Fluid Phase H_2 Storage Material Development

Tessui Nakagawa, Biswajit Paik, Benjamin Davis, Troy Semelsberger, Tom Baker, Larry Sneddon

2012 Annual Merit Review, May 17th

Los Alamos National Laboratory

LA-UR 12-20427

Project ID # ST040

Overview

Timeline

- Project Start Date: Oct 1st 2010
- Project End Date: 2014
- Percent Complete: 45%

Budget

- Total Project Funding:
  - DOE share: $ 330
  - Contractor share: $ 0
- Funding received in FY11: 400k
- Funding for FY12: 330k

Barriers

- Barriers Addressed
  - Weight/Volume
  - Efficiency
  - Durability/Operability
  - Discharging Rates
  - H_2 purity

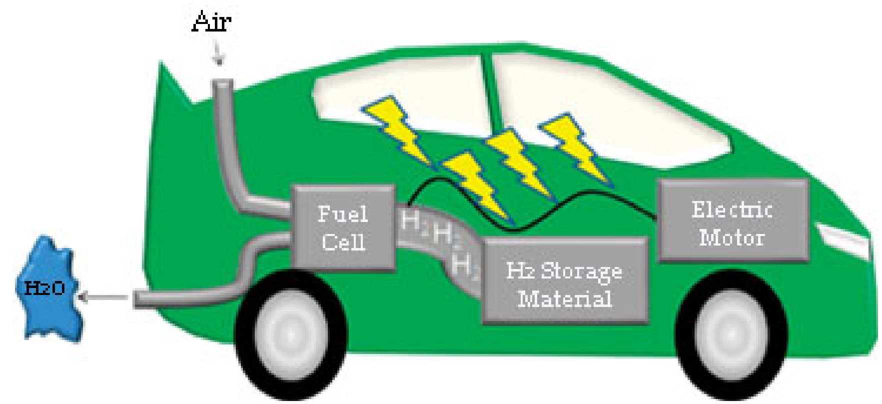
Partners

- LANL (lead)
- University of Ottawa
- UPenn (consulting)

Relevance

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

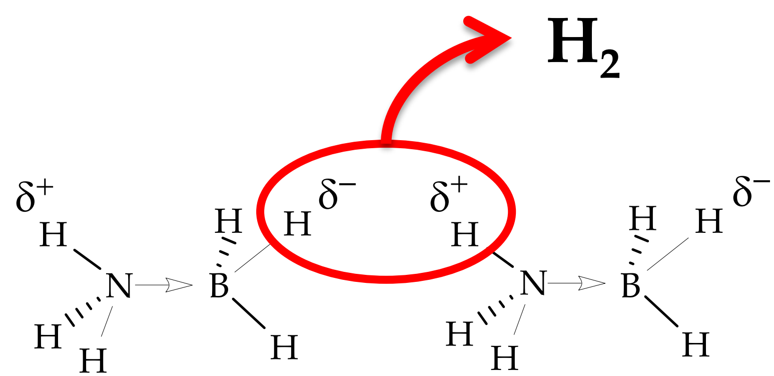
2017 system target = 5.5 wt. %; ultimate 7.5 wt. %



Objectives

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

Work with Hydrogen Storage Engineering Center of Excellence (HSECoE) to ensure compatibility with system designs.



Ammonia Borane

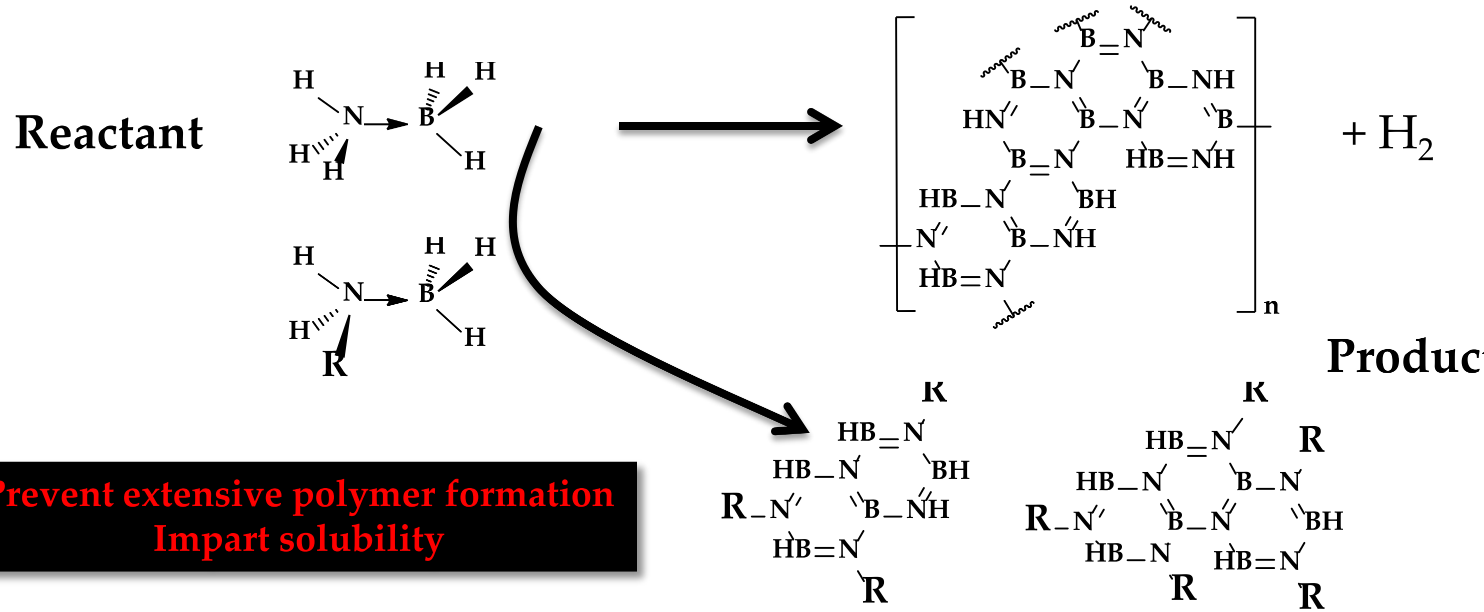
Approach #1

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

Our Method: Implement strategies to prevent or forestall phase change, define usable temperatures/times to guide HSECoE

2012 Goals:

1) Development solubility quantification method and screen ILs
2) Design additives which prevent solid formation



Prevent extensive polymer formation
Impart solubility

Solubility screening and additives will be used to address phase change

Approach #2

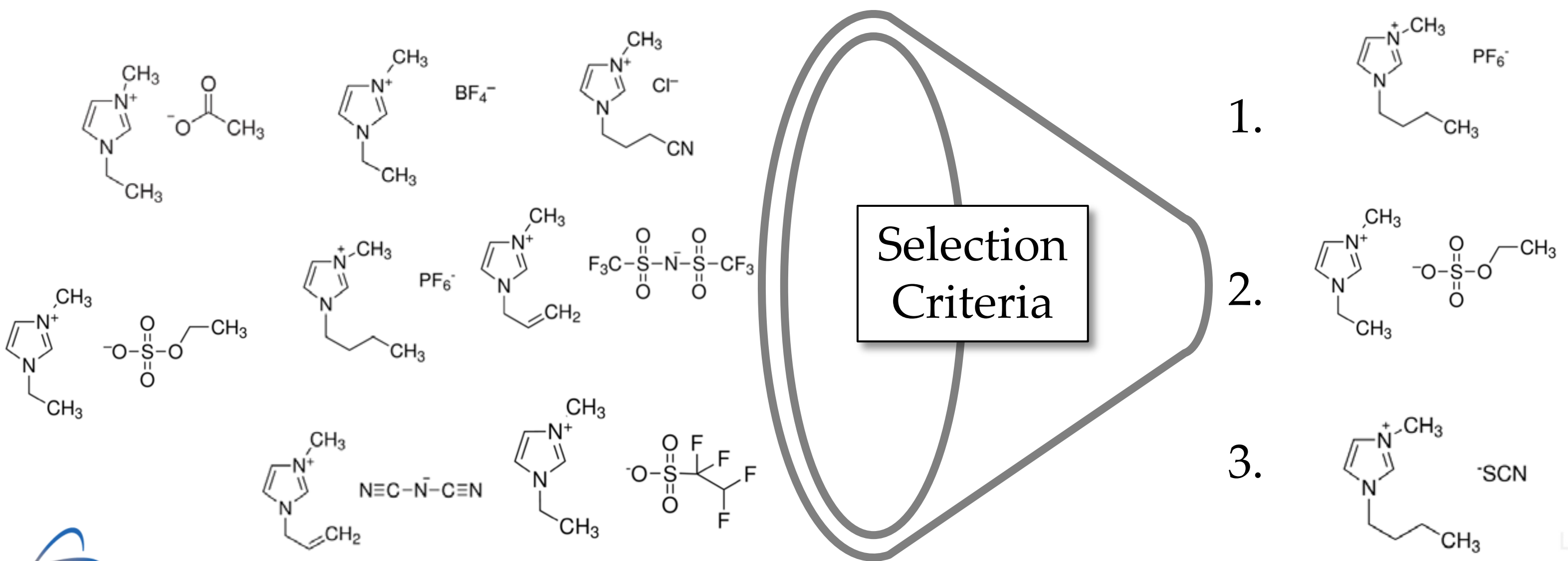
Knowledge Gap: Many ionic liquids, many AB fuel blend possibilities.

Our Method: survey fuel blends to meet DOE targets for hydrogen release rates, capacity, stability, and H_2 purity while maintaining fluid phase

HSECoE set 40 wt. % AB min in 2012

2012 Goals:

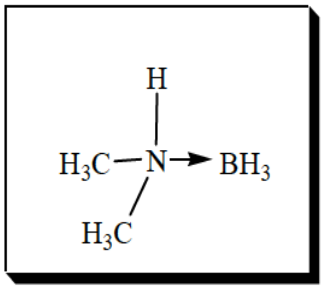
1) Use solubility measurements
   -> Maximize capacity
2) Continue short/long term stability
   -> ensure minimal H_2 loss
2) Develop impurity quantification method and use
   -> provide HSECoE with guiding data

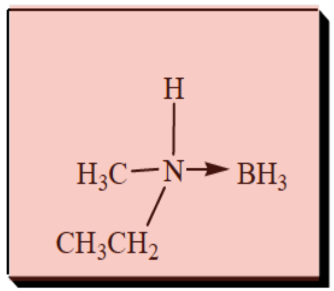


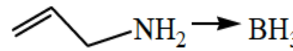
Additive Development

Additive Development

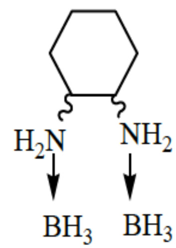
- CHSCoE originally explored alkylamine boranes to solubilize AB

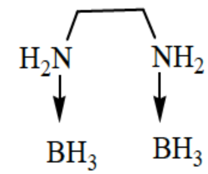






liquid at RT





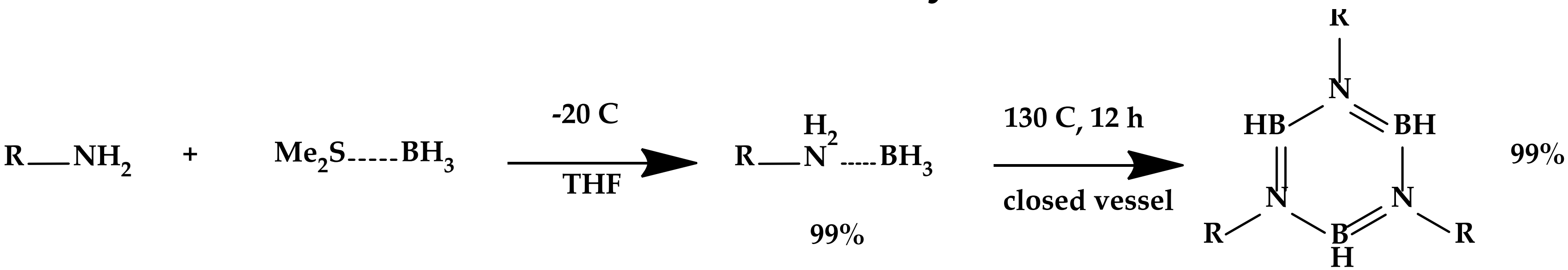
solid at RT

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

AB/IL + 5% dipentylamine →(85 C) solid (2.2 eq. H_2 released)

AB/IL + 5% trimethylborazine →(85 C) solid (2.3 eq. H_2 released)

2012: New Additives Synthesized



R = hexyl, methoxypropyl

Analogous syntheses by Framery, E.; Vaultier, M. *Heteroatom Chem*, **2000**, *11*, 218-225.

Liquid

Picture @ Room Temperature
Hexyl is Liquid = 0 C
Hexyl is Solid = -40 C

Liquid

Picture @ Room Temperature

Additive amine-boranes have 3-4 wt. % usable H_2 and maintain fluid phase

US Provisional Patent Application Number 61/615650

2012: Additives/AB Mixtures Yield Fluid Products

140 C

Picture @ Room Temperature

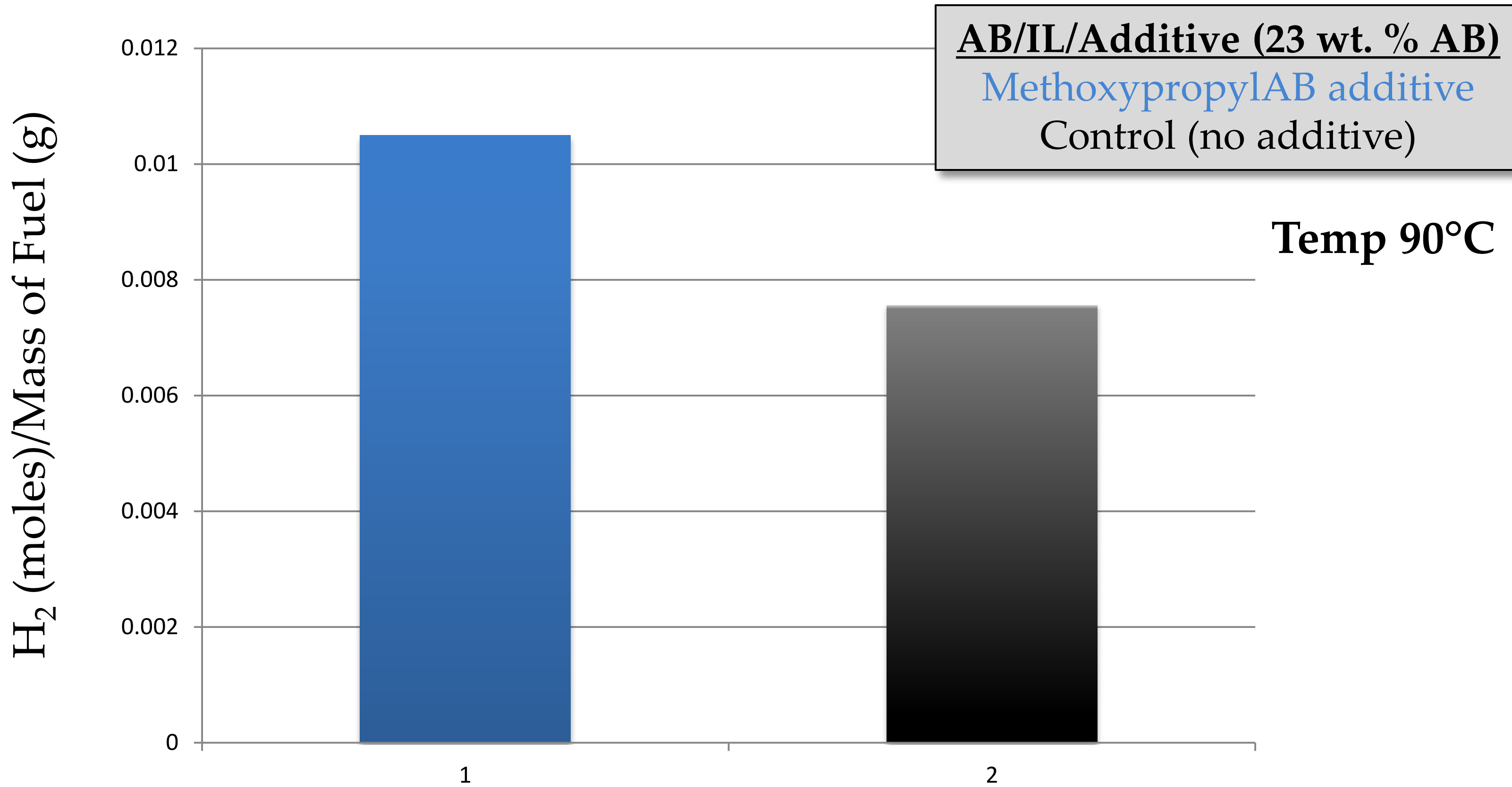
20 wt. %AB in hexylAB (6.0 wt. % H_2) transforms from a slurry to <u>liquid</u> upon dehydrogenation

Additives Can Impart Favorable Fluid Properties

US Provisional Patent Application Number 61/615650

Accomplishments

2012: H_2 Release Before Phase Change in AB/IL/additive Mixtures

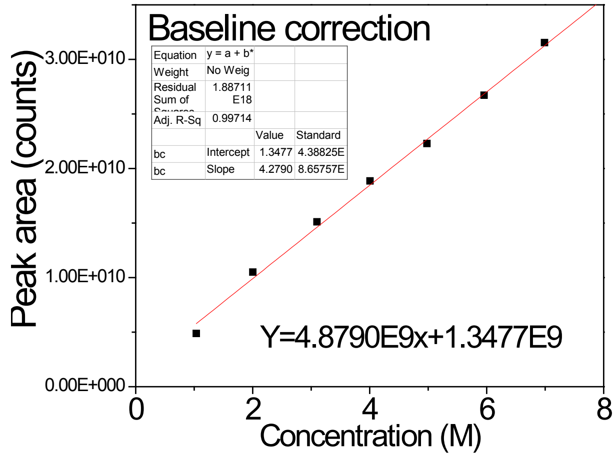


More H_2/g of fuel is released in AB/IL/additive mixtures before phase change

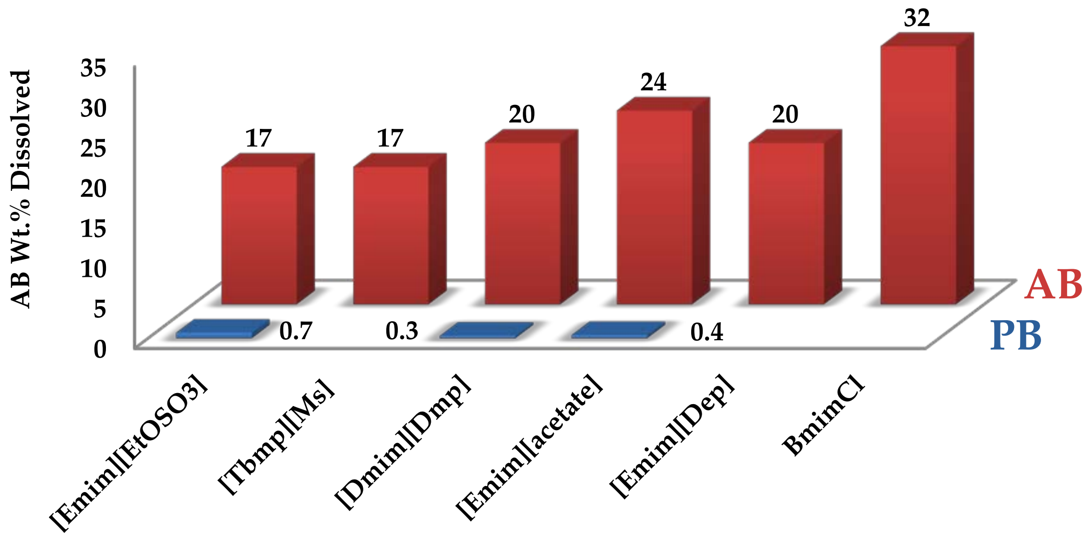
Ammonia Borane Ionic Liquid Survey

Accomplishments

2012: Ammonia Borane/Polyborazylene Solubility Measurements



^{11}B NMR quantification method only 'sees' dissolved species



Polyborazylene (PB) solubility properties depend on the route of formation

↓

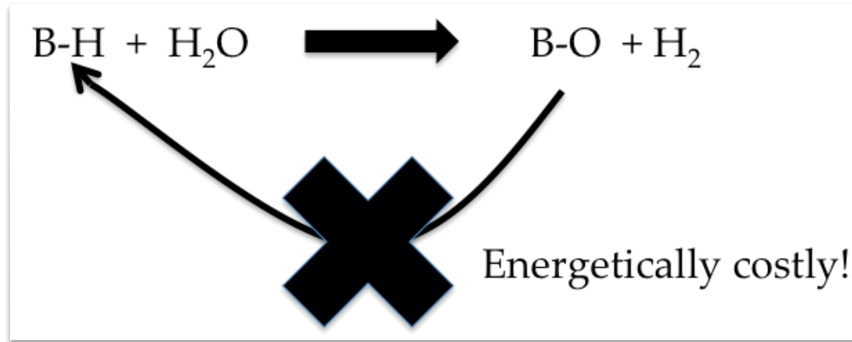
uOttawa will provide a PB from metal catalyzed decomposition of AB for us to test

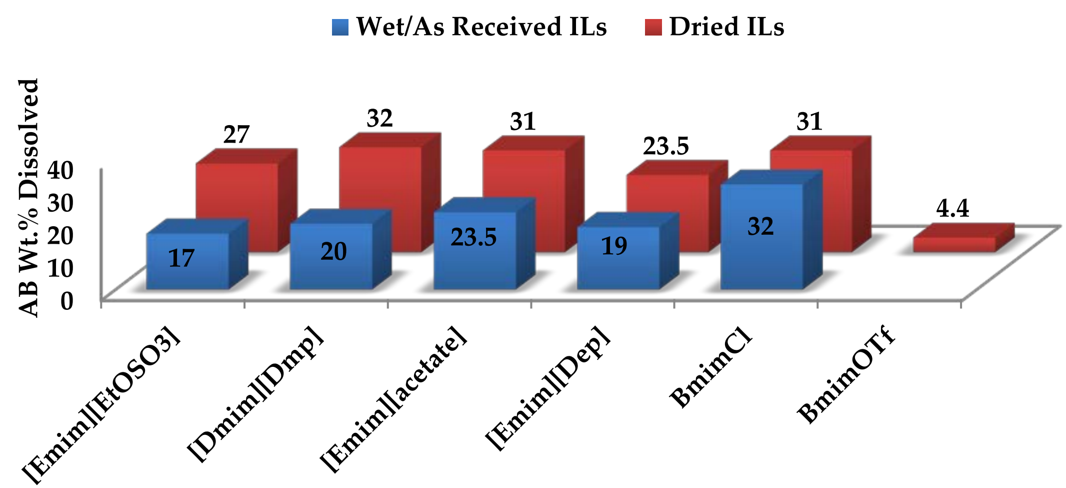
NMR solubility quant method completed, initial selection of ionic liquids assessed

2012: Water Impurities can alter AB solubility

Due to ionic nature, some ILs will absorb several wt. % H_2O if exposed to atmosphere

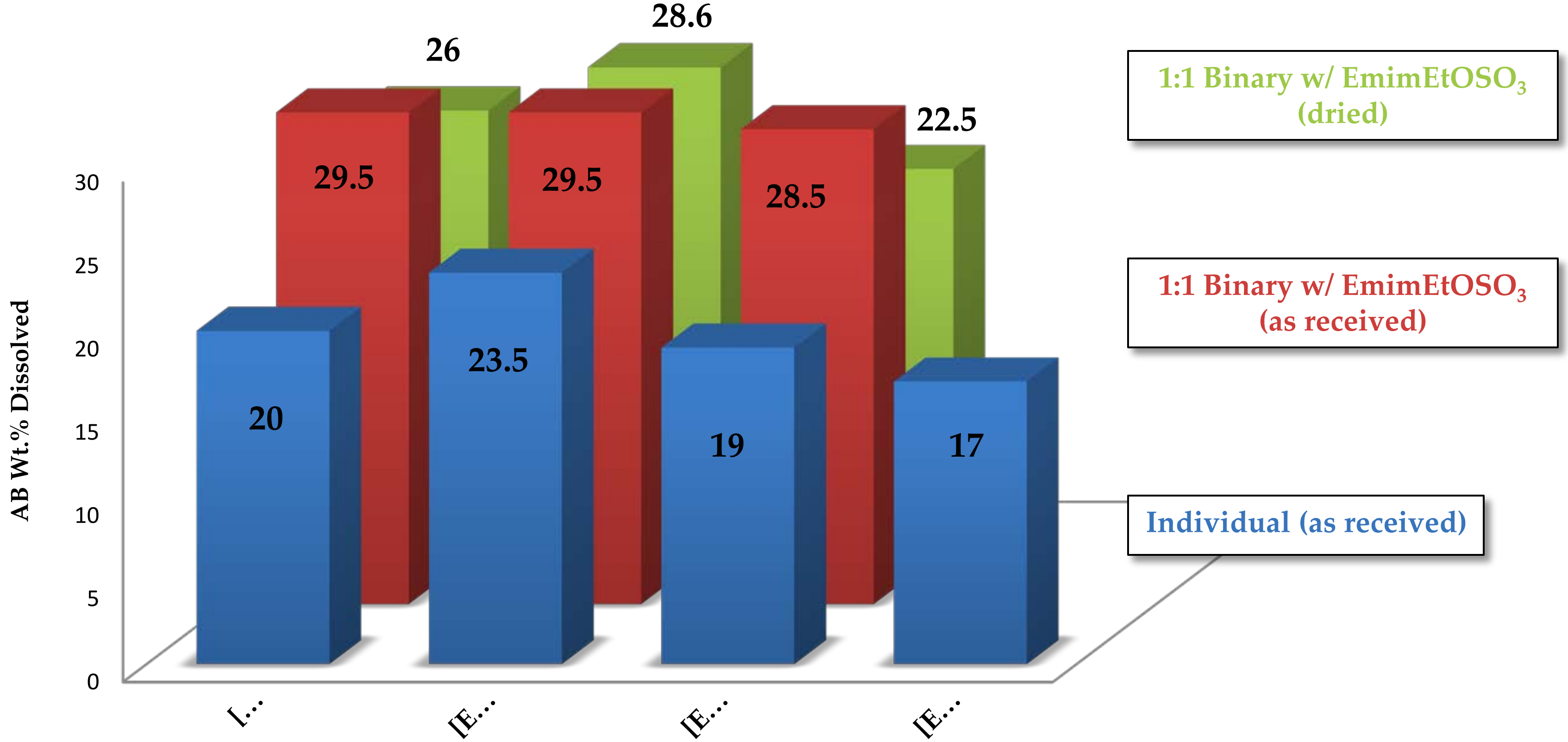
Ionic Liquid	As Received (ppm)	Dried (ppm)
$EmimEtOSO_3$	1600	80
DmimDmp	4000	250
EmimAcetate	1500	100
BmimCl	10,000	320
BmimOTf	450	< 30





Drying Methods Implemented, Solubility of AB Improves

2012: Ammonia Borane Solubility in Binary Ionic Liquids

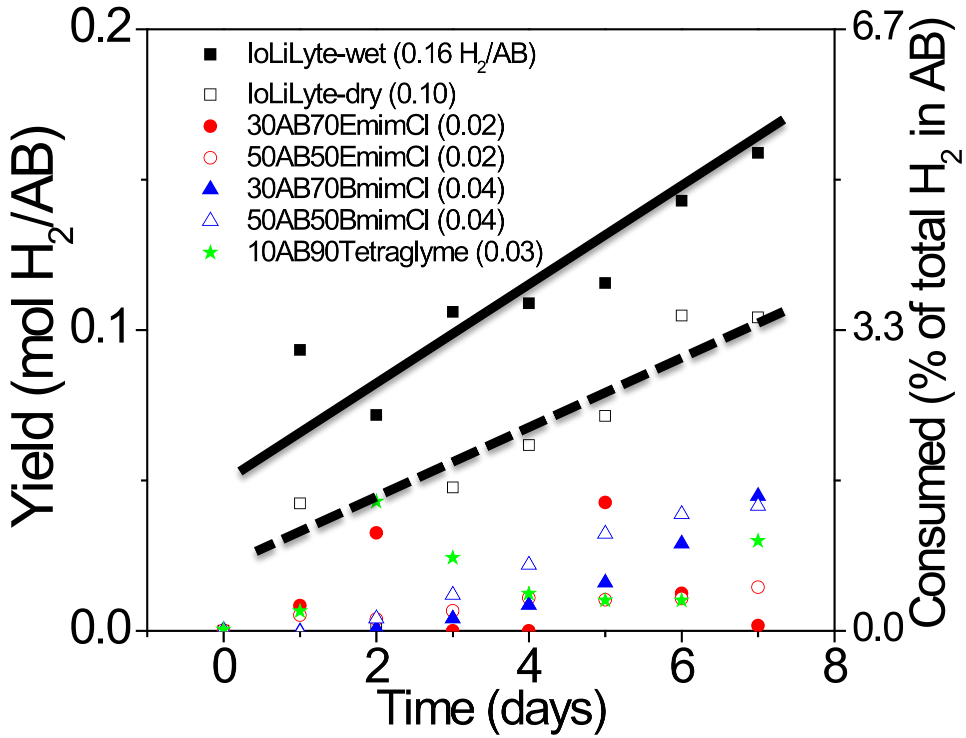


AB solubility measured in binary ILs, improves in some cases

2012: Stability Measurements Continued

Hydrogen Storage Engineering CENTER OF EXCELLENCE

Burette Measurements

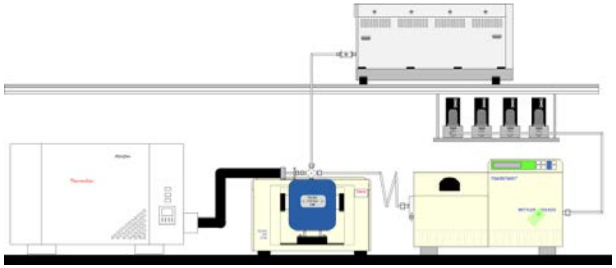


More sensitive Parr reactor Measurements initiated

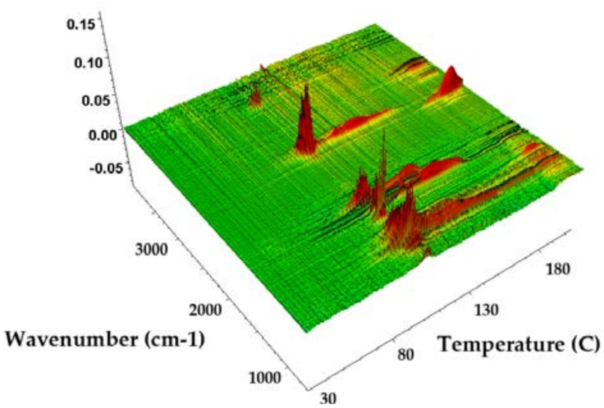
Stability improves with dry IL; More accurate, longer term studies initiated

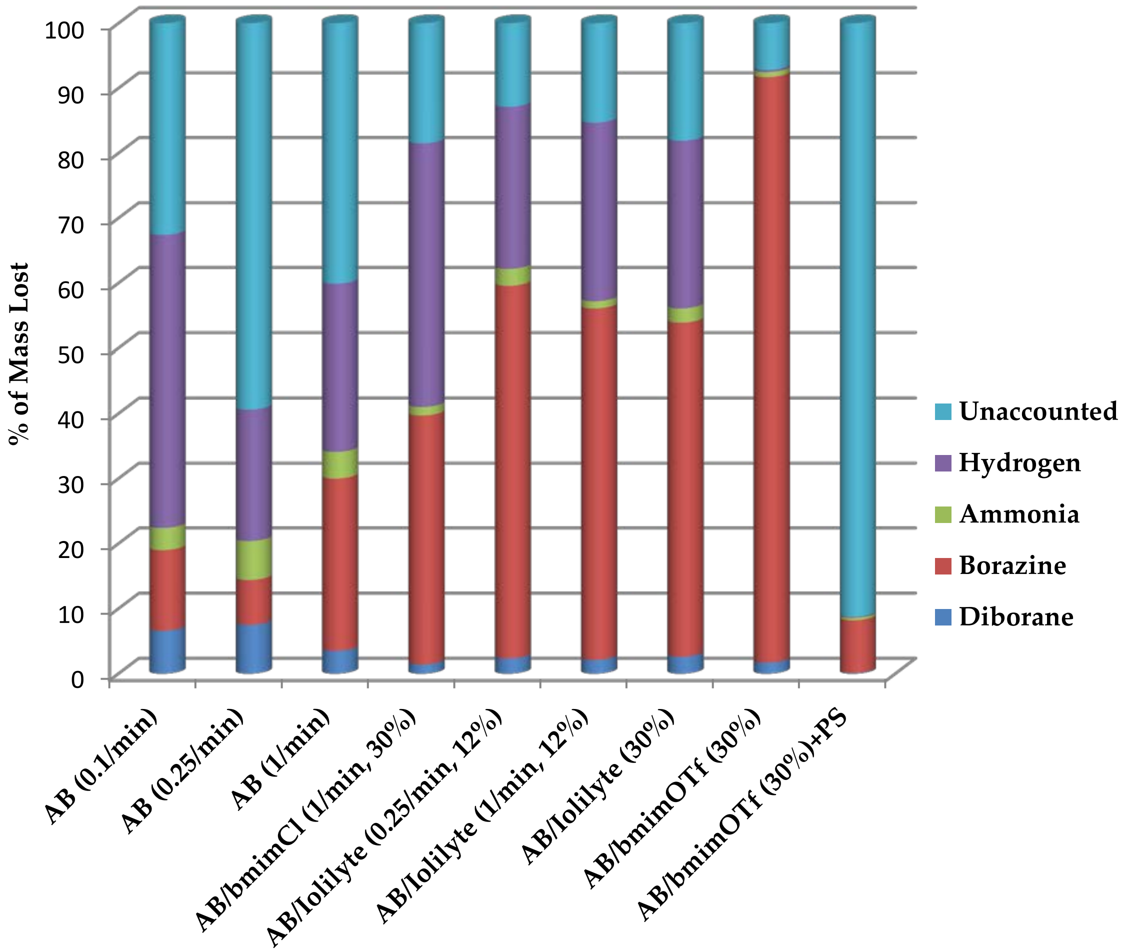
Hydrogen Storage Engineering CENTER OF EXCELLENCE

2012: Quantification Methods Developed, Validated, Initial Results



Evolved Gas Analysis Equipment





Quant Method Completed, Initial Results to Guide HSECoE

Collaborations

External Collaborators	Effort	Contact
H_2 Codes and Standards	General Guidance	C. Padro (LANL)
University of Ottawa	Additive Development	T. Baker
University of Pennsylvania	AB/IL Formulations	Larry Sneddon
Chemical Hydrogen System Architect	System Designs	Troy Semelsberger (LANL)
SSAWG	Technical Collaboration	G. Ordaz (DOE)
H_2 Storage Tech Team	General Guidance	Ned Stetson (DOE)
Argonne National Laboratory	Independent Analyses	R. Ahluwalia
Applied Energy Office	General Guidance	Kevin Ott (LANL)

Proposed Future Work

Synthesize, design, and test new additives

FY12 Measure AB/IL/additive liquid range

FY12, FY13 Synthesize/evaluate new additives

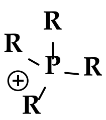
Continue solubility assessments and AB stability in new ionic liquids

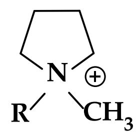
FY12 Solubility tests with new classes of ionic liquids

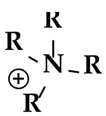
FY12 Test uOttawa PB/real spent fuel solubility

FY12 Initiate long term stability measurements

<u>FY12 Milestone</u>: complete solubility survey







Continue AB/IL impurity evaluation

FY12, FY13 Identify trends and tailor to HSECoE needs

Interface with HSECoE

FY12, FY13 Upscale candidate materials for HSECoE component validation

Summary

Additive Development

- New additives synthesized
- AB/additive slurries remain fluid after prolonged heating

Solubility Measurements

- Method Development Complete
- Water impurities identified, measured, and removed
- Effect of water on solubility observed
- Binary solubilities measured

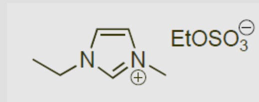
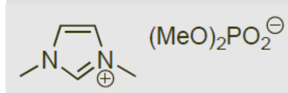
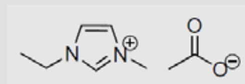
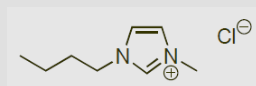
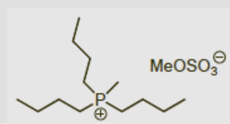
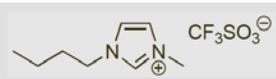
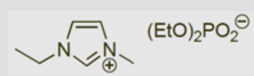
Impurity Quantification

- Method development complete
- Measurements on AB and AB/IL
- HSECoE guidance

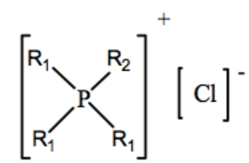
→ **Optimizing AB fuel blends for HSECoE use**

Technical Back-Up Slides

Ionic Liquid Nomenclature

Ionic Liquid	Abbreviation
	$EmimEtOSO_3$ (Iolilyte)
	DmimDmp
	EmimAcetate
	BmimCl
	TbmpMs
	BmimOTf
	EmimDep

Cyphos IL 101



R_1 = hexyl R_2 = tetradecyl

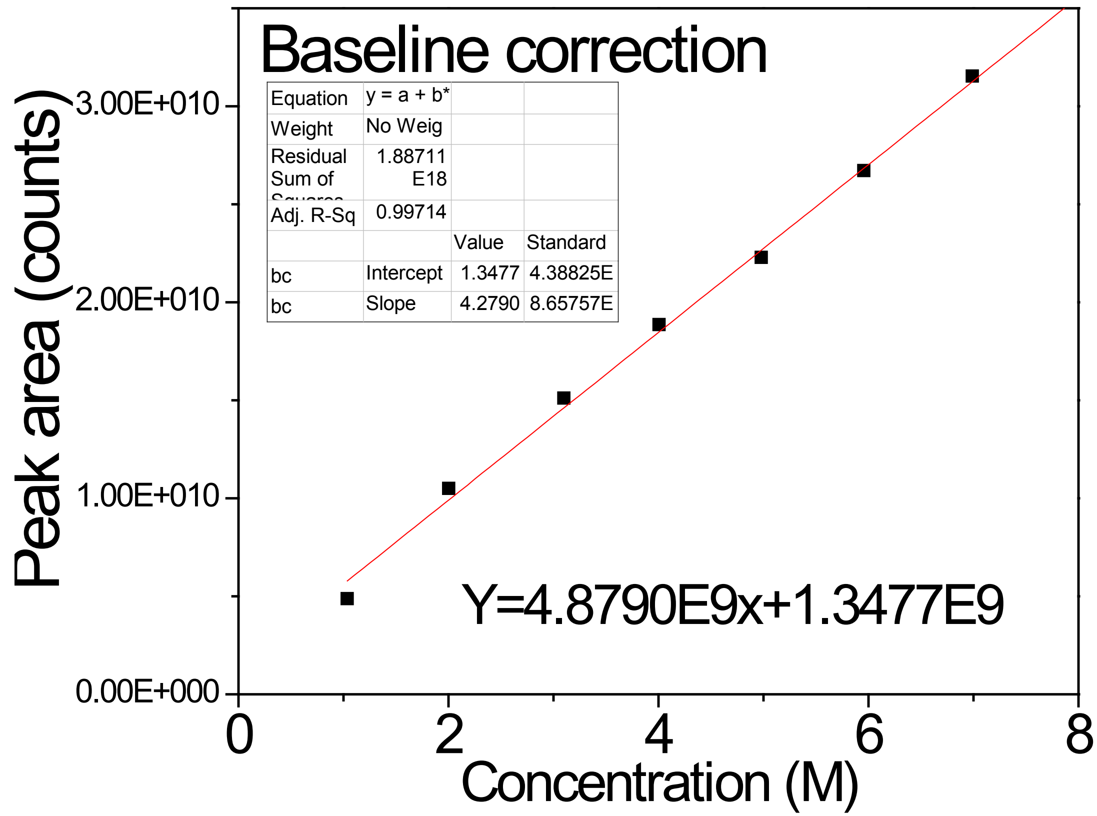
Previously examined ILs CHSCoE

CHSCoE IL
bmimCl
bmmimCl
bmimI
$bmimBF_4$
$bmimPF_6$
$mmimMeSO_4$
$emmimEtSO_4$
bmimOTf
emmimOTf
$pmmimTf_3C$

Limitations:
-> only imidazolium cations
-> only 1:1 ratio compositions
-> ILs were dried no H_2O quant

NMR Quantification Methodology

NMR was calibrated for boron loading using BF_3-etherate standards
When applied to a different boron species of known concentration, an excellent approximation of boron concentration was calculated



Full List of AB/IL Combinations Examined

sample	average (wt%)
IoLiLyte (IN-0026)	17.83
TetdpBtmp2P (IN-0009)	3.64
TbmpMs (IN-0013-TG)	16.58
BmimBF4	10.00
DmimDmp (IL-0053)	20.02
EmimAcetate (IL-0189)	23.56
EmimDep (IL-0052-HP)	19.43
Cyphos	10.59
BmimOTf	4.40