Fluid Phase H_2 Storage Material Development

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2013 Annual Merit Review, May 15th

Los Alamos National Laboratory

LA-UR-13-22354

Project ID # ST040

Overview

Timeline

- Project Start Date: Oct 1st 2010
- Project End Date: 2014
- Percent Complete: 73%

Barriers

- Barriers Addressed
  - A. Weight/Volume
  - C. Efficiency
  - D. Durability/Operability
  - E. Discharging Rates

Budget

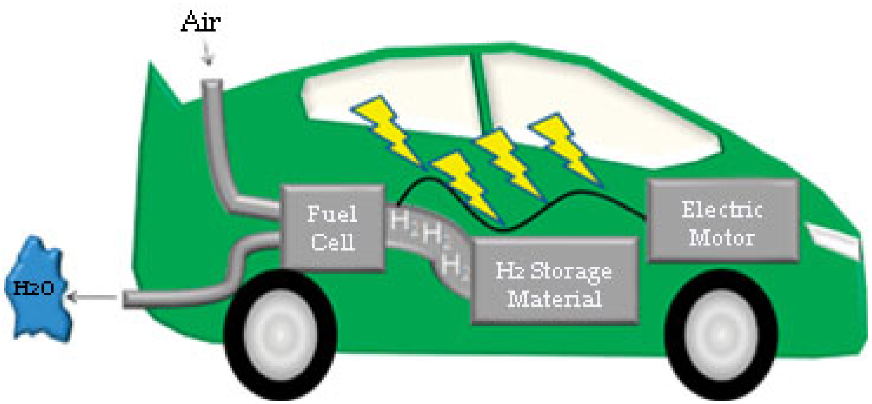
- Total project funding
  - DOE share: $ 225k
- Funding received in FY12: $ 330k
- Funding for FY13: $ 225k

Partners

- LANL (lead)
- University of Ottawa

Relevance

Materials with good H_2 storage capacity and efficient regeneration are required for transportation, stationary, and portable power applications.

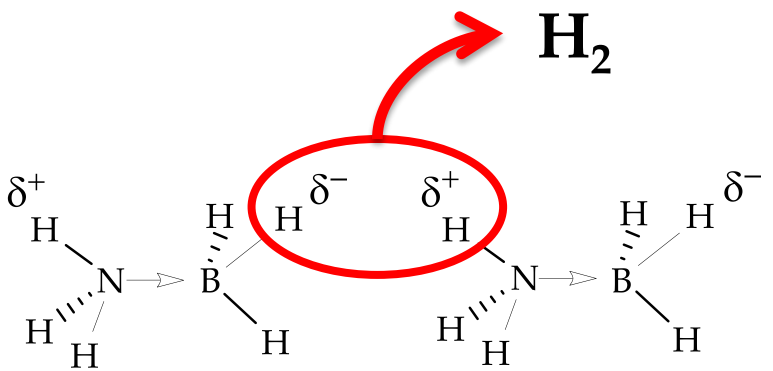


2017 system target = 5.5 wt. %; ultimate 7.5 wt. %

Objectives

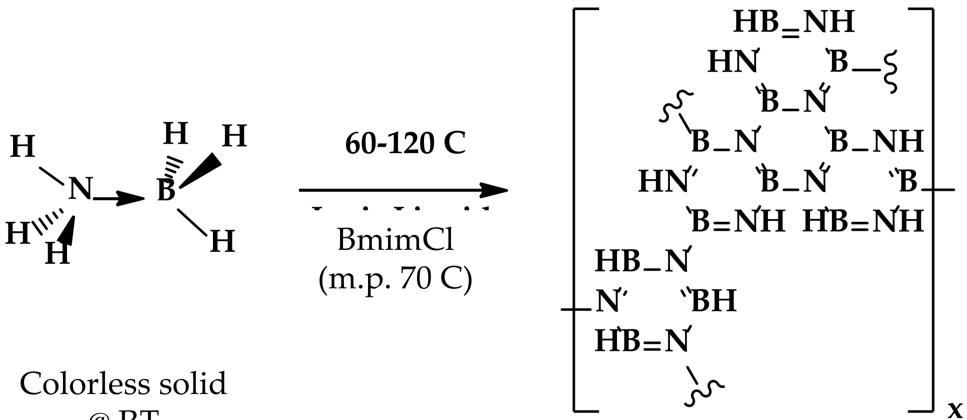
Develop liquid ammonia-borane (~15 wt. % usable H_2)/ionic mixtures that have sufficient H_2 capacity, release kinetics, stability, and fluid phase properties upon H_2 release.

Integrate design specifications from Hydrogen Storage Engineering Center of Excellence (HSECoE) and ensure compatibility with system designs.

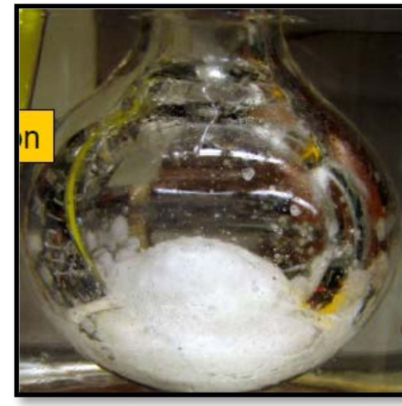


Ammonia Borane

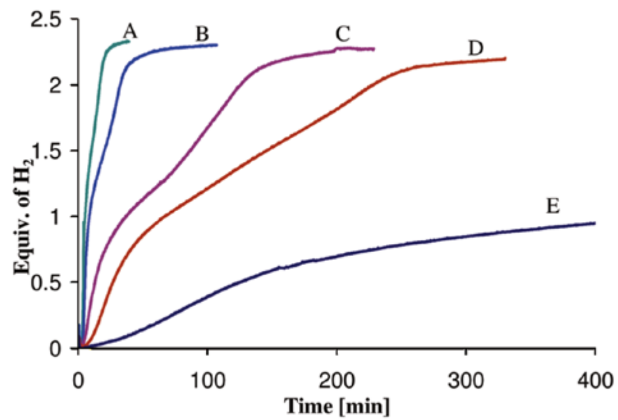
AB/IL: Good Capacity, Kinetics



Colorless solid
@ RT



7-11 wt. % H_2



A - 110 C
B - 105 C
C - 95 C
D - 85 C
E - 75 C

Larry Sneddon, UPENN

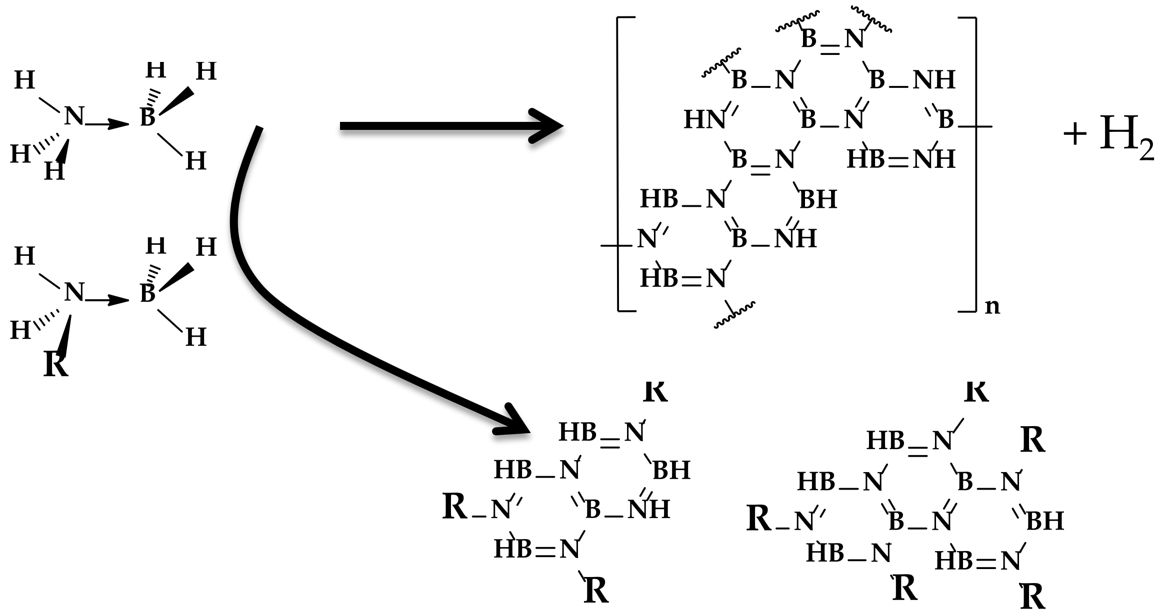
Approach

Technical Limitation: Ammonia borane mixtures can form insoluble products after extensive H_2 release

Our Method: Use additives which react with ammonia borane, yielding smaller molecular weight products that are less prone to precipitation. By adjusting the functionality of the additive, we can control solubility of the products in various media

2013 Goals:

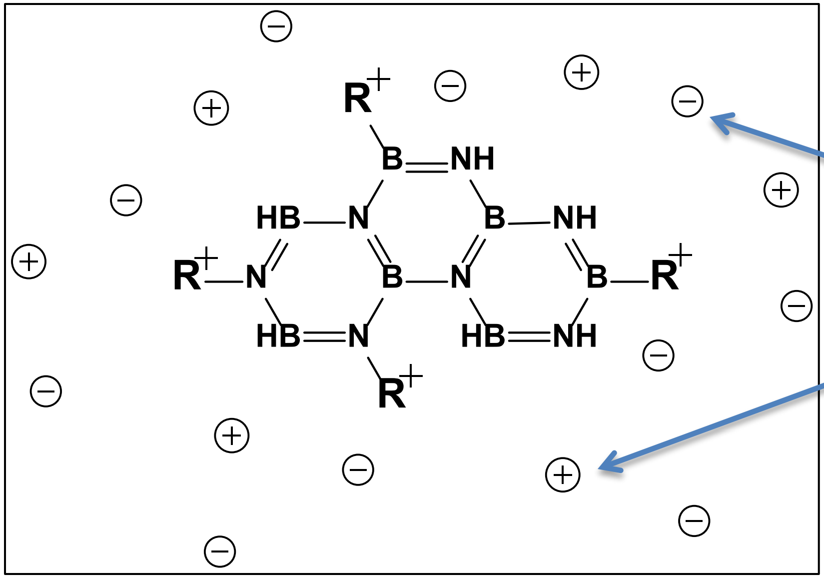
1) Design and synthesize amine-boranes tethered to ionic liquids
2) Characterize neutral functionalized amine-boranes and AB blends



Two different classes of additives will be used to address phase change

Approach – Ionic Additives

Advantage: excellent solubility in ionic liquids; less impurities



Ionic liquid represented by positive, negative symbols

Disadvantage: unknown compounds, must be synthesized

Ionic additives give better solubility in ionic liquids

Approach – Neutral Additives

Advantage: easy to synthesize; liquid products; good H_2 capacity

AB/hexylAB

140°C

→

6 wt. % H_2

Copolymer product (@ 20°C)

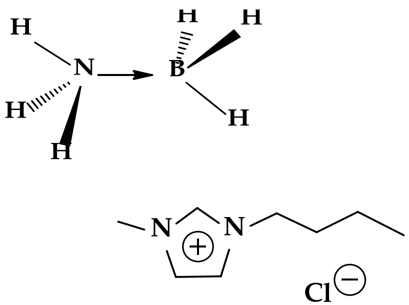
Disadvantage: may generate volatile intermediates

Neutral Additives Yield Promising Results in FY12

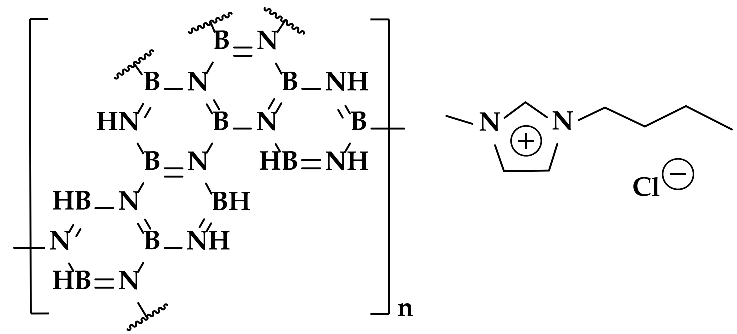
Ionic Additive Development

Approach

Initial Sneddon Mixture:

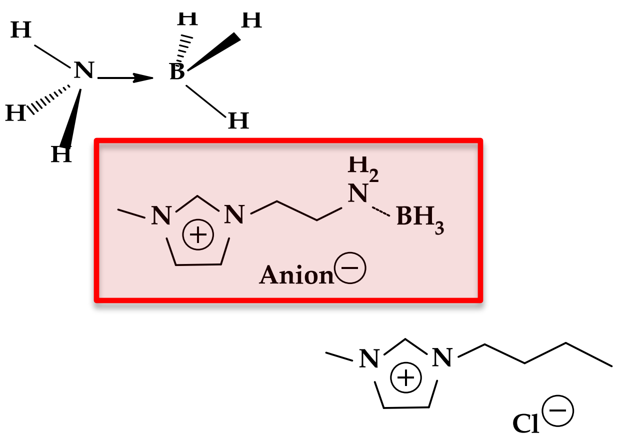


Final Sneddon Products:

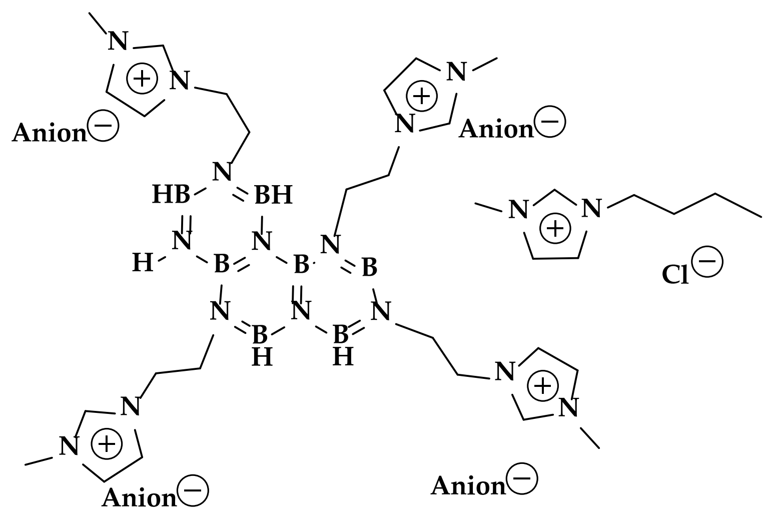


Insoluble

Proposed Target:



Proposed Products:

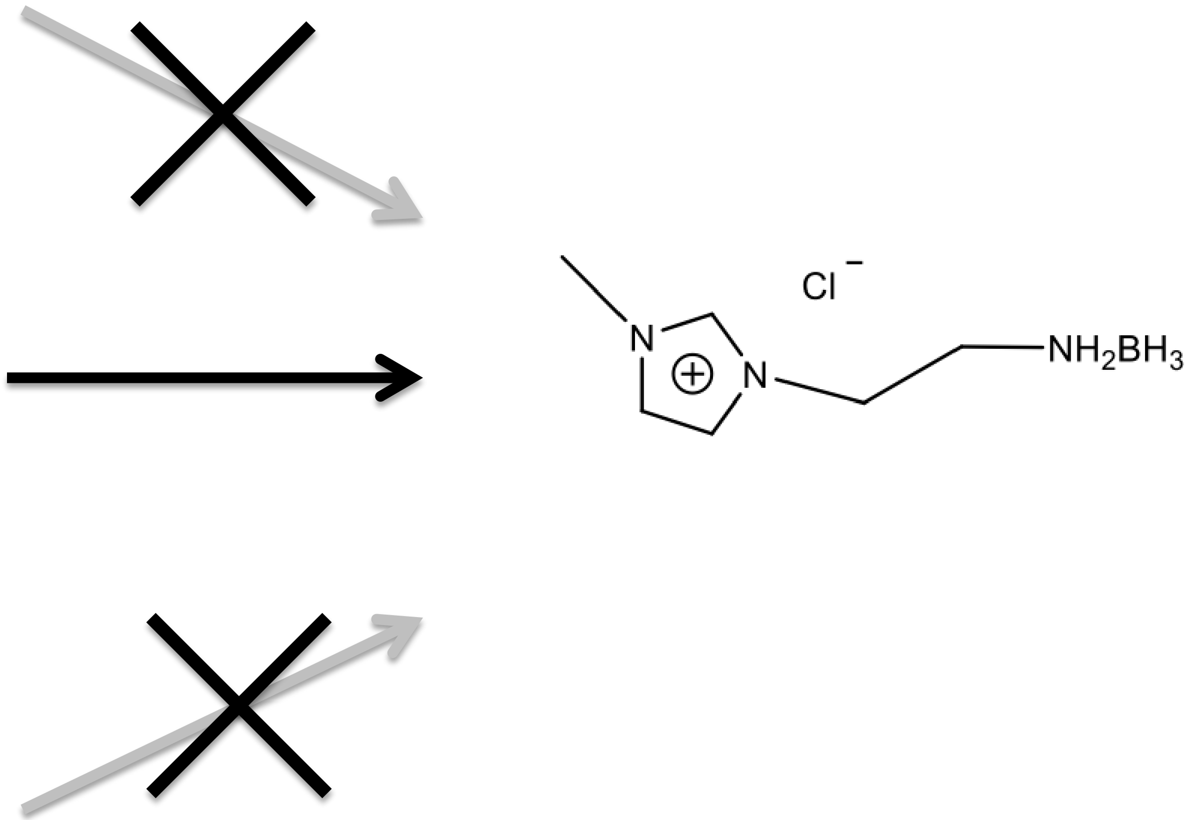


Attempted three independent syntheses

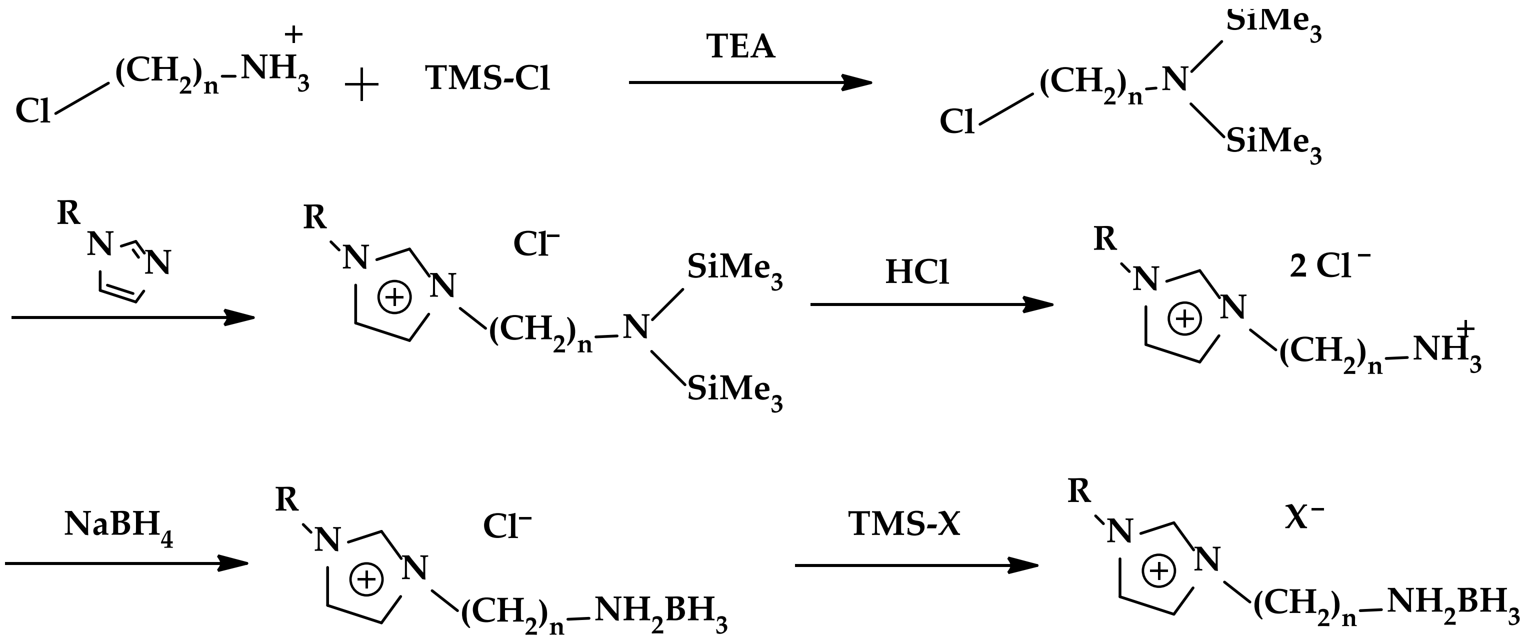
Gabriel Synthesis

Silyl Protecting Groups

Nitrile Precursors

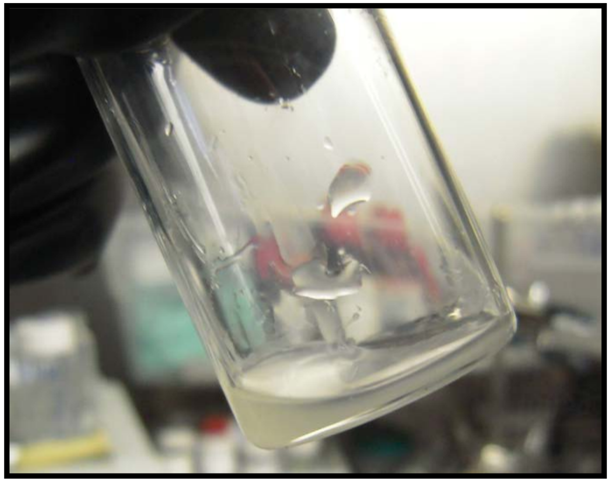


Successful Synthesis of Amine-Borane tethered to an Ionic Liquid

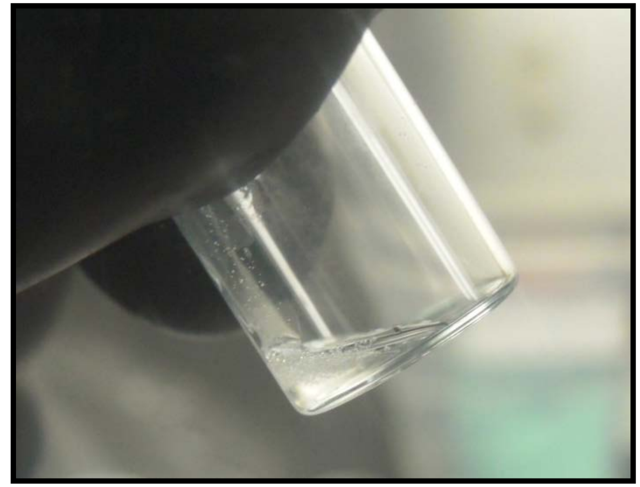


US Nonprovisional Application (#13850959)

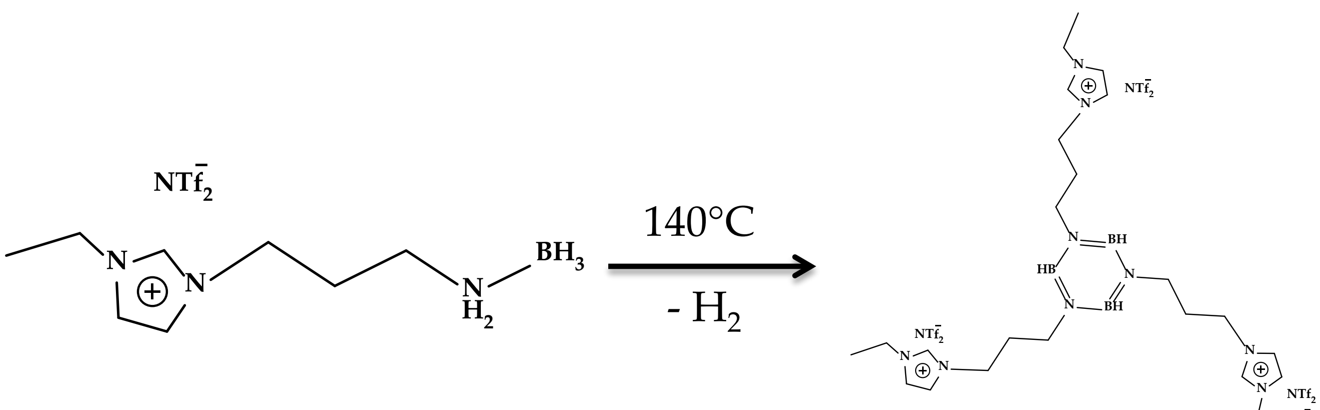
Tethered Ionic liquid/Amineboranes Remain Liquid!



H_2 Charged State (@ 20°C)

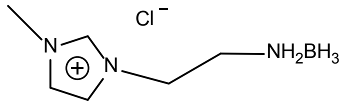
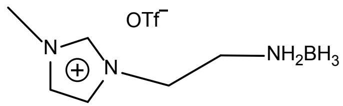
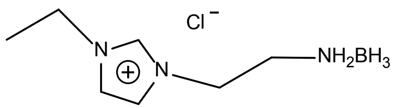
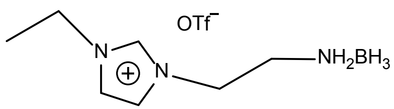
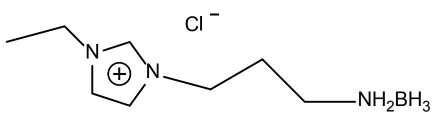
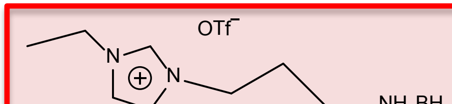
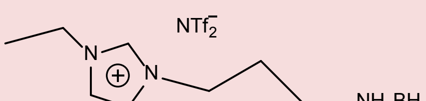


H_2 Released State (@ 20°C)



US Nonprovisional Application (#13850959)

First Round of Derivatives

Additive	Identifier	Initial State(20°C)	Spent State (20°C)	Wt. % H_2
	A	Solid	Solid	2.5
	B	Solid	Solid	1.5
	C	Solid	Solid	2.3
	D	Oily Wax	Solid	1.4
	E	Solid	Solid	2.1
	F	Liquid	Viscous liquid	1.4
	G	Liquid	Liquid	1.0

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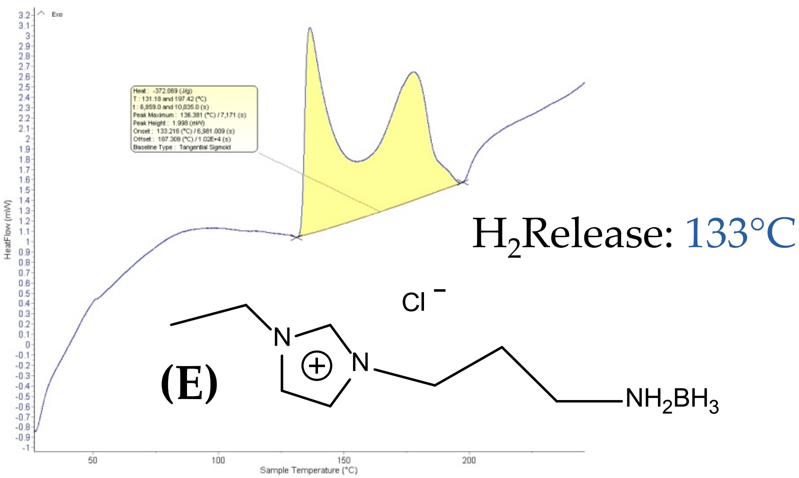
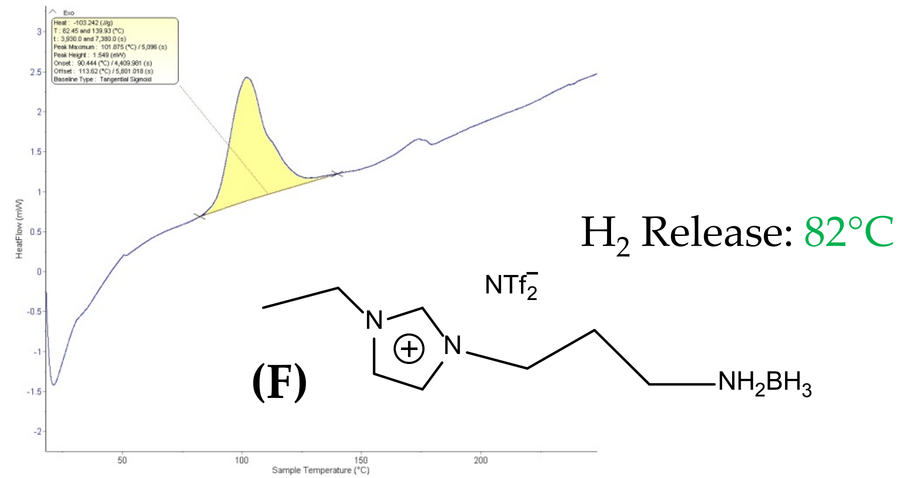
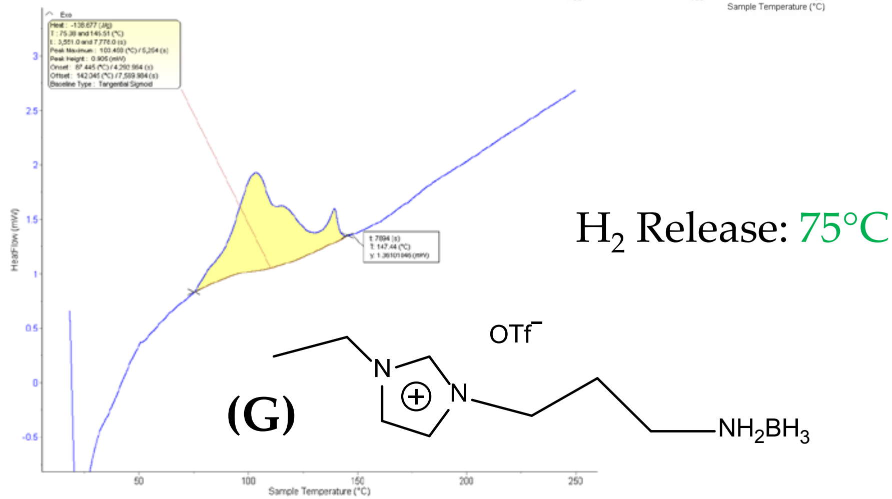
Anion Choice Has Pronounced Effect on Properties







Control H_2 release with anion choice; better match with AB = less impurities

Amineborane-IL/AB mixtures

Material	AB/Additive	Initial State (20°C)	Spent State (20°C)	Wt. % H_2
B	0.5	Solid	Solid	2.0
F	0.5	Milky Suspension	Solid	1.8
F	1	Milky Suspension	Flaky Solid	2.3
G	0.5	Milky Suspension	Viscous Liquid	1.3

Ionic Additives blended with AB yields fluid phase products

US Nonprovisional Application (#13850959)

Neutral Additive Development

Surveyed Alternative AmineBoranes

uOttawa

	n-C4	iso-C4	sec-C4	tert-C4	n-C5	iso-C5	sec-C5	1,2-DMP	neo-C5	n-C6
NRH_2 b.p. (C)	78	68	63	45	104	95	93	85	83	130
$RH_2N \bullet BH_3$ m.p.	10	65	0	96	5	85	-5	-	-	~-20

Synthesized by Ottawa

Amine	n-C5	iso-C5	sec-C5	1,2-DMP	neo-C5	n-C6
50g ($)	97	70	1390	128	264	17

Initial survey of related substituents did not reveal obvious solutions

Benzylamine-borane Pursued

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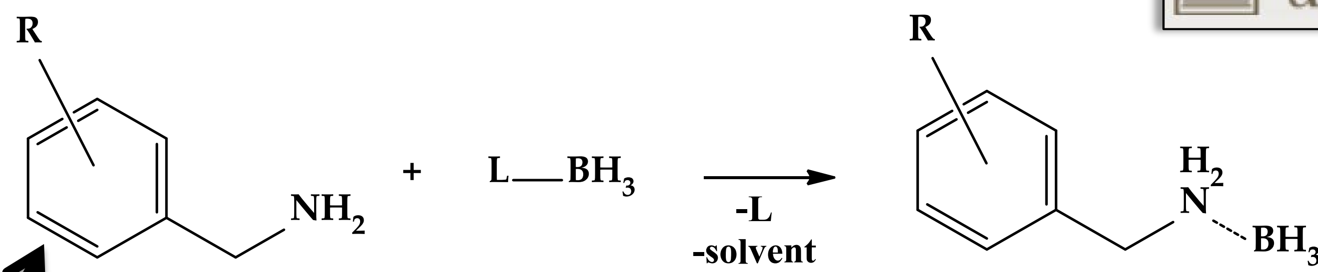
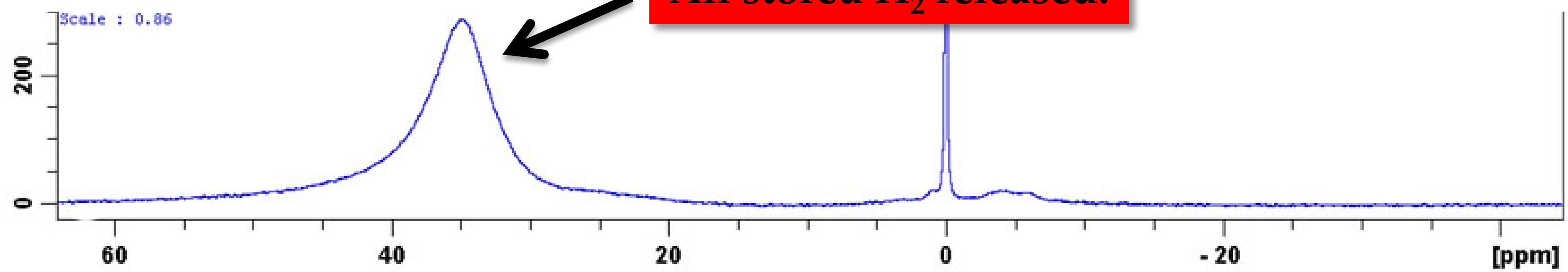


R = H, m.p. 10Ş "
R = o-CH3, m.p. = < 20°C
b.p. ~200°C

R = H, m.p. 57°C
R = o-CH3, m.p. = 110°C

Interact with ionic liquids = greater solubility

All stored H_2 released!



Benzylamine-borane/AB Mixtures

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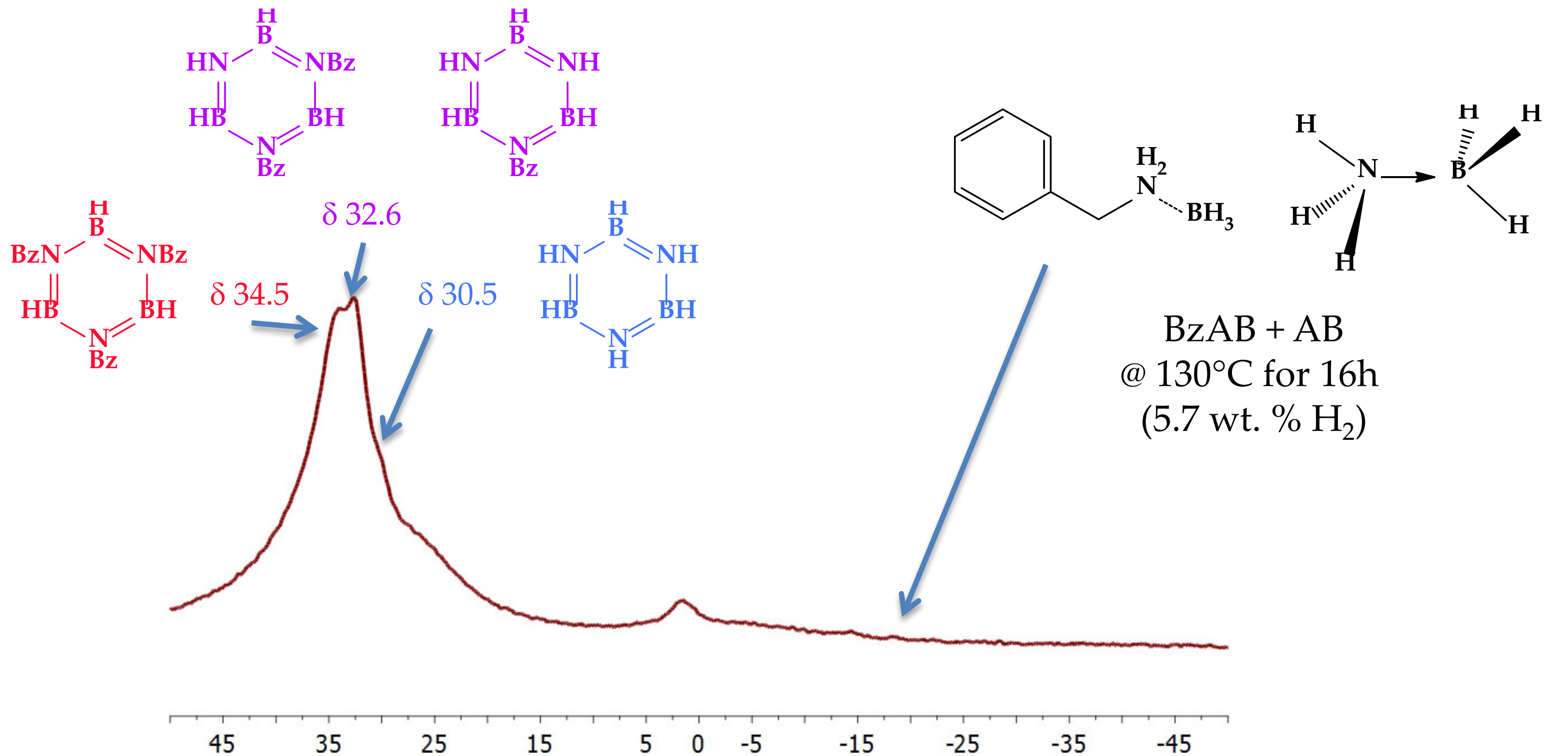


Spent fuel of BzAB + AB in [EMIm]$EtSO_4$ (1.8 wt. % H_2) still flows while above 100°C!

Evidence of copolymerization; 2 wt. % IL mixture flows above 100°C

Los Alamos NATIONAL LABORATORY EST. 1943

Benzylamine-Boranes Outselected

uOttawa

Fuel Blend	time (h)	temp (C)	solvent	Spent Phase?	Wt. % H_2
BzAB/AB	24	80	neat	RT: solid 80 C: liquid	5.7
BzAB/AB	18	130	neat	RT: solid 130 C: solid	5.7
BzAB/AB	22	130	$[EMIm]EtSO_4$	RT: liquid 130 C: liquid	0.5
BzAB/AB	18	130	$[EMIm]EtSO_4$	RT: solid 130 C: liquid	1.8
2-MeBzAB/AB	7	130	neat	RT: liquid 130 C: liquid	0.5
2-MeBzAB/AB	18	130	$[EMIm]EtSO_4$	RT: solid 130 C: liquid	1.7

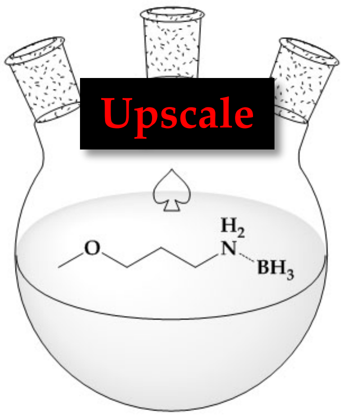
Benzylamineboranes outselected for future work

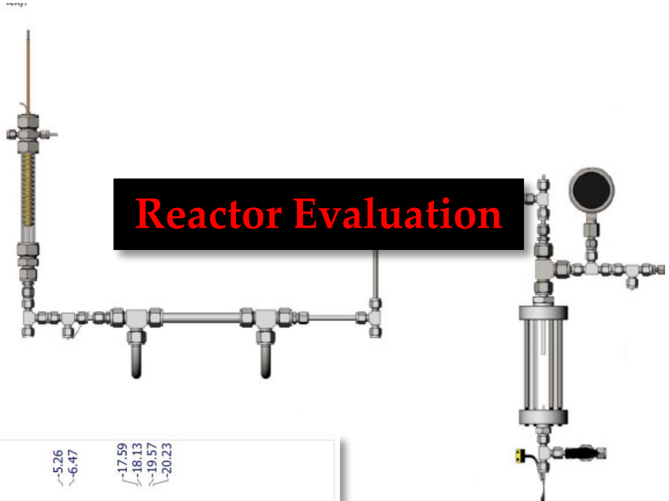
2013 Accomplishments (joint with ECoE)

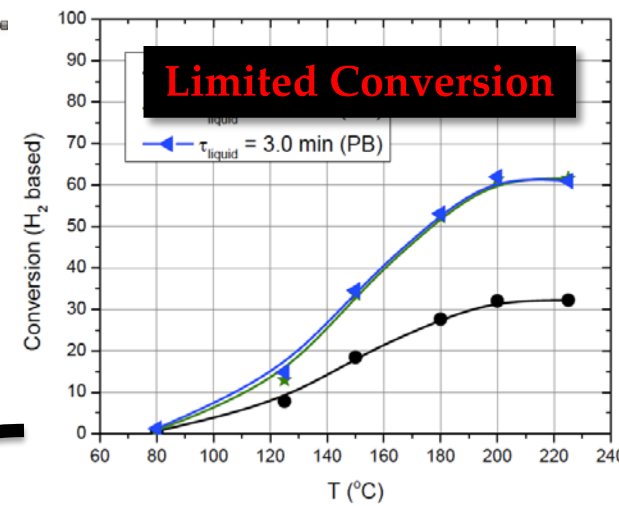
Volatility Limits Conversion

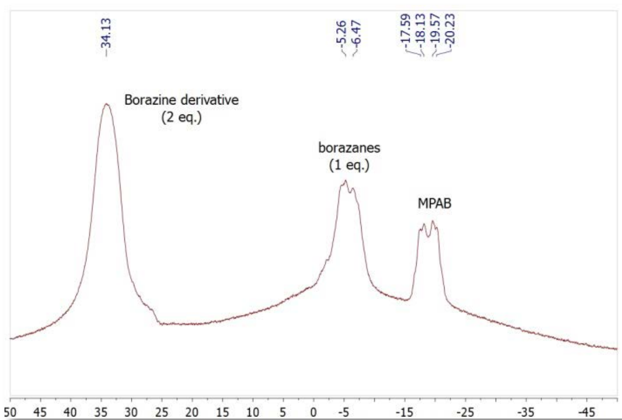
Materials Development

Hydrogen Storage Engineering CENTER OF EXCELLENCE



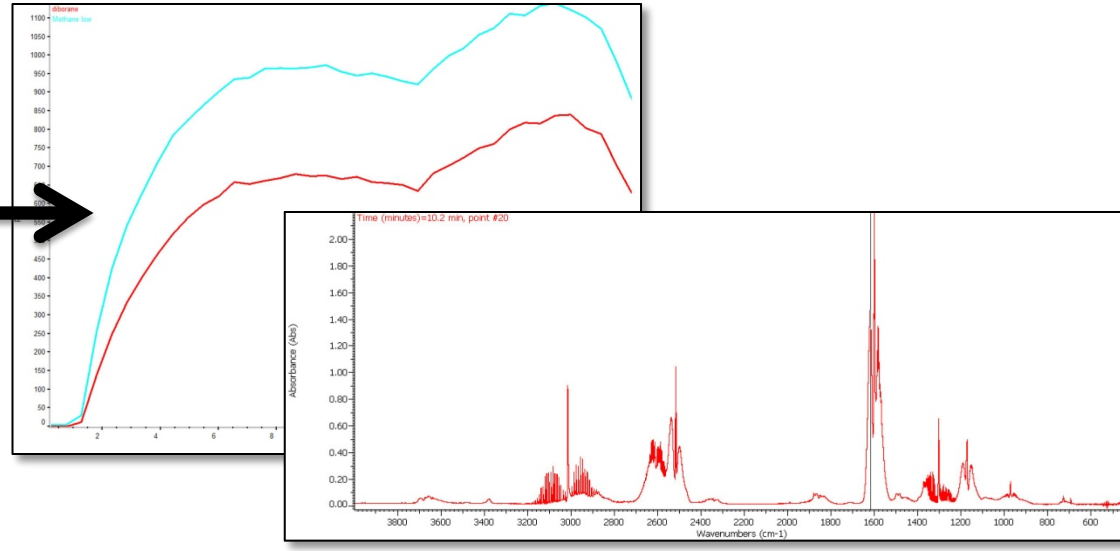




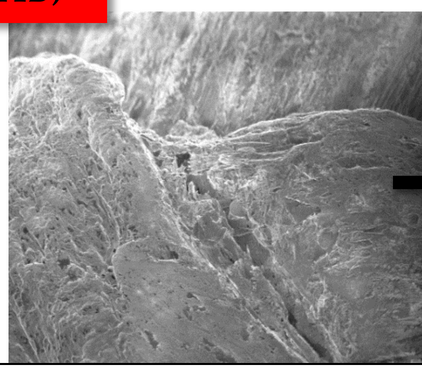


Non-volatile additives may facilitate greater conversion and prevent phase change

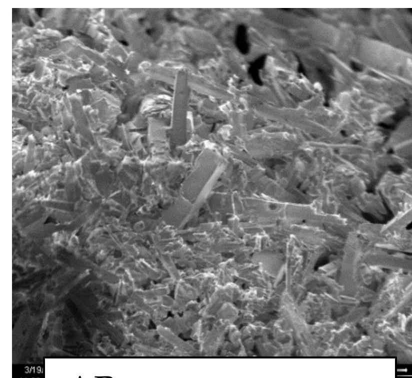
Neutral AmineBorane/AB Blends: Batch Evaluation



Heating to 130°C releases 98% of stored H_2 (assume 2.5 eq. for AB)



AB (JSC Aviobor, as received)



AB (finely dispersed)

Excellent H_2 release; Some impurities detected; Better AB mixing for future runs

Stability Additive Development

Stability Additives

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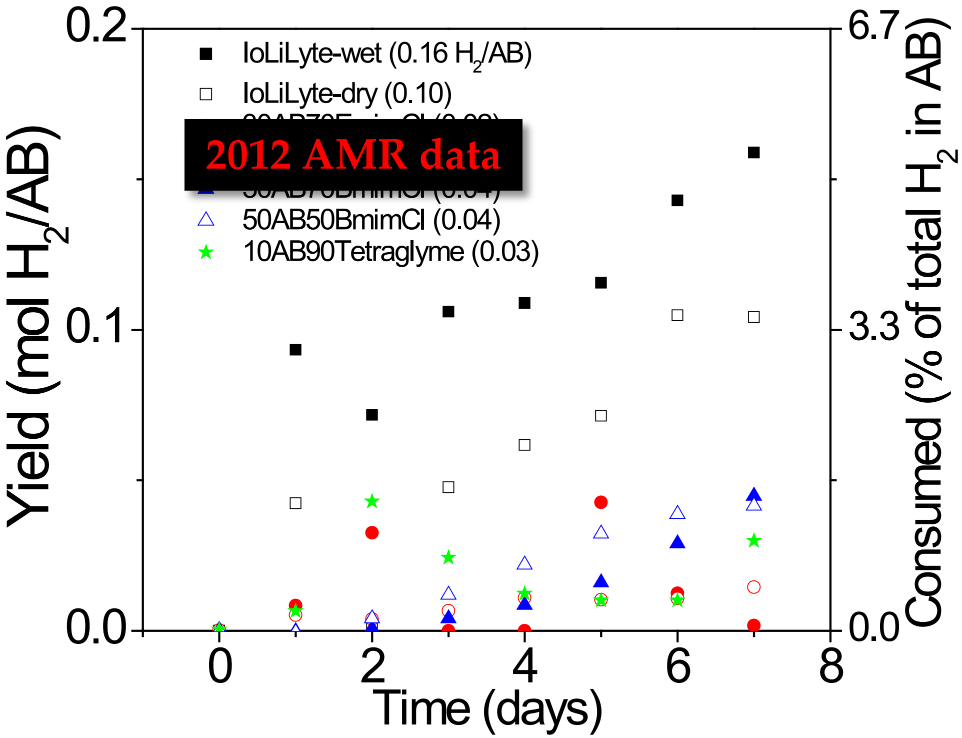
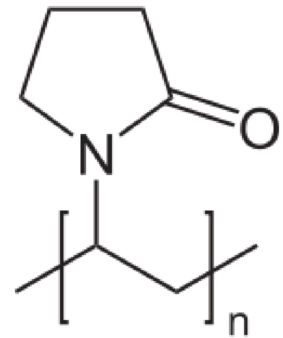




PVP – inert, nonvolatile

prevents isomerization and resulting H_2 release from glyme solutions at room temperature

PVP improves AB stability; related additives may work in ionic liquids

Collaborations

External Collaborators	Effort	Contact
H_2 Codes and Standards	General Guidance	C. Padro (LANL)
Centre for Catalysis Research and Innovation	Neutral Additive Design, Characterization	T. Baker (Ottawa)
Chemical Hydrogen System Architect (HSECoE)	System Designs	Troy Semelsberger (LANL)
Los Alamos Applied Energy Office	Fuel Cell Expertise, General Guidance	Rod Borup (LANL)

Proposed Future Work

Continue amine-borane/ionic liquid additive development

FY13 Upscale synthesis; determine maximum AB loading

FY13-FY14 Assess H_2 release, phase of AB blends

FY13-FY14 Incorporate ECoE feedback for better additive design

Assess efficacy of diaminoborane additives

FY13 Synthesize known materials

FY13 Evaluate product phase with borazine, polyborazylene

FY14 Generate AB blends and perform batch experiments

Interface with HSECoE

FY13-FY14 Upscale candidate materials for HSECoE reactor/component testing

Project Summary

Relevance: Developing materials that store H_2, supporting the HSECoE effort to meet the 2017 system target of 5.5 wt. %; 7.5 wt. % ultimate

Approach: Create amineborane additives which, when blended with ammonia borane, yield a good storage capacity material that remains fluid after H_2 release. Ionic and neutral additives were targeted.

Accomplishments and Progress: synthesized first amineborane/ionic liquid additive; demonstrated blends with AB remain liquid post H_2 release; searched for new neutral additives; evaluation of neutral additives in HSECoE reactor suggests volatility may limit conversion

Collaborations: Hydrogen Storage Engineering Center of Excellence

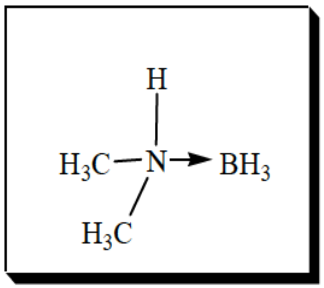
Proposed Future Research: Continue amineborane/ionic liquid additive development; investigate diaminoborane additives

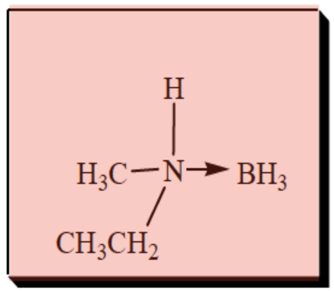
Benjamin Davis
bldavis@lanl.gov

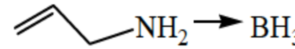
Technical Back Up Slides

Previous Additive Development

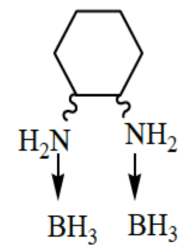
- Explored alkylamine boranes to solubilize AB

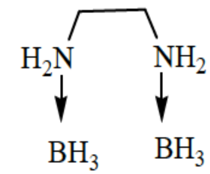






liquid at RT





solid at RT

- UPENN evaluated amine additives and substituted borazines to maintain fluid phase (2011)

AB/IL + 5% dipentylamine $\xrightarrow{85\ \mathrm{C}}$ solid (2.2 eq. H_2 released)

AB/IL + 5% trimethylborazine $\xrightarrow{85\ \mathrm{C}}$ solid (2.3 eq. H_2 released)