Chemical Hydrogen Storage R&D at Los Alamos National Laboratory

Project ST6

Ben Davis, Himashinie Diyabalanage, Charles Hamilton, Roshan Shrestha, Tom Baker, Anthony Burrell, Neil Henson, Michael Inbody, Kevin John, Troy Semelsberger, Frances Stephens, John Gordon, Kevin Ott

2008 DOE Annual Merit Review
Arlington, VA

This presentation does not contain any proprietary or confidential information

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Overview

Timeline

- Start: FY 05
- End: FY 09
- 60% Complete

Barriers

- Weight and Volume
- Flow Rate
- Energy Efficiency
- Cost
- Regeneration Process
- System Life-Cycle Assessments

Budget

•Estimated Project Funding
- $9.61 M

•FY 07
- $1,837 K

•FY 08
- $2,455 K

Partners

- Chemical Hydrogen Storage Center of Excellence
- IPHE (Singapore, UK, New Zealand)

Objectives

- Develop and demonstrate heterogeneous catalysts and continuous flow reactor operation for hydrogen release
- Develop liquid ammonia-borane (AB) fuels and increase rate and extent of hydrogen release
- Identify and demonstrate new materials and strategies for near-thermoneutral hydrogen release ($\Delta G°$ = ideally no less negative than ca. –0.8 kcal/mol)
- Demonstrate all chemical steps and conduct engineering assessment for energy efficient AB regeneration process (high yields, rates, and energy efficiency, integrate steps when possible)
- Develop materials and processes to minimize gas-phase impurities, and demonstrate adequate purity of hydrogen stream
- ✓ Provide materials chemistry support for PSU work on electrochemical conversion of B-O to B-H (completed as part of phase 1)

Milestones

Completed (green) In progress (yellow)

Q4 FY07	Completed	Complete down-selection process for 2010 engineering & 2015 science in collaboration with the entire Center
Q1	Completed	Define independent chemical steps for regeneration of spent fuel and document energy requirements per step. (DOE Joule Milestone)
Q2	In progress	Complete laboratory scale demonstration of regeneration chemistries for at least two approaches and document reaction yields. (DOE Joule Milestone)
Q3	Completed	Prepare and characterize variety of M-B-N-H compounds for high capacity, potentially reversible hydrogen storage
Q3	Completed	Determine thermodynamic efficiency of demonstrated spent fuel regeneration routes. (DOE Joule Milestone)
Q4	In progress	Develop heterogeneous catalysis for hydrogen release from AB
Q4	In progress	Use mechanistic results and theory to guide catalyst design for optimal rates and extent of hydrogen release from liquid amine-borane fuels
Q4	In progress	Develop chemical hydrogen storage regeneration methods at laboratory-scale, obtain initial data for efficiency and cost analysis, and demonstrate lab-scale reactions capable of at least 40 percent energy efficiency

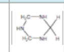
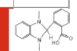
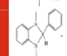
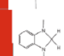
Approach: Los Alamos Technical Contributions

- Down-select materials and processes for Phase 2 to focus continuing research
- Engineering Guided Research
  - Use single cell PEM fuel cell for testing purity of hydrogen gas streams
  - Fabricate and operate continuous flow reactor for heterogeneous catalyst testing
- New hydrogen storage materials
  - Design and synthesis of near-thermoneutral release materials
  - Design and synthesis of liquid fuel compositions
- Hydrogen Release
  - Identify reaction pathways and mechanisms to maximal storage and release rates that lead to:
  - Design, synthesize, and demonstrate heterogeneous catalysts with high rates at T < 100 °C
- Regeneration
  - Use theory to guide toward most energy efficient matching of regeneration reactions
  - Demonstrate all individual steps to ammonia borane from spent fuel and begin process integration
  - Use ‘well-to-tank analysis’ and other engineering input to guide selection and improvement of reaction steps
- B-O to B-H *(completed: SBH go-nogo)*
  - Provide organic soluble borate salts for PSU electrochemistry

Down select results

Appendix 2. Decision Summary Spreadsheet

Organic hydrides, alkoxides, and nanoparticles

Material	Wt.%	Vol. % g H2/cc (target - .045	Onboard Regen	Offboard Regen.	Phase Change	Rate @ T (g H2/sec/kg) (target - .020)	Stability	If endothermic, Release T	Decision Summary: Disadvantages	Decision Summary: Advantages	Structure
Endothermic/ mildly exothermic Release Materials:											
Imidazolines											
hexahydrotriazine	6.9									Not demonstrated -- hypothetical	
N,N-9-dimethyl dihydrobenzimidazole/Pd	0.75	0.06	no	not demonstrated, but likely	l/l	<.01 @ rt	y	exo, room temp	Low Weight Fraction	Rates of release good at room temp.	
1,3-dimethyl-2-phenylbenzimidazoline/HoAc/Pd	0.85		no	not demonstrated, but likely	l/l	<.01 @ rt	y	exo, room temp	Low Weight Fraction	Rates of release good at room temp.	
1,3-dimethylbenzimidazoline	1.3		no	not demonstrated, but likely	l/l	<.01 @ rt	y	exo, room temp	Low Weight Fraction	Rates of release good at room temp.	
Coupled reactions											
Mg(OMe)2/H2O	7% @ 20 wt% catalyst		no	not demonstrated	s/s	.03g/s/kg @ 260 °C	y	onset 160 °C, max 260 °C	Endothermic, temperature release too high (>200), requires water, CO2 loss, not directly regenerable		

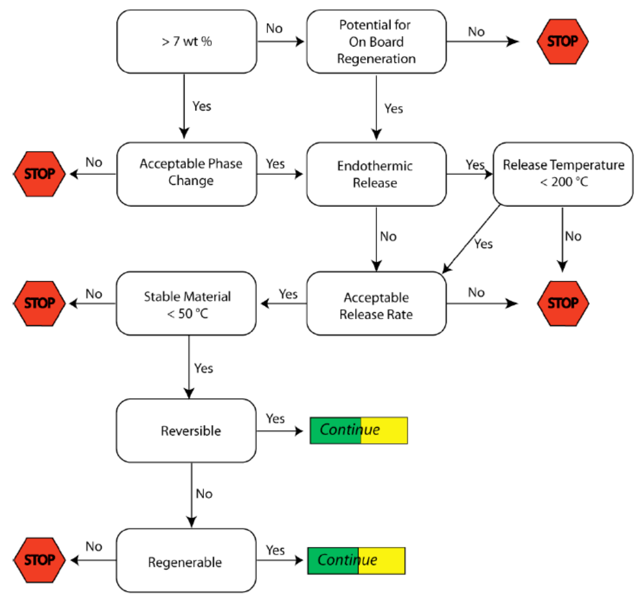
Metal Amidoboranes

Material	Wt.%	Vol. % g H2/cc (target - .045	Onboard Regen	Offboard Regen.	Phase Change	Rate @ T (g H2/sec/kg) (target - .020)	Stability	If endothermic, Release T	Decision Summary: Disadvantages	Decision Summary: Advantages
Exothermic Systems										
Metal Ammonia Borane Derivatives:										
LiAB	11	-	not demonstrated	not demonstrated	s/s	not quantified	to be determined	10 wt % < 90 °C	regeneration not yet determined,	Good rate to 11%, new work
Ca(AB)2	10	-	not demonstrated	not demonstrated	s/s	not quantified	good	7.2 % @ 170 °C	Temp release too high in solid state, possible for catalytic release, regeneration pathway not yet determined. New work.	
Li2Zn(AB)4	10		not demonstrated	not demonstrated	s/s	>.02	good	endo		Release temperature good, rate good, regen not yet determined. New work.
LiZn(AB)3	9						not stable @ rt		Good potential, but too unstable	
Ti(AB)4	10-12						to be determined			Demonstrated 11.9 % H2 released. Regeneration pathway not yet determined. New work.
Al(AB)3	10-12						not stable @ rt		Good potential, but too unstable	
17 mol %LiH/AB	10					.006 @ 85			Demonstrated 9.5 % H2	Generate borohydride, ammonia loss
9 mol% LiNH2/AB	10					.005 @ 85			Demonstrated 9.5 % H2	Generate borohydride, ammonia loss

Ammonia Borane Materials

Material	Wt.%	Vol. % g H2/cc (target - .045	Onboard Regen	Offboard Regen.	Phase Change	Rate @ T (g H2/sec/kg) (target - .020)	Stability	If endothermic, Release T	Decision Summary: Disadvantages	Decision Summary: Advantages
Ammonia Borane Materials:										
Solid AB demonstr.	17% in 1 hr @ 150 °C	.12 @ 150 °C	no	steps demo'd	s/foam	.005 @ 85; .30 @ 120 (peak rate)	good			High capacity, solid to solid transformation, rates to 7% good, work in progress on foaming, H2 impurities
AB 3 equiv	19.6	0.145	no	yes	s/foam		good			For Reference Only -- not experimental data
AB 2.5 eq. fully dense	16.3	0.121	no	yes	s/foam		good			For Reference Only -- not experimental data
AB 2.5 eq. packed pellet 60% voids	16.3	0.049	no	yes	s/foam		good			For Reference Only -- not experimental data
AB 2.5 eq. packed pellet 30% voids	16.3	0.085	no	yes	s/foam		good			For Reference Only -- not experimental data
1:1 AB/MCM scaffold	8									Low but acceptable wt. %, 3:1 more promising
3:1 AB/MCM scaffold	14.7	0.0735	no	not demo'd	no foam	nd	not yet determined			Demonstrated 14 wt % hydrogen at 85 °C.
MeAB	8.8 (2 eq.)		no	not demo'd	l/s		evolves H2 < 50 °C		Stability at room temperature not adequate	Low melting, good rate
20%MeAB/AB	12 wt % (2 eq.)		no	not demo'd	l/s	similar to AB	evolves H2 < 50 °C		Stability at room temperature not adequate	Low melting, good rate
EDBB with catalyst	9.1 (2 eq.)		no	not demo'd	l/l		promising			New work, appears promising liquid composition, liquid to liquid, good rate to 6% with catalyst; stability needs to be verified
EDBB/AB with catalyst	11.3		no	not demo'd	l/l		promising			New work, appears promising liquid composition, liquid to liquid, good rate to 6% with catalyst; stability needs to be verified. Additional components may be added to increase liquid range
20%AB/diglyme, Bronsted acid catalyst	3.5%		no	not demo'd	l/s	.0003 @ 60			Poor hydrogen capacity, v. slow.	
20% AB/% BPh3/diglyme	3.9		no	as AB	l/s	.0004 @ 65 °C			Poor hydrogen capacity, v. slow.	
AB THF, or glymes (xM) with tm catalyst	ca. 1 @ 1.5 M		no	steps demo'd	l/s	rates good to 1st equivalent down to rt	good		Solubility in THF, glymes insufficient	
MeAB THF (xM) with catalyst	ca. 1 @ 1.5 M		no		l/l		?		Solubility in THF, glymes insufficient	

Figure 2. Decision Tree for the CHSCoE Materials Down-Selection Process



Key accomplishments since last review

- New materials have been prepared that have lower exothermicity, higher rates to higher extents of release at lower temperatures compared to ammonia borane which exceed 2010 targets
- Liquid fuel compositions have been expanded, and liquid range to - 30 °C has been demonstrated
- Heterogeneous base metal catalysts for hydrogen release have been prepared and demonstrated to have high rates of release to > 9 wt % H_2 at 70 °C
- All individual steps in a “first pass” AB regen cycle have been proven with overall yield of spent fuel digestion through reduction steps exceeding 70%
- Flow reactor for catalyst screening and process development has been assembled and screening heterogeneous catalysts underway
- Hydrogen stream purity analysis system has been assembled and is operating to identify and quantify impurities in H_2 stream
- PEM fuel cell apparatus for hydrogen stream purity testing has been assembled and is operating

New solution routes to new AB derivatives

Extensive portfolio of storage materials with lower exothermicity, higher rates and extent of release, with reduced impurities in H_2 stream

Metal Amidoborane Derivatives

$MgCl_2 + 2NaNH_2BH_3 \rightarrow Mg(NH_2BH_3)_2 + 2NaCl$
$MgCl_2 + NaNH_2BH_3 \rightarrow Mg(NH_2BH_3)Cl + NaCl$
$ZnCl_2 + 2NaNH_2BH_3 \rightarrow Zn(NH_2BH_3)_2 + 2NaCl$
$TiCl_4 + 4NaNH_2BH_3 \rightarrow Ti(NH_2BH_3)_4 + 4NaCl$
$LiNH_2 + NH_3BH_3 \rightarrow LiNH_2BH_3 + NH_3$

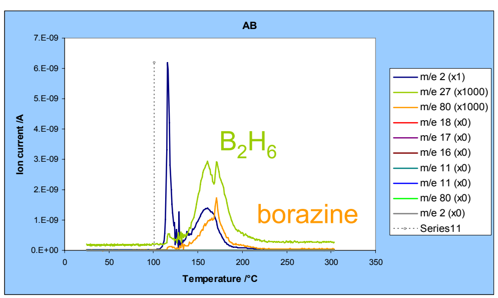
$NaH + NH_3BH_3 \rightarrow NaNH_2BH_3 + H_2$
$CaH_2 + 2NH_3BH_3 \rightarrow Ca(NH_2BH_3)_2 + 2H_2$
$AlH_3 + 3NH_3BH_3 \rightarrow Al(NH_2BH_3)_3 + 3H_2$
$LiAlH_4 + 4NH_3BH_3 \rightarrow LiAl(NH_2BH_3)_4 + 4H_2$
$Li_2(ZnH_4) + 4NH_3BH_3 \rightarrow Li_2Zn(NH_2BH_3)_4 + 4H_2$
$Li(ZnH_3) + 3NH_3BH_3 \rightarrow LiZn(NH_2BH_3)_3 + 3H_2$

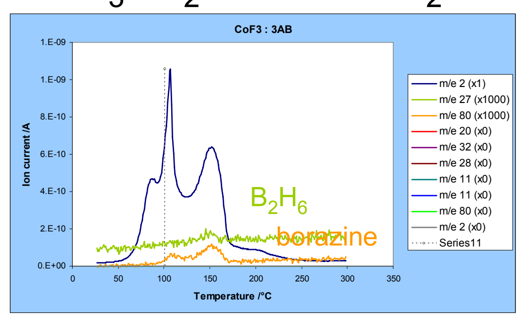
Example
$W(NH_2BH_3)_6$ = 8.3 wt%

e.g. $Ca(NH_2BH_3)_2$ has greater thermal stability than AB but undergoes faster catalytic release of H_2 at room temperature

Fluoride systems

$$NH_3BH_3 + MF_n \rightarrow NH_3BH_2F + M + ½H_2$$





- Future Examination of potential for direct rehydrogenation to explore potential of onboard regeneration

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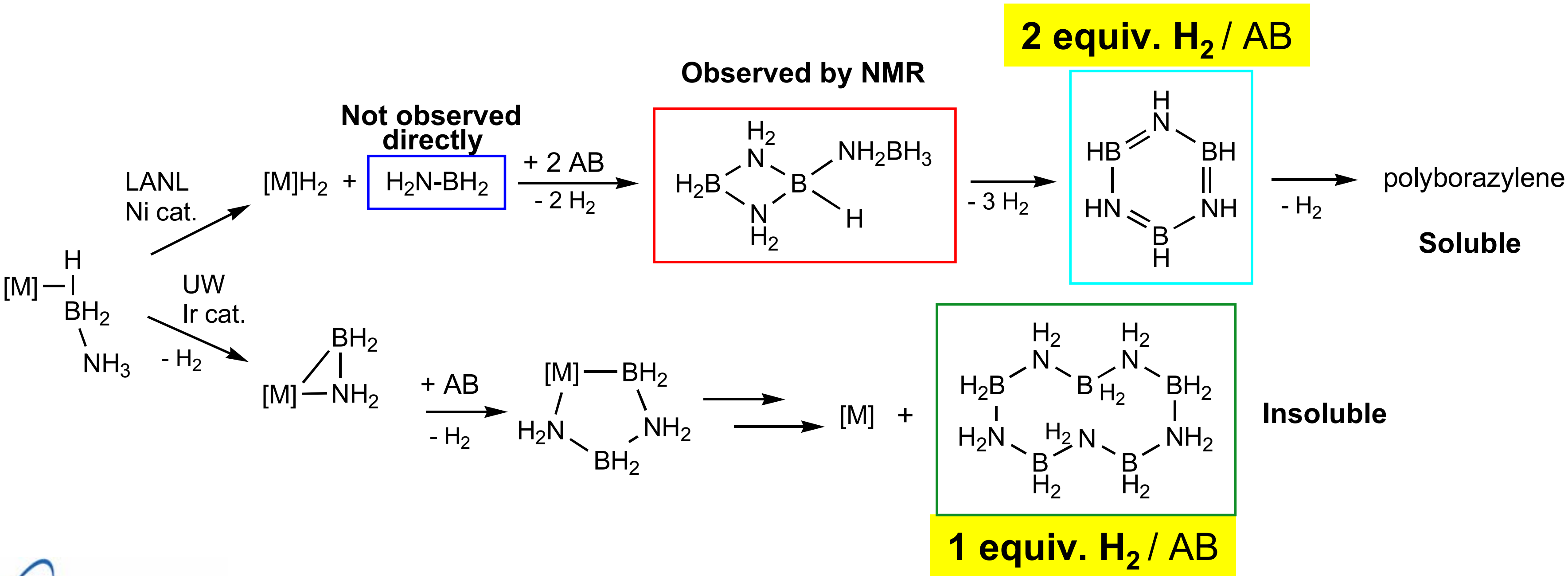
We Now Understand the Catalytic Mechanism of H_2 Release from Ammonia-Borane to Guide Catalyst Design

$$H_3NBH_3 \rightarrow n\,H_2 + (H_2NBH_2)_n \rightarrow n\,H_2 + (HNBH)_n \rightarrow n\,H_2 + BN$$

6.5 wt% | 13.1 wt% | 19.6 wt%

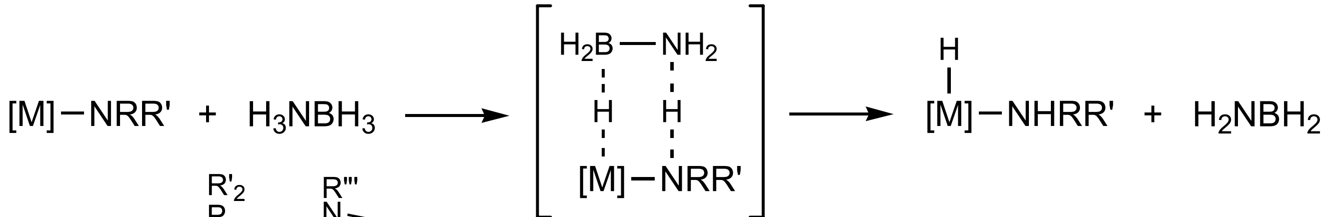
- 2007: proposed that ejection of reactive aminoborane (H_2NBH_2) from metal center allows for release of > 2 equiv. of H_2
- 2008: confirmed mechanistic details*

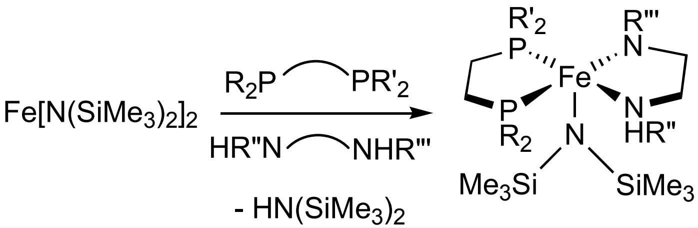


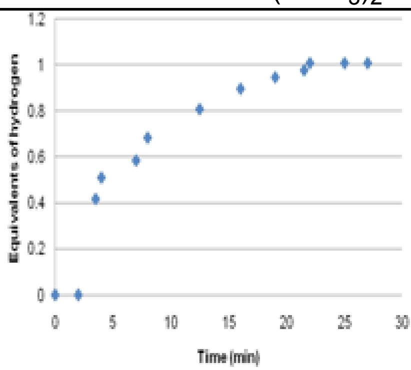
*V. Pons (DEFG02-05ER15719-AO)

Understanding Mechanism Leads to New Class of Modular Iron Hydrogen Release Catalysts

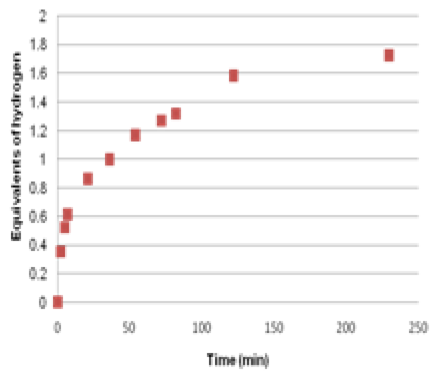
2008 work



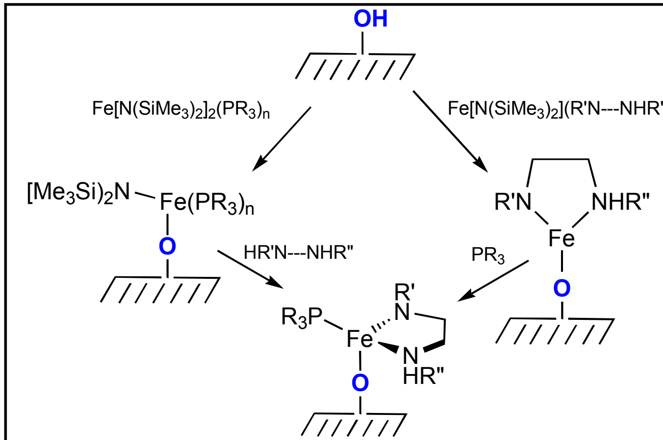




(dcpe)(dpen)Fe[N(SiMe$_3$)$_2$]
Fast but only 1 Equiv. H$_2$
0.026 g s^{-1} kW^{-1}



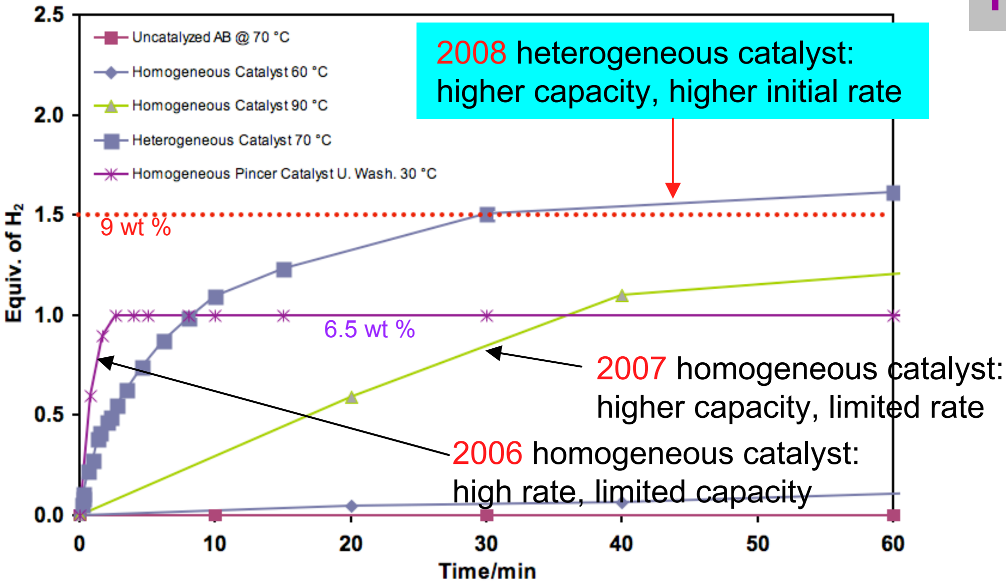
(PCy$_3$)$_2$Fe[N(SiMe$_3$)$_2$]$_2$ > 1 H$_2$ but slower
0.004 g s^{-1} kW^{-1}



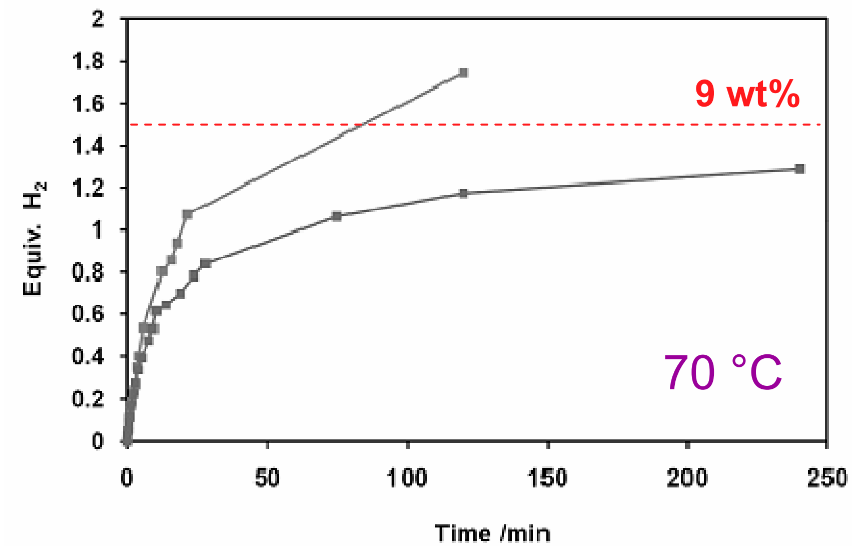
Route to Supported Iron Dehydrogenation Catalysts

• Future Improved rates of hydrogen release from new catalysts that can be prepared on supported catalysts employing the new synthesis robot

2008: Identified Effective Heterogeneous Catalysis for the Release of H_2 with cleaner hydrogen stream



Non-precious metal catalyst identified!



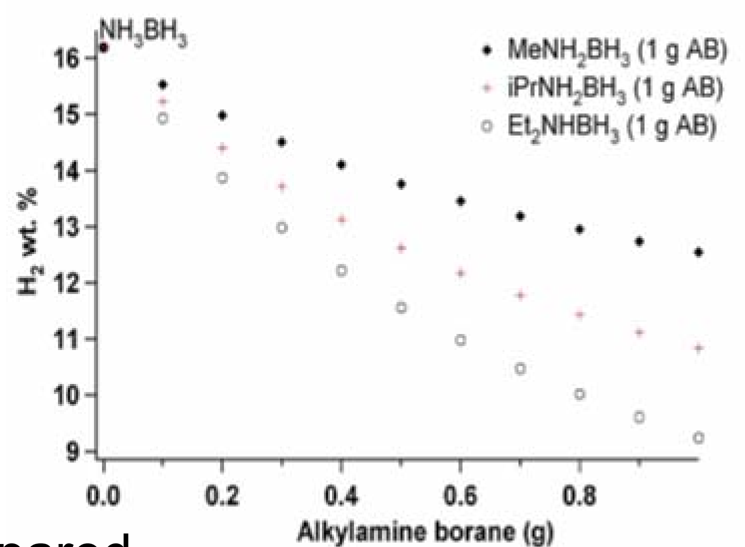
DOE target 0.02 g s^{-1} kW^{-1}
Measured for Heterogeneous catalyst 0.04 g s^{-1} kW^{-1}
With no borazine detected!

- Future Find additional non-precious metal catalysts with high rates and stability under continuous flow reaction conditions

22	23	24	25	26	27	28	29	30
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
47.867	50.942	51.996	54.938	55.845	58.933	58.693	63.546	65.39

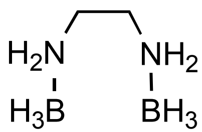
New Fuels that are Liquid Down to -30 °C Have Been Developed

- 2007 Initial work using methylamine-borane was terminated in 2008 due to volatility and instability of MeAB containing liquid mixtures

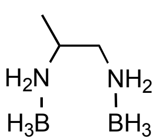


- 2008 New liquid systems have been prepared

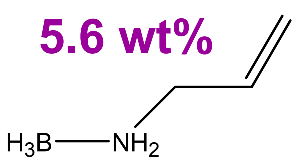
9.1 wt%



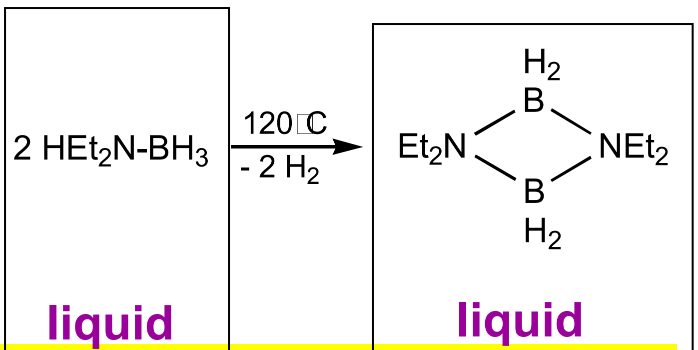
7.8 wt%



5.6 wt%



2.3 wt%



- Future Optimize fuel mixture for highest wt% H_2 and target liquid range using synthesis robot

Regeneration: Demonstrated spent fuel recycle

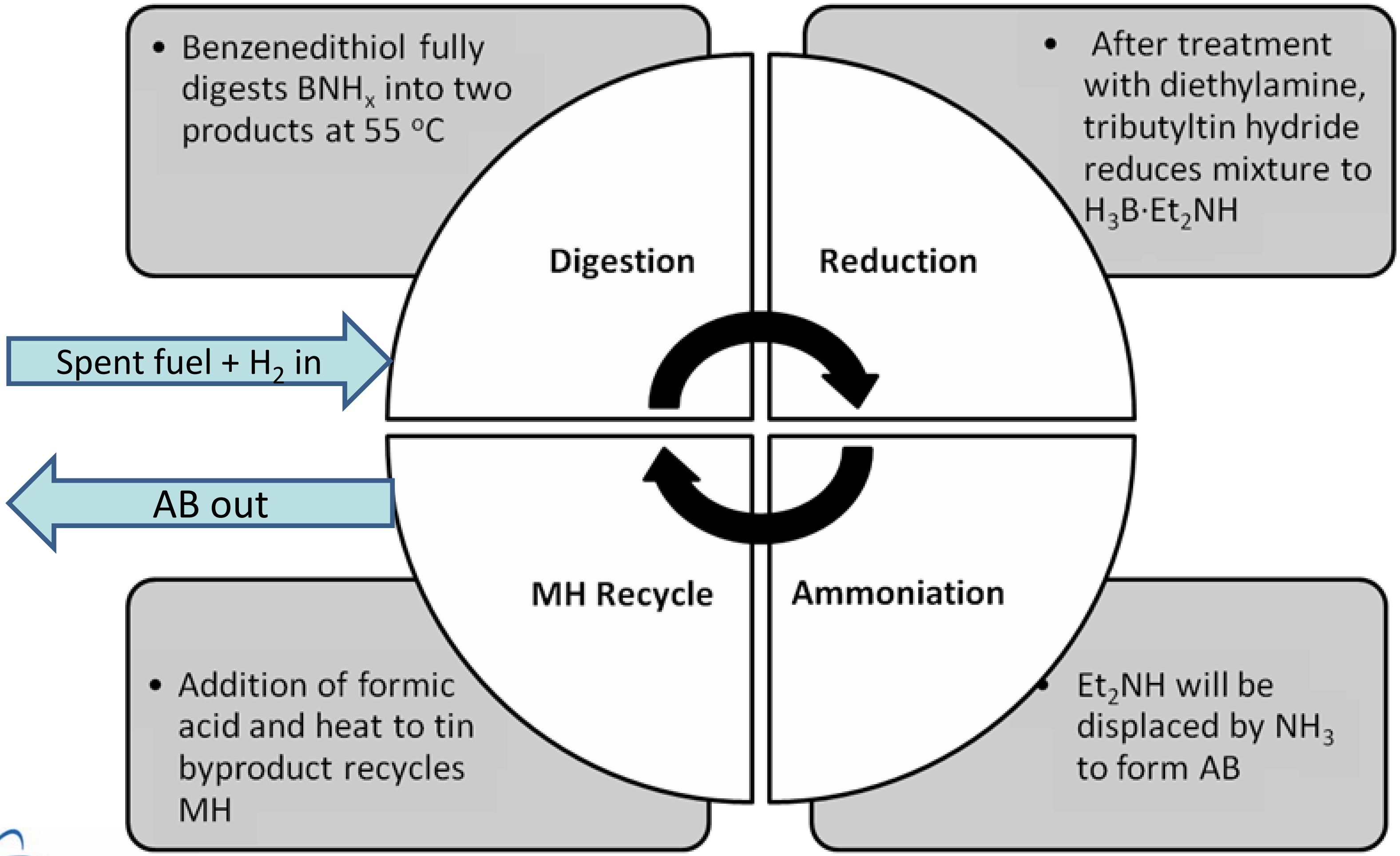
2007

- Amines digested spent fuel, but products **did not** undergo other required reactions
- Proposed thiols as digestion agents
- Screened a variety of reducing agents with a variety of B-X bonds; showed that the boron-sulfur bond in $B(SPh)_3$ could be reduced by Bu_3SnH
- Route for tin hydride recycling via formate route was proposed

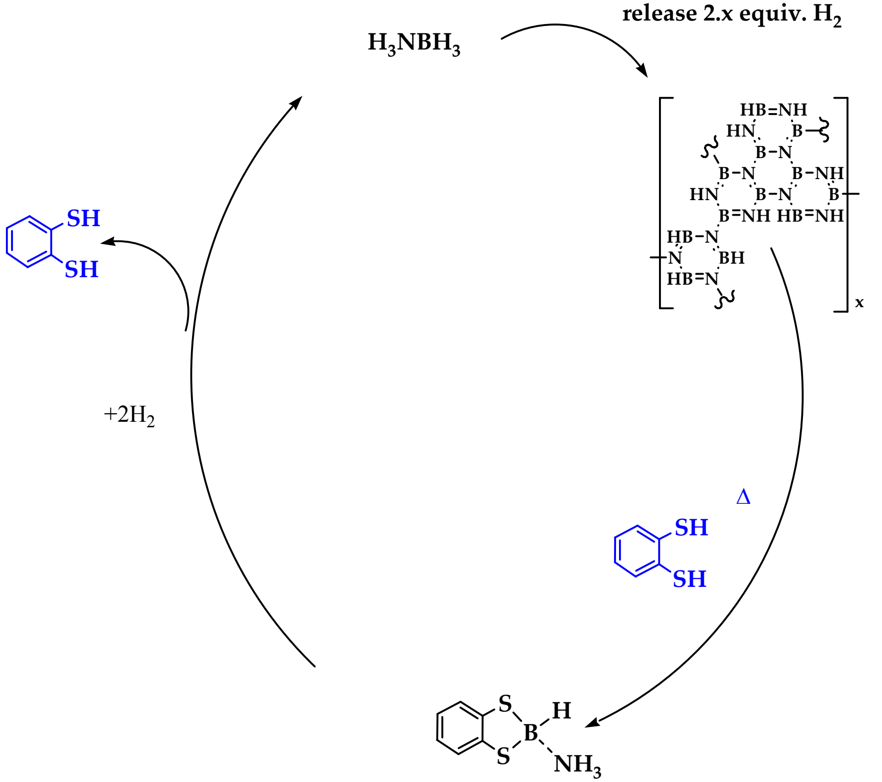
2008 Progress

- **New digestion agent:** Demonstrated that benzenedithiol digests spent fuel in high yield (100% isolated yield)
- Demonstrated that thiol-based digestion products undergo reduction to yield AB (70% isolated yield of LBH_3)
- **Tin hydrides reduce digestion products and can be recycled:**
  - Extensive calculations *and* experiment confirm tin mono- and dihydrides as reducing agents for digestates
  - Decreased reaction temperature for reduction enabled using auxiliary ligands -- results in higher yields, rates of reduction
  - Reduction co product $(C_6H_4S_2)(SnBu_3)_2$ reacts with formic acid en route to recycling the MH (ongoing work)
  - Direct hydrogenation replaces formic acid steps

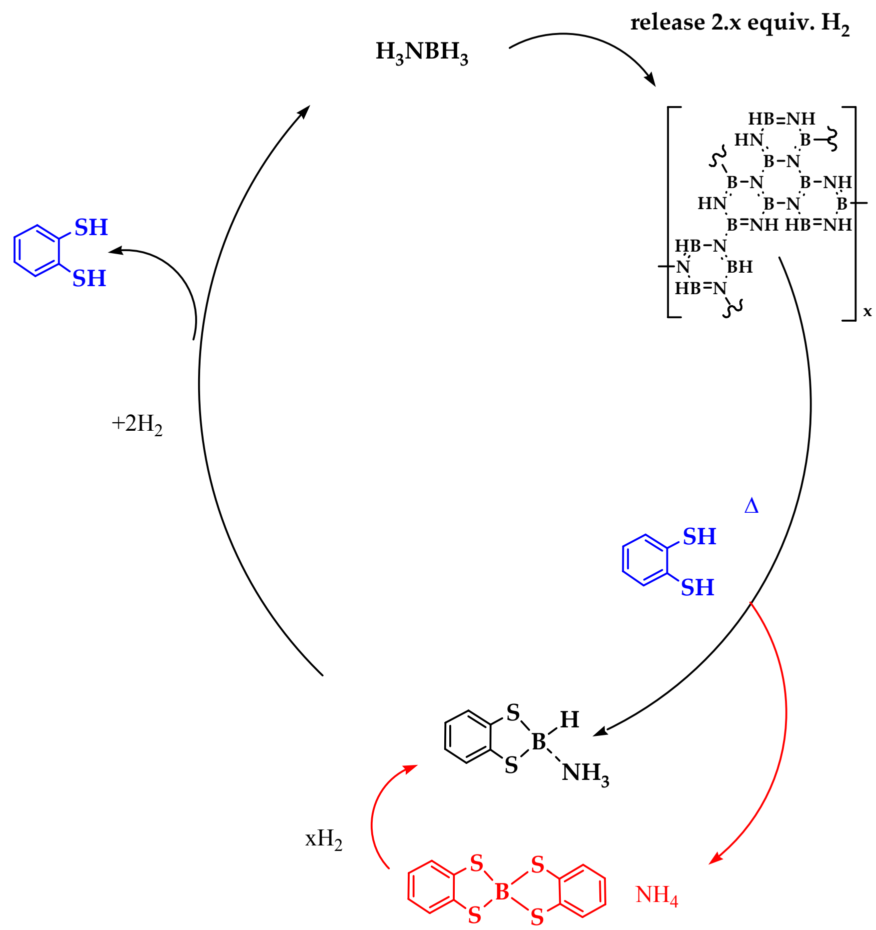
LANL Has Demonstrated Fuel Regeneration Process



Stepwise Regen of AB: Solving the Problems



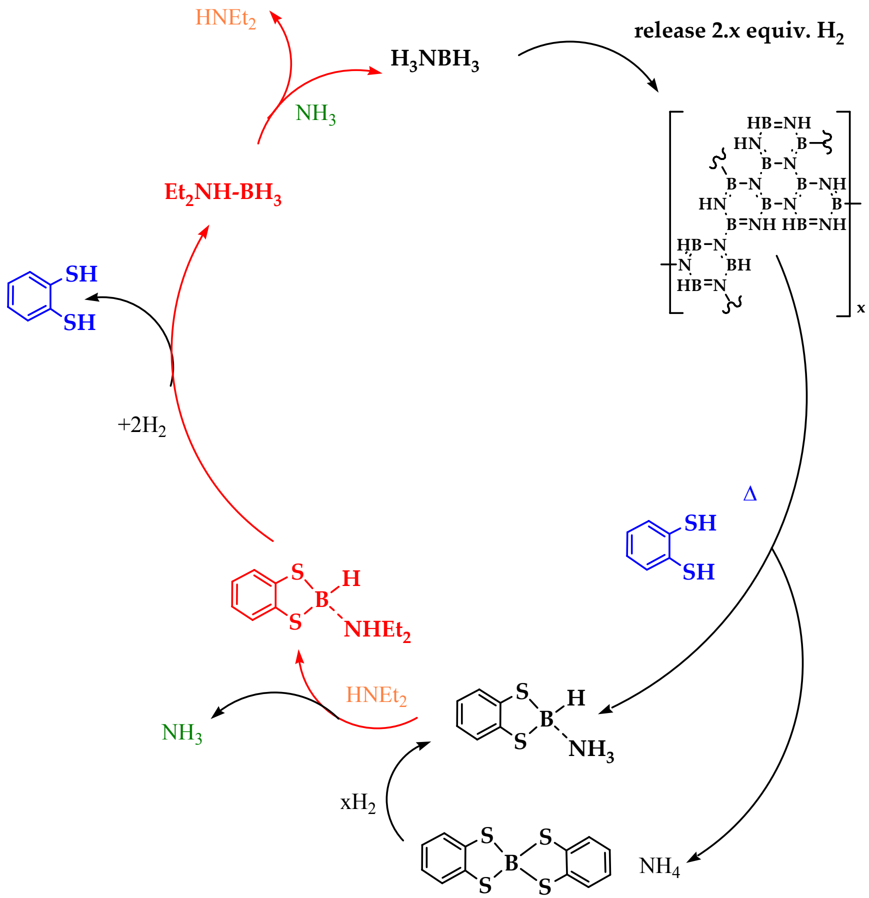
Cycle as envisioned



1st problem = co product chemistry

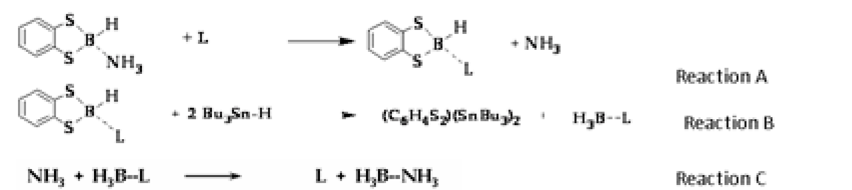
✓ solved

How we utilize the Theory – Experiment Interface: Choosing the Best Ligand for Reduction and Ammoniation by Matching Energetics



2nd problem = matching digestion with reduction chemistry ✓ **solved**

- Tech Team 08: LANL showed exchange of NH_3 for NEt_3 permitted reduction of $HB(C_6H_4S_2)\cdot L$ at lower temperature
- Now energy balance required for Rxns A-C: $HNEt_2$ (ongoing work)



L =

Reaction A	ΔH	-5.5	-4.5	-1.0	6.2
	ΔG	-3.7	-3.3	1.0	9.2
Reaction B	ΔH	1.5	2.7	0.1	-4.7
	ΔG	11.6	13.0	10.0	5.6
Reaction C	ΔH	6.8	4.6	3.7	1.3
	ΔG	5.9	4.1	2.8	-1.0

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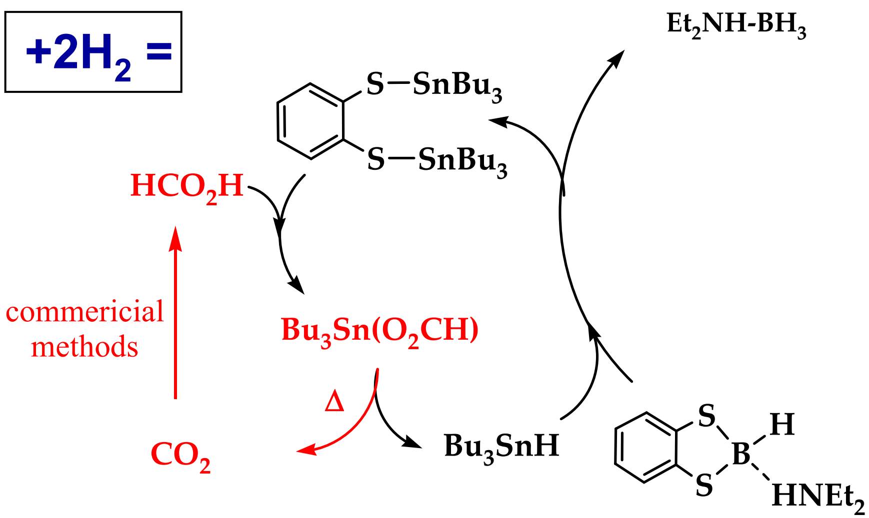
ANL Engineering Assessment Identifies CO_2 Compression as a Major Energy Concern in Regen Cycle

Have to replace CO_2 as a hydrogen transfer reagent

$+2H_2$ =



(HOOC)$SnBu_3$ → CO_2 + $HSnBu_3$ 12.9 kcal/mol
H_2 + CO_2 → HCOOH -22.5 kcal/mol

3rd problem = engineering issues in formic acid synthesis

Theory

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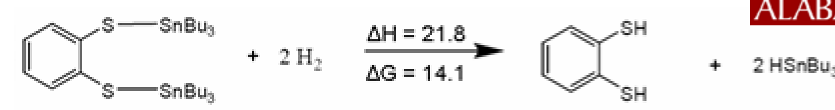


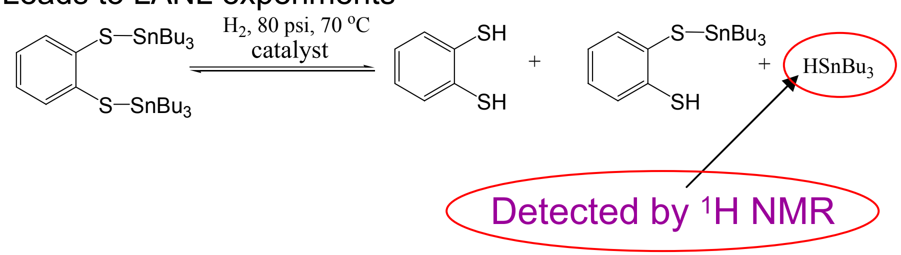
$C_6H_4(SSnBu_3)_2$ (l) + 2 H_2 (g) → $C_6H_4(SH)_2$ (l) + 2 Bu_3SnH (l) 4.2

Relevant work at PNNL using rhodium homogenous catalysis

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

RhH + $B(OPh)_3$ → Rh^+ + $HB(OPh)_3^-$

Leads to LANL experiments



Examining alternatives to tin for easy hydrogenation (Philip Power, Davis)

2008 Top Priority
Investigate
Direct Rehydrogenation

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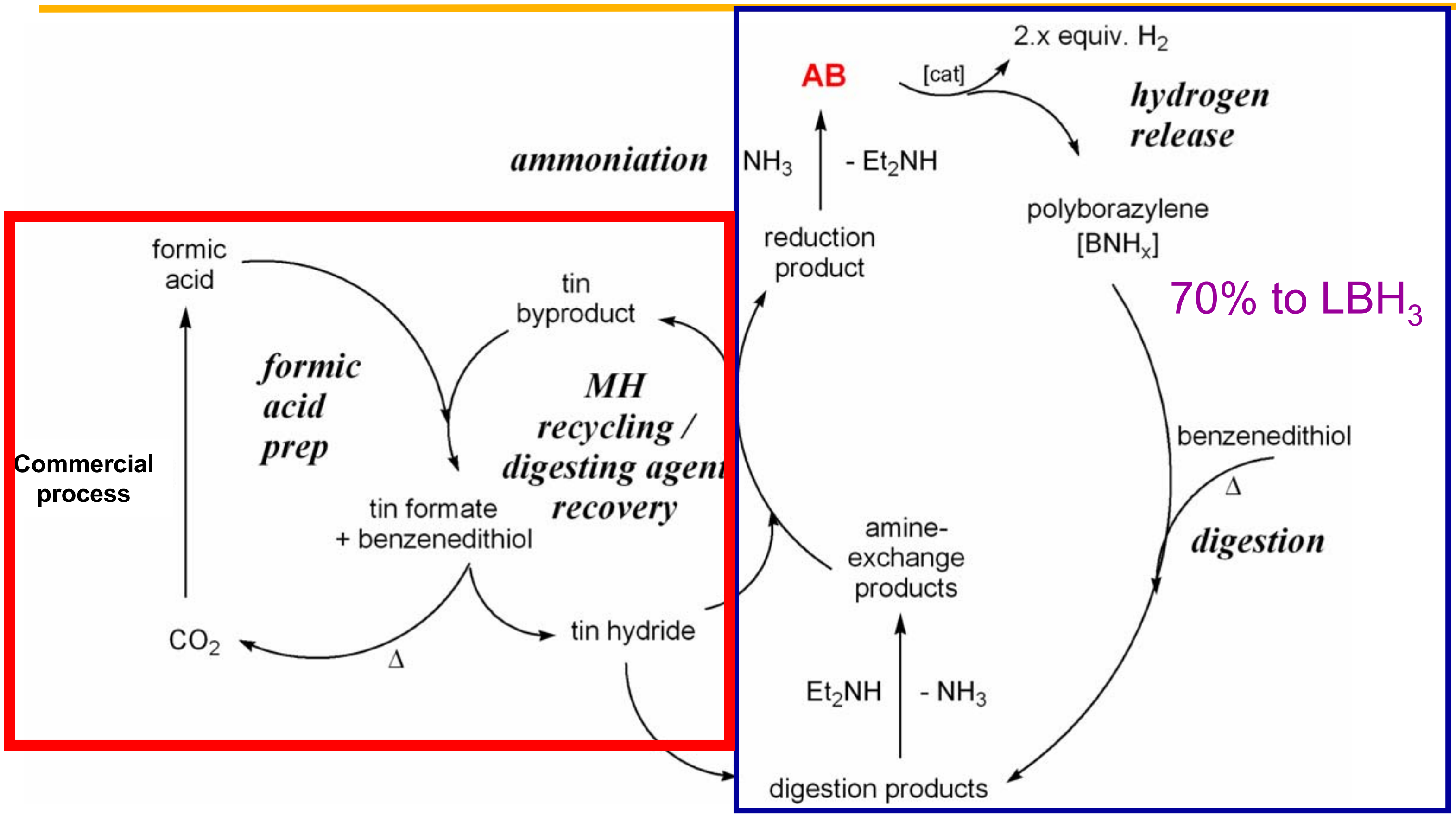
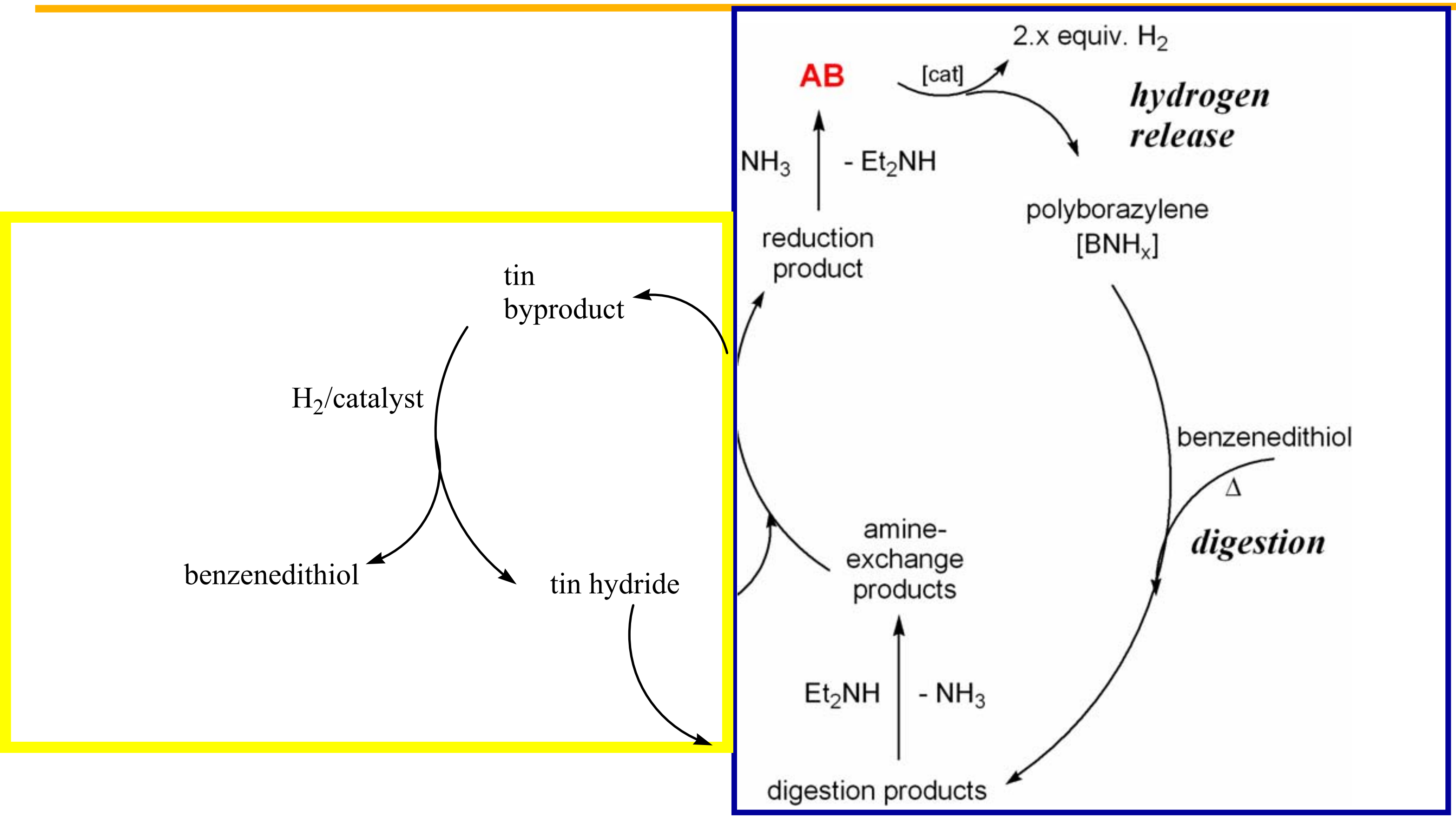
LANL's Current Engineering-Guided Ammonia-Borane Regeneration Process



Future: Complete most steps in one pot, with separations facilitated by solid-supported reagents and identify an energy efficient, non-gas phase hydrogen transfer reagent (in progress)

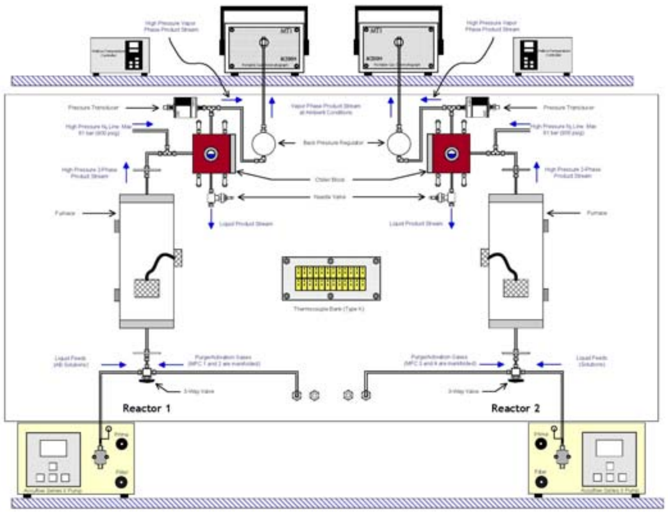
LANL's *NEW* Engineering-Guided Ammonia-Borane Regeneration Process



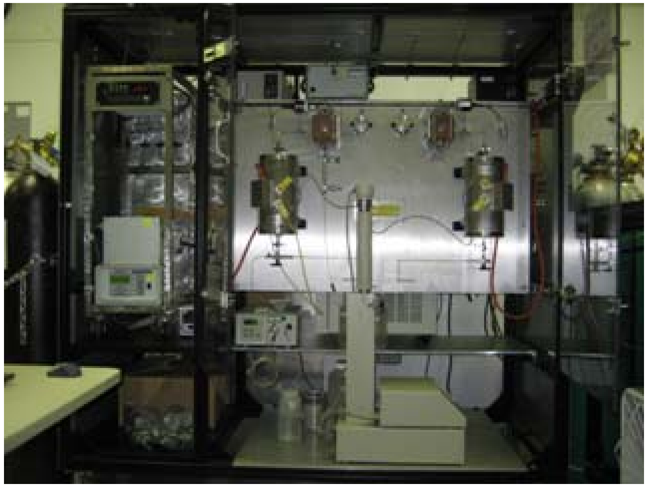
Future: Complete most steps in one pot, with separations facilitated by solid-supported reagents and identify an energy efficient, non-gas phase hydrogen transfer reagent (in progress)

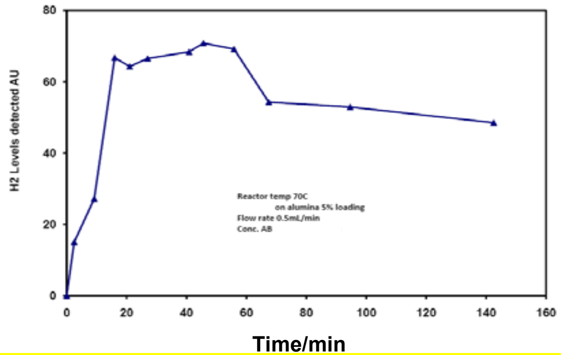
Engineering Assessment of Catalysts/Processes using Continuous Flow Reactor is Underway to Determine Catalysis Lifetime Issues

2007 bread-board designs



2008 reactor assembled and testing underway

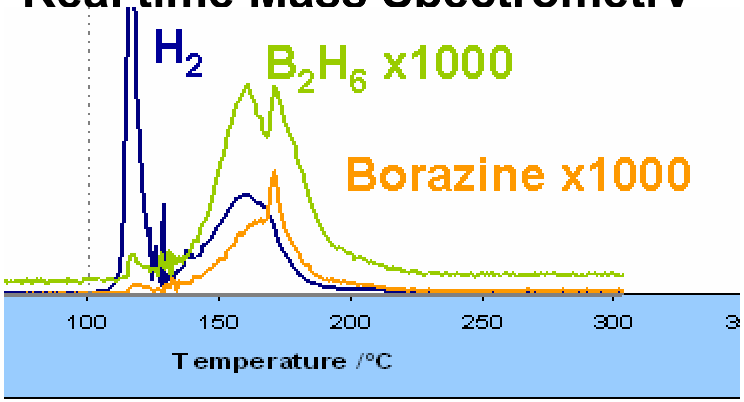


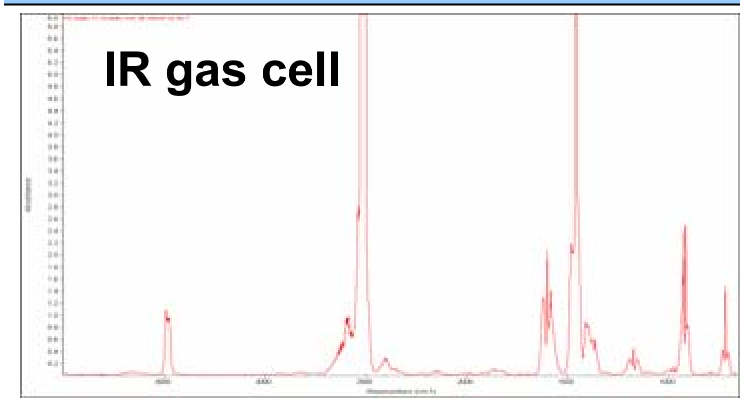


- Future All heterogeneous metal catalysts will be characterized in the flow reactor

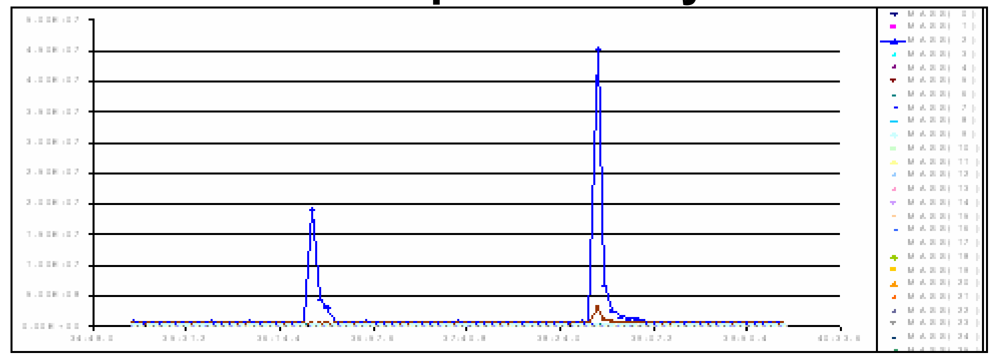
Hydrogen Stream Purity Capability is Enhanced

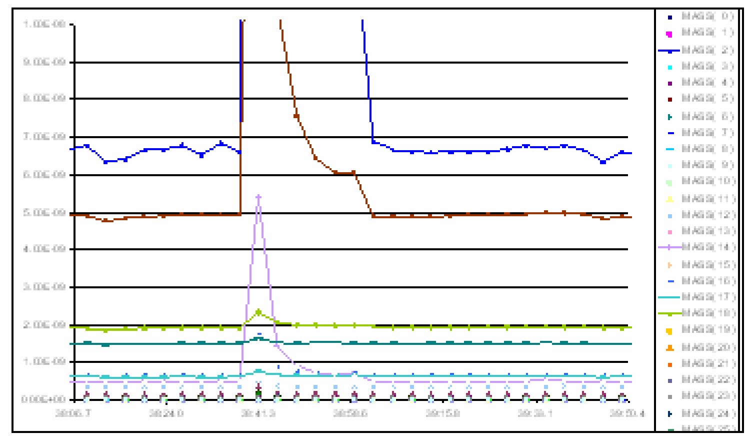
Real time Mass Spectrometry





Mass Spectrometry





We can use spectroscopy and spectrometry for determining H_2 purity
But what about effects of very small, perhaps undetectable contaminants over long operating times?

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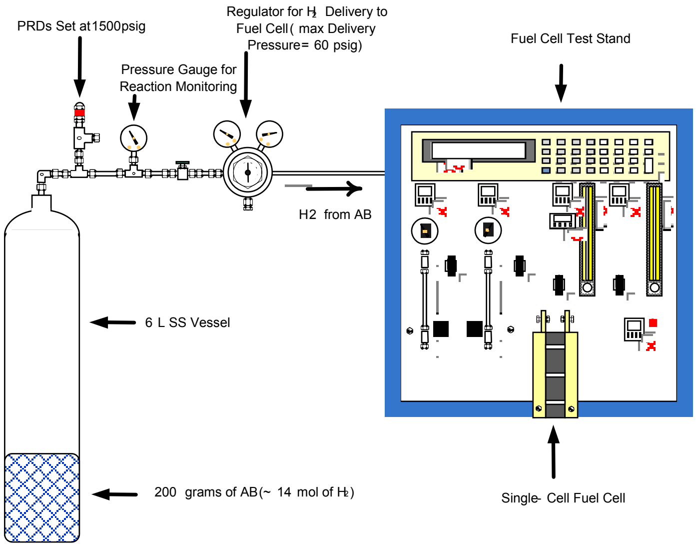
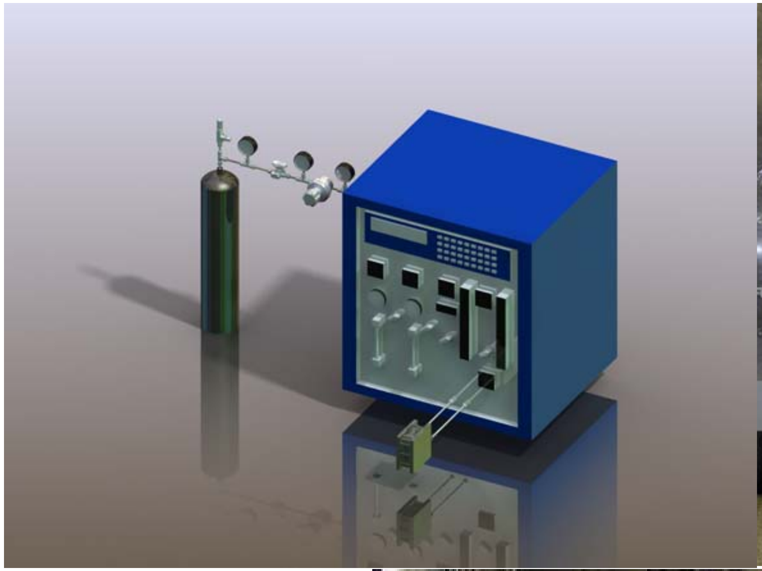
PEM Fuel Cell Provides the Final Word On H_2 Purity





2008 reactor assembled and testing underway

Small surface area fuel cell (1 cm²) is used as a sensitive detector of hydrogen purity -- and acts as a dosimeter

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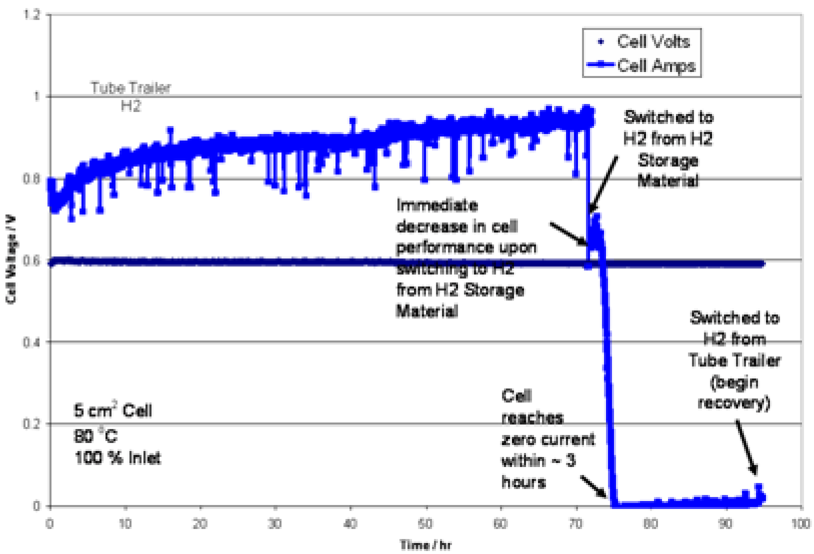
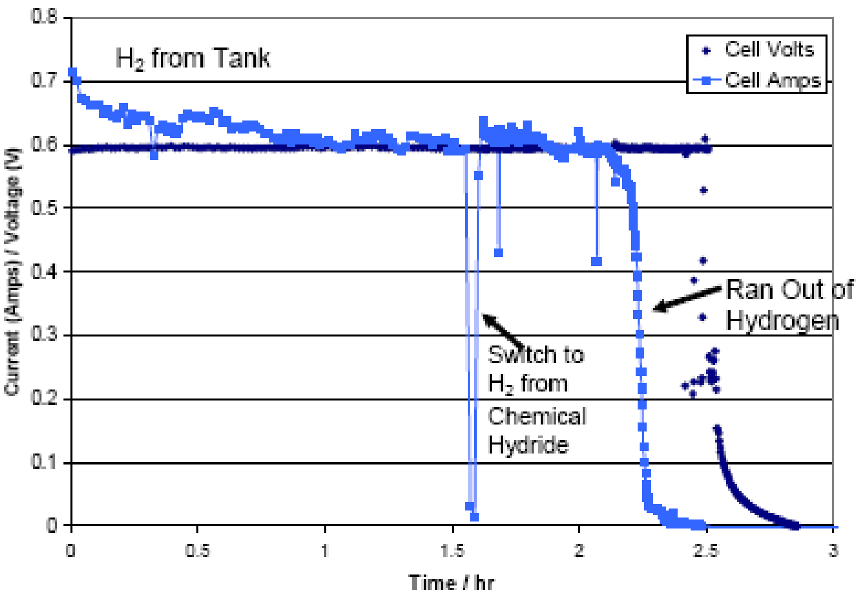
Impacts from the H_2 Stream on Fuel Cell Operation can be determined



Raw H_2 from thermal treatment of AB contains borazine, which is known to poison Pt fuel cell catalyst



Simple inline filter removes borazine, FC performance unaffected

Fuel cell recovered under clean hydrogen and analysis indicates catalysis was poisoned, not the membrane.

- Future Test hydrogen release systems H_2 purity using long term fuel cell operation

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Collaboration with Rod Borup of the LANL Fuel Cell Durability Team

Future Work

- Storage materials
  - Prepare fuels that meet DOE targets for operability (temperature,stability)
  - Identify, test new materials with potential for on-board regeneration
- Release
  - Identify, demonstrate additional non-precious metal heterogeneous catalyst with yet higher rates and with high durability for AB release
- Regeneration of AB
  - Improve process efficiency (replace CO_2 in the hydrogen transfer step)
  - Optimize and quantify yield of recycle using "real" spent fuel
  - Lab scale integrated regen process demonstration
- Engineering Guided Research
  - Hydrogen purity testing of release materials (including regenerated fuel using fuel cell as dosimeter)
  - Identify and mitigate any impacts of impurities using *in situ* FC performance and *post-mortem* analysis of FC components
  - Flow reactor catalysis testing of catalyst (kinetics, durability, extent)
  - Process modeling of liquid systems, regen complete cycle and energy efficiency analysis

Summary of LANL Technical Accomplishments

- Engineering integration is now the major driver for the chemical storage systems under development
- Heterogeneous catalysis have been identified and proven to be effective with hydrogen release from AB
- Liquid storage options for AB fuels are major priority and have multiple paths forward
- Large numbers of new materials are now under investigation for direct rehydrogenation potential for onboard regeneration
- Regen scheme is being optimized with input from ANL, with replacement of major energy intensive steps the priority
- Hydrogen gas stream purity is being examined with working fuel cell and multiple paths forward for preventing impurities
- As we move along in Phase 2 greater communication with the new Engineering Center of Excellence will be vital

Materials Comparisons and Progress; Selected Results

	Thermolysis			Catalysis					
	Ca-amidoborane	LiZnAB3	$ScAB_3$	Homog. Fe catalyst-1	Homog. Fe catalyst-2 *2007*	Heterog. Pt	Heterog. Cu	Heterog. Mn	Heterog. Ni
Grav. density (Mat. wt%)	7.2	9.3	11.1	1 eq. H_2/AB	1.8 eq. H_2/AB	1.91 (Eq. H_2 per AB)	1.82 (Eq H_2 per AB)	0.16 (Eq H_2 per AB)	0.11 (Eq H_2 per AB)
H_2 Flow Rate (g/s) per kg*	.02	.02	New work	.058	.008 *0.00015*	0.057	0.076	0.004	0.002
Vol. density (kg-H_2/L	.05 (est.)	.07 (est.)	.05 (est.)	Not measured	Not measured	New Work	New Work	New Work	New Work

* DOE target = .02 g/s/kW;
rate/kg is roughly equal to rate/kW

DOE System Targets for Hydrogen Storage Systems

Gravimetric Density (wt%)	Volumetric Density (Kg-H_2/L)
4.5 ***(2007)***, 6.0 ***(2010)***, 9.0 ***(2015)***	0.036 ***(2007)***, 0.045 ***(2010)***, 0.081 ***(2015)***

Team & Collaborators

Chemical Hydrogen Storage COE Partners

IPHE Partners