeneration that exploited the high hydrogen density and facile H<sub>2</sub>-elimination reactions of amineboranes.

## **Ammonia Borane H<sub>2</sub>-Release**



# Approach and Specific Objectives

## Penn Project Approach

**Hydrogen-Release:** Enhance the rate and extent of H<sub>2</sub>-release from amineboranes using the activating effects of (1) **ionic liquids**, (2) **chemical promoters** and (3) **metal-catalysts**.

**Regeneration:** Develop spent fuel regeneration methods based on digestion of BNH<sub>x</sub> to boron trihalides, then conversion to AB via sequential coordination, reduction and displacement reactions.

### Specific Objectives for the Past Year

- Develop an understanding of the activating effects and reaction mechanisms of ionic-liquid and base promoted AB H<sub>2</sub>-release.
- Identify optimal temperature/composition conditions for AB H<sub>2</sub>-release in ionic liquids and provide high quality kinetic data for system analyses at Argonne.
- Optimize base-promoted AB H<sub>2</sub>-release.
- Find new metal catalysts for promoting AB H<sub>2</sub>-release in ionic liquids.
- Make final Go/No-Go Decision on boron halide based spent-fuel regeneration processes.



### Penn Research Team

PI: Larry Sneddon

Students:

Dan Himmelberger  
Bill Ewing  
Emily Berkeley

## *Approach*

**Penn Approach to H<sub>2</sub>-Release. Increase the Rate and Extent of AB H<sub>2</sub>-Release by Activation with:**

**1. Ionic Liquids**

**2. Chemical Promoters**

**3. Metal-Catalysts/Ionic-Liquids**

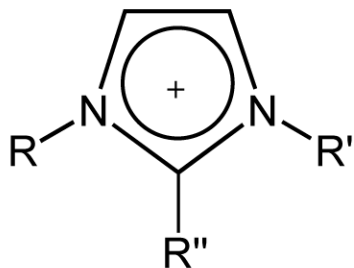


## Approach

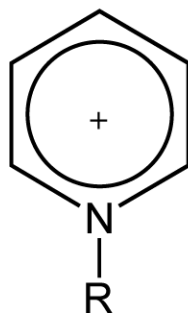
# 1. Why Ionic Liquids for Amineborane H<sub>2</sub>-Release?

### Ionic Liquids

Cations:



N,N'-imidazolium



N-pyridinium

Anions:

*Reactive:* AlCl<sub>4</sub><sup>-</sup>, Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>

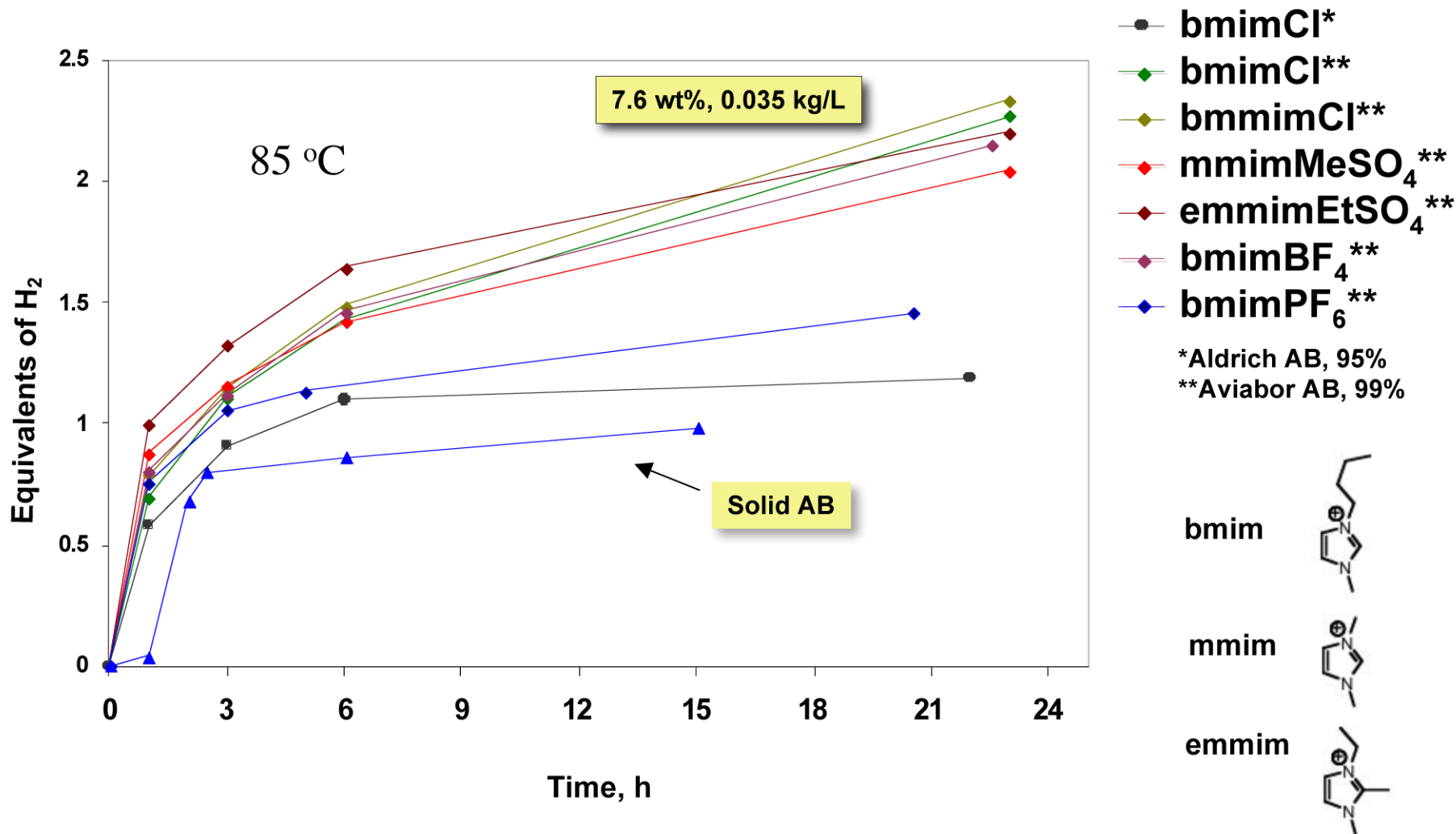
*Inert:* PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>

### Advantages

- Negligible vapor pressures
- Dissolve both neutral and ionic species
- Thermally stable to elevated temperatures
- Non-coordinating anions and cations provide an inert, polar reaction medium
- **Promote the formation of ionic or polar intermediates and transition states**

# Technical Accomplishments

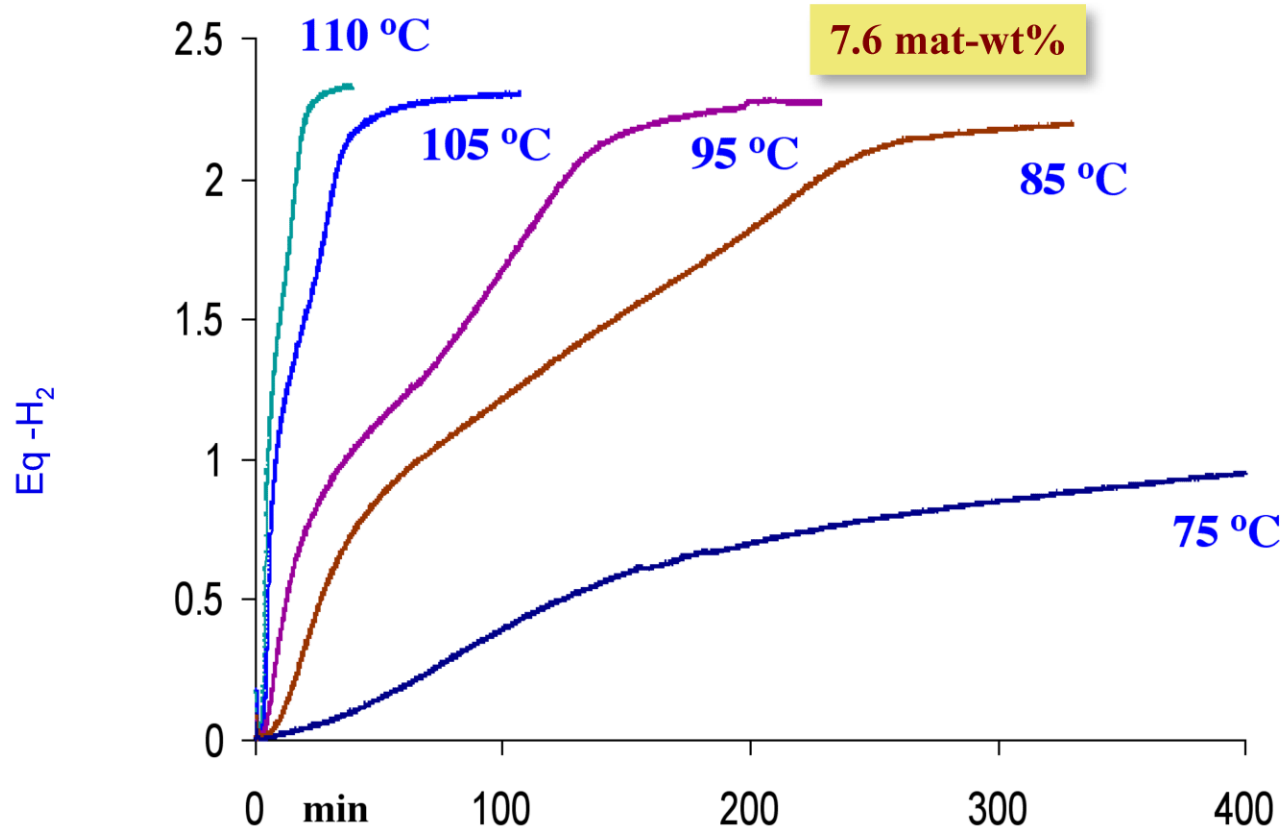
## Ionic Liquids Increase the Rate and Extent of AB H<sub>2</sub>-Release and Eliminate Induction Period



## Technical Accomplishments

# Significantly Faster Rates for AB H<sub>2</sub>-Release In Ionic Liquids with Only Small Temperature Increases

AB H<sub>2</sub>-Release versus Temperature for 50 wt% bmimCl/AB



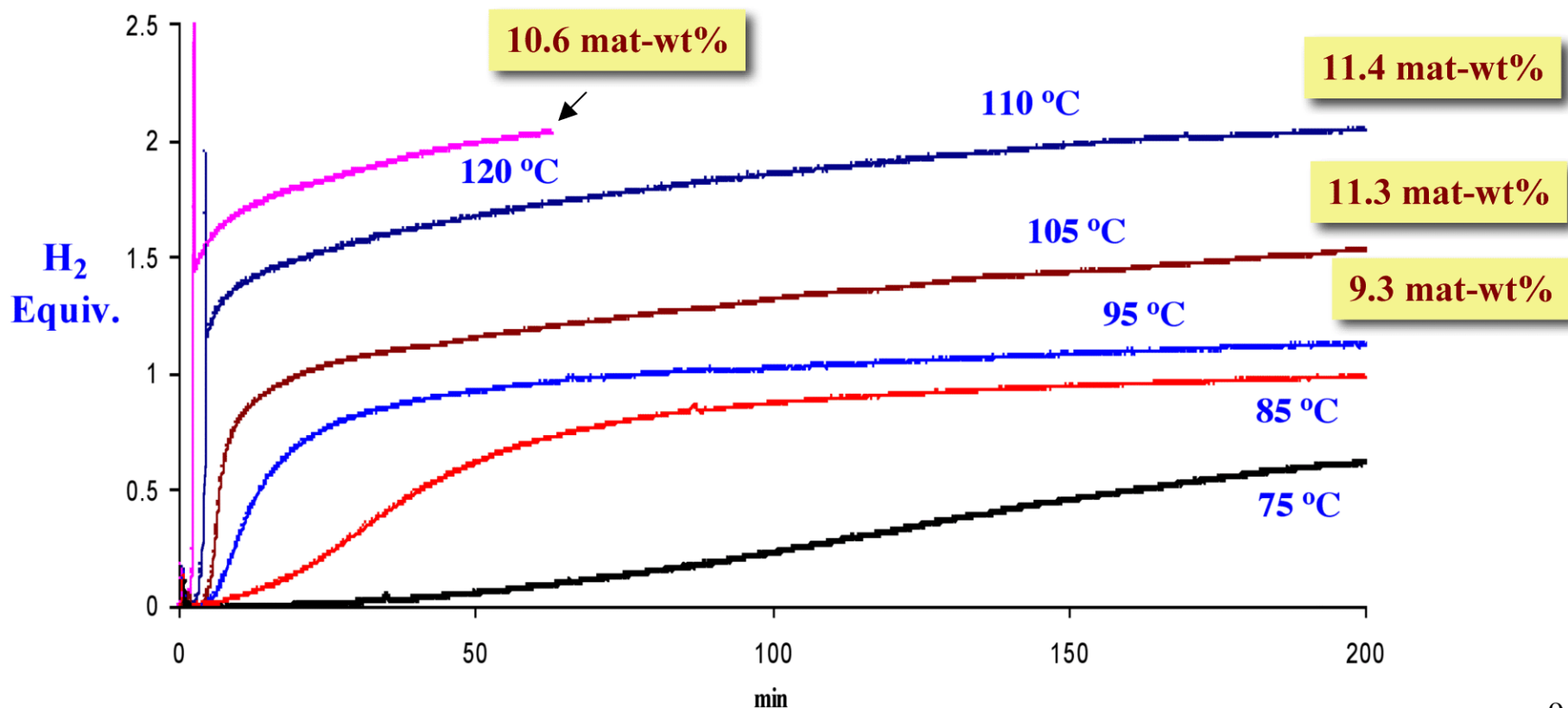
**Conclusion: Fast H<sub>2</sub>-Release at higher temperatures, but need to increase mat-wt% by decreasing % ionic liquid**



## Technical Accomplishments

**Fast Rate and a 11.4 mat-wt% H<sub>2</sub>-Release was Demonstrated for 20 wt% ionic-liquid/AB at 110 °C**

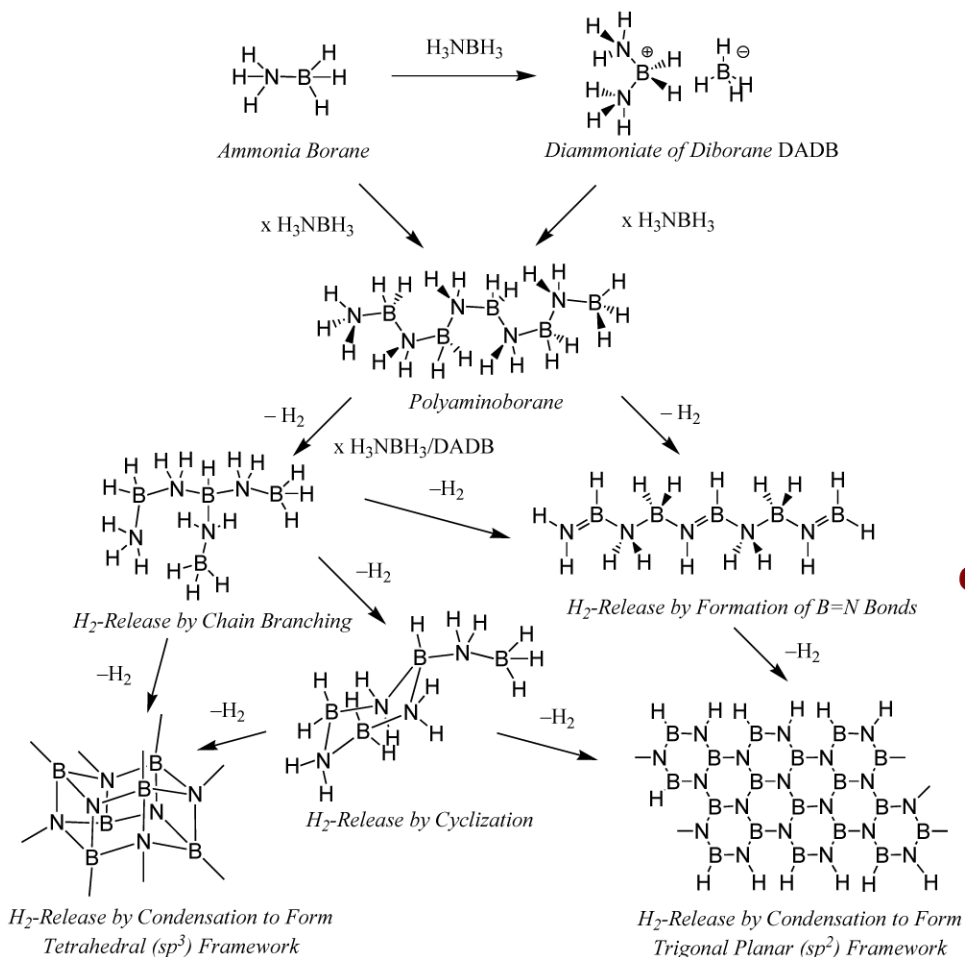
**AB H<sub>2</sub>-Release versus Temperature in 20 wt% bmimCl**



# Technical Accomplishments

## How Do Ionic Liquids Activate AB H<sub>2</sub>-Release?

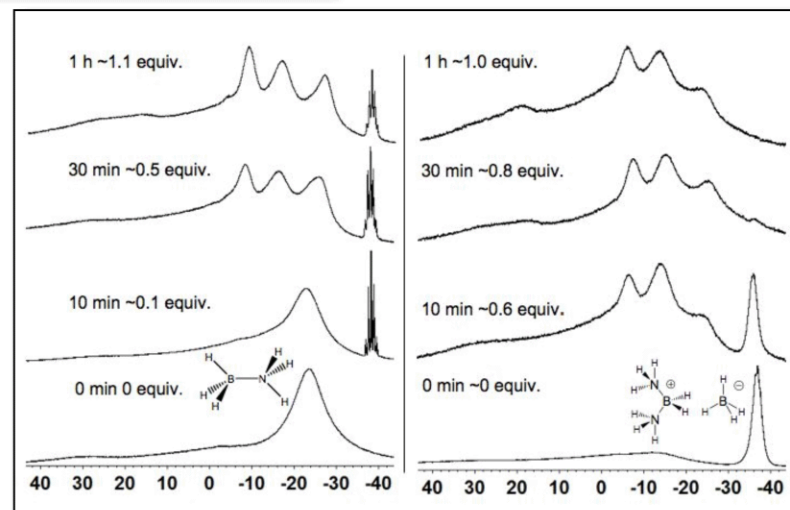
### Possible Mechanistic Steps



Himmelberger, D.; Alden, A.; Bluhm, M. E.; Sneddon, L. G. *Inorg. Chem.* **2009**, *48*, 9883-9889

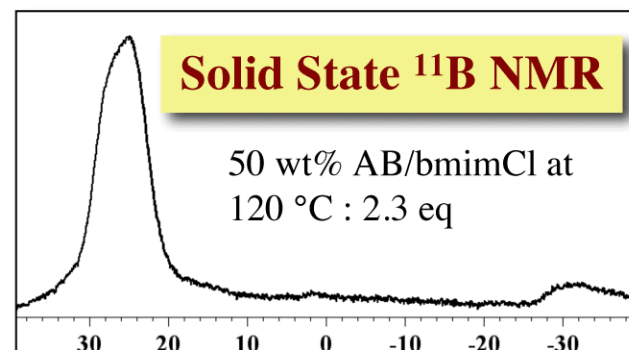
### Solution <sup>11</sup>B NMR

10 wt% AB and DADB in bmimOTf at 85°C



**Conclusion: Both DADB formation and decomposition is enhanced in ionic liquids**

### Solid State <sup>11</sup>B NMR

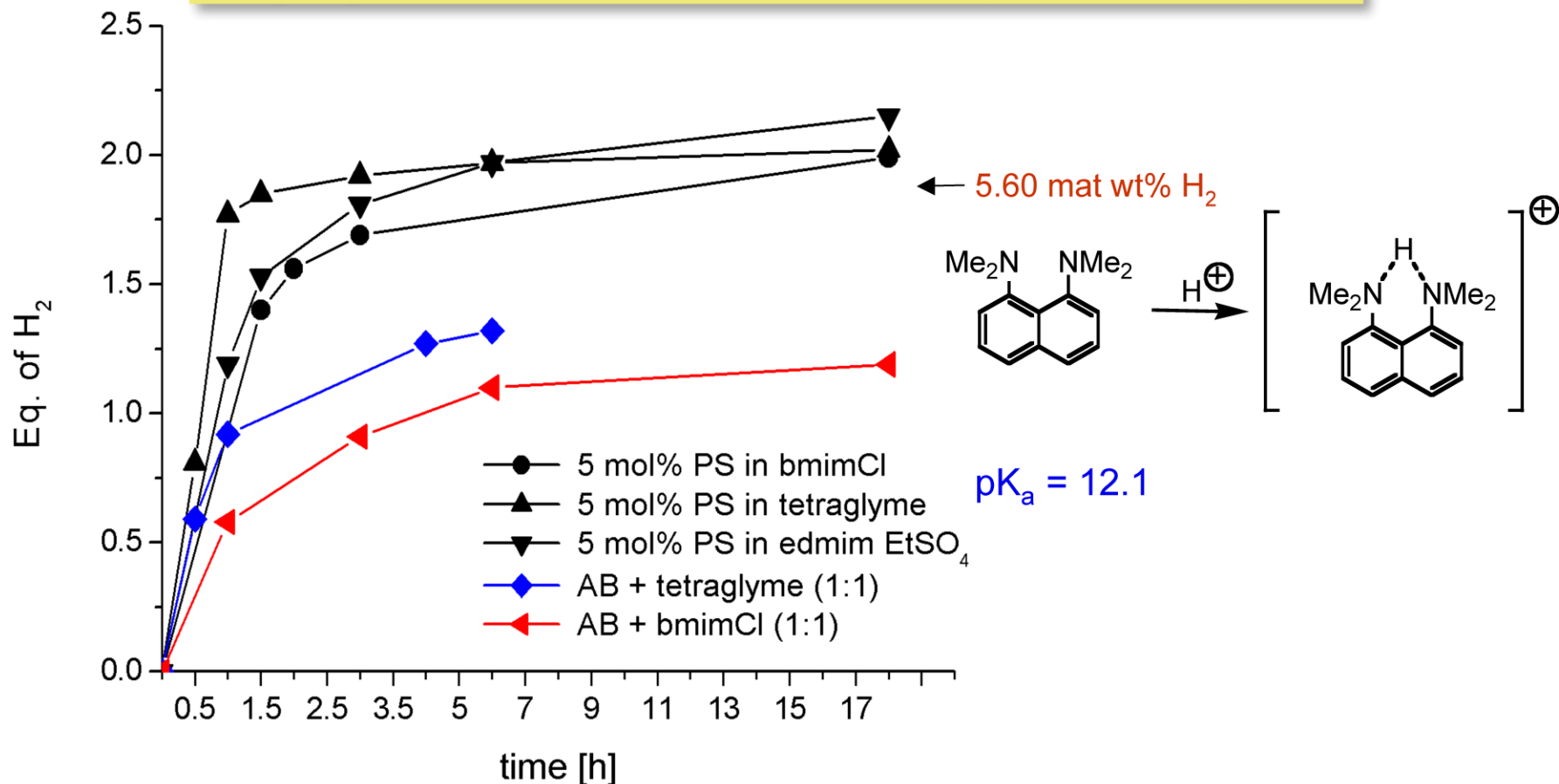


**Conclusion: Final Spent Fuel Product has sp<sup>2</sup>-type framework**

# Approach and Technical Accomplishments

## 2. Enhanced AB H<sub>2</sub>-Release with Proton Sponge in Ionic Liquids or Tetraglyme with Reduced Foaming

**NH<sub>3</sub>BH<sub>3</sub> + 5 mol % PS at 85 °C in Ionic-Liquids or Tetraglyme**

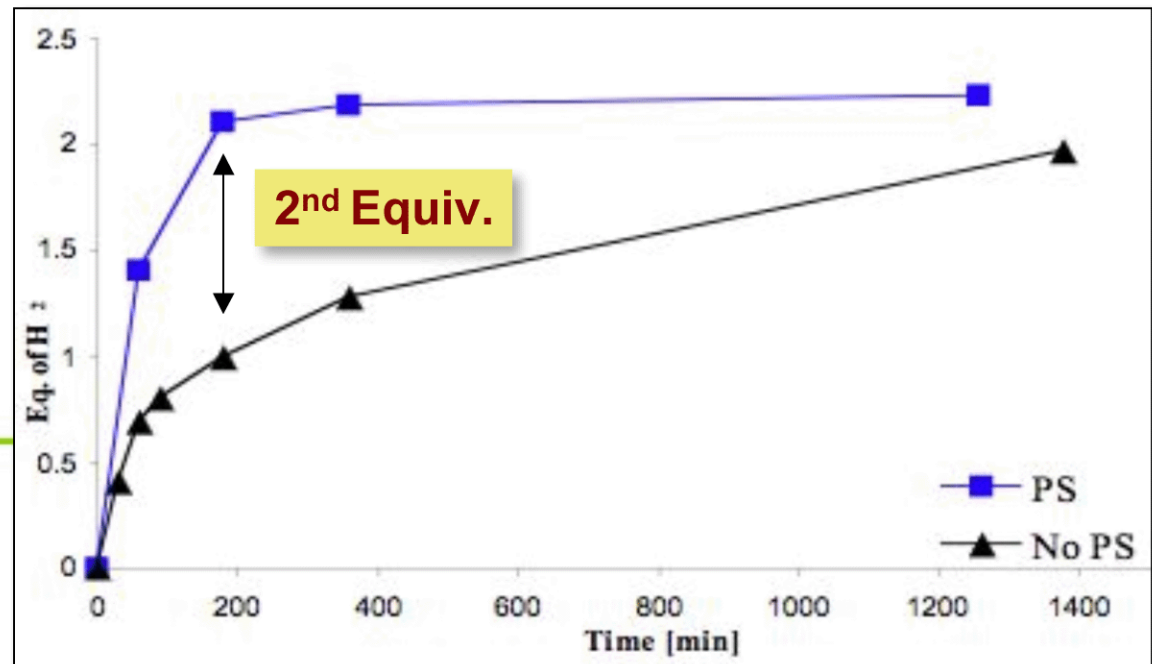
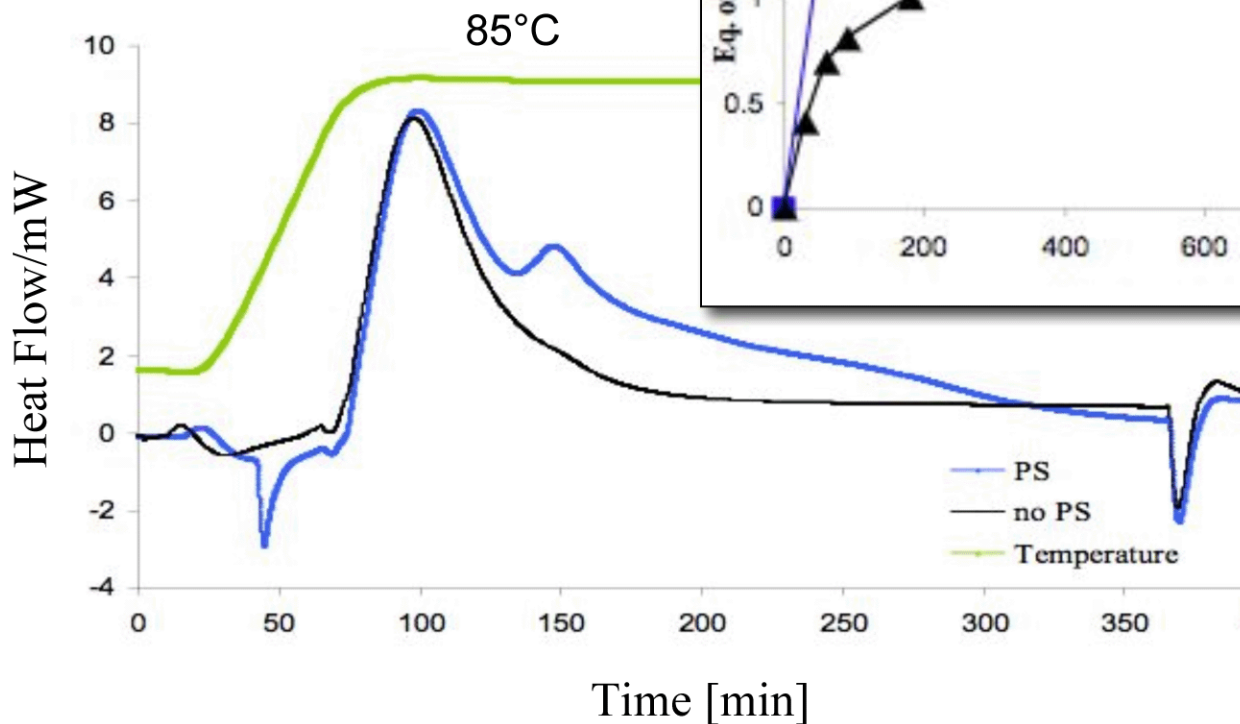


Himmelberger, D.; Yoon, C. W.; Bluhm, M. E.; Carroll, P. J.; Sneddon, L. G.  
*J. Am. Chem. Soc.* **2009**, *131*, 14101-14110.

# Technical Accomplishments

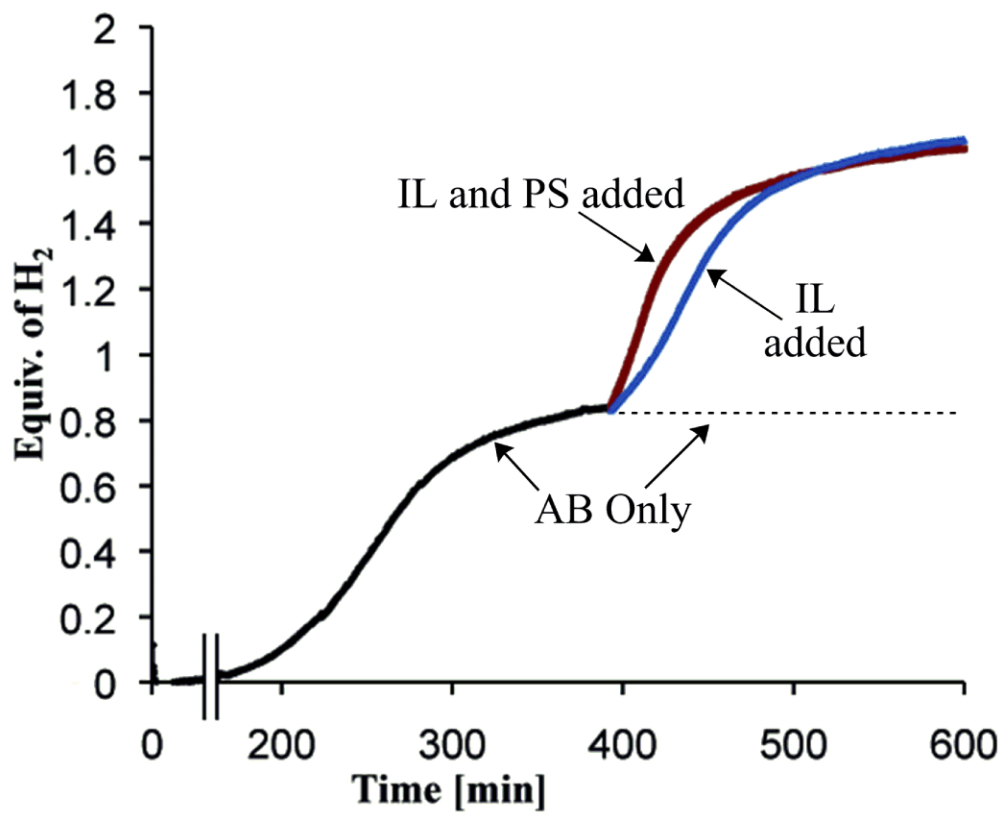
## Proton Sponge Increases the Release Rate of the Second Equivalent of H<sub>2</sub> from AB

AB with 5 mol% PS  
in bmimCl at 85 °C

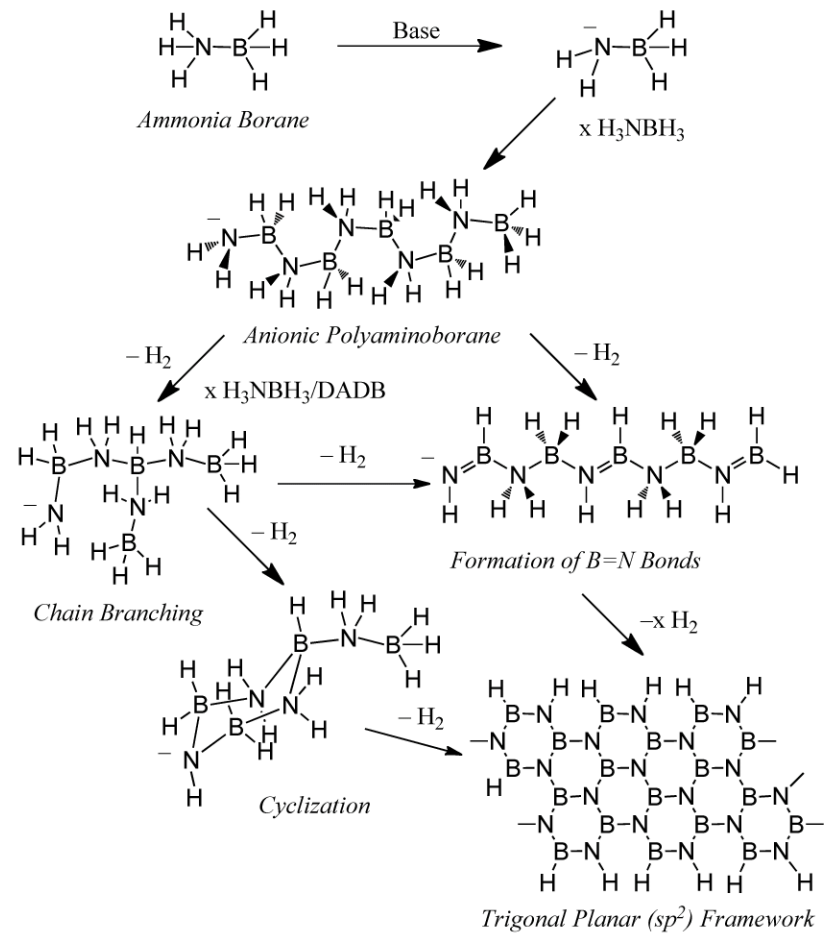


# Technical Accomplishments

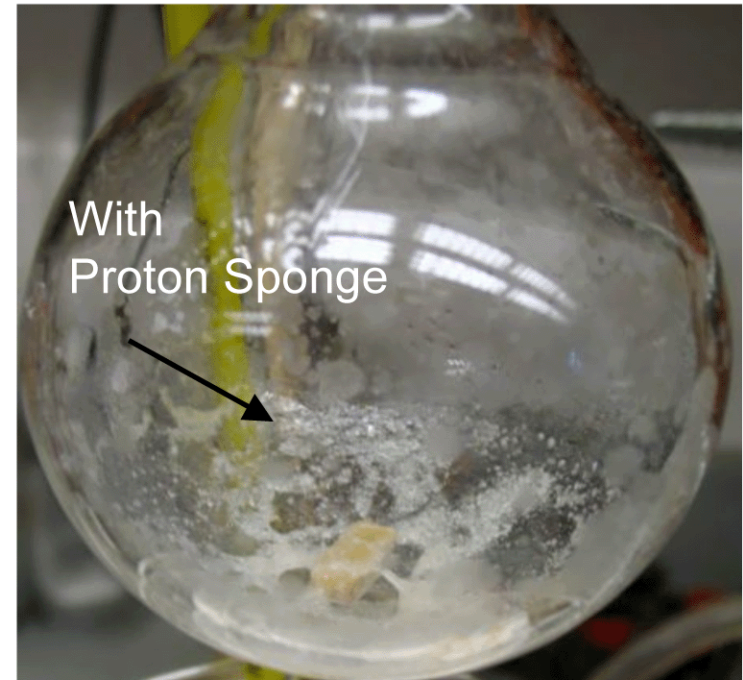
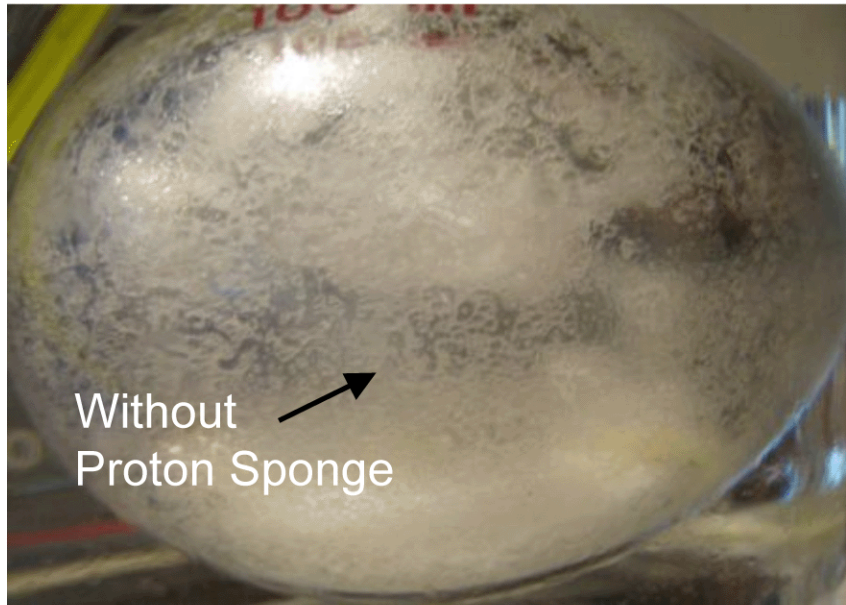
## Proton Sponge Induces Loss of a Second H<sub>2</sub>-Equivalent from Thermally Dehydrogenated AB



### Possible Mechanistic Steps



## Foaming Suppressed with Proton Sponge



### **3. Why Use Metal Catalysts for Amineborane Dehydrogenations in Ionic Liquids?**

Catalysts in Conjunction with Ionic Liquids Could Provide:

- **Faster H<sub>2</sub>-Release**
- **Better Control of H<sub>2</sub>-Release Rates**
- **Lower Temperature Reactions**
- **Synergistic Release Mechanisms**

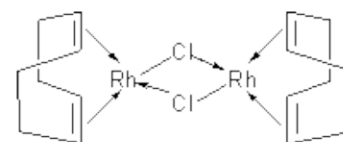
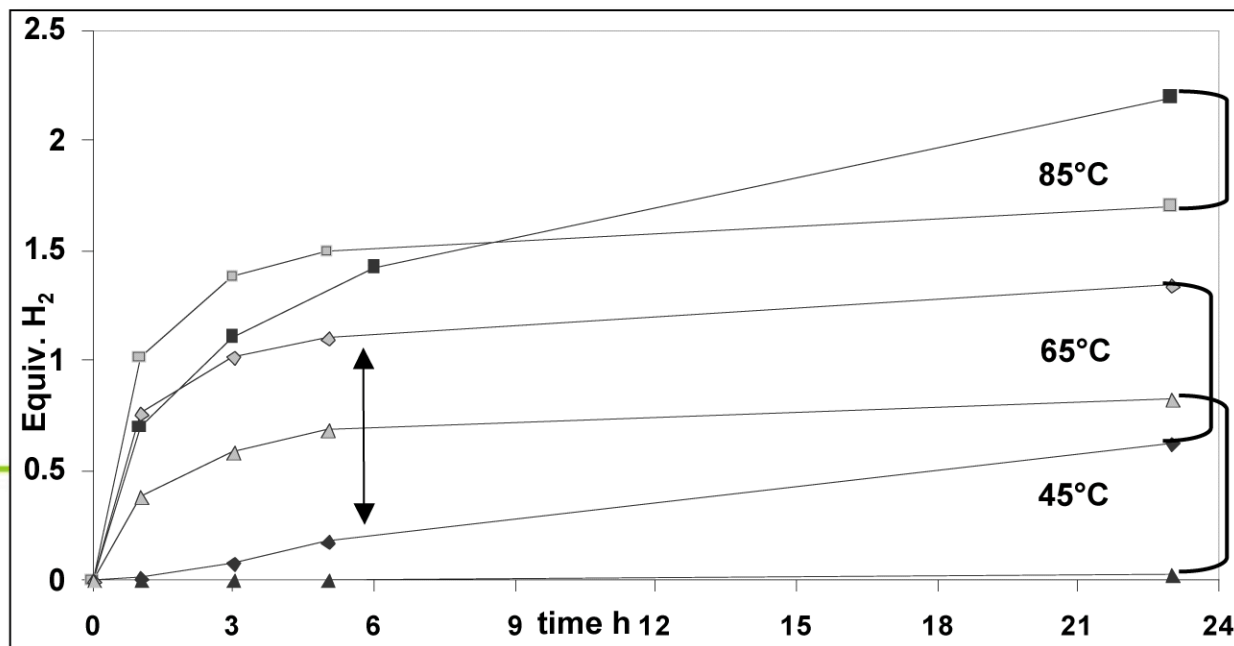
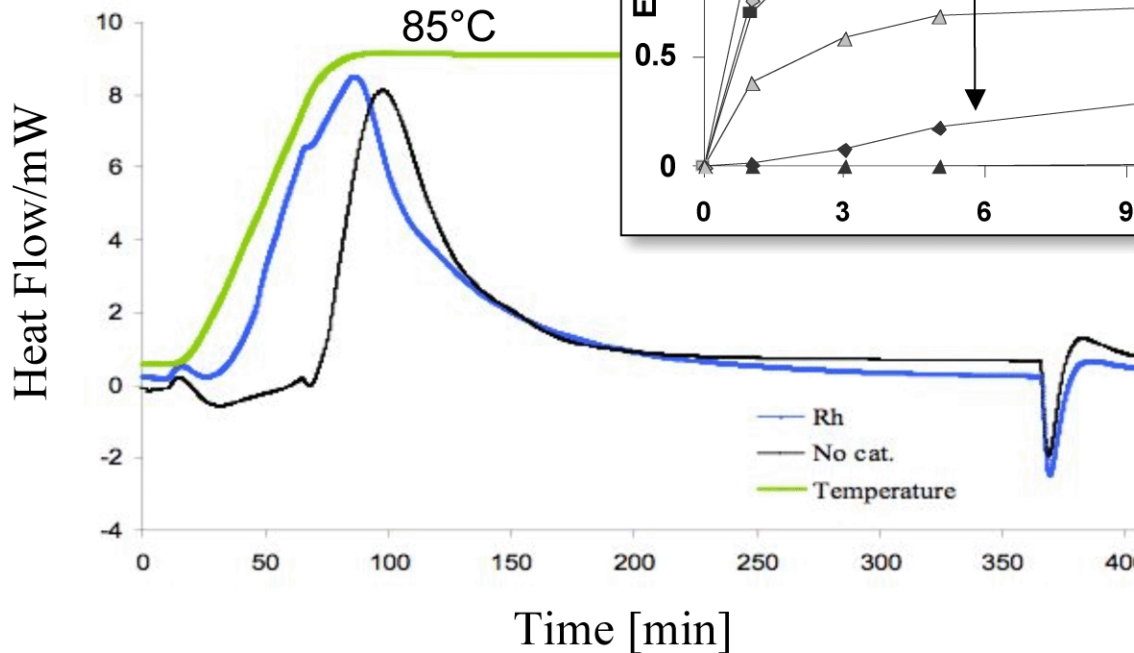
Center Partners (LANL and U Washington) have previously demonstrated metal catalyzed AB H<sub>2</sub>-release in organic solvents.

# Technical Accomplishments

## Rh Catalyst Increases Release Rate of the First Equivalent of H<sub>2</sub> from AB in Ionic Liquids

50 wt% AB  
in bmimCl  
5 mol% Rh

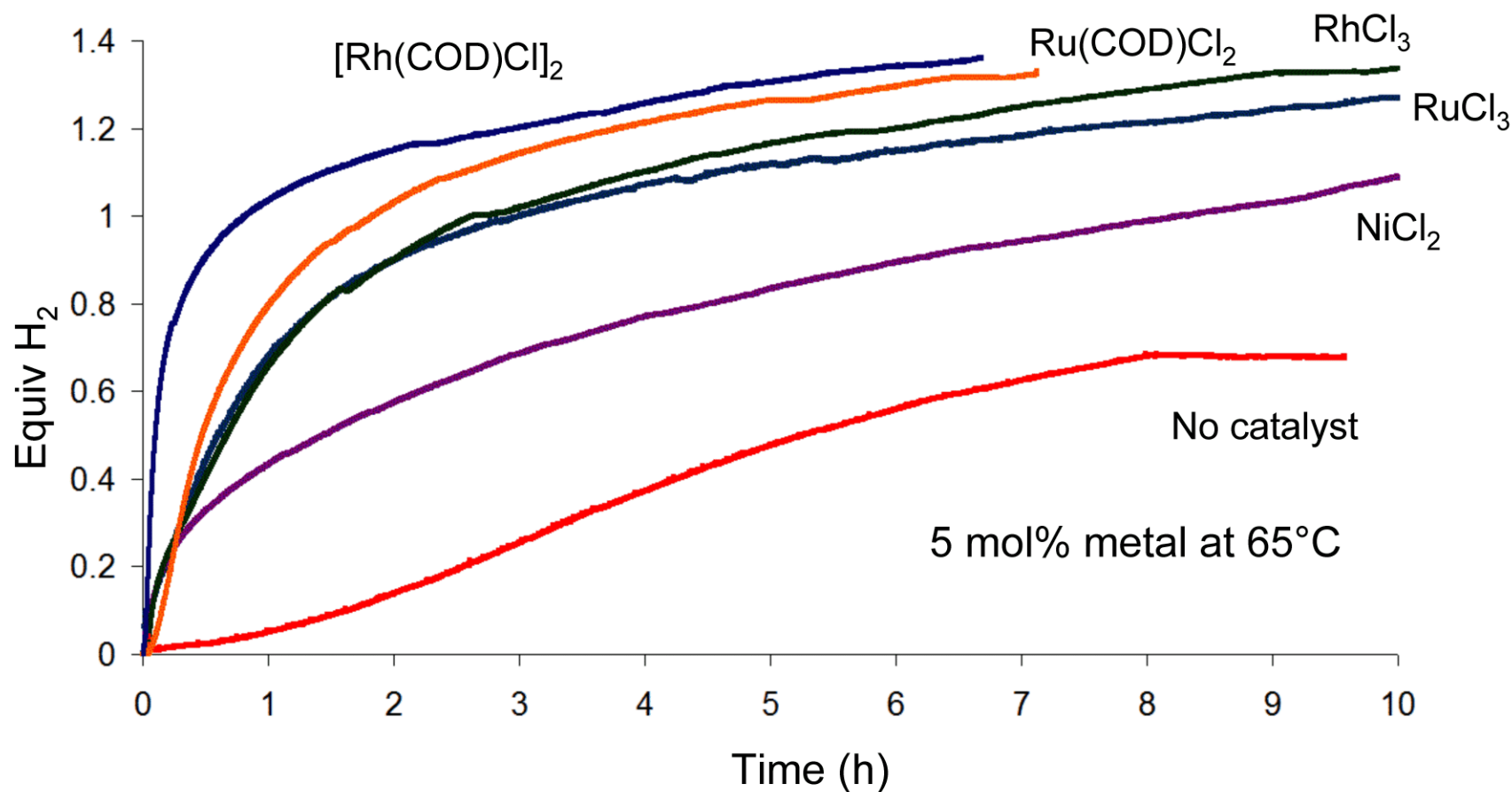
DSC



- 85°C
- ◆ 65°C
- ▲ 45°C
- 85°C w/ Rh
- ◆ 65°C w/ Rh
- ▲ 45°C w/ Rh



## Other Metal Catalysts Increase the Rate of AB H<sub>2</sub>-Release in Ionic Liquids



## Technical Accomplishments

# H<sub>2</sub>-Release Systems Show Significant Increases in the Mat-Wt% and Rate of H<sub>2</sub>-Release

	AB and 20 wt% bmimCl		AB and 50 wt% bmimCl		AB and 50 wt% bmimCl 5 mol % PS
	120 °C Two equiv. in 52 min	110 °C Two equiv. in 157 min	<b>120 °C Two equiv. in 7 min</b>	110 °C Two equiv. in 22 min	<b>110 °C Two equiv. in 9 min</b>
Initial Rate (mol/sec)	4.4x10 <sup>-5</sup>	1.8x10 <sup>-5</sup>	2.3x10 <sup>-5</sup>	8.3x10 <sup>-6</sup>	2.1x10 <sup>-5</sup>
Grav. density (Mat. wt%)	11.4 2.2 Equiv.	<b>11.4 2.16 Equiv.</b>	7.2 2.06 Equiv.	6.9 2.11 Equiv.	6.1 2.21 Equiv.
Vol. density (Kg-H <sub>2</sub> /L Mat.)	0.089	0.095	0.067	0.063	0.057
H <sub>2</sub> Flow Rate (g/s) per kg Material	0.47	0.193	0.08	0.056	0.119
Kg of Mat. for 0.8 mol/sec	3.4	8.4	10	29	13

### DOE Total System Targets for Hydrogen Storage Systems

Gravimetric Density (wt%)

4.5 (2007), 6.0 (2010), 9.0 (2015)

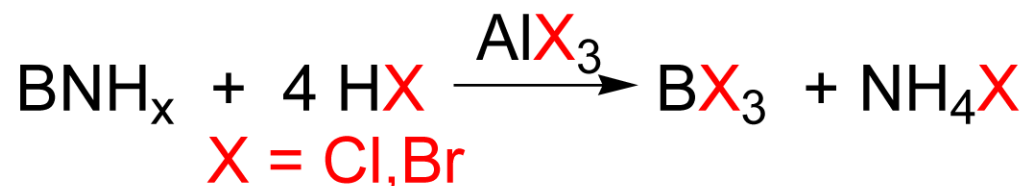
Volumetric Density (Kg-H<sub>2</sub>/L)

0.036 (2007), 0.045 (2010), 0.081 (2015)

## Approach

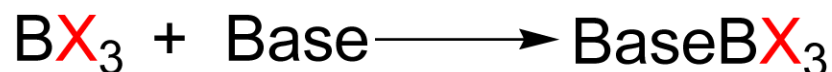
# Penn Approach to Regeneration: Super-Acid/Halide-Reduction Process

## First Step: Digestion of Spent Fuel by Super Acidic Halo-Acids

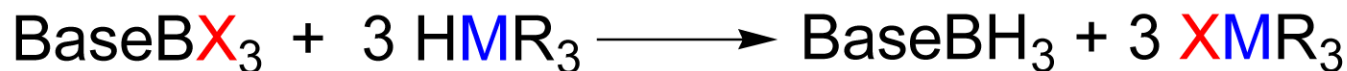


## Second Step: One-Pot Conversion of $\text{BX}_3$ to AB

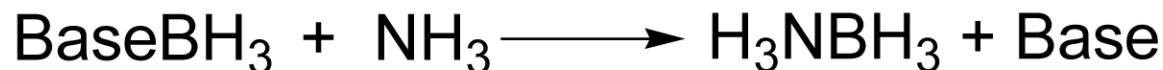
### Coordination of $\text{BX}_3$



### BX Reduction



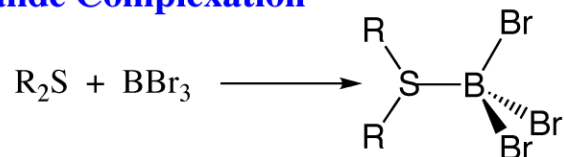
### Base Displacement by $\text{NH}_3$ Yields AB



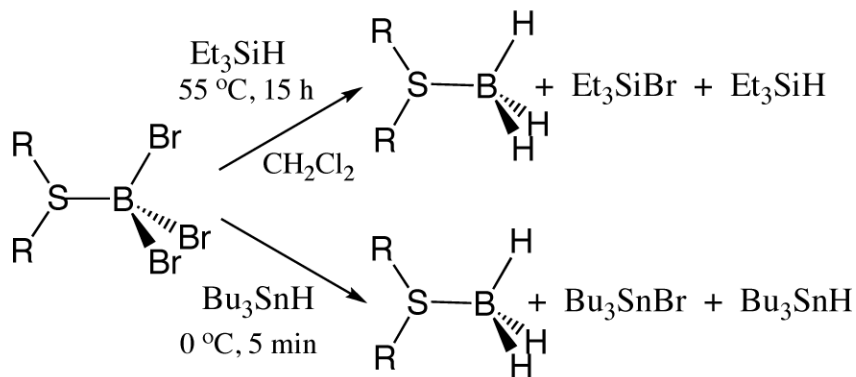
# Technical Accomplishments

## Step 2: Boron Halide Reduction Processes are Simple, Quantitative and Allow Separation and Recovery of All Products

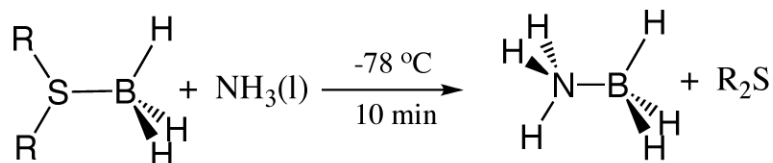
### Boron Halide Complexation



### Complex Reduction with Silanes or Stannanes

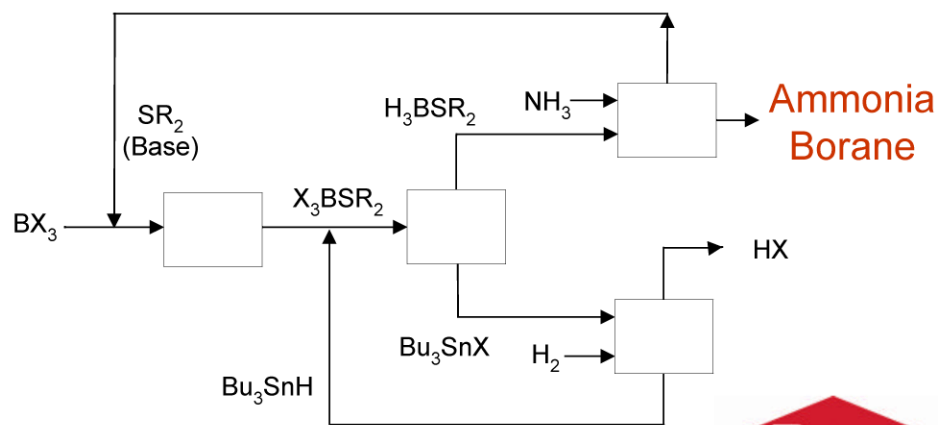


### Displacement with Ammonia



### Demonstrated Advantages:

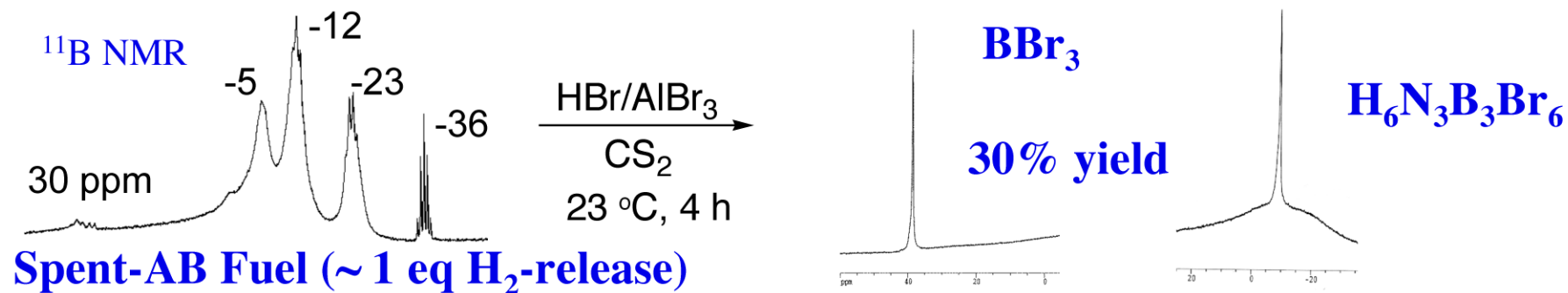
- (1) high, 96-100%, yields on multi-gram laboratory scale-ups
- (2) avoids the formation of B-O bonds
- (3) avoids the formation of  $B_2H_6$
- (4) simple product isolation based on volatility with separation/recovery of all materials
- (5) 2008-9 Rohm and Haas analysis indicates a scalable process



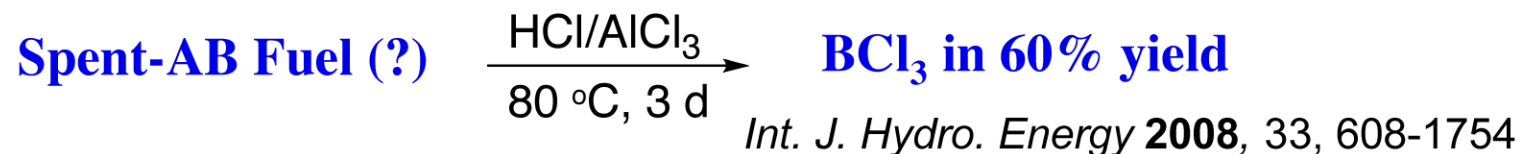
# Technical Accomplishments

## Step 1: Progress on Spent Fuel Digestion to $BX_3$

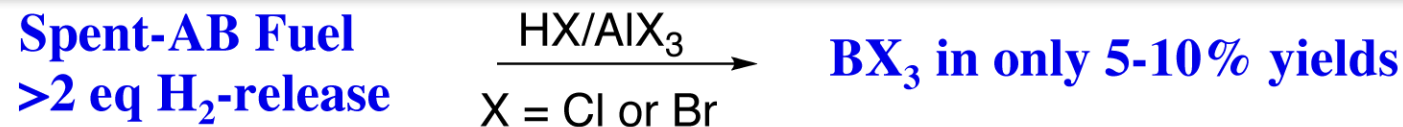
### 2007 Penn: Superacidic $HX/AlX_3$ Solutions Digest Spent-Fuels



### 2008: Mertens et. al. Report Digestion with Superacidic $HCl/AlCl_3$



### 2009-10 Penn: Superacidic Conditions Do Not Give Good Yields of $BX_3$ from Highly Dehydrogenated Fuels



**Conclusion: Super-Acid Approach is No-Go Owing to Unsatisfactory Spent Fuel Digestion**

## Summary of Project Accomplishments/Conclusions



- Significant rate enhancements with reduced borazine formation and a high mat-wt% H<sub>2</sub>-release (up to 11.4%) were achieved with 20 wt% ionic-liquid/AB mixtures at 110 °C.
- Base-induced H<sub>2</sub>-release in ionic liquids increases the release rate of the second AB H<sub>2</sub>-equivalent and reduces foaming.
- Metals catalyze AB H<sub>2</sub>-release in ionic liquids with significant increases in the rate of loss of the first AB H<sub>2</sub>-equivalent.
- Generated quality kinetic data for Argonne zero-order onboard system analysis.
- A simple, quantitative boron halide reduction process was developed that allowed the separation and recovery of all products, but a No-Go decision was made on the overall Penn regeneration process owing to incomplete spent fuel digestion.



# Collaborations and Technology Transfer

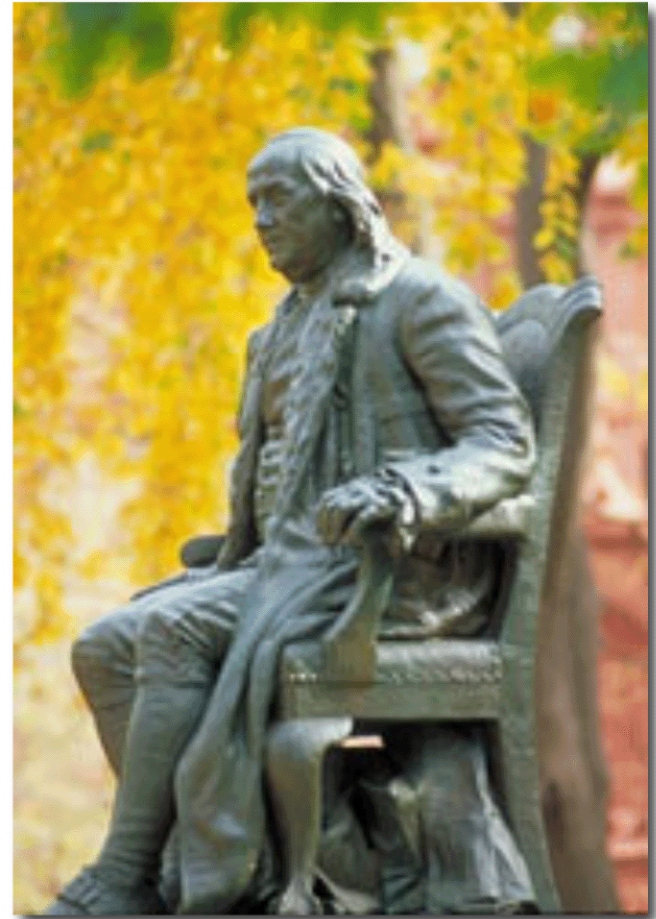
**Penn work on H<sub>2</sub>-Release/Regeneration was Highly Coordinated with Partners by Frequent “Brainstorming” Discussions, Laboratory Visits, and Sample and Measurement-Sharing.**

## *Some Examples of Collaborations and Technology Transfer*

- Provided Penn kinetic data on AB/ionic-liquid H<sub>2</sub>-release to Argonne for their zero-order onboard system analysis.
- PNNL postdoctoral visited Penn to learn how to perform the borazine synthesis at PNNL.
- Penn students and postdoctoral carried out research at PNNL on several extended visits to use the unique capabilities at PNNL in DSC, solid-state NMR and H<sub>2</sub> measurements to study H<sub>2</sub>-release from the Penn ionic liquid based systems.
- PNNL provided essential help in constructing two PNNL-designed gas burette systems at Penn. These systems have enabled much of the key H<sub>2</sub>-release measurements on Penn systems.
- Penn and Dow (Chen and Lipiecki) evaluated the scale up feasibility of the of the boron halide reduction/separation step for regeneration.
- U. of Ottawa (Baker) and Penn carried out joint investigations of the mechanisms of AB H<sub>2</sub>-release.

# Some Important Future Questions

- Can new fuels or fuel/mixtures be developed that will generate liquid spent fuel products in ionic liquids?  
AB/alkyl-boranes/additives?  
AB/ammonia-triboranes?
- Can new ionic liquids be developed that will extend the liquid range of the spent fuels?
- What is the most effective metal catalyst that can be used in conjunction with ionic liquids to promote H<sub>2</sub>-release?
- Can other efficient synergistic methods be developed to activate H<sub>2</sub>-release?
- Borazine formation is reduced in ionic liquids, but can it be completely eliminated?
- Can spent fuels be directly regenerated in ionic liquids?





# Project Summary

**Relevance:** *The development of efficient hydrogen storage systems are essential to the success of the DOE Hydrogen Initiative for transportation.*

**Approach:** *Enhance the rate and extent of H<sub>2</sub>-release from amineboranes using the activating effects of (1) ionic liquids, (2) chemical promoters, and (3) metal-catalysts and develop high yield halide-based regenerations.*

**Technical Accomplishments and Progress:** *Significant increases in both the rate and extent of AB H<sub>2</sub>-release were attained.*

**Technology-Transfer/Collaborations:** *Active partnerships and collaborations across the Chemical Hydride Center.*

**Future Research:** *Some key issues for future research have been identified.*

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