Hydrogen Storage Engineering
CENTER OF EXCELLENCE

Chemical Hydride Rate Modeling, Validation, and System Demonstration

LANL Team

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DOE Fuel Cell Technologies Program Annual Merit Review,
EERE: Hydrogen, Fuel Cells and Infrastructure Technologies Program
Washington, DC May 14-18, 2012
Technology Development Manager : Ned Stetson

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U.S. Department of Energy
Energy Efficiency and Renewable Energy
Bringing you a prosperous future where energy is clean, abundant, reliable, and affordable

The Institute for Hydrogen and Fuel Cell Research

Project ID: ST007

LANL Project Overview and Relevance

Timeline

- Project Start Date: Feb FY09
- Project End Date: FY14
- Percent Complete: 55%

Budget

- Total Project Funding: $4.7M
  - DOE Share: $4.7M
- Funding:
  - 2011: $480K
  - 2012: $900K

Barriers

- **Barriers Addressed**
  - *Efficiency*
  - *Gravimetric Capacity*
  - *Volumetric Capacity*
  - *Durability/Operability*
  - *H_2 Discharging Rates*
    - *Start time to full flow*
    - *Transient Response*
  - *H_2 Purity*
  - *Environmental, Health & Safety*

Project Timeline

Phase 1									Phase 2						Phase 3					
2009			2010				2011		2011		2012				2013				2014	
Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2

System Architect Accomplishments/Highlights

- Technology Team Lead for:
  - ✓ System Design Concepts and Integration: *delivered preliminary design concepts*
    - *Fluid-phase chemical hydrogen storage*
      - *AB compositions*
      - *Alane compositions*

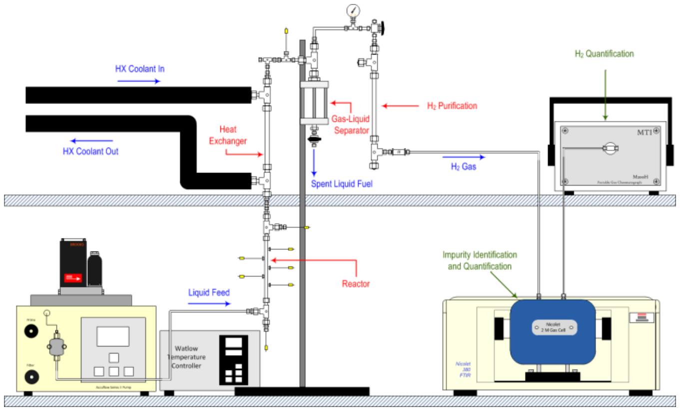
- Chemical Hydrogen Storage **System Architect & Fluid-Phase System Designer**

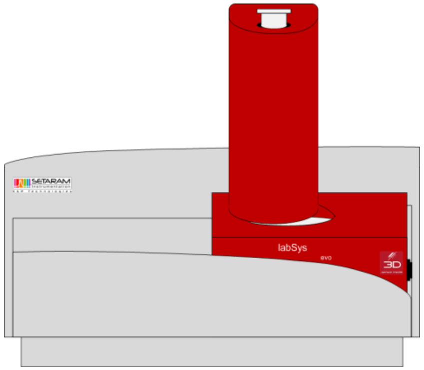
  Monitored progress on chemical hydrides technology across the technology areas for needed features to be advanced and to insure needed communication across groups and areas occurs

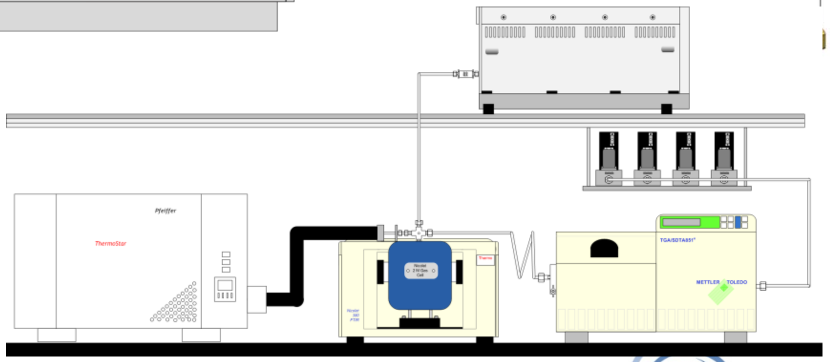
  - ✓ Assessed endothermic and exothermic systems
  - ✓ Performed FMEA analyses on fluid-phase chemical hydrogen systems
  - ✓ Performed Chemical Hydrogen downselections, discontinuations, and GO/NO-GO decisions (*details in Reviewer Only Slides*)
  - ✓ Refocused Chemical Hydrogen research efforts (*details in Reviewer Only Slides*)
    - Component targeted research
      - — SMART milestones
      - — Deliverables

Accomplishments

- ✓ **Reaction Characteristics**
- ✓ **Chemical Compatibilities**
- ✓ **Viscosities**
- ✓ **Reactor Design**
- ✓ **Hydrogen Purification**
- ✓ **Discontinued Research**







Reviewer Only Slides

- ✓ Startup Energy
  - Endothermic vs. Exothermic

Fluid-Phase Chemical Hydrogen Media

Compositions

$$(AB)_{solubility} = \frac{(mass)_{AB}}{(mass)_{solvent}} = fcn\left[\{T\}, \begin{Bmatrix} Ionic \\ Liquid \end{Bmatrix}_{i=0,1,2}, \begin{Bmatrix} Mass \\ IL \end{Bmatrix}_{i=0,1,2}, \begin{Bmatrix} IL \\ Purity \end{Bmatrix}_{i=0,1,2}, \begin{Bmatrix} AB \\ Purity \end{Bmatrix}, \begin{Bmatrix} H_2Prod \\ Additive \end{Bmatrix}^{synthesized}_{j=0,1,2}, \begin{Bmatrix} Mass \\ Additive \end{Bmatrix}^{synthesized}_{j=0,1,2}\right]$$

Thermo-Physical Properties

- Phase change
- Solubility
- Freezing/Boiling points
- Solvent Compatibility
- Viscosity
- Solvent Stability

Dissolution Kinetics

- Particle Size
  - sublimation,
  - recrystallization
- Temperature
- Mixing

Health & Safety Conscious

- Human
- Environmental

Cost Conscious

Dehydrogenation Kinetics

- Space-time yield
- Selectivity
- Conversion
- Stability

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HSECoE

Reaction Characteristics

- Synthesize/ Identify
- Determine Stability
- Combine with AB
- RXN Characteristics
- Reactor Design & Operation

Relevance:
To quantify reaction characteristics that will aid in the development of low mass and low volume system components (i.e., gas-liquid separators, reactors, hydrogen purification components, ballast tanks, fuel tanks, etc.,)

Accomplishments: Reaction Characteristics

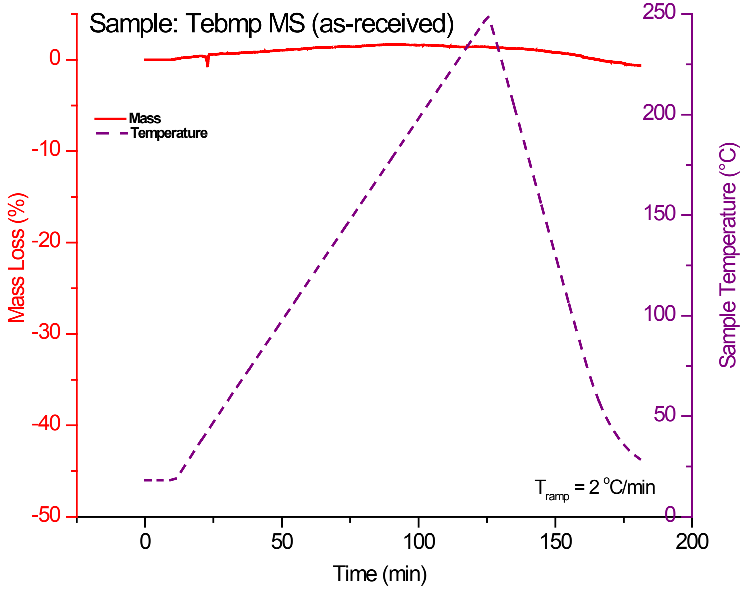
Solvent Stability is critical

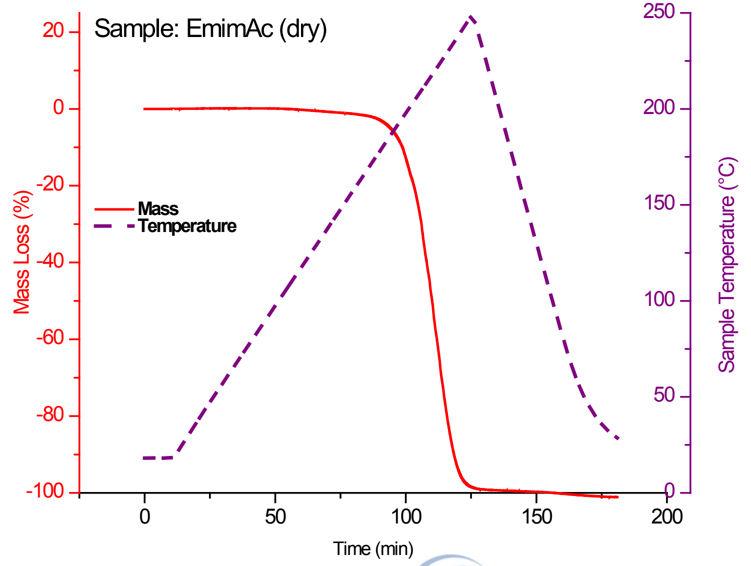
- Maintain fluid phase
- Eliminate reactor fouling
- Reduces gas-phase impurities

Solvent Requirements

- High boiling point
- Chemically inert
- High solubilities for AB
- Thermally stable
- Low freezing point

AB solvating candidates have been identified (Ben Davis, LANL)

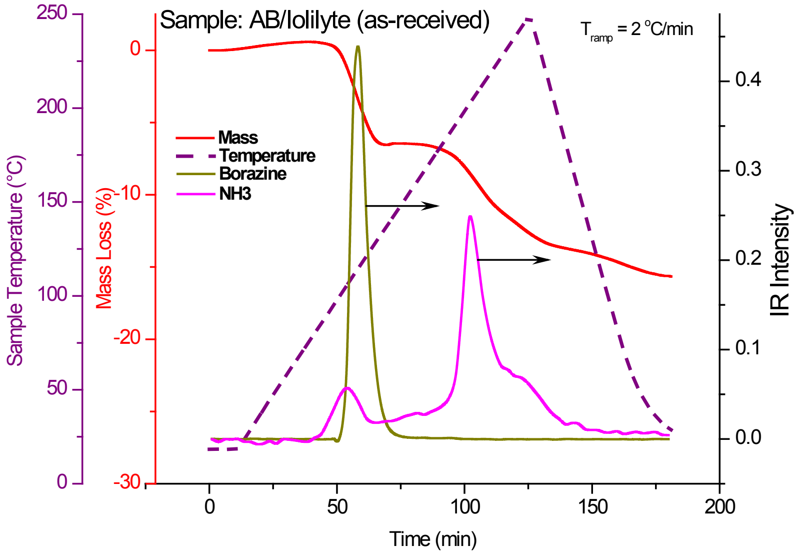




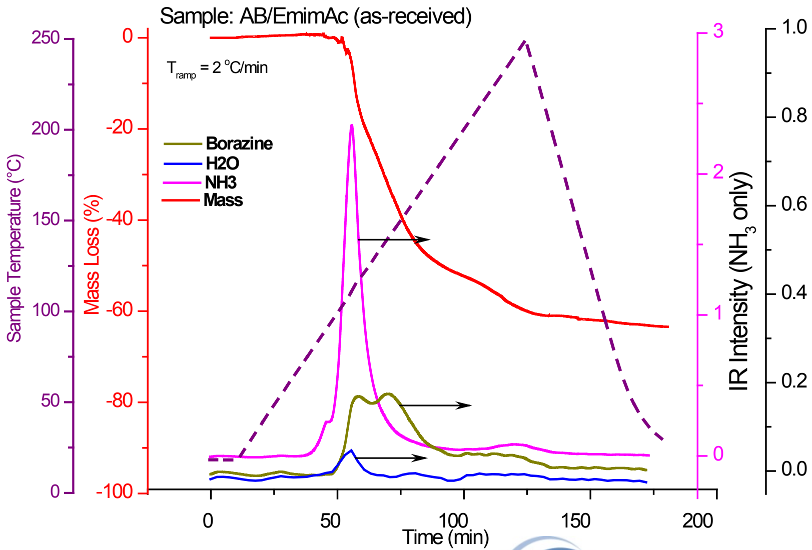
Accomplishments: Reaction Characteristics

Fluid-phase AB compositions

- Temperature operability range
- Impurities
- Hydrogen yields
- Phase changes



Reaction characteristics AB compositions determine the reactor design and operation

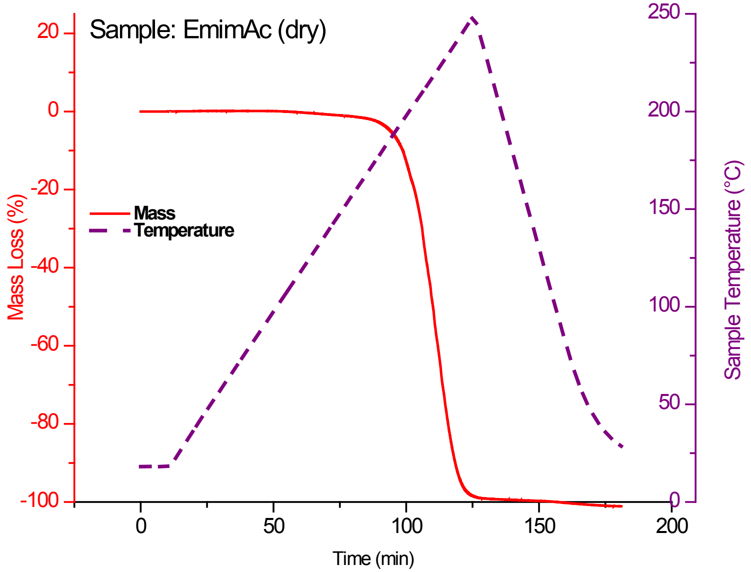


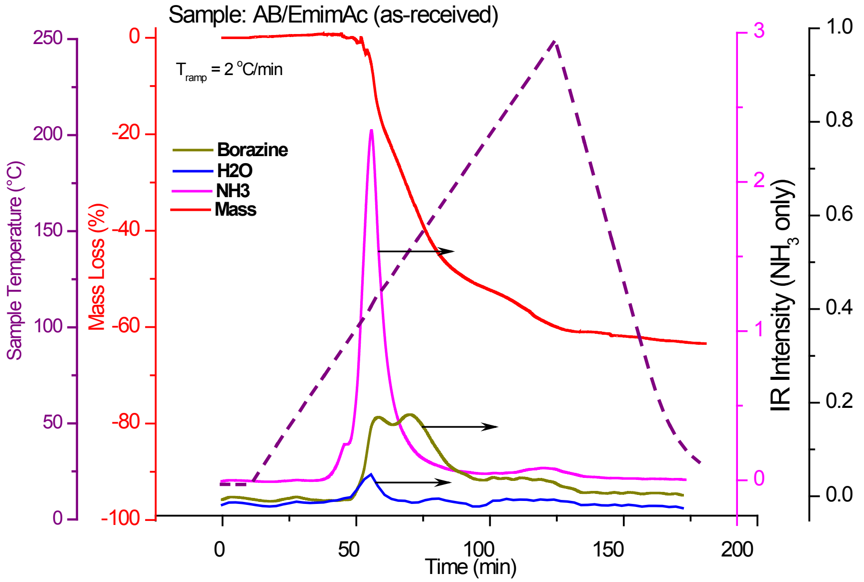
Accomplishments: Reaction Characteristics

Determine Stability

Combine with AB

RXN Characteristics





$$r_{solvent\ rxn} \neq 0 \ \ for\ T < 140°C \quad \Rightarrow$$ Discontinued

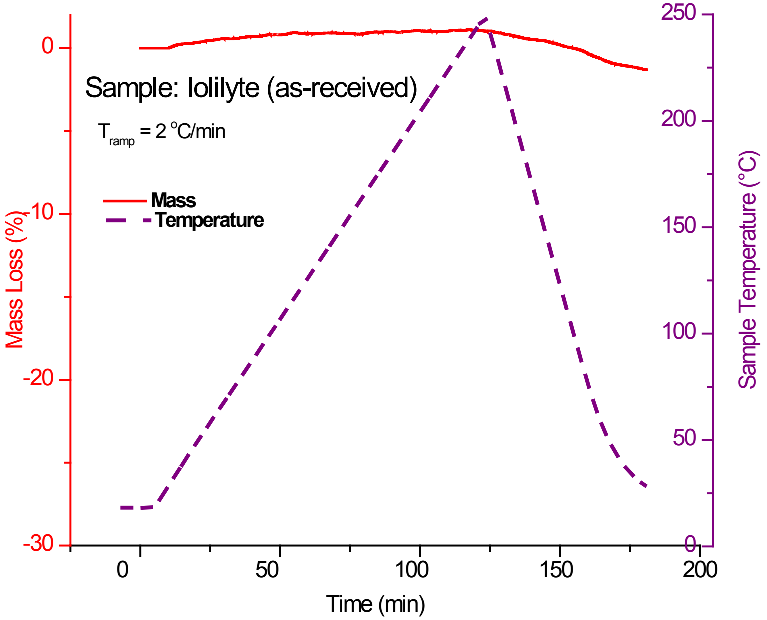
Overlapping kinetics result in poor reaction selectivity control

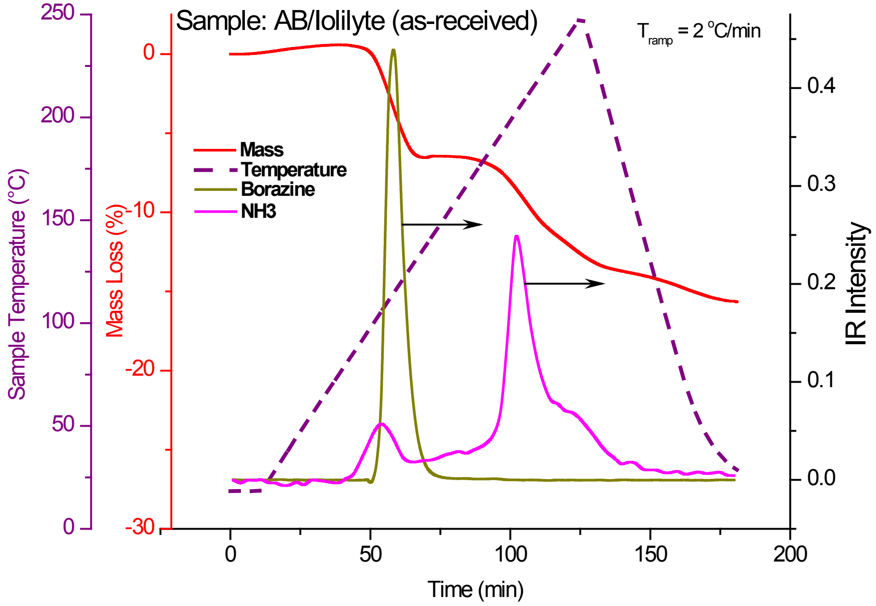
Accomplishments: Reaction Characteristics

Determine Stability

Combine with AB

RXN Characteristics





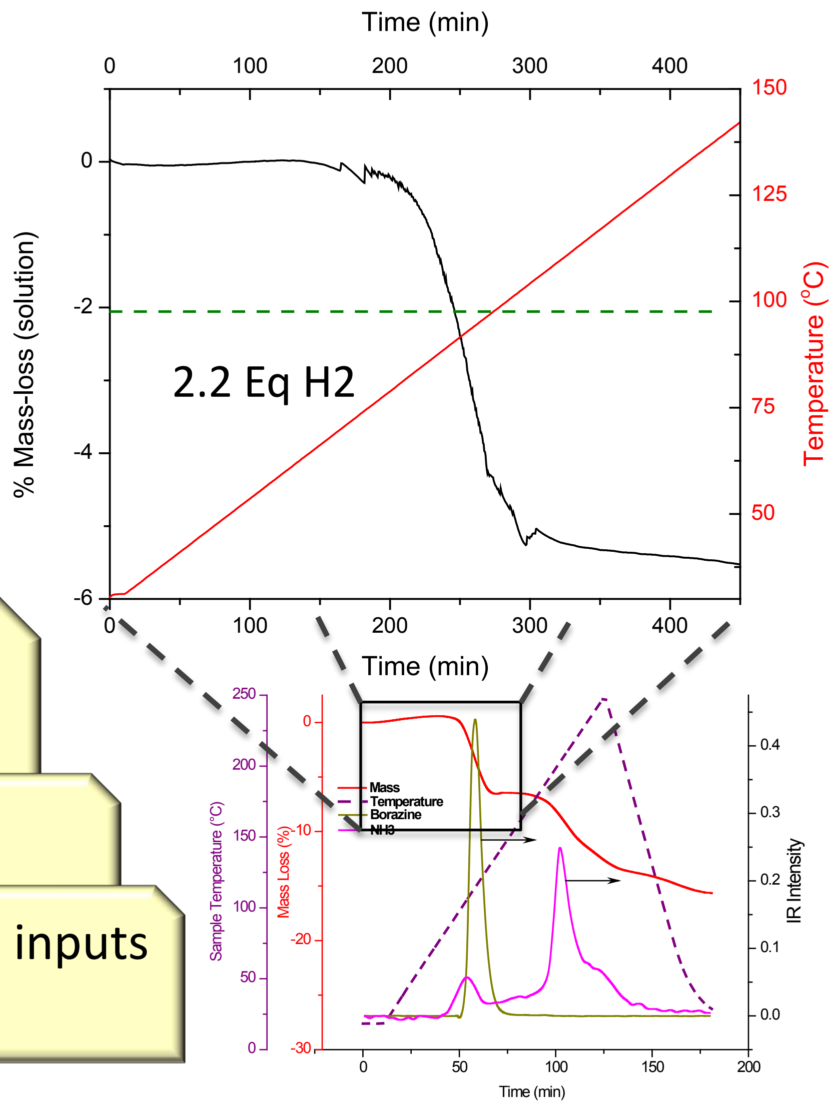
$$r_{H_2} >> r_{solvent\ rxn} \quad for\ T < 140°C$$

Engineered compositions must demonstrate clearly distinct kinetics regions

Accomplishments: Reaction Characteristics

Identified optimal reactor conditions

1. Maximize H_2 selectivities
2. Reduce impurity production
3. Mitigate reactor fouling
4. Mitigate solvent decomposition
5. Reactor designs
6. System level modeling inputs

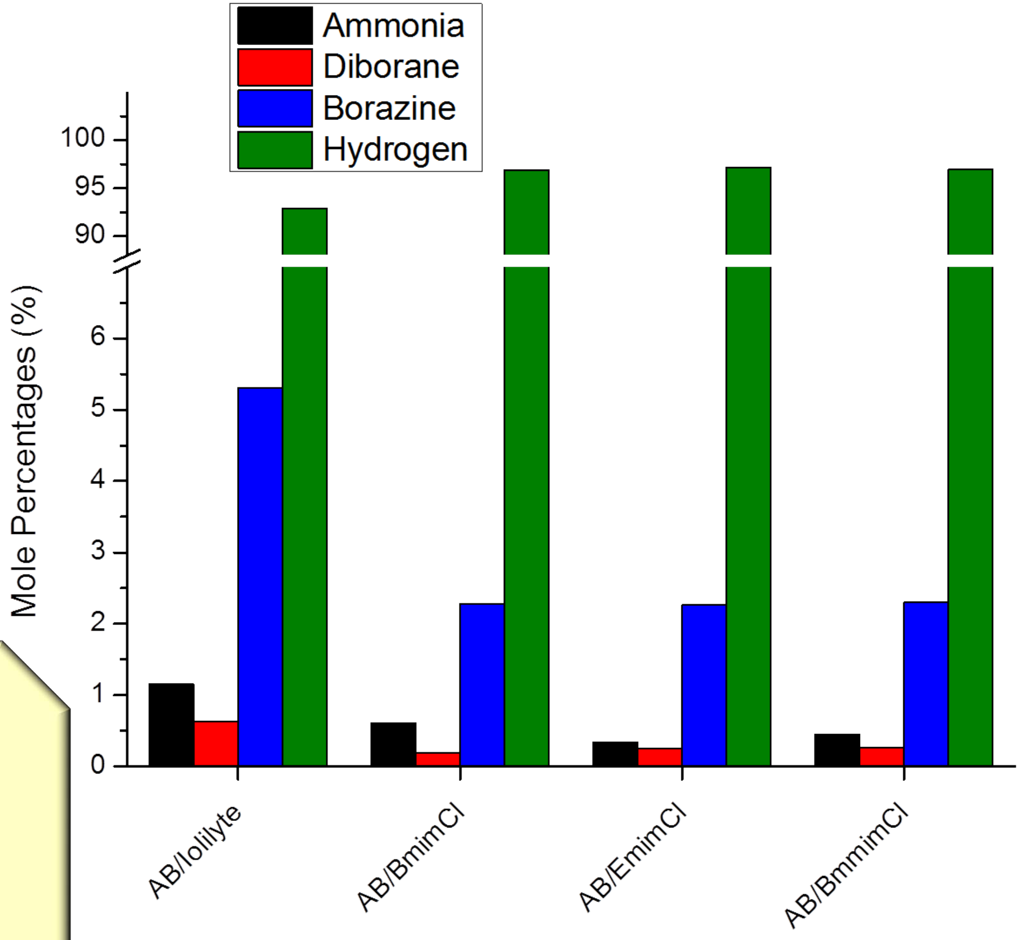


Accomplishments: Reaction Characteristics

Fully characterized reaction profiles

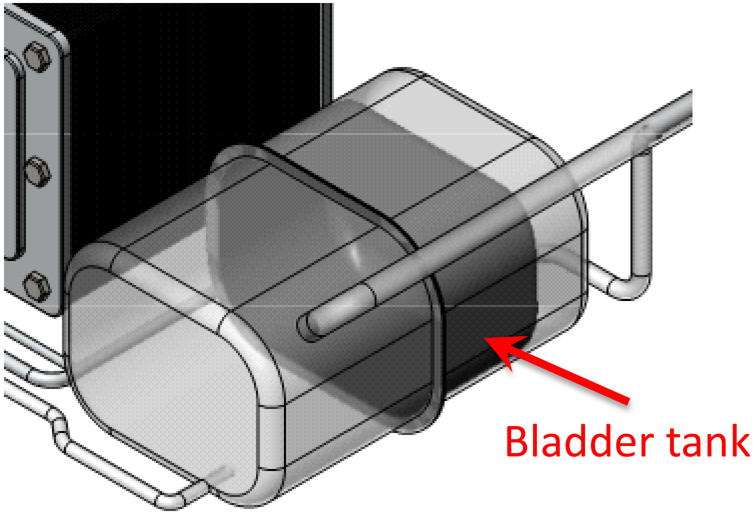
1. Selectivity as a fcn of temperature

2. *In situ* quantification
   - ✓ Hydrogen
   - ✓ Diborane
   - ✓ Ammonia
   - ✓ Borazine



2.2 Eq H_2 @ T_{max} = 140°C

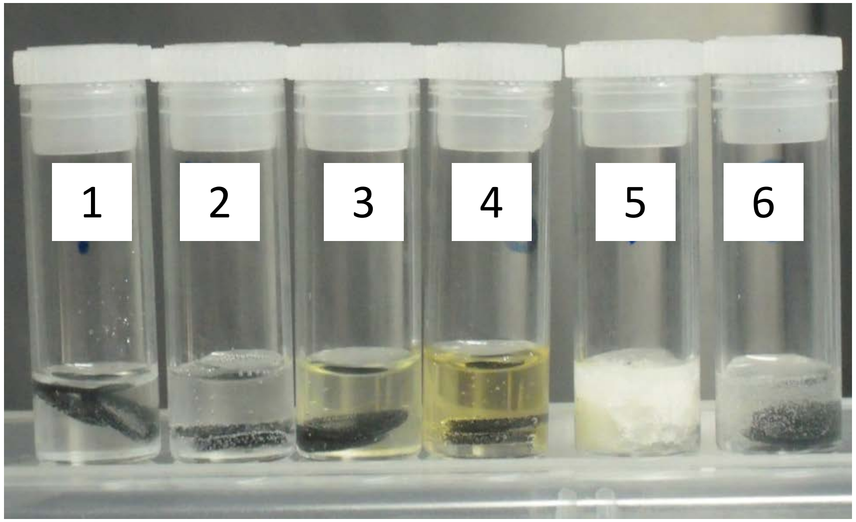
Accomplishments: Chemical Compatibilities



1: AB/Iolilyte (2 months)
2: AB/TbmpMS (2 months)
3: AB/DmimDmp (2 months)
4: AB/EmimAc (2 months)
5: AB/EmimDep (2 months)
6: AB/BmimCl (2 months)
7: PNNL AB Slurry (2wks)

No physical degradation of bladder material when exposed to various AB compositions

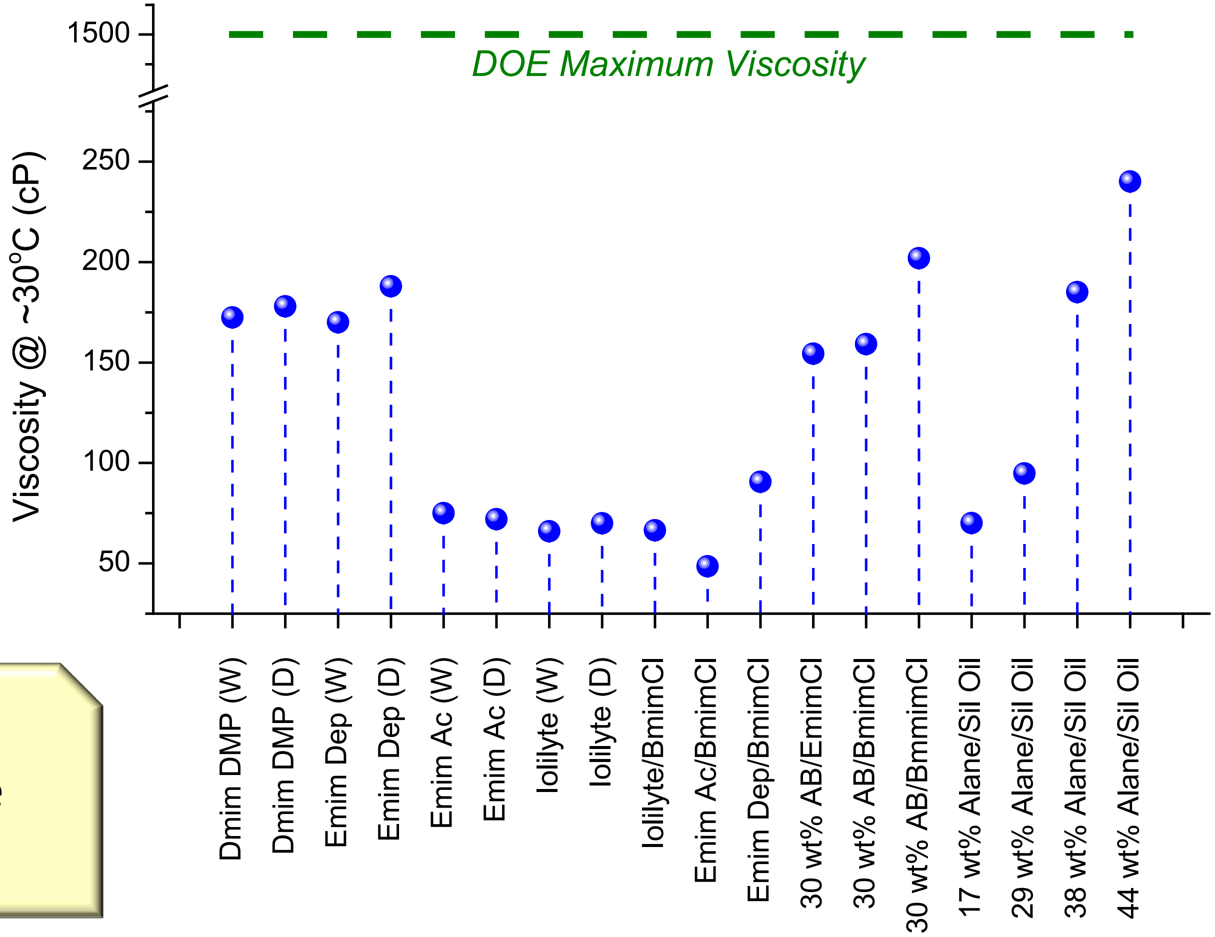
1. Need to quantify chemical and physical changes to bladder material



Accomplishments: AB & Alane Fluid-Phase Viscosities

All neat and as-prepared fluid-phase AB and alane compositions have viscosities well below ECoE targets

1. Low temperature viscosities needs to be quantified



$$\uparrow \mathit{Viscosity} \Rightarrow \uparrow \mathit{Pump\ Power} \Rightarrow \downarrow \mathit{System\ Efficiency}$$

Subscale Reactor Design

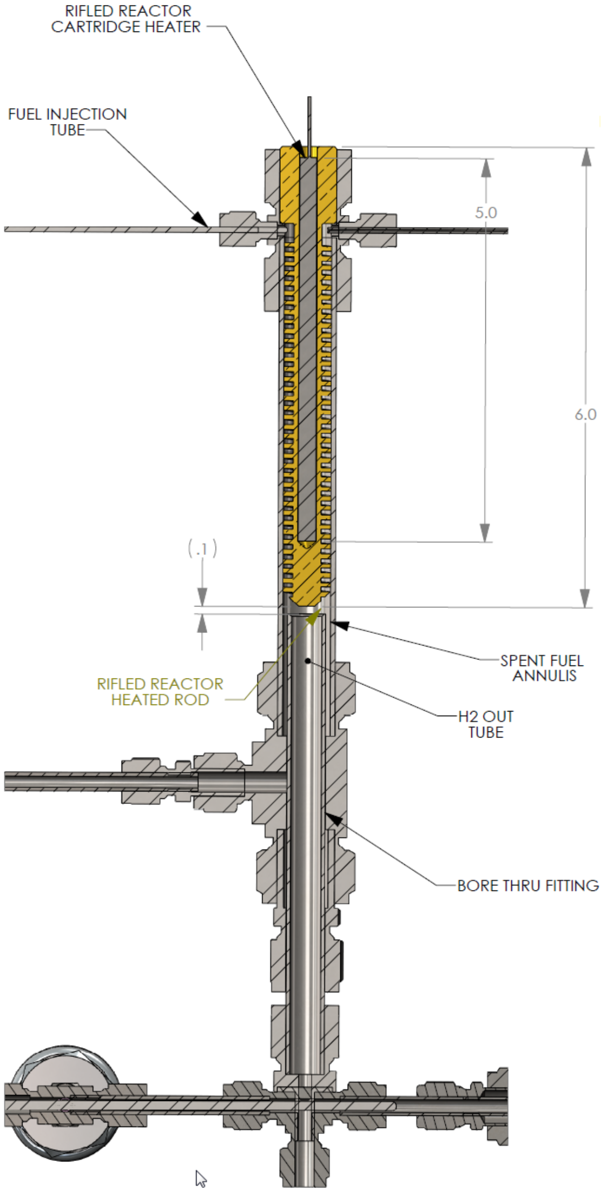
1. To assess reactor performance as a function of design
    - *Space-Time Yield*
    - *Reactor Durability*
    - *Reactor Operability*
    - *Impurities*
    - *Downstream Effects (i.e., GLS, Purification, etc.)*

2. To down-select the most viable reactor design

Relevance: Develop and demonstrate novel reactors

- ✓ High hydrogen space-time yields
- ✓ High heat transfer rates
- ✓ Promote gas-liquid separation
- ✓ Mitigate reactor fouling

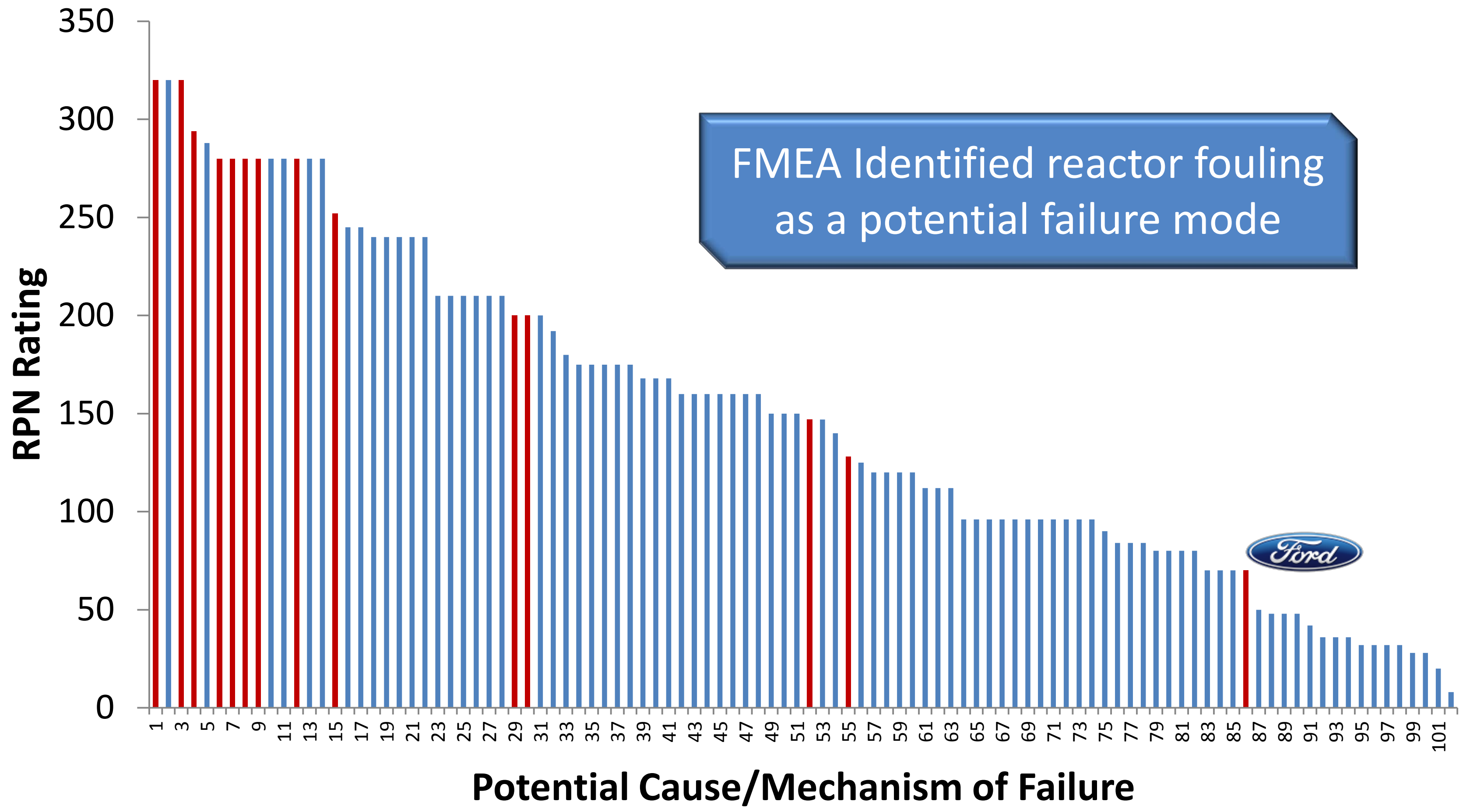
Accomplishments: Reactor Design



Reactors will be tested and benchmarked

1. Maximum H_2 space-time Yield
2. Promote gas-liquid separation
3. Mitigate fouling

Accomplishments: Reactor Design



FMEA Identified reactor fouling as a potential failure mode

Brick colored bars indicate failure mechanisms resulting from fouling

Accomplishments: Reactor Design

Liquid Composition:

- 5 wt.% AB/tetraglyme

Reaction Conditions:

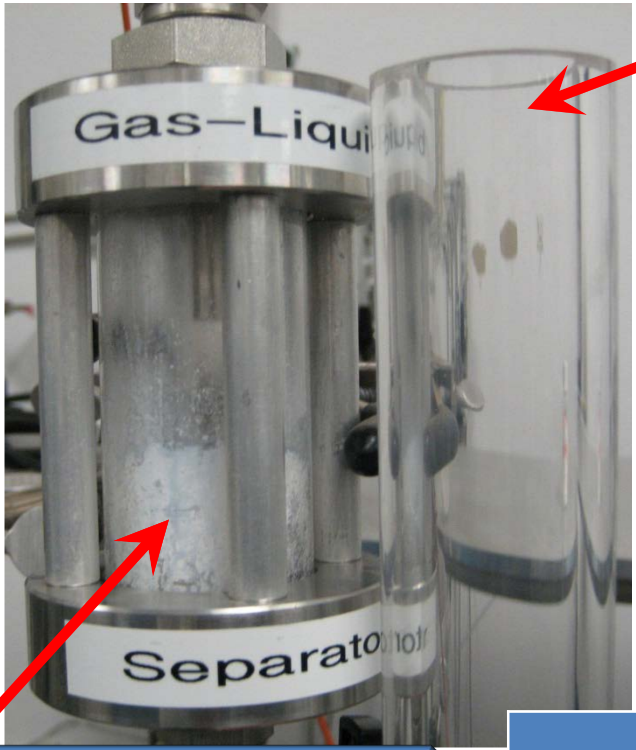
- T_{stpt} = 190 °C
- Space-time ≈ 0.5 min

Reactor Type:

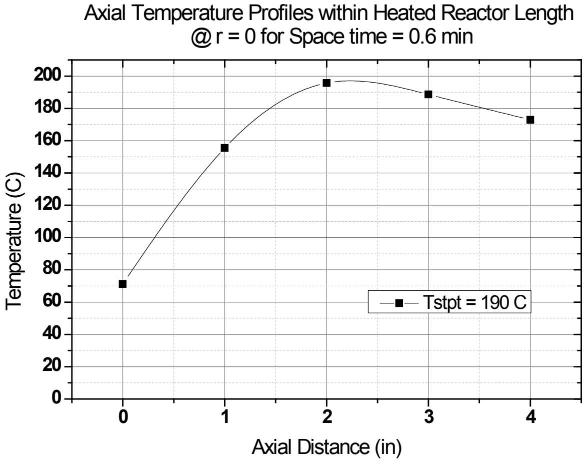
- Vertical flow reactor

Reaction Type:

- Uncatalyzed thermal decomposition



As-received material of construction



Tetraglyme

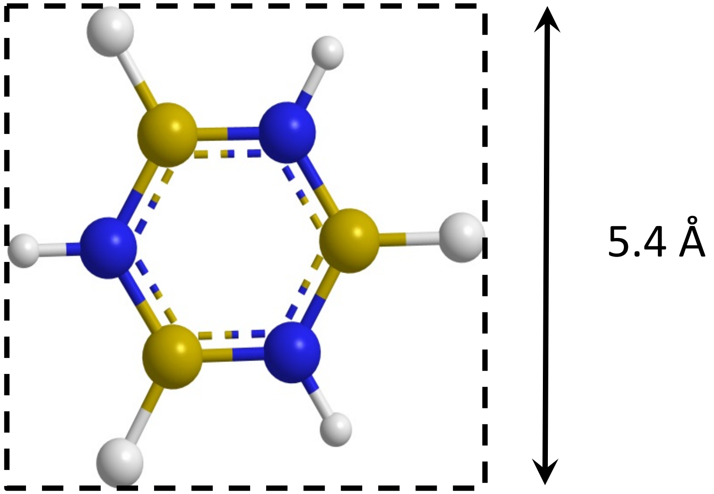
Parameter	Value
Boiling Point (°C @ 760 mm Hg)	275
Freezing Point (°C)	-29.7
Vapor Pressure (mm Hg @ 20°C)	< 0.01
Viscosity (cP @ 20°C)	4.1

Fouling was not observed in the gas-liquid separator at temperatures ≤ 200 °C for a 5 wt.% AB-tetraglyme composition

Note: Tetraglyme was discontinued as a solvent agent due to low AB solubility

Hydrogen Purification

- Borazine Scrubber Targets:
    - Adsorbent mass = 4 kg
    - Adsorbent volume = 3.6 L

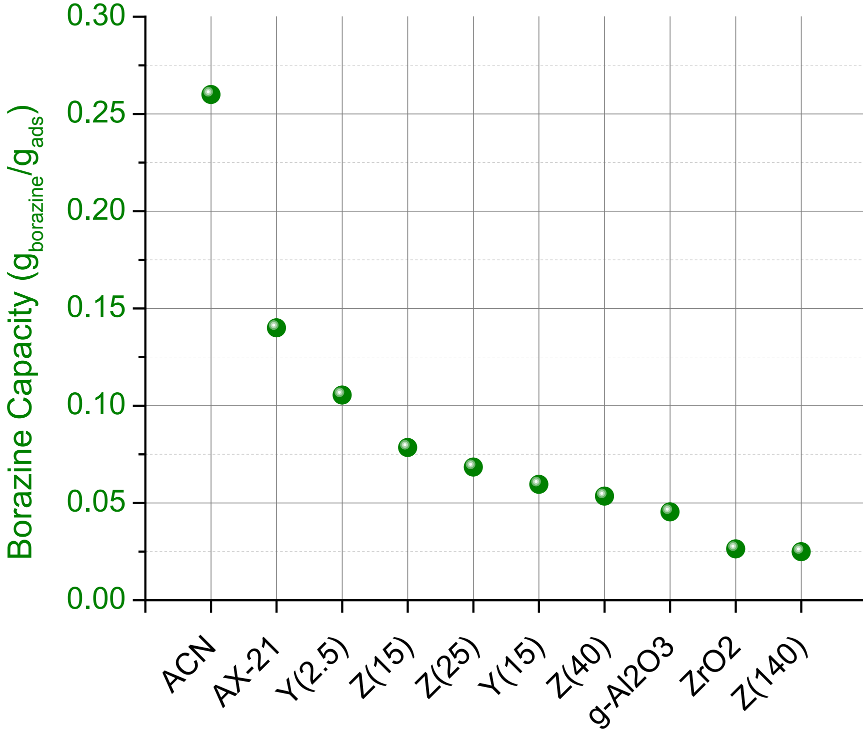


Borazine

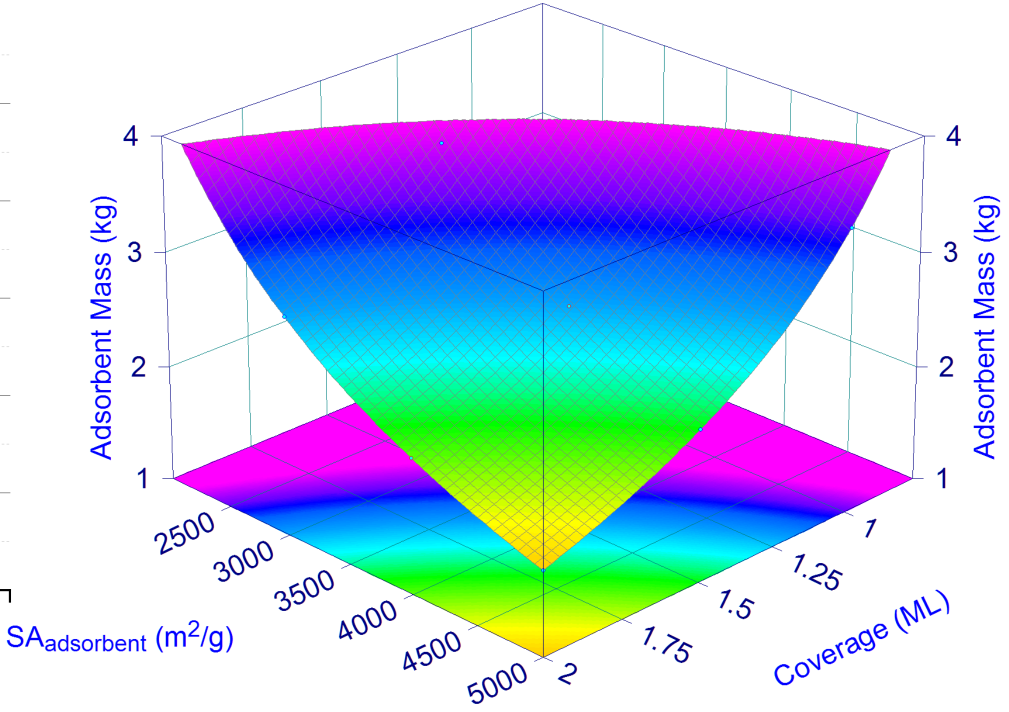
Relevance: To develop and demonstrate hydrogen purification technologies that produce fuel-cell grade hydrogen meeting DOE purity targets

Accomplishments: Borazine Adsorption

Borazine Scrubber
Target Mass = 4 kg



Borazine Scrubber
Target Volume = 3.6 L



Adsorbents have been identified that effectively adsorb borazine

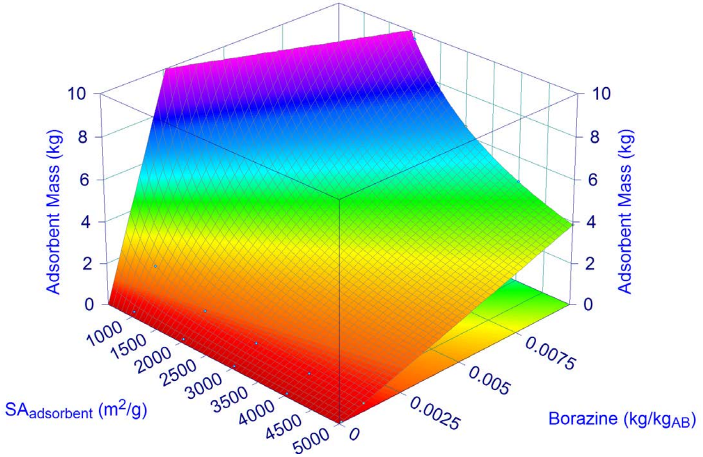
Accomplishments: Borazine Adsorption

- Zeolite Shortcomings:
  - Low coverage's due to acid site density
  - Low surface area
- Need to explore higher surface area chemically active adsorbents
  - Activated Carbon
  - MOFs (BASF)

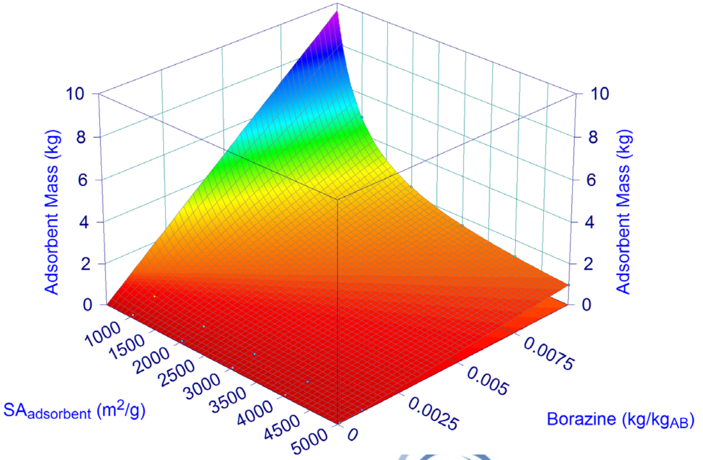
Physical Adsorbents can meet borazine scrubber ECoE mass targets if

1. Chemically modify adsorbent
2. Reduce borazine via reaction selectivity
3. Increase adsorbate coverages to greater than one

Adsorbent Mass (kg) required for an 1800 mile replacement interval as a fcn of adsorbent surface area (m^2/g) and borazine produced (kg/kg_{AB}) for a borazine coverage of 0.25 monolayers



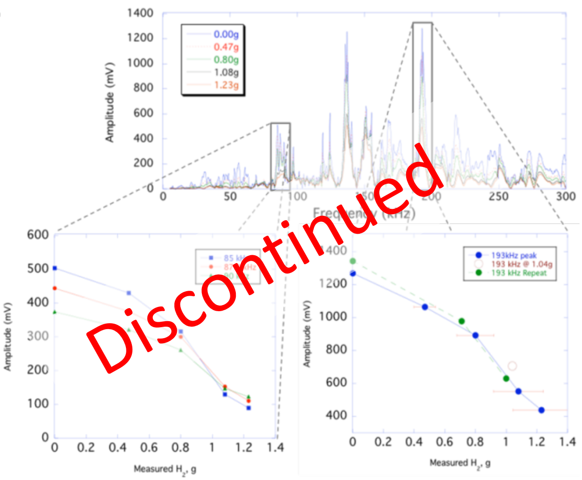
Adsorbent Mass (kg) required for an 1800 mile replacement interval as a fcn of adsorbent surface area (m^2/g) and borazine produced (kg/kg_{AB}) for a borazine coverage of 1.00 monolayers

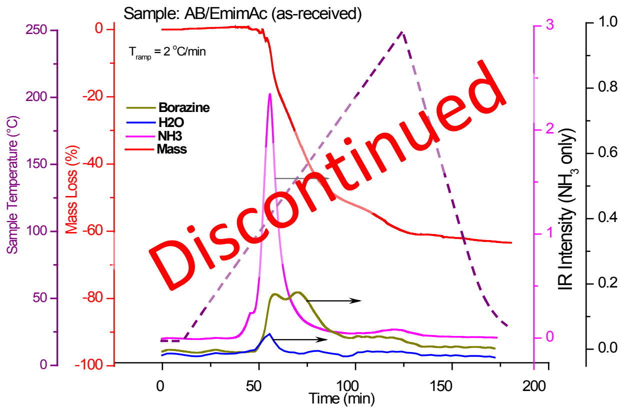


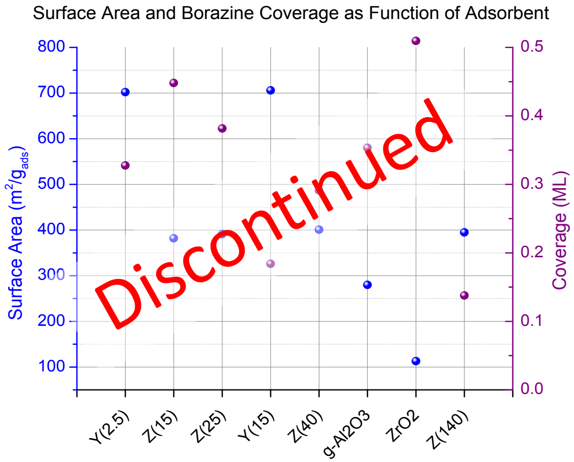
Discontinued Research

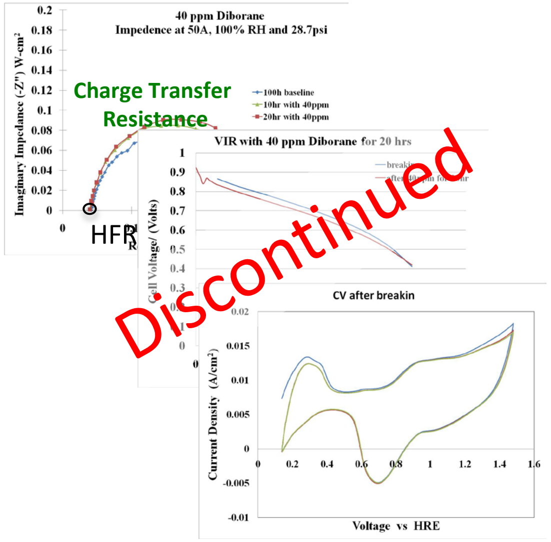
Accomplishments: LANL Discontinued Research

- Various liquid-phase hydrogen bearing additives (e.g., sec-butyl AB)
- Various AB solvating agents (e.g., EmimAc, EmimDep, etc.)
- Various physical adsorbents for high impurity concentrations
- Fuel gauge sensor research scope
- Fuel cell tolerance testing research scope









LANL Accomplishments Summary

1. *In situ* quantification of all gas phase products generated from fluid-phase AB compositions
2. Identified reactor operating conditions that
   - maximize hydrogen selectivities,
   - minimize impurities production, and
   - eliminate solvent decomposition
3. Demonstrated that borazine can be scrubbed with regenerable adsorbents
4. Demonstrated that reactor fouling can be mitigated by reactor operating temperature
5. No apparent incompatibilities observed with bladder materials and fluid-phase AB compositions
6. Designed and built novel fluid flow reactors
7. Demonstrated fuel gauge sensor for metal hydrides and chemical hydrogen storage media
8. Refocused Research Efforts of the Chemical Hydrogen Research Group
9. Performed Downselections, Discontinuations, and GO/NO-GO Decisions
10. Developed a comprehensive component testing plan for the Chemical Hydrogen Research Group

LANL Future Work

Task	Material Tested	Test Apparatus	Task Outputs	System Engineering Inputs (as necessary)
Reactor Fouling/ Impurities	Slurry Alane (6.0 wt. % H2)	Flow through reactor	● Degree of reactor fouling ● Reactor efficiency ● Reaction selectivity	● System design strategies for mitigating reactor fouling ● Impurity levels for H2 purification sizing ● Reactor design improvements ● Preliminary observations of GLS fouling
	20 wt. % AB slurry			
	40 wt. % AB slurry			
	Fluid phase AB (6.0 wt. % H2)			
Borazine Purification	Chemically modified adsorbents	EGA	● Required mass and volumes of adsorbent materials	● Updated system mass and volume projections
Novel Reactor Design and Testing	Fluid-phase AB compositions	Novel reactors with gas analysis	● Degree of reactor fouling ● H2 space-time yield ● Reaction selectivity	● Reactor performance ● Impurity levels for H2 purification sizing ● Reaction characteristics ● Preliminary observations of GLS fouling
Materials Engineering / quantification	Fluid-phase chemical H2 storage media	TGA, EGA, DSC, etc.,	● viscosity ● impurities ● freezing points	● System design modifications ● System design/operation limitations ● Reaction characteristics

LANL Milestones

Component	Phase 2 S*M*A*R*T Milestones
Materials Engineering	Report on ability to develop a 40wt. % liquid AB material having viscosity less than 1500cP pre- and post-dehydrogenation and kinetics comparable to the neat.
Reactor	Report on ability to develop a flow through reactor capable of discharging 0.8 g/s H2 from a 40 wt.% AB fluid-phase composition having a mass of no more than 2 kg and a volume of no more than 1 liter.
Borazine Scrubber	Report on ability to develop a borazine scrubber with a minimum replacement interval of 1800 miles of driving resulting in a minimum outlet borazine concentration of 0.1 ppm having a maximum mass of 3.95 kg and maximum volume of 3.6 liters.

Collaborations

External Collaborators	Effort	Contact
H_2 Codes and Standards	General Guidance	C. Padro (LANL)
Chemical Hydrogen Storage Researchers	Materials Updates	J. Wegrzyn (BNL)
		T. Baker (U. Ottawa)
		B. Davis (LANL)
H_2 Production & Delivery Tech Team	WTT Analyses	M. Pastor (DOE)
		B. James
LANL Fuel Cell Team	General Guidance Fuel Cell Impurities	T. Rockward (LANL)
		R. Borup (LANL)
H_2 Safety Panel	General Guidance/Concerns	S. Weiner
SSAWG	Technical Collaboration	G. Ordaz (DOE)
H_2 Storage Tech Team	General Guidance	Ned Stetson (DOE)
Argonne National Laboratory	Independent Analyses	R. Ahluwalia

ECoE Collaborators	Effort	Contact
UTRC	Ammonia Scrubbing	B. van Hassel
	Simulink® Modeling	J. Miguel Pasini
PNNL	MOR	E. Ronnebro
	System Modeling	K. Brooks/M. Devarakonda
	BOP	K. Simmons
NREL	Vehicle Modeling	M. Thornton

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Fuel Cell Technologies Program: Hydrogen Storage Technology Development Managers:

Ned Stetson and Jessie Adams

Backup Slides

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