



# Amineborane-Based Chemical Hydrogen Storage

Department of Chemistry  
University of Pennsylvania

DOE Chemical Hydrogen  
Storage Center of Excellence

2009 DOE Hydrogen Program Review

May 19, 2009      Project ID: st\_16\_sneddon

This presentation does not contain any proprietary or confidential information

# Project Overview

## Timeline

Project Start: FY 2005  
Project End: March 2010  
Percent complete: 80%

## Budget

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

DOE Funding in 08: \$300,000  
DOE Funding in 09: \$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 methods that can meet the DOE targets for hydrogen storage is key to enabling the use of hydrogen as an alternative energy carrier for transportation.*

## **Project Objectives**

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

In collaboration with Center Partners, the focus of this project is to develop new methods for H<sub>2</sub>-release and regeneration that exploit the high hydrogen density and facile H<sub>2</sub>-elimination of amineboranes for chemical hydrogen storage.

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



## 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 regeneration methods that: (1) give high yields; (2) avoid formation of B-O bonded intermediates; (3) avoid formation of hazardous diborane; (4) recover all products. Penn method focuses 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



#### Penn Research Team

PI: Larry Sneddon  
Postdoctoral: Laif Alden  
Students:  
Dan Himmelberger  
Bill Ewing  
Emily Berkeley

- Identify optimal temperature/composition conditions for AB H<sub>2</sub>-release in ionic liquids
- Optimize and expand studies of base-promoted AB H<sub>2</sub>-release.
- Find new metal catalysts for promoting AB H<sub>2</sub>-release in ionic liquids.
- Refine boron halide based regeneration processes.

## **Summary of Important Penn Accomplishments/ Milestones Since 2008 AMR**

- Significant rate enhancements along with high mat-wt% H<sub>2</sub>-release (up to 11.4%) were demonstrated with 20 wt% ionic-liquid/AB mixtures at 110 °C.
- Base-induced H<sub>2</sub>-release in ionic liquids was extended to new bases and shown to increase the release rate of the second AB H<sub>2</sub>-equivalent
- A variety of metals were found to catalyze AB H<sub>2</sub>-release in ionic liquids with significant increases for the rate of loss of the first AB H<sub>2</sub>-equivalent.
- The boron halide reduction step in the regeneration scheme was demonstrated to be simple, quantitative and allow the separation and recovery of all products. Initial Rohm and Haas analysis indicates a scalable separation process.

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

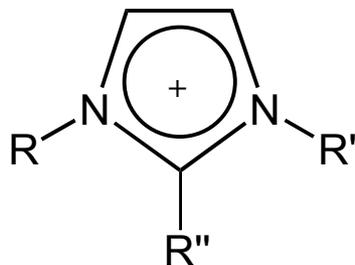
- 1. Ionic Liquids**
- 2. Chemical Promotors**
- 3. Metal Catalysts/Ionic-Liquids**



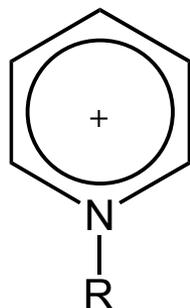
## Why Ionic Liquids for Amineborane H<sub>2</sub>-Release?

### 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>

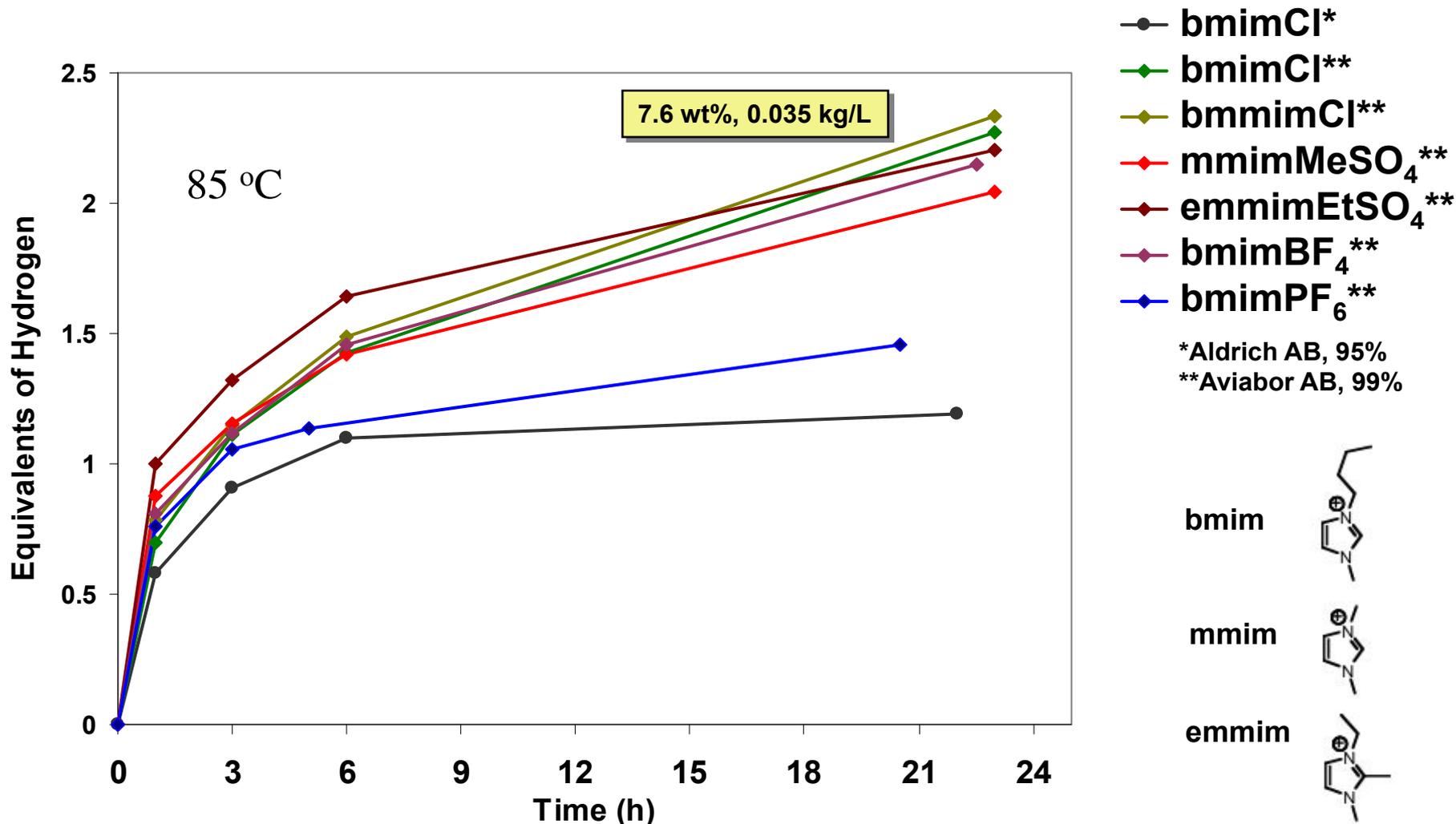
*Inert:* PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>

### 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**

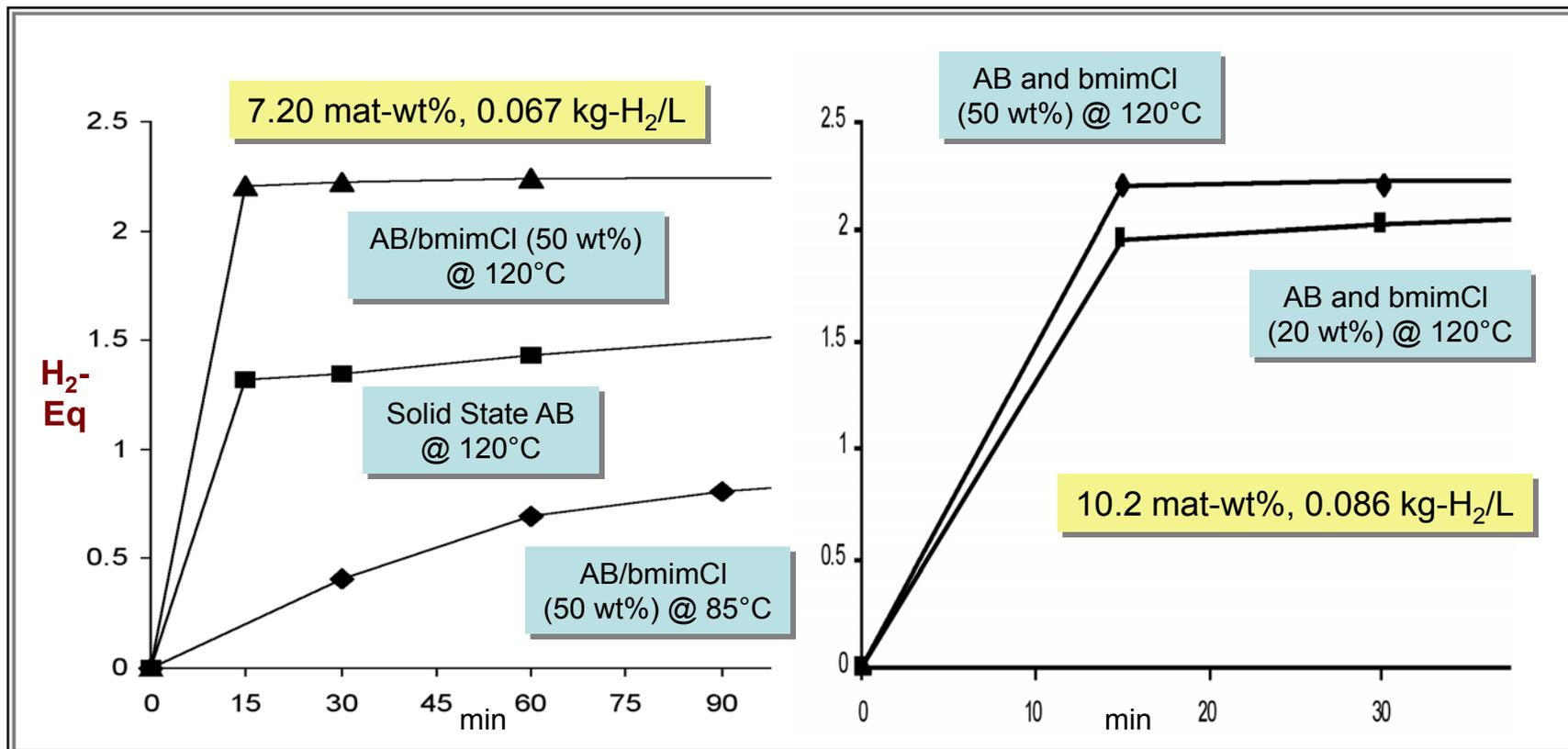
# Technical Accomplishments

## 2006-7: Ionic Liquids Increase the Rate and Extent of AB H<sub>2</sub>-Release and Eliminates Induction Period



## Technical Accomplishments

### 2008: Initial Studies Show AB H<sub>2</sub>-Release Rates in Ionic Liquids Are Greatly Increased at 120 °C

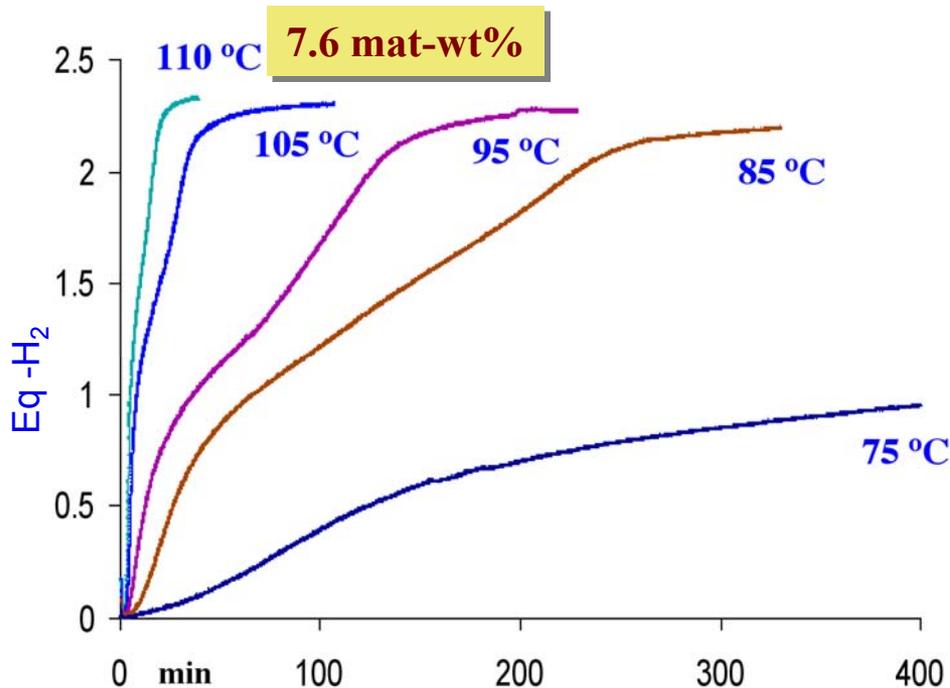


**2009 Goal: Identify Optimal Temperature/Weight Conditions for AB H<sub>2</sub>-Release in Ionic Liquids**

## Technical Accomplishments

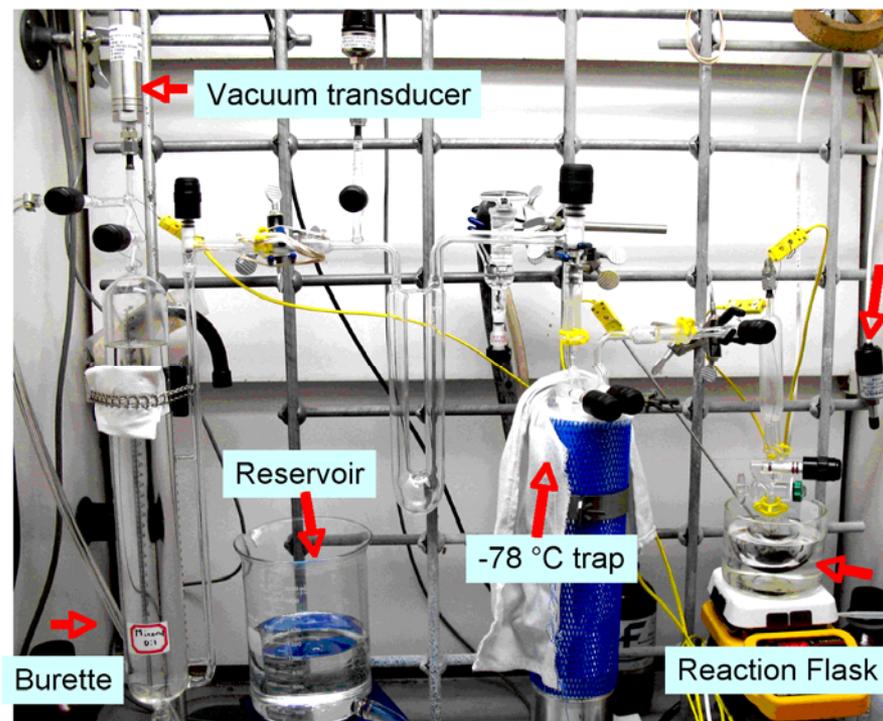
# 2009: Significantly Faster Rates for AB H<sub>2</sub>-Release In Ionic Liquids with Only Small Temperature Increases

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**

PNNL-Designed Automatic Gas-Burette Used for Continuous H<sub>2</sub>-Release Measurements

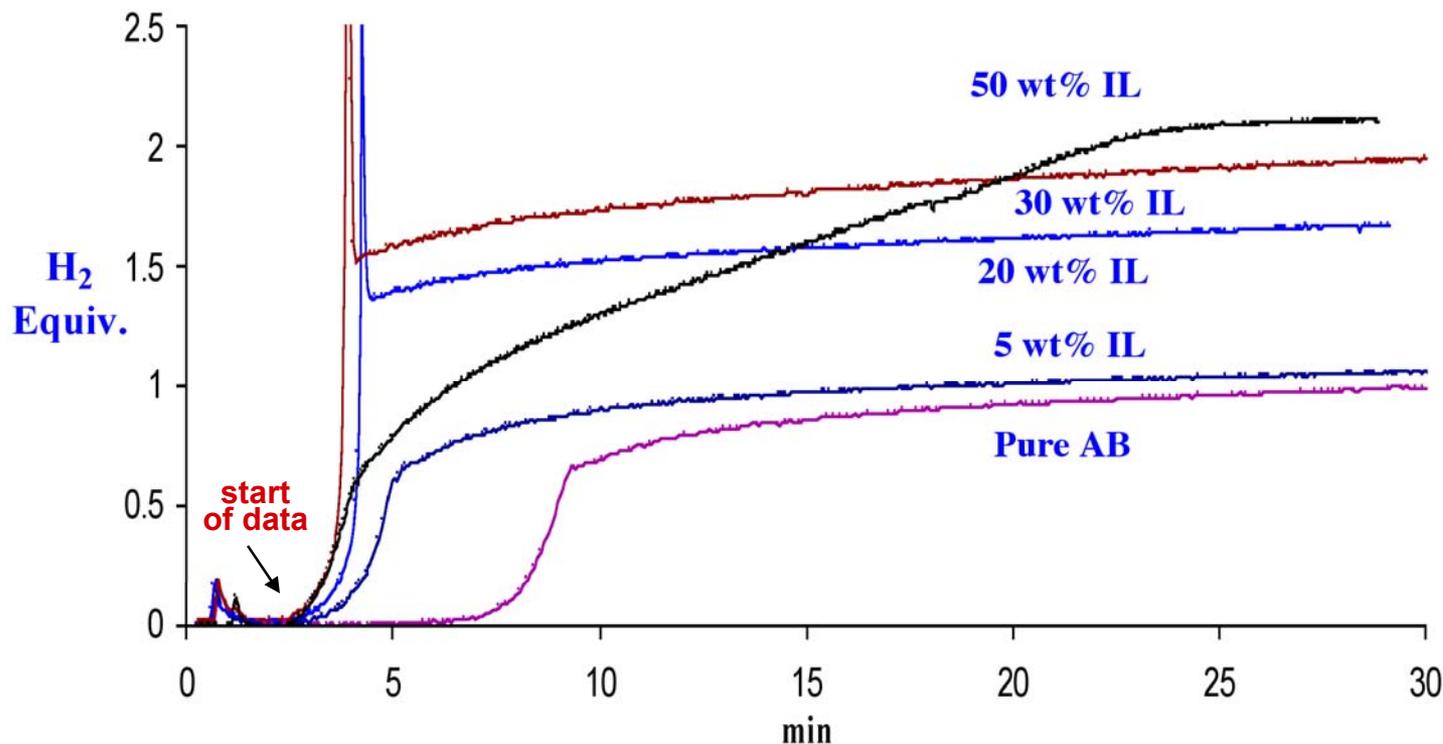


Zheng et. al. *Rev. Sci. Instrum.* **2008**, 79, 084103

## *Technical Accomplishments*

### **2009: Reactions at 110 °C with Only 20 wt% Ionic Liquid Still Have Fast H<sub>2</sub>-Release Rates**

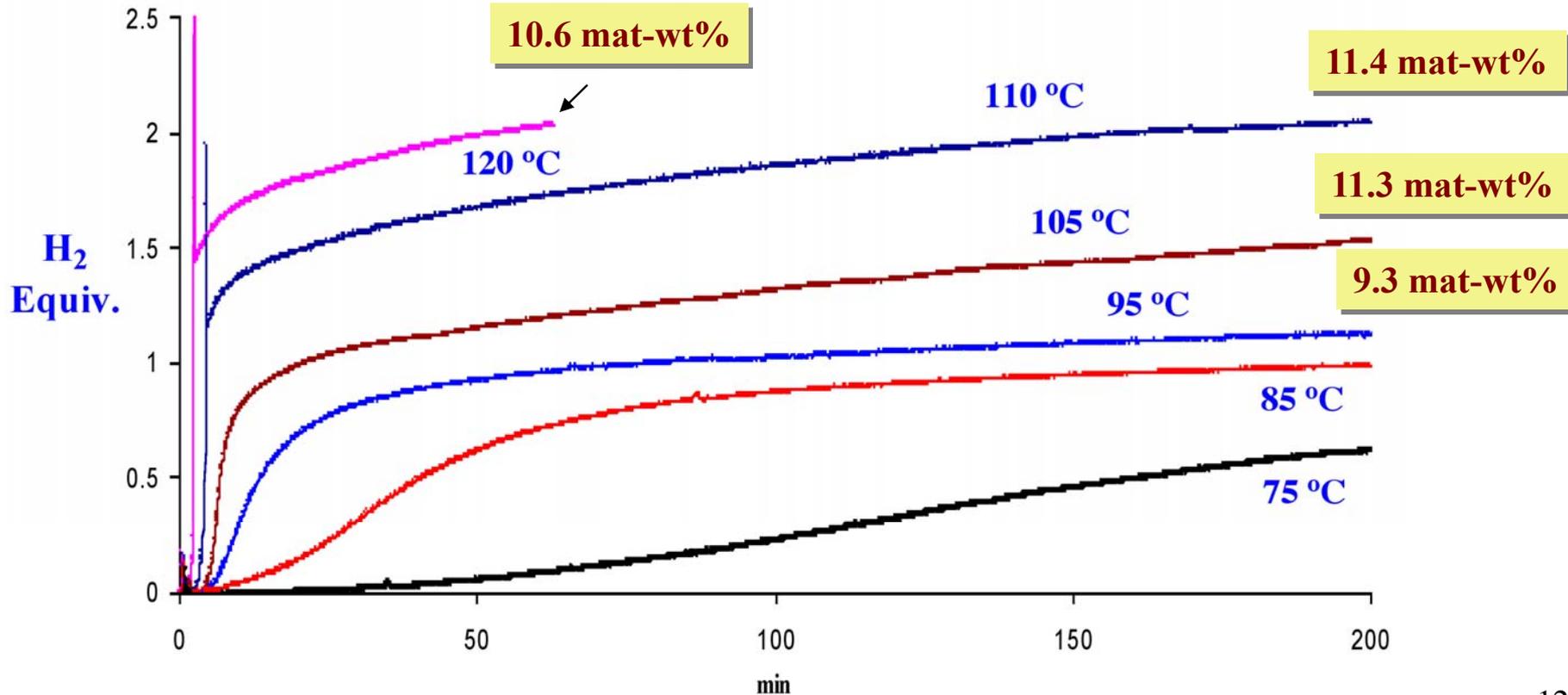
**Initial AB H<sub>2</sub>-Release versus bmimCl wt% at 110 °C**



## Technical Accomplishments

**2009: 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**

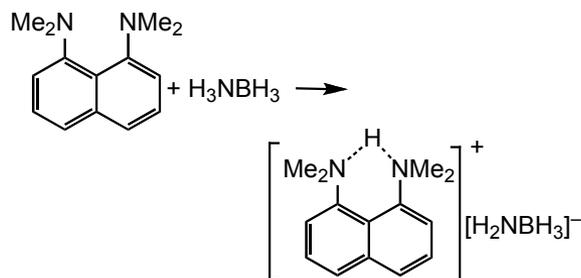


# Approach and Technical Accomplishments

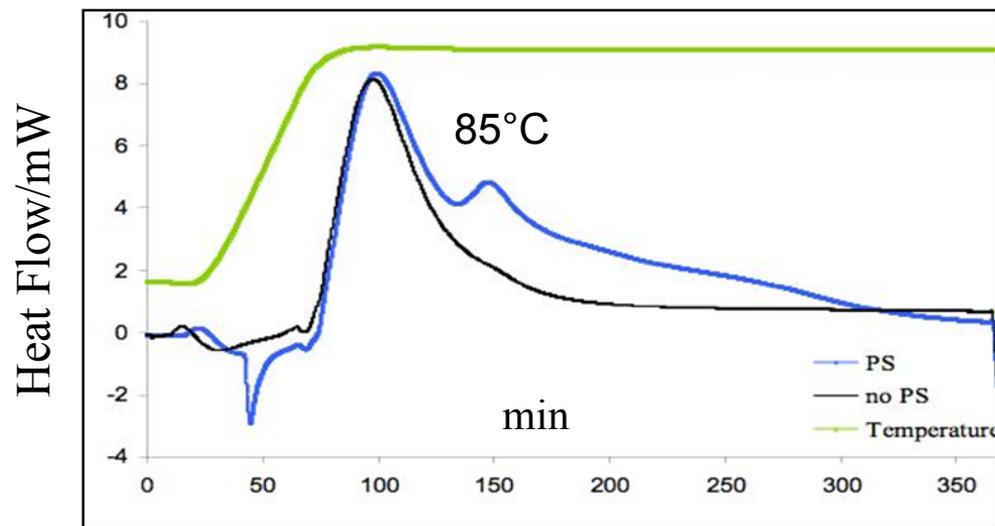
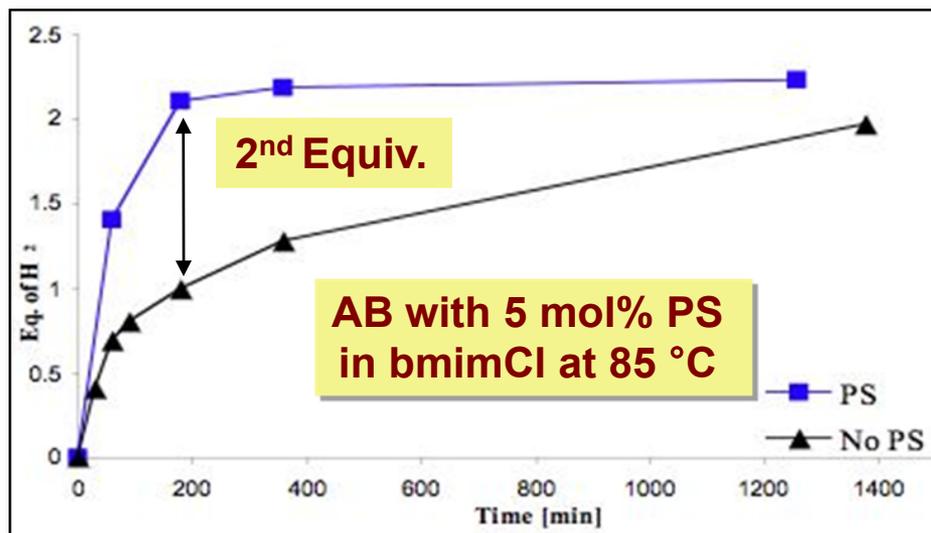
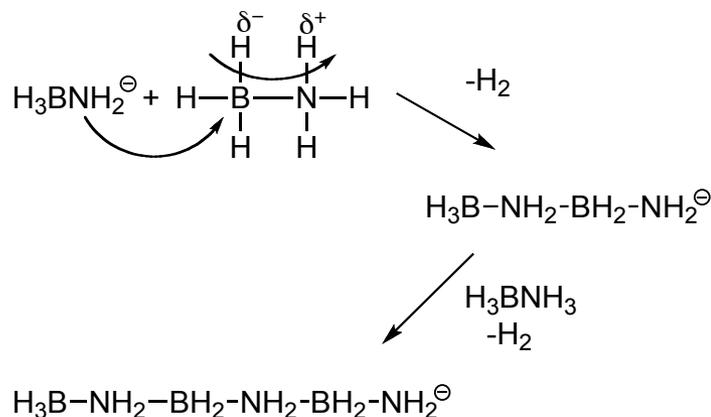
## 2008: Proton Sponge Increases the Release Rate of the Second H<sub>2</sub>-Equivalent from AB and Reduces Foaming

### Approach: H<sub>2</sub>-Release by AB Anionic Polymerization

#### Initial Step



#### Chain-Growth/H<sub>2</sub>-Release

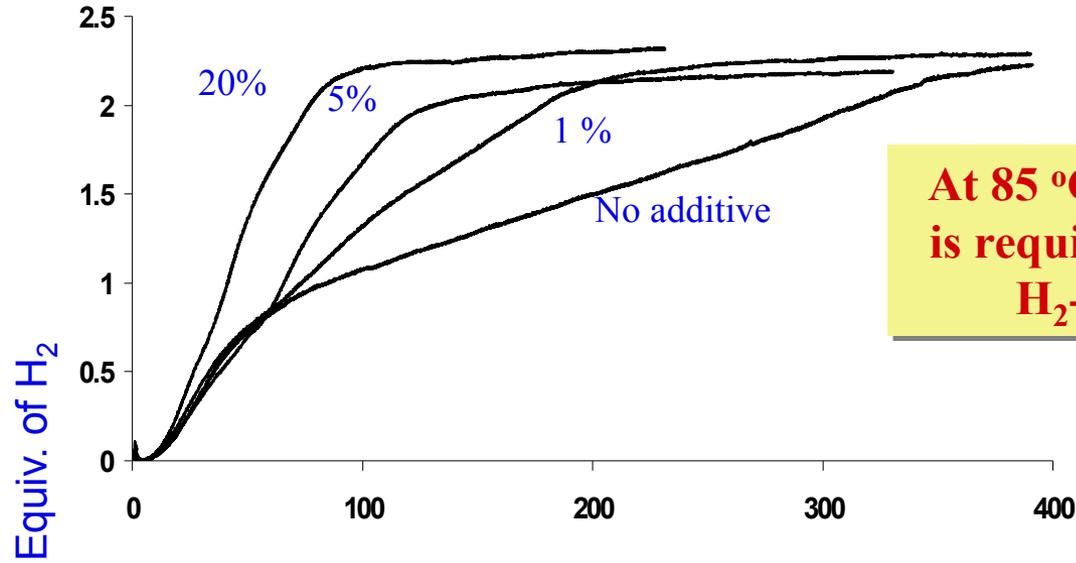


# Technical Accomplishments

## 2009: Less Base is Required at Higher Temperatures

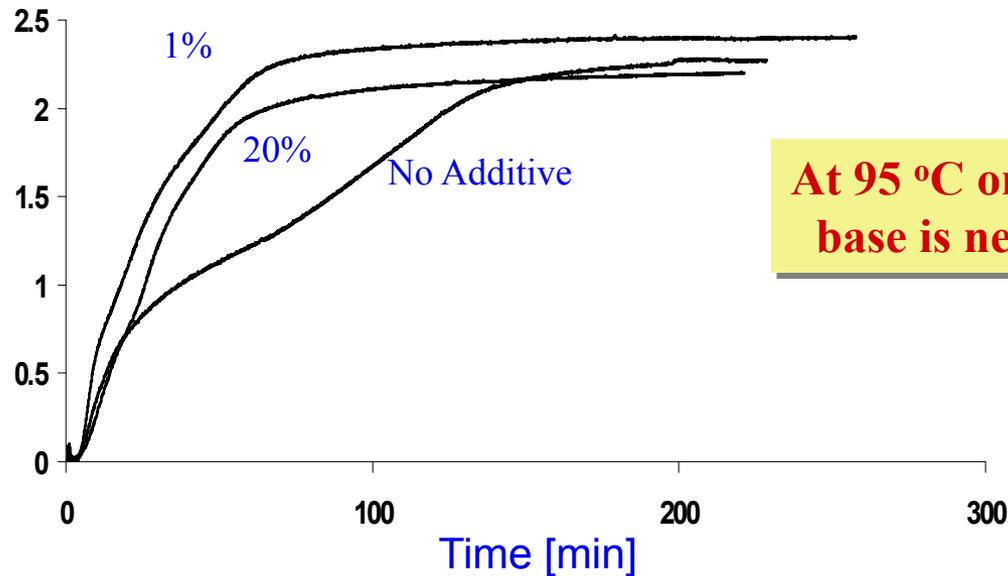
150 mg AB and  
150 mg bmimCl

85 °C



At 85 °C 20% base  
is required for fast  
H<sub>2</sub>-release

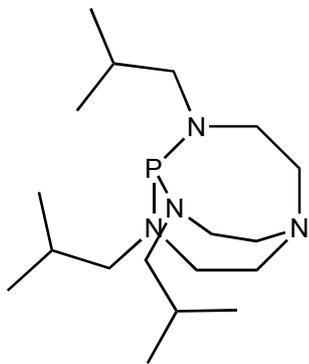
95 °C



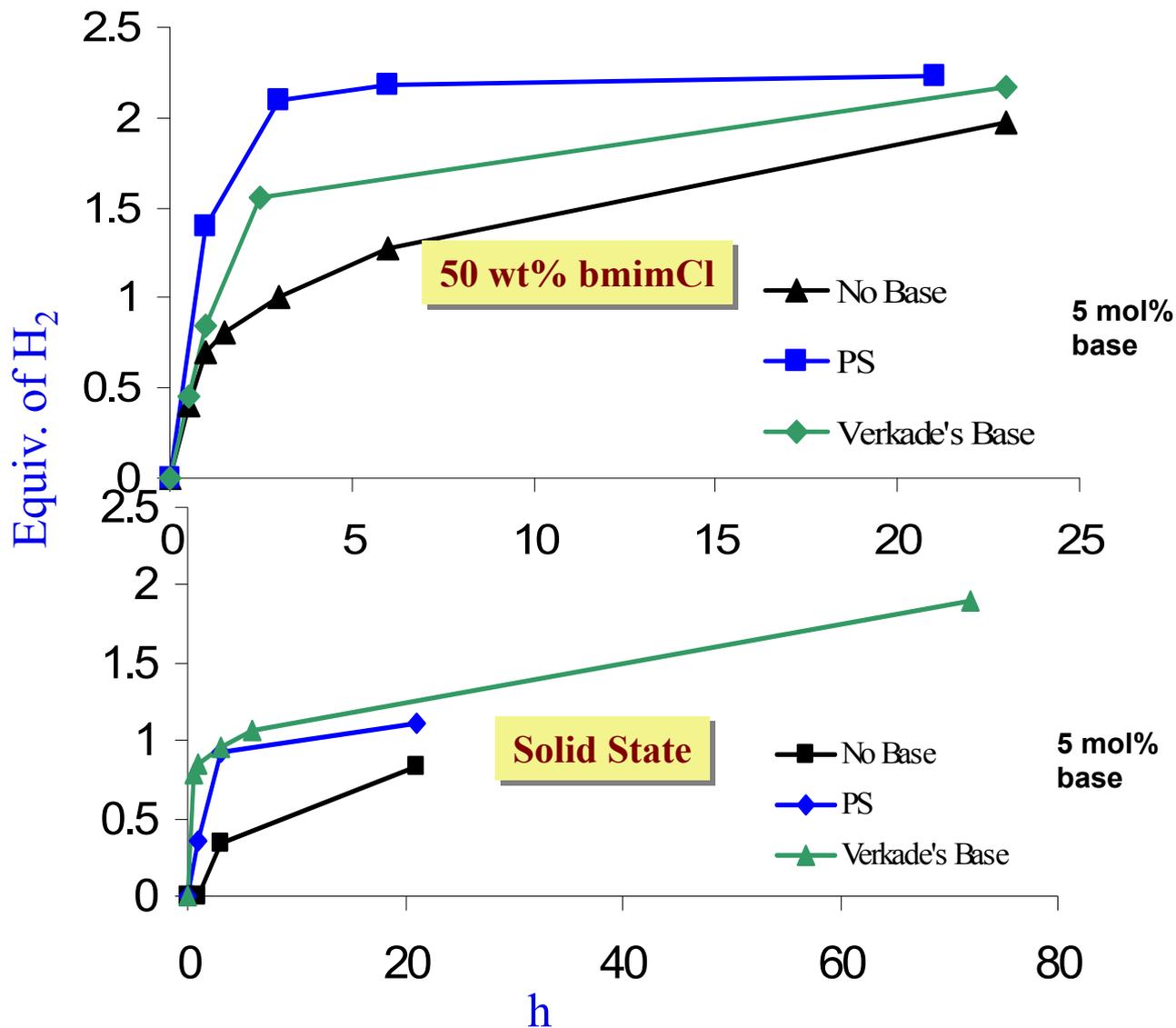
At 95 °C only 1%  
base is needed!

# Technical Accomplishments

## 2009: Other Strong Bases Also Activate AB H<sub>2</sub>-Release



Verkade's Base



## Technical Accomplishments

### 2009: 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</b> <b>Two equiv. in</b> <b>7 min</b>	110 °C Two equiv. in 22 min	<b>110 °C</b> <b>Two equiv. in</b> <b>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</b> <b>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)

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

Catalysts in Conjunction with Ionic Liquids Could Provide:

- (1) **Faster H<sub>2</sub>-Release**
- (2) **Better Control of H<sub>2</sub>-Release Rates**
- (3) **Lower Temperature Reactions**
- (4) **Synergistic Release Mechanisms**

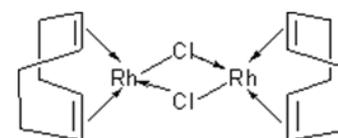
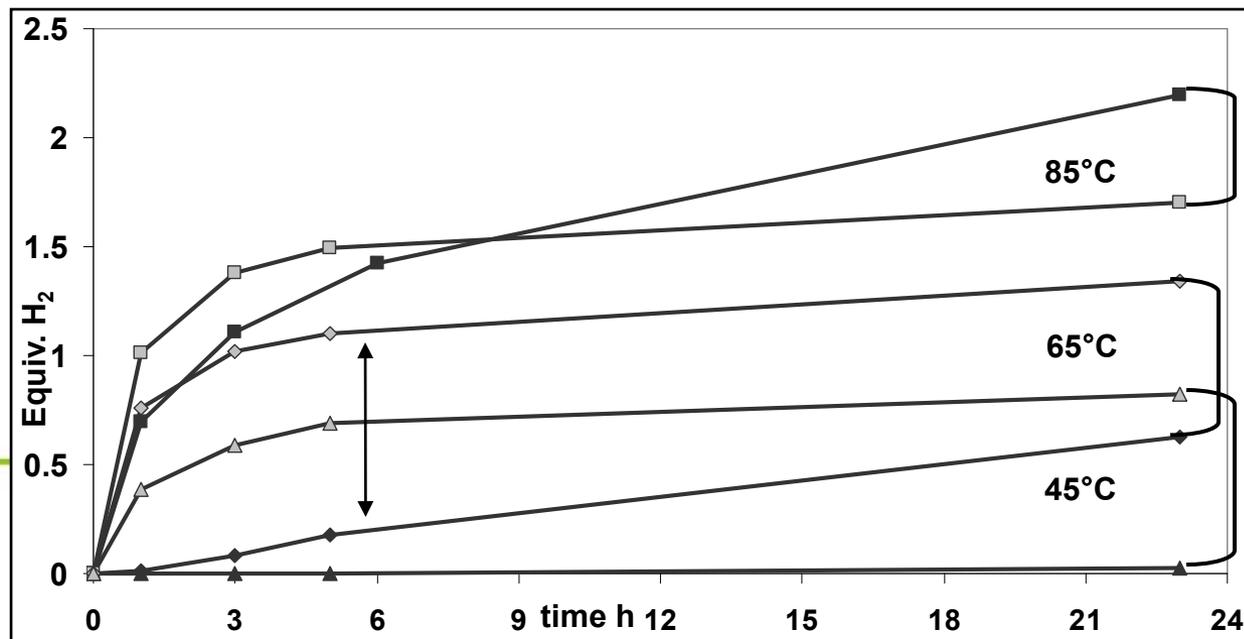
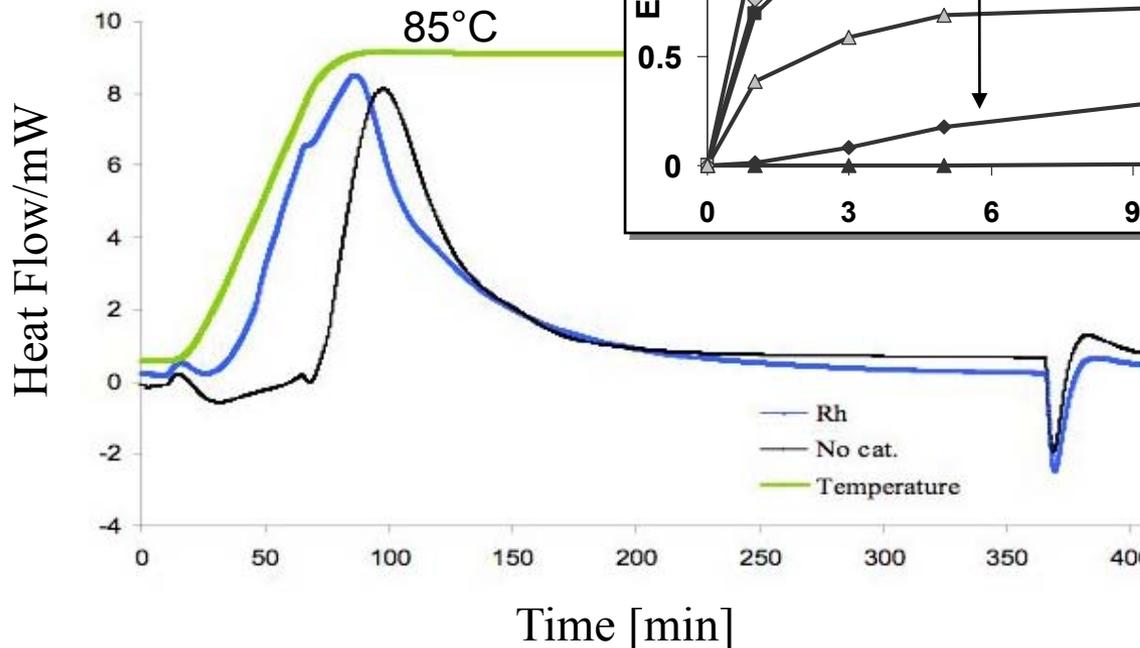
Center Partners (LANL and U Washington) have previously demonstrated metal catalyzed AB H<sub>2</sub>-release in organic solvents.

# Technical Accomplishments

## 2008: 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

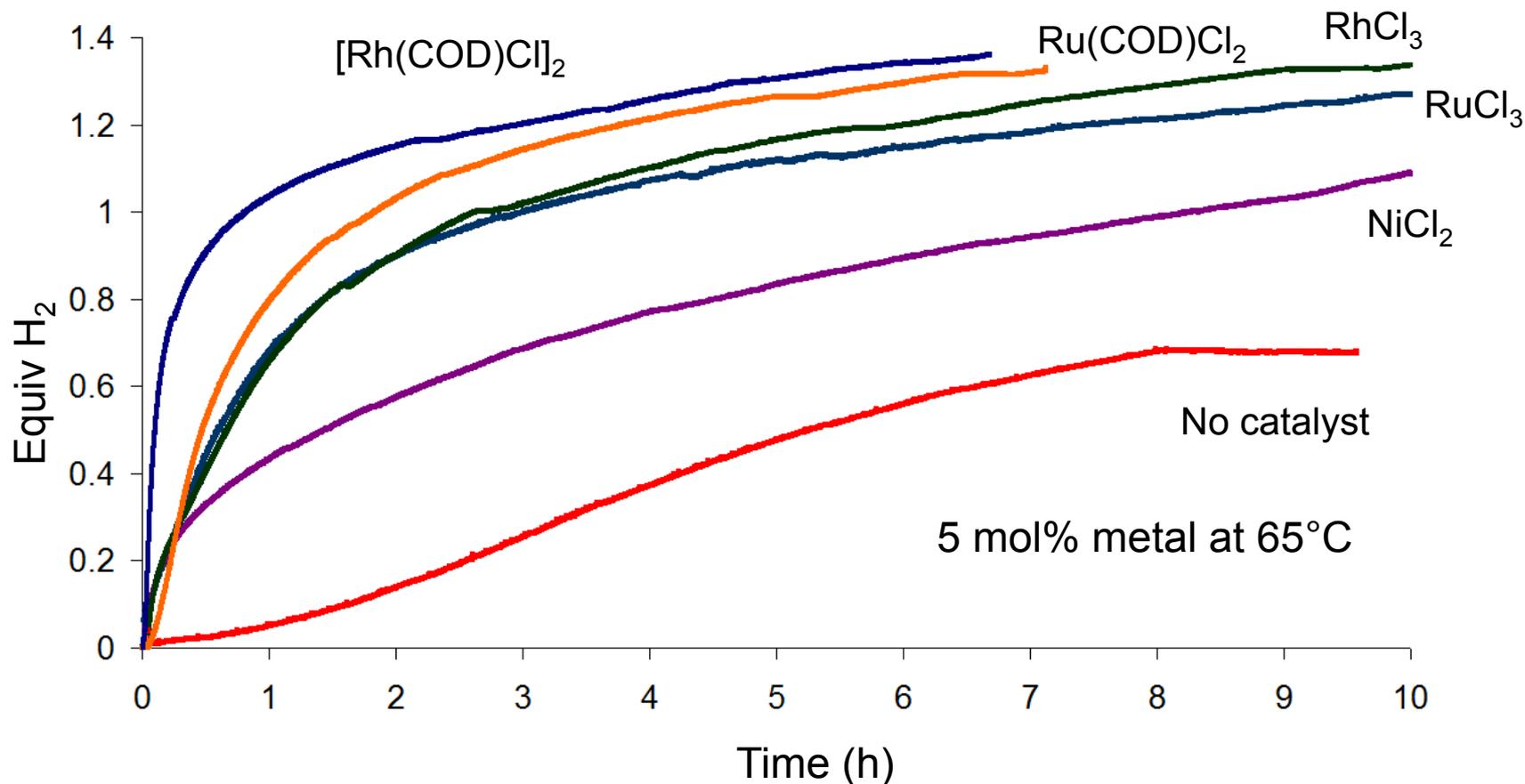
DSC



- 85°C
- ◆ 65°C
- ▲ 45°C
- ◻ 85°C w/ Rh
- ◊ 65°C w/ Rh
- ◄ 45°C w/ Rh

## *Technical Accomplishments*

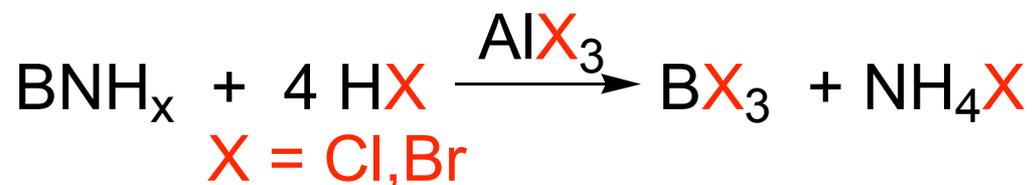
### **2009: Other Metal Catalysts have been found to Increase the Rate of AB H<sub>2</sub>-Release in Ionic Liquids**



## Approach

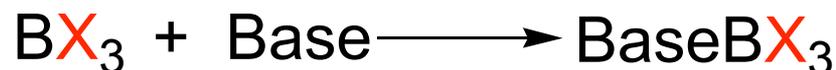
# Penn Approach to Regeneration: Super-Acid/Halide-Reduction Process

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

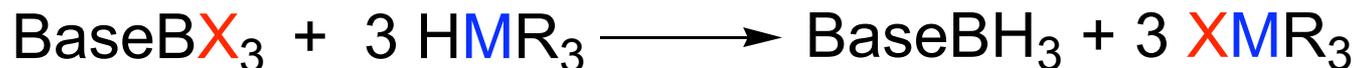


### Second Step: One-Pot Conversion of $\text{BX}_3$ to AB

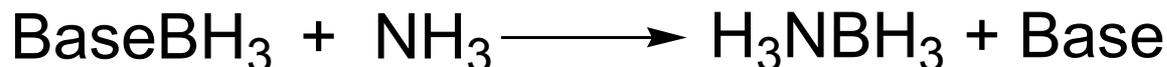
#### Coordination of $\text{BX}_3$



#### BX Reduction



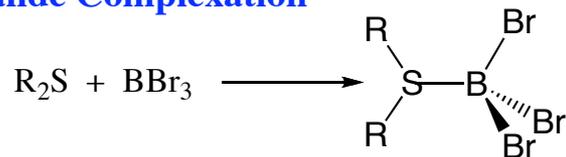
#### Base Displacement by $\text{NH}_3$ Yields AB



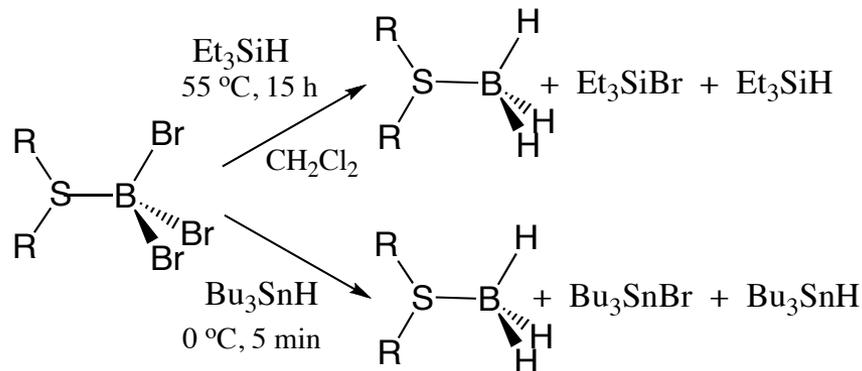
# Technical Accomplishments

## 2008-2009: Step 2: Boron Halide Reduction Processes are Simple, Quantitative and Allow Separation and Recovery of All Products

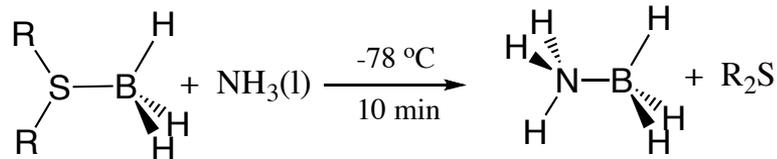
### Boron Halide Complexation



### Complex Reduction with Silanes or Stannanes

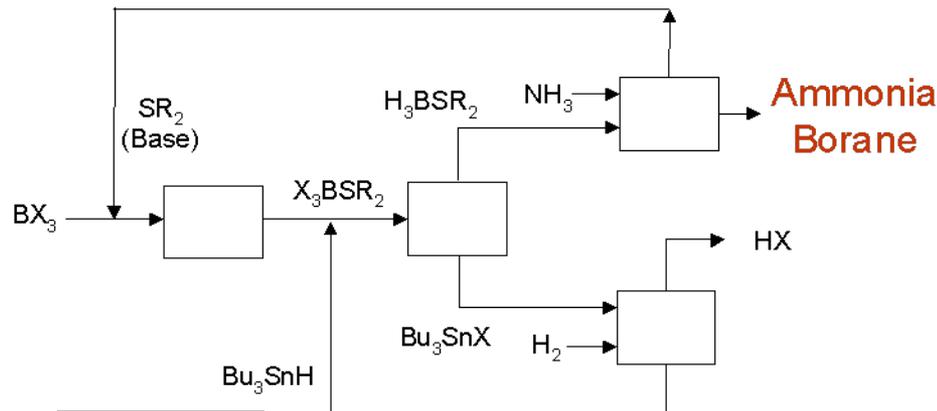


### Displacement with Ammonia



### Demonstrated Advantages:

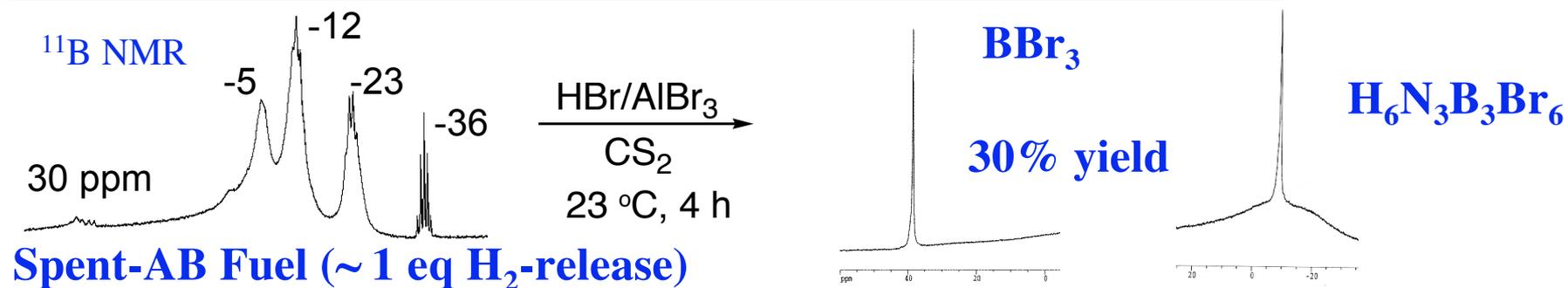
- (1) high, 96-100%, yields on multi-gram laboratory scale-ups
- (2) avoids the formation of B-O bonds
- (3) avoids the formation of  $B_2H_6$
- (4) simple product isolation based on volatility with separation/recovery of all materials
- (5) 2008-9 Rohm and Haas analysis indicates a scalable process



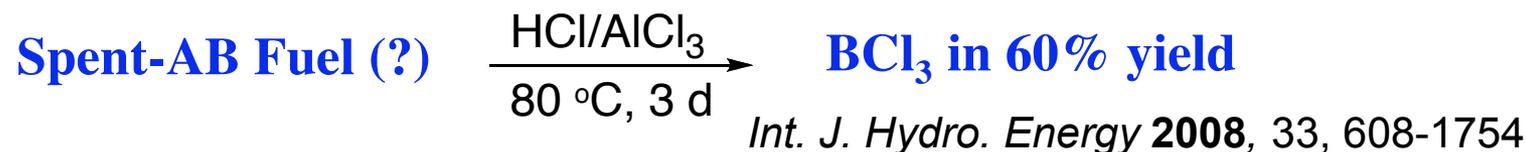
# Technical Accomplishments

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

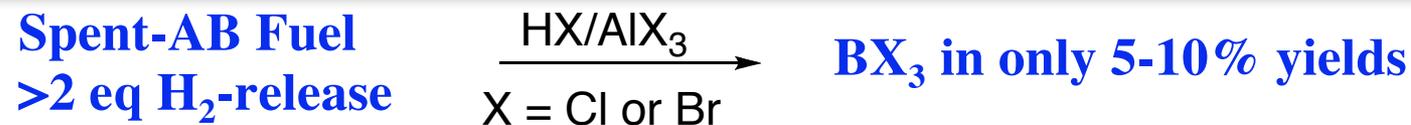
### 2007 Penn: Superacidic $HX/AlX_3$ Solutions Digest Spent-Fuels



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



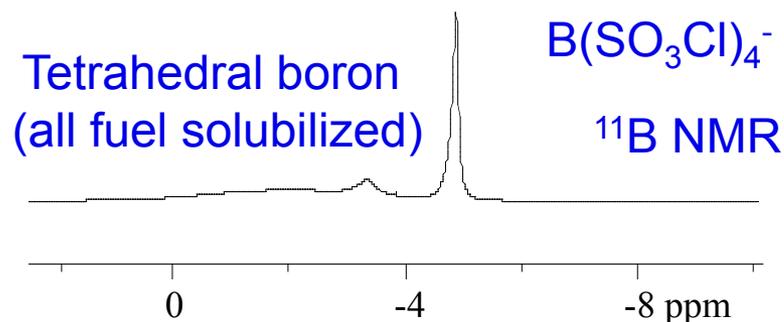
### 2008-9 Penn: Superacidic Conditions Do Not Give Good Yields of $BX_3$ from Highly Dehydrogenated Fuels



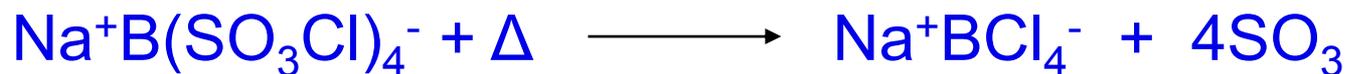
**2009 Conclusion: Spent Fuel Digestion to  $BX_3$  Must be Improved for a Halide-Based Regeneration to be “Go”**

## Examples of Alternative Methods Under Study for Spent Fuel Conversion to $BX_3$

### 1. Spent Fuel Digestion in Chlorosulfonic Acid



### Conversion to Boron Halides?



Drache et. al. *Bull. Soc. Chim. Fr.* **1976**, 1749-1754

### 2. Reactions with Halogen/Oxidant Systems



# Future Studies



- Complete H<sub>2</sub>-release studies for: (1) ionic-liquid/AB mixtures at different temperatures, (2) base-initiated ionic-liquid/AB mixtures, and (3) metal-catalyzed ionic-liquid/AB.
- Complete the optimization of the temperature/weight-ratios for ionic liquid based H<sub>2</sub>-release.
- Continue to develop and optimize new chemical-promoter systems with improved H<sub>2</sub>-release rates
- Explore the activities of non-precious metal catalysts in ionic liquids for improving the rate of AB H<sub>2</sub>-release.
- Take advantage of synergistic mechanisms to improve H<sub>2</sub>-release rates.
- Explore alternative methods for the formation of boron trihalides
- Explore, with Center partners, the development of hybrid regeneration methods

# Collaborations and Technology Transfer

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

## *Some Examples of 2008-9 Collaborations and Technology Transfer*

- PNNL postdoctoral visited Penn to learn how to perform the borazine synthesis at PNNL.
- Penn students and postdoctoral carried out research at PNNL on two 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 PNNL (Linehan) began a collaboration on identifying the nature of the active catalyst in the rhodium catalyzed AB H<sub>2</sub>-release in ionic liquids.
- Penn and Rohm and Haas (Chen and Lipiecki) began evaluating the scale up feasibility of the of the boron halide reduction/separation step for regeneration.
- U. of Ottawa (Baker) and Penn are carrying out joint investigations of the mechanisms of AB H<sub>2</sub>-release.

# 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 and a key barrier to boron-halide based regeneration was identified.*

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

**Proposed Future Research:** *Broad based experimental studies on both H<sub>2</sub>-release and regeneration that build on past discoveries.*

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# **Additional Slides**

# H<sub>2</sub>-Release Systems Reported at 2007 Program Review

Metrics	Hydrolysis 22 °C	Thermolysis at 85 °C					
		Solid-State			Solution-State		
	22.7 wt% aq. AT (1.1 mol%Rh)	AB/LiNH <sub>2</sub> (9 mol%)	AB/LiH (17 mol%)	AB/AT(5mol%) /PS(5mol%)	AB/PS(5mol%) /bmimCl	AB/edmimCl	AB/AT(5mol%) /PS(5mol%)/bmimCl
Grav. density (Mat. wt%)	6.1, 4h	5.9, 3h 9.3, 15h	5.7, 3h 9.4, 15h	5.1, 1h 6.9, 3h	5.1, 3h 5.8, 6h	3.1, 1h 4.2, 3h 5.3, 6h	5.3, 1h 6.5, 3h
Vol. density (Kg-H <sub>2</sub> /L Mat.)	0.090, 4h	0.047, 3h 0.074, 15h	0.045, 3h 0.073, 15h	0.044, 1h 0.059, 3h	0.047, 3h 0.054, 6h	0.018, 1h 0.023, 3h 0.030, 6h	0.049, 1h 0.060, 3h
H <sub>2</sub> Flow Rate (g/s) per kg Material	0.0042, 4h	0.0055, 3h 0.0017, 15h	0.0053, 3h 0.0017, 15h	0.014, 1h 0.0064, 3h	0.0047, 3h 0.0027, 6h	0.0086, 1h 0.0038, 3h 0.0024, 6h	0.015, 1h 0.0060, 3h
Kg of Mat. for 0.8 mol/sec	377, 4h	295, 3h 938, 15h	304, 3h 931, 15h	114, 1h 250, 3h	342, 3h 599, 6h	186, 1h 420, 3h 670, 6h	108, 1h 267, 3h

# H<sub>2</sub>-Release Systems Reported at 2008 Program Review

Metrics	AB Thermolysis at 120°C		
	Solution-State (15 min, ~2 Eq. H <sub>2</sub> )		
	50 wt% BmimCl	40 wt% BmimCl	20 wt% BmimCl
Grav. density (Mat. wt%)	7.2	8.7	10.2
Vol. density (Kg-H <sub>2</sub> /L Mat.)	0.067	0.078	0.086
H <sub>2</sub> Flow Rate (g/s) per kg Material	0.08	0.097	0.114
Kg of Mat. for 0.8 mol/sec	20	17	14