Liquid Hydrogen Storage Materials

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Project ID #
ST040

Overview

Timeline

- Project start date: 1st Oct 2010
- Project end date: 31st Sept 2011
- Percent complete: *50%*

Barriers

- **Weight and Volume**
- **Flow Rate**
- **Energy Efficiency**
- **Cost**
- **Regeneration Process**

Budget

- Total project funding
  - DOE share: $400
  - Contractor share: $0
- Funding for FY11: $400

Partners

- University of Pennsylvania
- LANL

Relevance - Objectives

- Develop liquid ammonia-borane (AB) fuels and increase rate and extent of hydrogen release
  - Liquid before and after hydrogen release
  - >10 Wt% H_2
  - Maximum liquid range for both fuel and product
  - Thermal stability at 50 C
  - Compatible with hydrazine regen
  - Low cost

Approach

- Determine design criteria for Ionic Liquids as supports for ammonia
  - What cations are suitable?
  - What anions are suitable?
  - What is a suitable viscosity?
  - What is maximum liquid range?

- Assess compatibility of “fuel” with known ammonia borane regen process
- Determine maximum ammonia borane mix in “fuel”
- Determine kinetics for thermal release
- Discover catalyst to improve cold start

Establish thermal stability limits for cations and anions

DSC, TGA, TGA-MS etc

Determine chemical compatibilities of cations and anions with ammonia borane

NMR, TGA, burette measurements

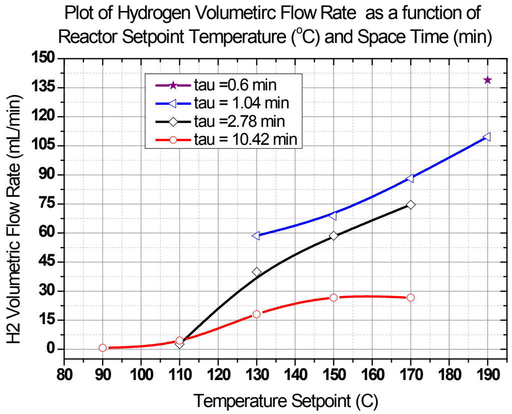
Liquid Properties of ionic liquid and ammonia borane : Ionic Liquid

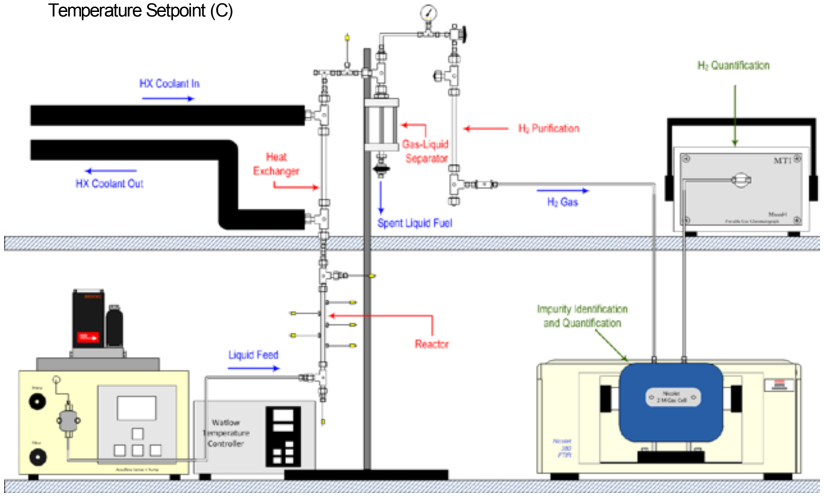
DSC, viscosity, etc

Collaboration with

Hydrogen Storage Engineering
CENTER OF EXCELLENCE

- Validated fluid-phase CH reactor
- Designed, built, assembled, and validated modular fluid-phase CH system test bed equipped with analytics
  - Reactors
  - Gas-liquid separator
  - Hydrogen purification





No significant progress without strong interaction between materials and engineering

AB Ionic Liquids

Summary – LANL and UPenn Down Selects for 2010 (AMR 2010)

Conclusion from AMR 2010

Ionic Liquid systems with catalysts look promising but need to tailor catalyst and ionic liquids combination - continued

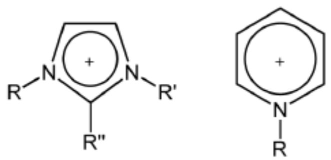
State of the art was Penn ionic liquids

Approach

1. Why Ionic Liquids for Amineborane H_2-Release?

Ionic Liquids

Cations:



N,N'-imidazolium N-pyridinium

Anions:

Reactive: $AlCl_4^-$, $Al_2Cl_7^-$

Inert: PF_6^-, BF_4^-, Cl^-

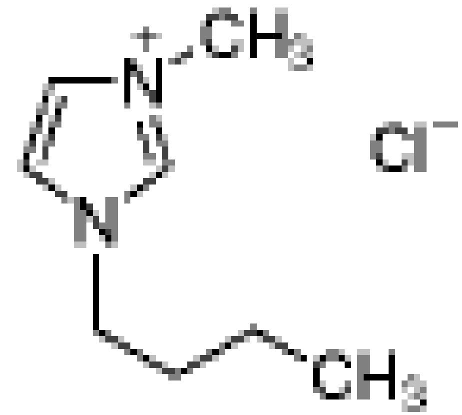
Advantages

- 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**

Basic feature of BmimCl

- name: 1-Buthyl-3-methylimidazolium chloride
- chemical formula: $C_8H_{15}ClN_2$
- density: 1.08 g/cm^3
- heat capacity: 322-330 J/mol K
- molecular weight: 174.67
- decomposition: 250°C
- melting point: ~70°C
- glass transition: -76°C
- eutectic by mixing AB at RT (mixture at RT: liquid phase)

Structure of BmimCl



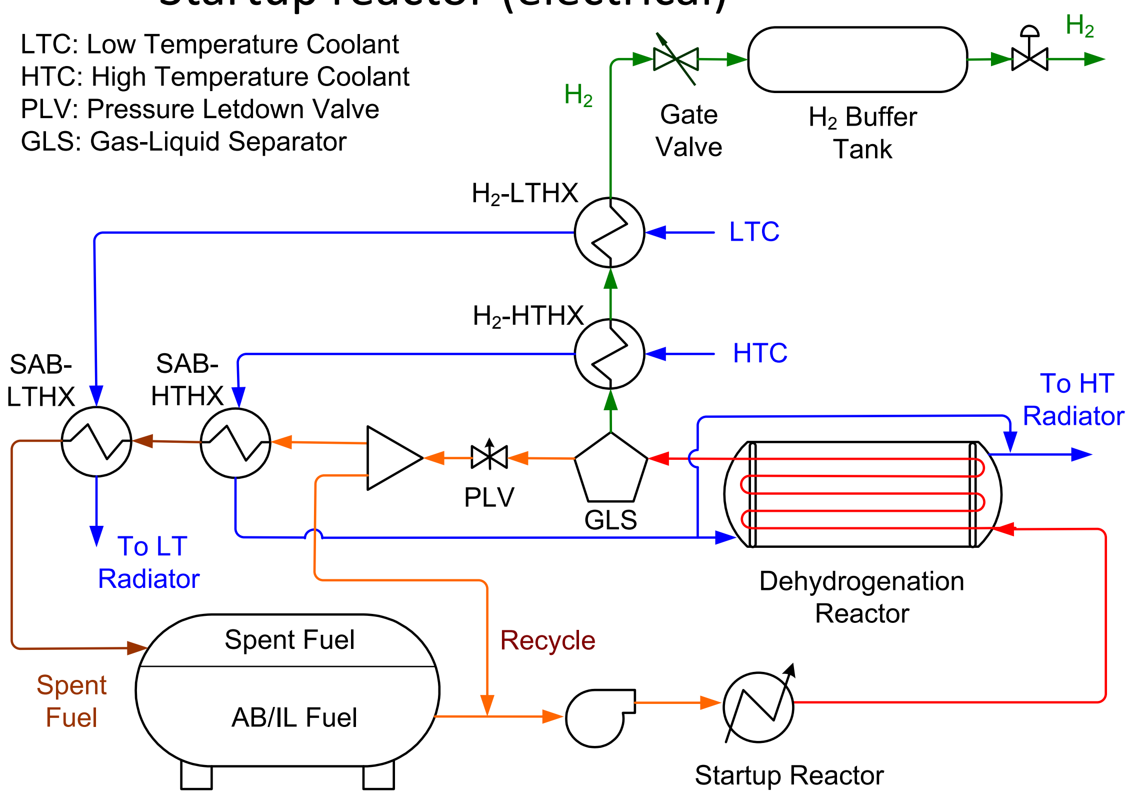
Collaboration HSECoE helped determine what properties of IL are most important for effective fuel.

R. K. Ahluwalia, J-K Peng, and T. Q. Hua
Argonne National Laboratory
October 10, 2010

On-board System Configuration

- Volume exchange tank design for storing fresh and spent fuel
- Adiabatic vs. non-adiabatic dehydrogenation reactor
- Buffer hydrogen tank
- Heat transfer system (FCS HT and LT coolants)
- Gas liquid separator (coalescing filter)
- Startup reactor (electrical)

LTC: Low Temperature Coolant
HTC: High Temperature Coolant
PLV: Pressure Letdown Valve
GLS: Gas-Liquid Separator

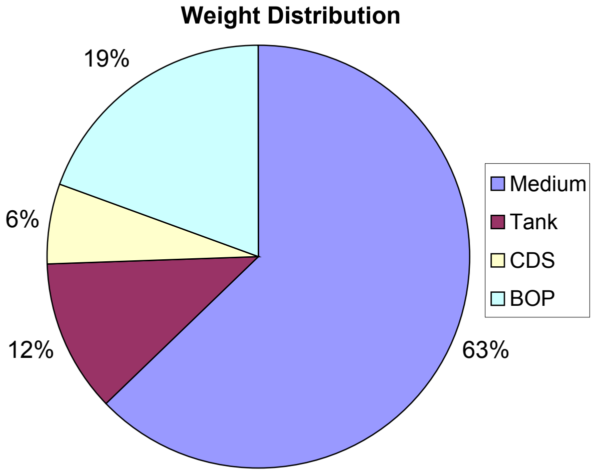


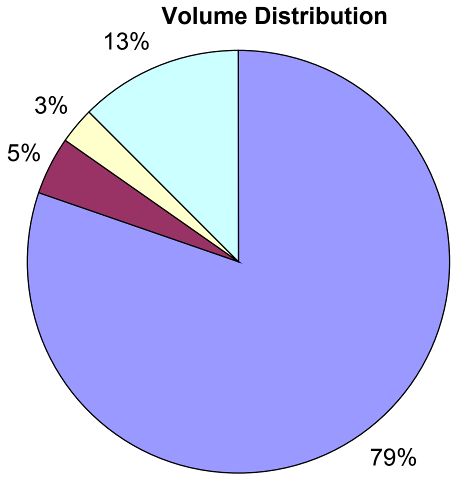
ANL analysis indicates on board system is possible

R. K. Ahluwalia, J-K Peng, and T. Q. Hua
Argonne National Laboratory
October 10, 2010

Preliminary System Weight and Volume

- Startup reactor, incremental W and V of FCS radiators to be included





	W (kg)	V (L)
Fuel Tank (full, 5.6 kg H_2 usable)	84.7	80.6
H_2 Buffer Tank (20 g H_2 capacity at 20 atm)	2.0	15.2
Dehydrogenation Reactor	5.0	1.1
High Temperature H_2 Cooler	1.6	2.1
Low Temperature H_2 Cooler	1.0	1.2
High Temperature Recuperator	2.9	3.0
Low Temperature Recuperator	0.9	0.8
Pump	1.5	1.0
Startup Heater	2.0	2.0
Gas/Liquid Separator	1.0	1.0
BOP		
Check Valves	0.6	0.2
Manual Valve	0.2	0.1
Excess Flow Valve	0.2	0.1
Service Vent Valve	0.2	0.1
Shutoff Valves	1.8	1.3
Relief Valves	0.6	0.2
Pressure Transducer	0.1	0.0
Temperature Transducer	0.1	0.0
Pressure Regulator	0.5	0.3
Pressure Relief Device	1.0	0.6
Pipings/Fittings	4.0	1.0
Fill System Control Module	1.0	1.0
Miscellaneous	2.0	0.5
System Total	**114.9**	**113.1**
Gravimetric Capacity, wt%	**4.9**	
Volumetric Capacity, g H_2/L		**49.5**

ANL analysis indicates reasonable initial Gravimetric capacity

Requirements for fuel Based upon Engineering Analysis

Hydrogen Storage Engineering
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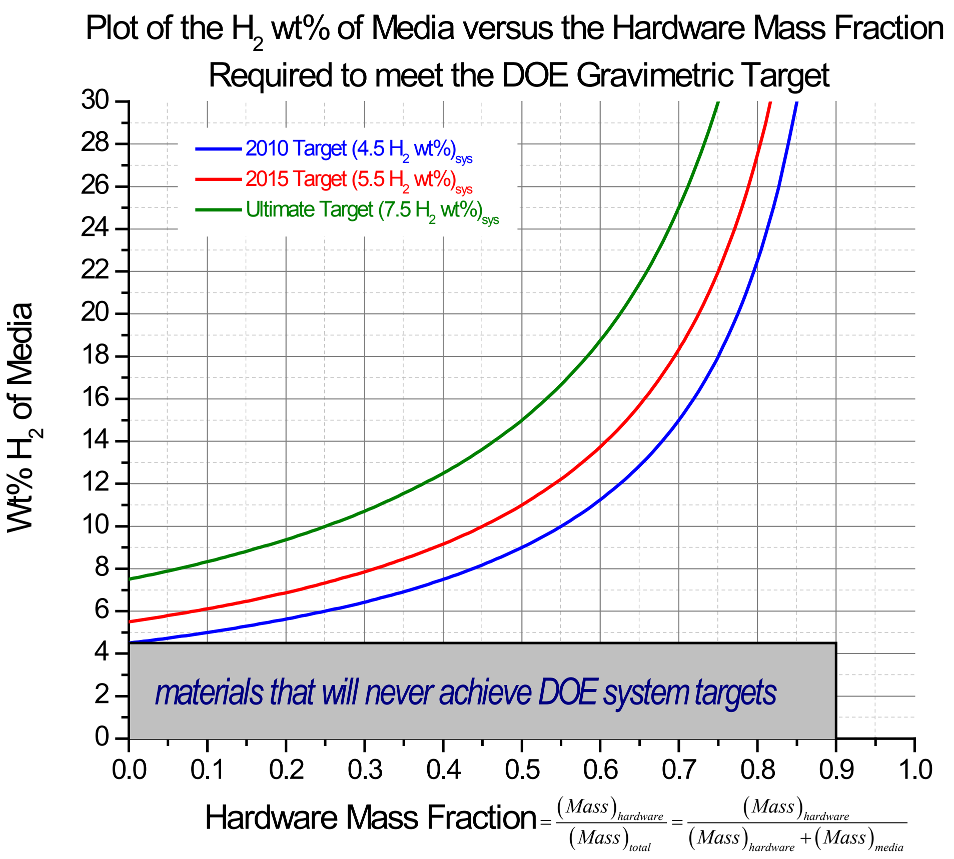
R. K. Ahluwalia, J-K Peng, and T. Q. Hua
Argonne National Laboratory
October 10, 2010

Argonne

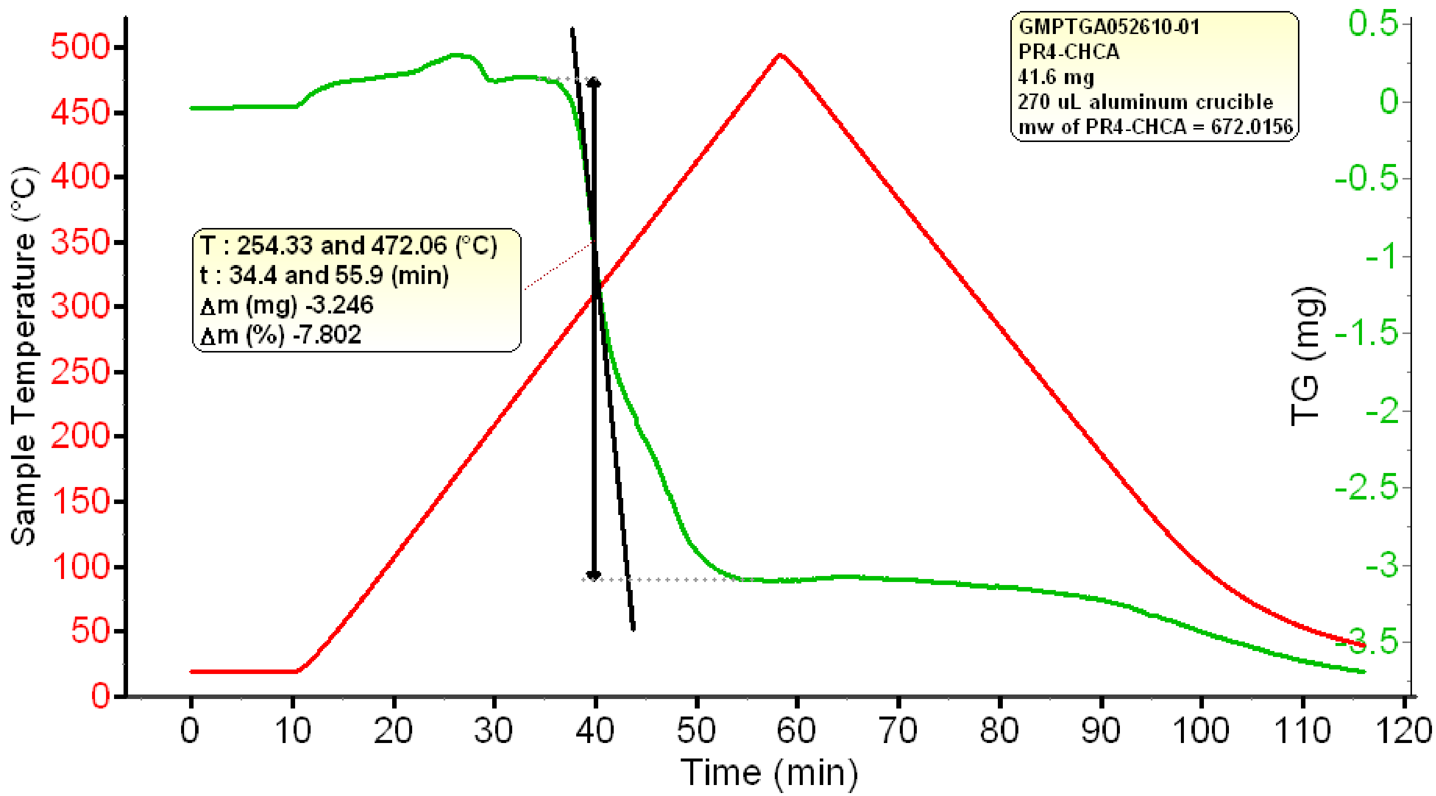
Required:
Liquid before and after hydrogen release
>10 Wt% H_2
Maximum liquid range
Thermal stability at 50 C
Compatible with hydrazine regen
Low cost

Desirable:
Compatible with stainless steel
Stable in air
Catalytic hydrogen release demonstrated



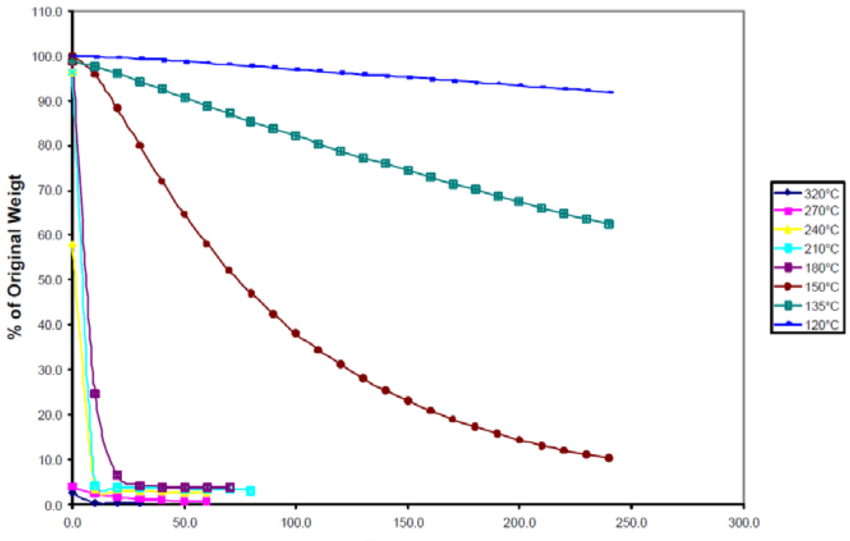
Based upon HSECoE analysis at 50:50 materials : balance of plant balance require that materials have >10 Wt% hydrogen to meet 2015 targets (**material independent**)

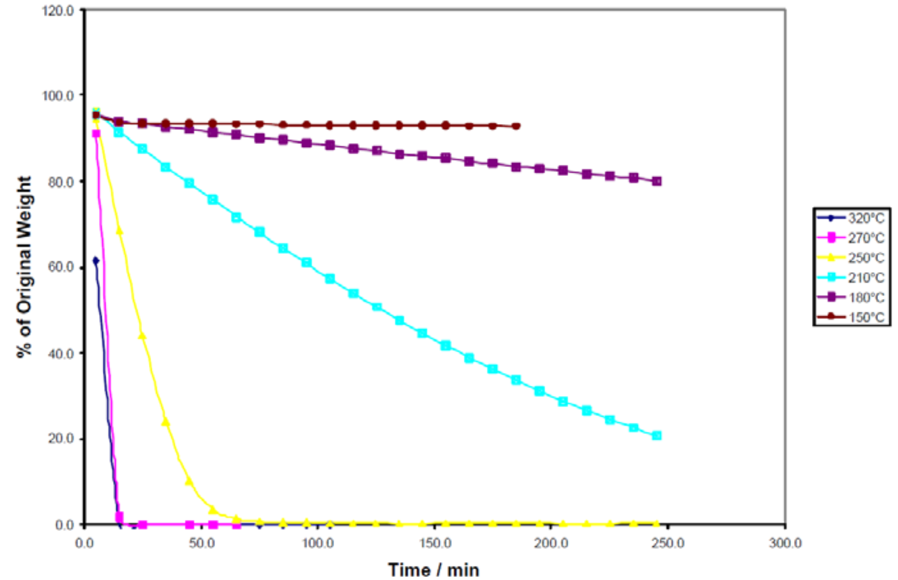
Thermal stability of ionic liquids is a critical issue

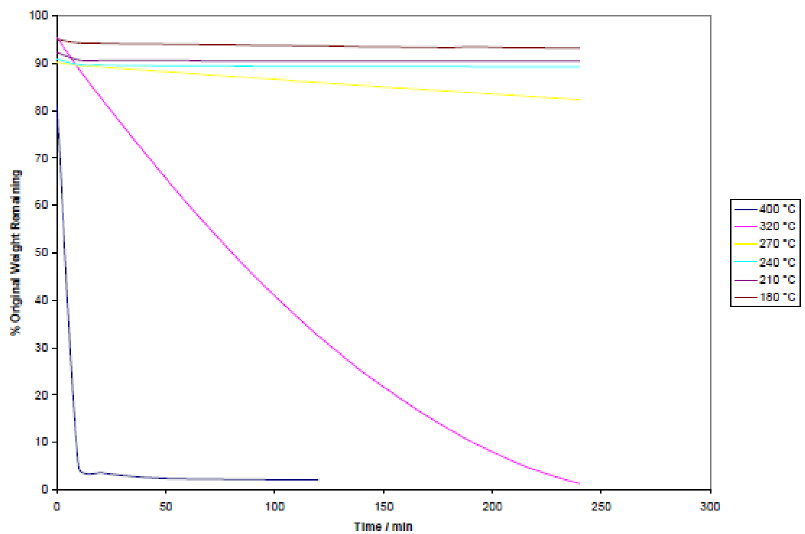


Thermal stability of the ionic liquids we have looked at appears to be dominated by choice of cation

Isothermal TGA Plots of Ionic liquids under N_2

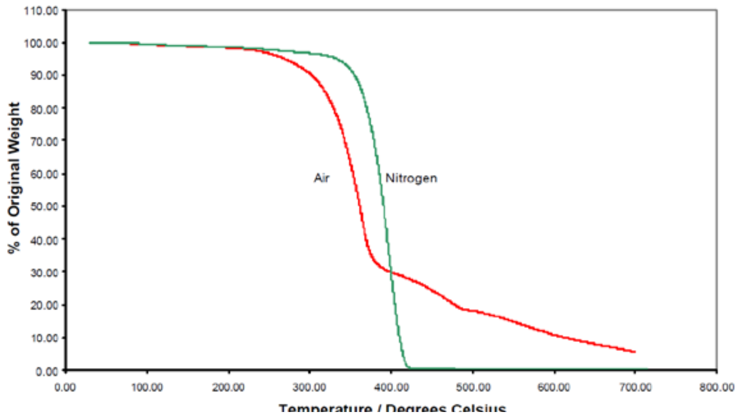


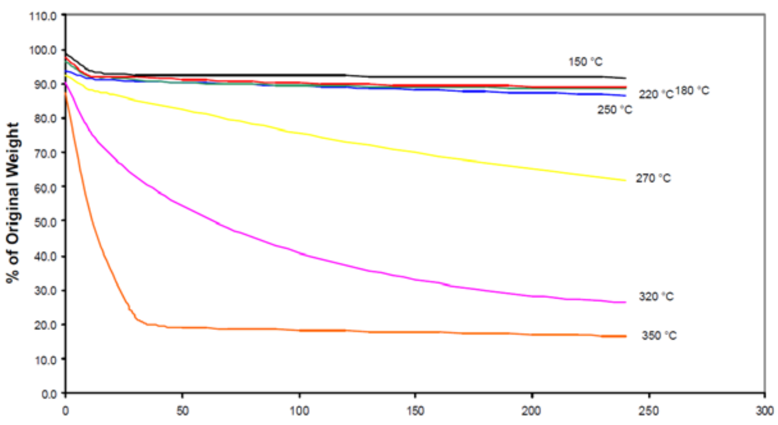


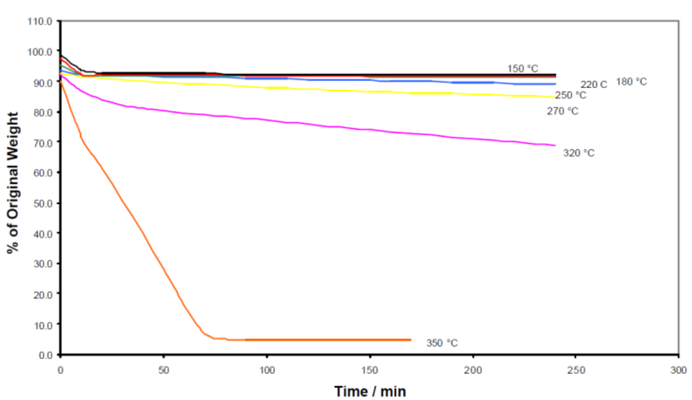


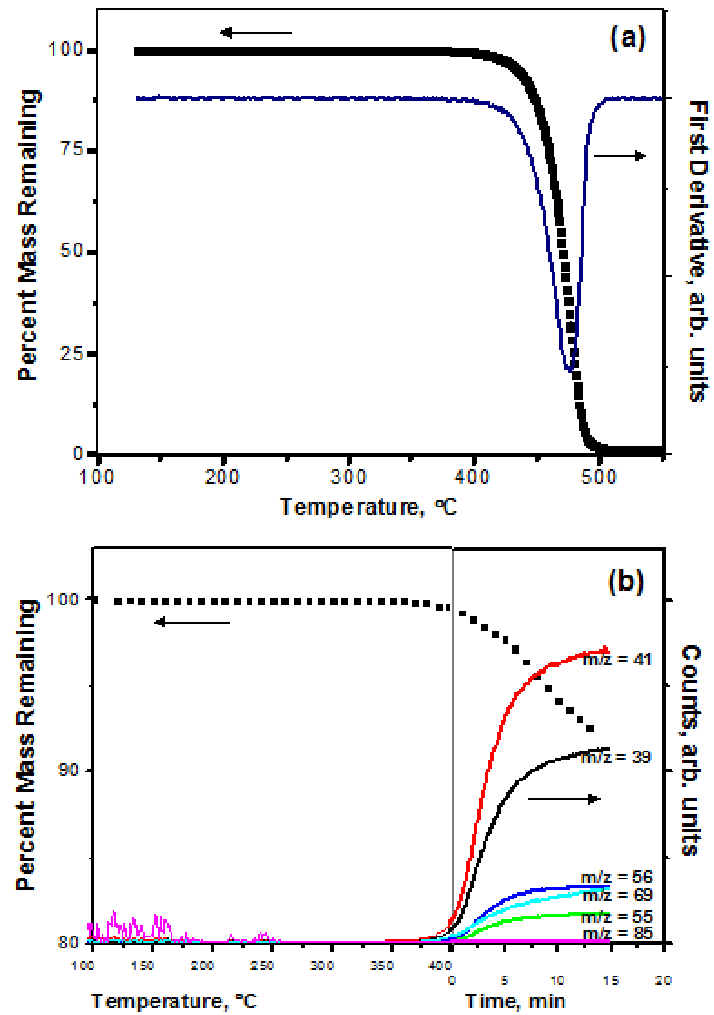
Decomposition rates will help determine limits for reactor contact times. These are examples of poor performers

Ionic Liquids with Good Thermal Stability



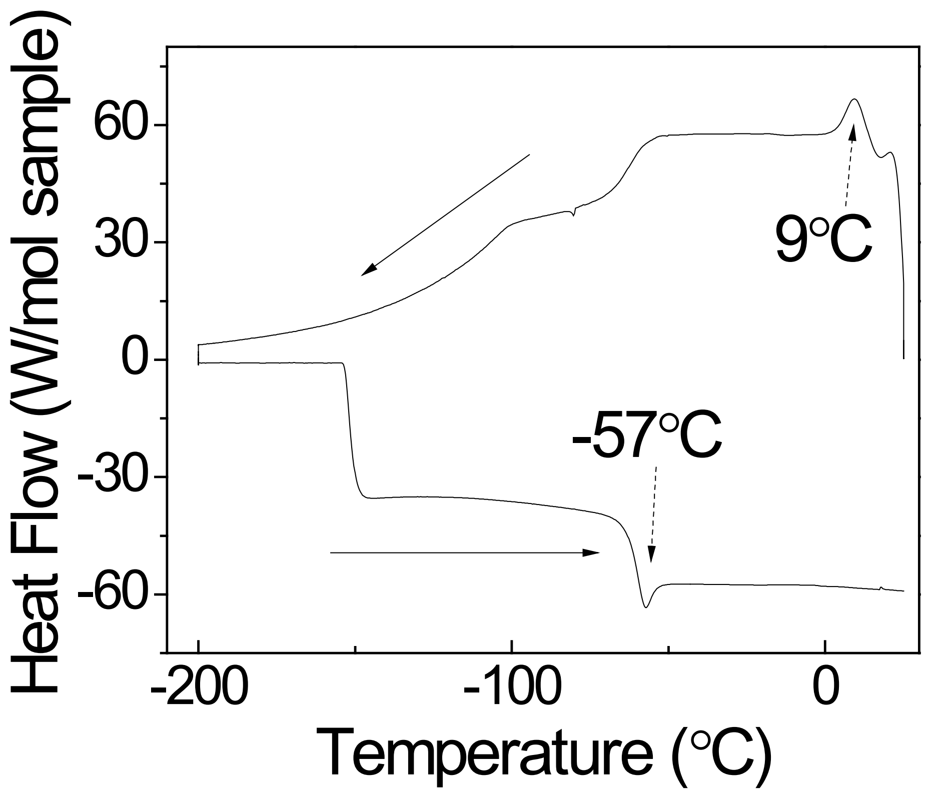






We have identified IL's that have good thermal stability

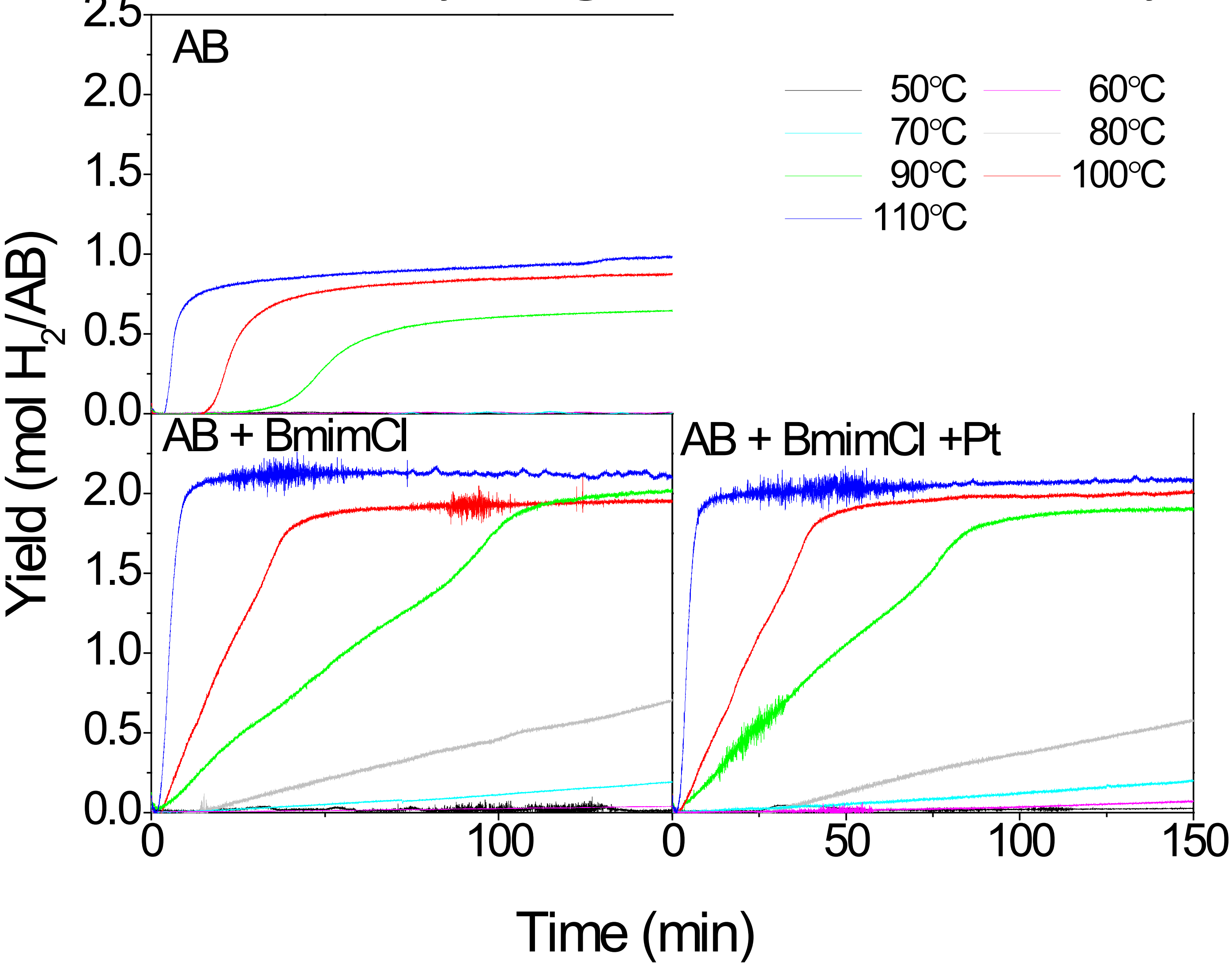
Low Temperature DSC used for determining phase changes in mixed IL:AB systems



Freezing: 9°C, Melting: -57°C → strange?

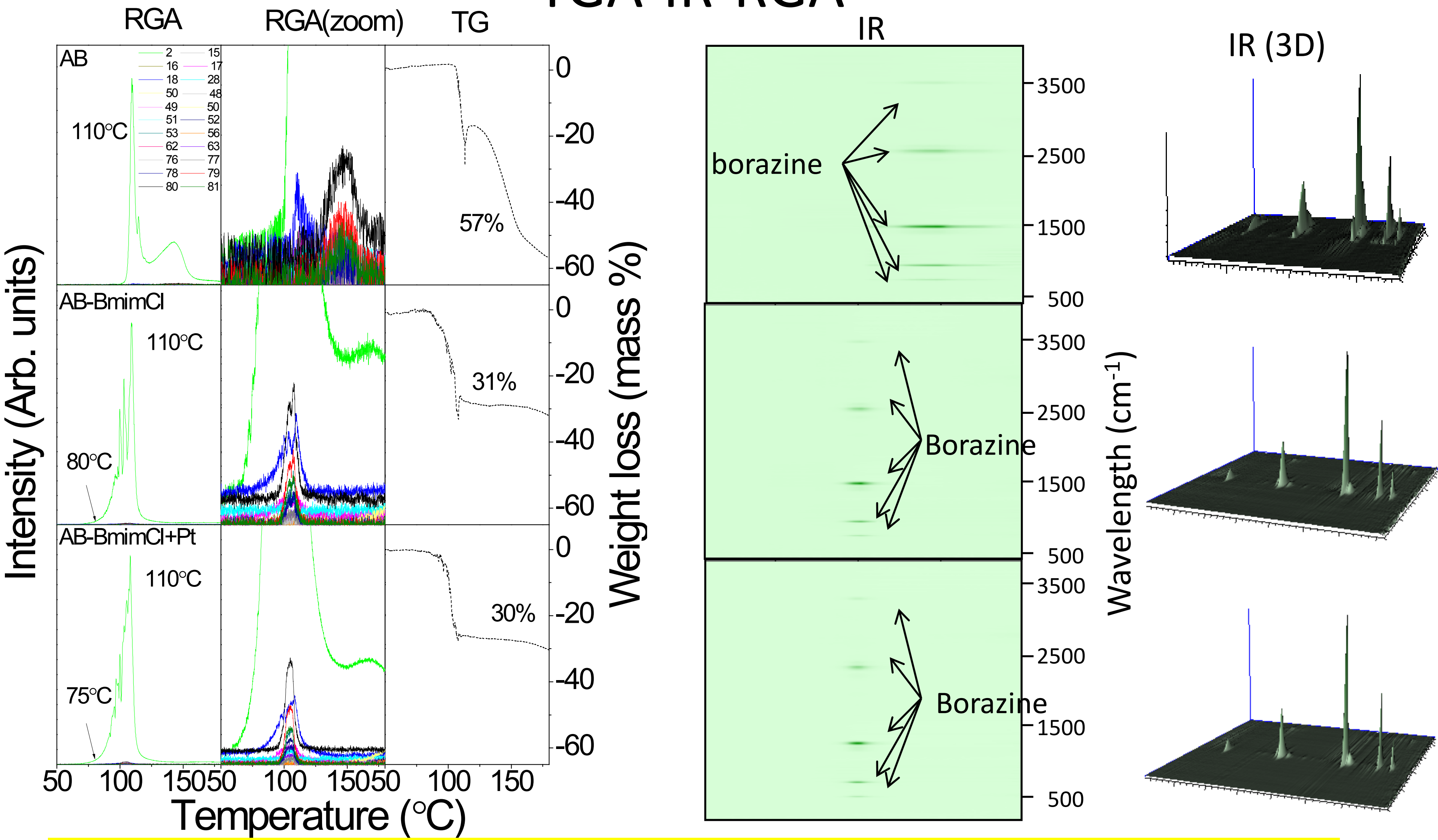
Unusual phase change behavior in mixed ionic liquid ammonia borane materials may have impact on storage life and must be considered when choosing an IL

Hydrogen Release in IL system



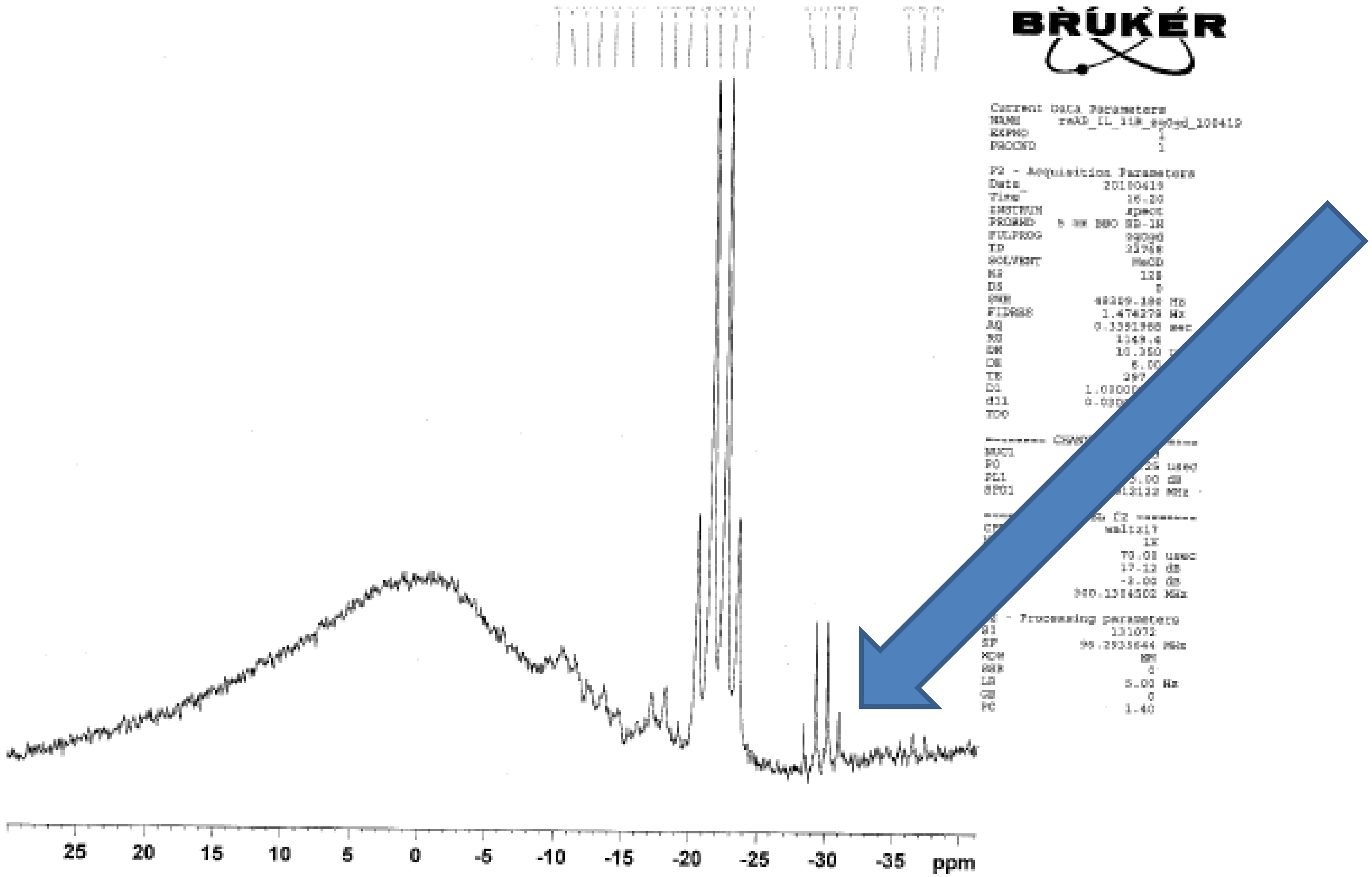
Platinum catalysts no longer show the significant improvements in kinetics observed in organic solves. Therefore for ionic liquid systems initial reactor kinetics, in collaboration with HSECoE, will involve simple thermal release

TGA-IR-RGA



- main impurity: borazine
- IL decreased impurities observed in gas phase and we believe catalysis will further improve hydrogen purity

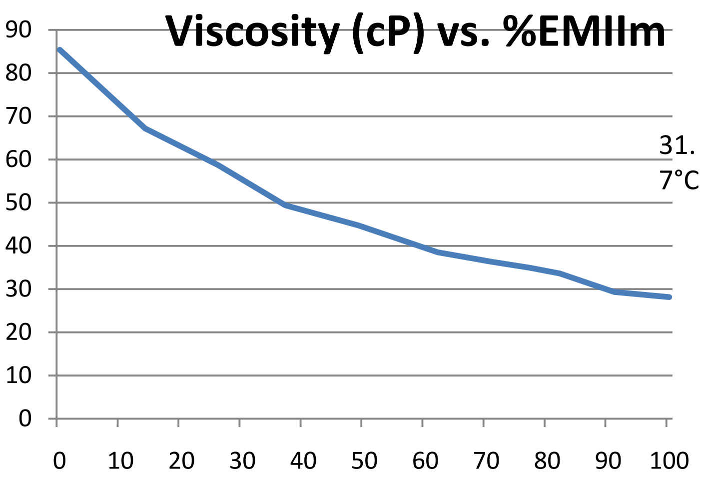
Compatibility with hydrazine regen

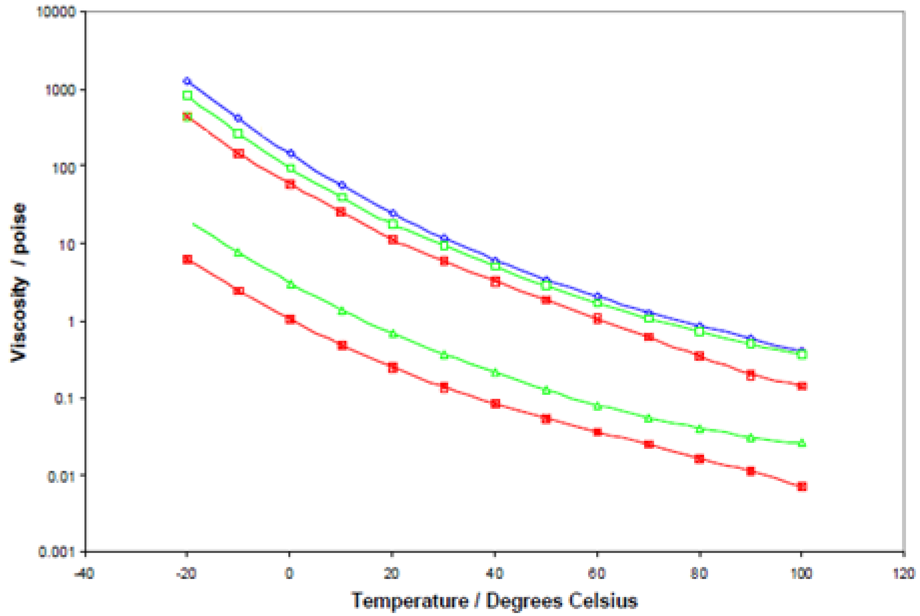


Impurity involves reaction of regen BH_3 with cation of IL

Ionic liquid can produce impurities in some cases! Yet another down select requirement.

Mixing IL's can change viscosity





Overall viscosity can be manipulated. Need to think about cost (mixed IL's) versus pump requirements (balance of plant)

Proposed Future Work

- Catalyst development
- Identify materials with NO PHASE CHANGES in operating temperature region
- Determine the limits of Wt% H_2 in an all liquid IL system?

Collaborations

Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Argonne NATIONAL LABORATORY

Penn UNIVERSITY of PENNSYLVANIA

Mandatory Summary Slide

- Cations have been identified that do not interfere with regeneration chemistry
- Anion selection rules understood
- No “volatile” solvents permitted
- Viscosity range (less than 2500 cP) determined in collaboration with Hydrogen Storage Engineering CENTER OF EXCELLENCE
- Liquid systems testing underway
- Catalysts development ongoing