Overview

Timeline
• Start date: Jan - April 2005
• End date: Jan. 2010
• Completion: Approx. 40%

Barriers Addressed
• Hydrogen release capacities
• Hydrogen release rates
• Regeneration of spent fuel
• Regeneration efficiency

Budget
• FY07 -- 50/300K PNNL/LANL: Center Coordination Funding

Partners: 2 NLs, 7 Universities, 4 Companies
Objectives

Identify, research, develop and validate advanced on-board chemical hydrogen storage systems to overcome technical barriers and meet 2010 DOE system goals with the potential to meet 2015 goals:

- Develop materials, catalysts and new concepts to control thermochemistry and reaction pathways
- Assess concepts and systems using engineering analysis and studies
- Select most promising chemical systems for engineering development
- Develop life cycle inventory and demonstrate a 1 kg storage system
Approach to Technical Barriers

• CAPACITY
  – Develop, synthesize, test compounds with high hydrogen density, favorable energetics, and potential pathways
  – Theory and modeling for insight to materials discovery and optimization

• HYDROGEN RELEASE
  – Develop materials and pathways that avoid large thermodynamic sinks and non-productive byproducts
  – Study mechanisms to enhance rates, extents of release, and to aid in the design of catalysts
  – Develop and optimize catalysts and catalytic processes

• REGENERATION
  – Develop pathways close to thermodynamic limits
    • Avoid high energy intermediates
    • Use recyclable intermediates

• ENGINEERING ANALYSIS
  – Provide early assessment of viability
  – Develop viable candidates toward prototype

Theory ↔ Experiment ↔ Assessment
Performance-Based Approach

Viable Chemical Hydrogen Storage System

- **On-board system** - optimized for weight, volume, transient, and cyclic use
- **Off-board system** - Chemical plant optimized for cost and energy efficiency

System Engineering Assessment

- Engineering Assessment
- Experimental Demonstration
- H₂ Capacity
- Theoretical Maximum efficiency

Potential Candidates

Hydrogen Release

Carrier Regeneration
Overview of Current Center Activities

- Tier I Sodium Borohydride
  - Regeneration Pathways Assessment
  - Electrochemical Reduction
  - On-board Engineering Assessment
- Tier II: Alternative Boron Chemistries
  - Amine Borane (AB/MeAB) Dehydrogenation
    - Mechanisms
    - Modifiers; chemical additives
    - Liquid fuel compositions
    - Catalyst development
  - AB Regeneration
    - Digestion of spent fuel, followed by
    - Reduction and ammoniation back to AB
    - Integration of all process steps
  - Polyhedralborane hydrolysis
- Tier III: Advanced Concepts
  - Organic systems
  - Nanomaterials
  - Coupled reactions
  - Metal amine boranes (with International Partnership for the Hydrogen Economy, IPHE -- new collaboration)
## Center Capabilities

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Rapid Screening</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Characterization</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Electrochemistry</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen Release</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Regen Chemistry</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Theory</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst Synthesis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eng. Assess.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction Eng.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process Design</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prototyping</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Center Integrates Capabilities to Enhance Progress

**Tier I**
- BO to BH
- Engineering Assessment
- Theory and Modeling
- Reactor Modeling
- Electrochemistry
- Regeneration Chemistry
- Process Design

R&H, PSU, LANL, PNNL, Ala, MCEL

**Tier II**
- Alternative Boron Chem.
- Materials Synthesis
- Characterization
- Theory and Modeling
- Regeneration Chemistry
- Rapid Screening
- Hydrogen Release
- Catalyst Synthesis
- Catalysis
- Engineering Assessment

Penn, NAU, Ala, Washington, LANL, PNNL, Missouri, Intematix, Davis

**Tier III**
- Advanced Concepts
- Materials Synthesis
- Characterization
- Theory and Modeling
- Regeneration Chemistry
- Rapid Screening
- Hydrogen Release
- Catalyst Synthesis
- Catalysis

Ala, Davis, LANL, PNNL
Theory and Modeling Crosscut Center Efforts for Early Assessment and to Guide Experiment

• Tier I Sodium Borohydride
  – Hydride reduction energetics (Rohm and Haas)
  – On-board reactor modeling (PNNL, MCEL)

• Tier II Alternative Boron Chemistries
  – Calculation of energetics of dehydrogenation reactions and reaction intermediates (Alabama, LANL, PNNL)
  – NMR chemical shift prediction in support of experiment (Penn, Alabama, LANL)
  – Thermochemistry of AB spent fuel regeneration: digestion, disproportionation, hydride transfer (Alabama, PNNL, LANL, Penn, UC Davis)

• Tier III Advanced Concepts
  – Calculation of Si-H vs. B-H bond energies to predict energetics of nanoparticle chemistries (Alabama, UC Davis)
  – Heats of formation and reaction enthalpies for heteroatom organics (Alabama, Washington)
  – Thermochemistry of IPHE project materials (Alabama, LANL, PNNL)
Engineering Assessment & Coordination Crosscuts Center Activities (PNNL Lead)

- Analysis: Rohm & Haas (lead), Millennium Cell, PNNL, LANL
- Fuel Stability: PNNL (lead), Rohm & Haas, NAU
- Hydrolysis Systems: Millennium Cell (lead), PNNL
- New Process Concepts: PNNL, LANL, Rohm & Haas, Millennium Cell
- AB Regeneration: LANL, Rohm & Haas, PNNL
- Catalysis requirements: LANL, PNNL

Coordination between engineering and scientific advances critical to Center success
Key Milestones
and technical barriers to be addressed

• DOE’s SBH Go/No-Go decision 4QFY07

• Near-term regeneration:
  – Achieve near-quantitative mass balance for regeneration
  – Achieve > 60% thermodynamic efficiency with optimized recycle chemistry

• Near-term AB H₂ release:
  – Catalysis: achieve >2 equiv. H₂ at higher rates
  – Thermolysis: Demonstrate solid AB reactor and process

• Down-select 2-3 materials and processes within the Center for engineering and development studies to meet 2010 targets (1QFY08)

• Down-select materials for further research to meet 2015 targets (1QFY08)

• Demonstrate chemical hydrogen regeneration laboratory-scale process for 2010 targets and for materials with potential to meet 2015 targets
### SBH Go/No-Go Milestones: FY07

<table>
<thead>
<tr>
<th>Quarter</th>
<th>Milestone Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>Finish computational analysis of Sodium Borohydride (SBH) regeneration options (chemical and electrolytic) that meet regeneration efficiency criteria (efficiency target of 50%)** and identify at least one process for laboratory demonstration. (quarterly report from Rohm and Haas)</td>
</tr>
<tr>
<td>Q2</td>
<td>Complete conceptual on-board system design that includes a path forward to meet the 2010 targets for on-board gravimetric and volumetric density. (quarterly report from Millennium Cell/PNNL)</td>
</tr>
<tr>
<td>Q3</td>
<td>Determine if laboratory demonstration of all non-commercial or unproven SBH formation steps are possible and estimate the efficiency** of the overall process. Prepare preliminary SBH production/regeneration cost estimate that contains a sensitivity analysis and qualifies the estimate in terms of degree of confidence (quarterly report from PSU, PNNL, ROH, LANL).</td>
</tr>
<tr>
<td>Q4</td>
<td>Determine feasibility and provide a go/no-go recommendation for SBH hydrolysis on-board storage system based on modeling of on-board storage system and laboratory-scale experimental demonstration of energy efficient** regeneration off-board. (recommendation from Center Coordinating Council)</td>
</tr>
</tbody>
</table>

**DOE’s Independent Review Panel scheduled to convene early September**
## Materials Down Select Process

<table>
<thead>
<tr>
<th>DOE 2010 Target</th>
<th>Metric</th>
<th>Material 1</th>
<th>Material 2</th>
<th>Material n</th>
</tr>
</thead>
<tbody>
<tr>
<td>System gravimetric Capacity (6 wt %)</td>
<td>g hydrogen released/g lab vessel</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>System Volumetric Capacity (.045 kg/L)</td>
<td>kg hydrogen/L lab vessel</td>
<td>✓</td>
<td>?</td>
<td>✓</td>
</tr>
<tr>
<td>H₂ Flow rate (0.02 g/s/kW (80 kW stack)</td>
<td>ml lab reactor to achieve .8 mole H₂/sec</td>
<td>✓</td>
<td>✓</td>
<td>no</td>
</tr>
<tr>
<td>Regen Efficiency &gt; 60 %</td>
<td>Based on LHV H₂, regen thermodynamics, demonstrated chemistry</td>
<td>✓</td>
<td>?</td>
<td>--</td>
</tr>
<tr>
<td>Auxiliary physical and chemical properties metrics</td>
<td>Solids, liquids, slurries, reactivity, handling, stability, byproducts, safety, etc.</td>
<td>?</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Materials down selections (current and to Phase 2) are based on progress (tracked quarterly) toward meeting DOE Targets.
Phase 1 to Phase 2 Transition

PHASE 1

- FY05
- FY06
- FY07
- FY08
- FY09

PHASE 2

- 2010 Targets
- Prototype

- R&D for 2015
- DOE Targets
Phase 1 to 2 Down Selection Process: Partner Capabilities Mapped to Down Selected Materials

<table>
<thead>
<tr>
<th>Partner Capabilities</th>
<th>Material 1</th>
<th>Material 2</th>
<th>Material n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials synthesis and characterization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalysis and catalyst synthesis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kinetics and Mechanism</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Theory and Modeling</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction engineering</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process modeling</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Systems integration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Continued partner participation in Phase 2 will be determined within Center and based on capabilities required to achieve Phase 2 goals on down selected materials.
Tier I: Technical Accomplishments

- Regeneration of BO to BH pathways assessed and proof-of-principle demonstrated
- Engineering assessment of SBH hydrogen release delivered
- Go/No-Go milestones developed with DOE

Metal reduction
- R&H demonstrates proof-of-principle borate reduction

\[
\text{NaBO}_2 + 2x/y \text{ M} + 2\text{H}_2 \rightarrow \text{NaBH}_4 + 2/y \text{ MxO}_y
\]

Electrochemistry
- PSU demonstrates proof-of-principle borate reduction
\[
\text{B(OH)}_4^- + 4\text{H}_2\text{O} + 8\text{e}^- \rightarrow \text{BH}_4^- + 8\text{OH}^-
\]

Engineering assessment:
- MCEL preliminary design package delivered
- R&H assessed regeneration pathways
- Implemented H2A analysis model
Key Results
Tier II: Complex Boranes

- Hydrolysis of ammonia triborane (AT) \((\text{NH}_3\text{B}_3\text{H}_7 + 6\text{H}_2\text{O})\)
  - Rh catalysed hydrolysis releases 6.1 wt. % \(\text{H}_2\)
  - 2010 and 2015 system targets not attainable with AT hydrolysis
  - Completed AT hydrolysis work at Penn

- Hydrolysis of \(\text{K}_2\text{B}_{10}\text{H}_{10} + \text{32 H}_2\text{O}\)
  - Rh catalysed hydrolysis releases 5.6 wt. % \(\text{H}_2\)
  - pH and counter ions for polyhedral borane anions have little effect on rate, extent of \(\text{H}_2\)
  - Go/No-Go tied to SBH decision

DOE System Targets: 2007, 4.5 wt%; 2010, 6.0 wt%; 2015, 9.0 wt%
Tier II: Alternative Boron Materials

Because of their protonic N-H and hydridic B-H hydrogens, amineboranes, ABs, are unique in their ability to store and release hydrogen while avoiding B-O formation.

\[
\begin{array}{c}
\delta^- H \quad H^\delta^+ \\
\downarrow \downarrow \\
\text{AB: } H_2B-NH_2 \rightarrow \text{--HB-NH-- + H}_2 \\
\end{array}
\]

<table>
<thead>
<tr>
<th>Material</th>
<th>H$_2$ wt%, H$_2$ density (assumes conv. to ‘BN’)</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$BH$_4$</td>
<td>24.5%, 0.2 kg-H$_2}$/L; Unstable &gt; -20°C</td>
<td></td>
</tr>
<tr>
<td>AB: NH$_3$BH$_3$</td>
<td>19.6, 0.16</td>
<td>Crystalline solid</td>
</tr>
<tr>
<td>Cyclotriborazane: B$_3$N$<em>3$H$</em>{12}$</td>
<td>14.9, 0.11</td>
<td>Crystalline solid</td>
</tr>
<tr>
<td>Borazine: B$_3$N$_3$H$_6$</td>
<td>7.5, 0.06</td>
<td>Liquid, bp 55 °C</td>
</tr>
<tr>
<td>AT: NH$_3$B$_3$H$_7$</td>
<td>17.8, 0.14</td>
<td>Crystalline solid</td>
</tr>
<tr>
<td>MeAB: BH$_3$NH$_2$CH$_3$</td>
<td>8.9, 0.08 (assuming 2H$_2$/MeAB)</td>
<td>Solid, mp 55 °C</td>
</tr>
</tbody>
</table>

DOE System Targets: 2007 4.5 wt %, 0.036 kg-H$_2$/L; 2010: 6.0 wt. %, 0.045 kg-H$_2$/L; 2015: 9.0 wt%, 0.081 kg-H$_2$/L
Tier II: Selected Results from Hydrogen Release from Amine Boranes

- Mechanistic understanding has led to increased capacities and rates
  - Penn: Anionic mechanism in ionic liquids
  - LANL: Metal catalyzed mechanisms explain selectivity, capacities, and guide catalyst design

- Understanding of chemistry and engineering issues has led to new liquid amine borane formulations
  - PNNL and LANL provide proof-of-principle for RNH$_2$BH$_3$
  - NAU discovers liquid formulation of MeAB/AB
  - U. Washington demonstrates high rates of H$_2$ release

- Solid AB: >16 wt % release (PNNL)

- Large parameter space requires rapid throughput screening
  - LANL - new rapid throughput for homogeneous catalysts for H$_2$ release
  - Intematix - Solid catalysts for H$_2$ release
  - Future -- Regeneration
Key Results: AB Hydrogen Release

- **Thermolysis/Chemical Promoters**
  - Anionic polymerization mechanism enhances extent, rates of release
  - Ionic liquids avoid induction period, promote reactivity, improve rates and extent of release from AB
  - Chemical promoters alter reaction pathway, enhance extent of release

- **Solid AB Thermolysis**
  - Mechanistic understanding of release from solid AB
  - Chemical additives reduce induction period, alter ‘nucleation and growth’ phase
  - Demonstrated up to 16 wt. % $H_2$
  - Fuel stability studies ongoing

- **Metal Catalysis**
  - Improved mechanistic understanding drives catalyst design
  - Equally rapid release of 1 $H_2$ from AB and MeAB with Ir catalysts at room temperature
  - Greater extent of $H_2$ with inexpensive base metal catalysts at improved rates at $T > 60 \, ^\circ C$ (patents)
  - Liquid fuel compositions: MeAB/AB
  - MeAB/AB release rates and capacities improving with better catalysts
  - MeAB dehydrogenation (-1$H_2$) results in soluble spent fuel products

- **Completed Bronsted acid-catalysed release from AB at LANL**
Tier II: Regeneration of Spent Fuel from ABs

- Significant increase in resources directed at regeneration chemistry
- Regeneration of spent fuel demonstrated by two pathways
  - Spent fuel $\rightarrow$ BBr$_3$ $\rightarrow$ AB
  - Spent fuel $\rightarrow$ BSR$_n$ $\rightarrow$ AB
  - Capture of residual B-H
  - Theory input guided experiments
- Recycle of reducing agents
  - UC Davis and Alabama working on M-X to M-H recycle and energetics
  - Crucial to overall efficiency
- Overall regeneration efficiencies calculated, e.g. spent fuel-BSR$_n$-SnH-AB:
Key Results: Spent Fuel Regeneration

Placed substantially more resources on regeneration this year

• FY06 Status: proof-of-principle chemistry studies initiated
  – Penn demonstrated trifluoroacetic acid digestion
  – Penn demonstrated amine AlH$_3$ reduction to amine borane
  – LANL demonstrated Sn-H reduction of Cl-BCat to make HBCat; subsequent disproportionation to BH$_3$ (patent)
  – LANL: possible recycle of Sn-Cl to Sn-H with formate (patent)

• FY07 Status - all steps of two potential regen chemistries demonstrated and efficiencies calculated
  – Penn: Br approach
  – LANL: SR approach (patent app. pending)
  – UC Davis: exploring M-X to M-H recycle

• Routes to ‘save’ B-H in spent fuel
  – PNNL: strained alkoxides to (RO)$_2$B-H, ammonia digestion
  – LANL: spent B-H to (RS)$_2$B-H; +NH$_3$(liq.) directly to AB
Tier I&II: Materials Comparisons and Progress
Selected Results

<table>
<thead>
<tr>
<th>Metrics</th>
<th>Hydrolysis</th>
<th>Thermolysis/Chemical Promoters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Penn AT (1.1 mol % Rh)</td>
<td>PNNL AB solid 155 °C (avg. rate to n H₂)</td>
</tr>
<tr>
<td></td>
<td>MCEL 30 wt% aq. SBH</td>
<td>Penn AB/LiNH₂, 85 °C, 3 hr</td>
</tr>
<tr>
<td></td>
<td>Missouri K₂B₁₀H₁₀Rh</td>
<td>Penn AB/AT/PS, solid state 85 °C, 3 hr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Penn AB/AT/PS, ionic liquid, 85 °C, 3 hr</td>
</tr>
<tr>
<td>Grav. density (Mat. wt%)</td>
<td>6.1, 4h</td>
<td>7 &gt;13</td>
</tr>
<tr>
<td></td>
<td>Material 7.3% System 4.5%</td>
<td>&gt;16</td>
</tr>
<tr>
<td></td>
<td>5.6</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.5</td>
</tr>
<tr>
<td>Vol. density (kg-H₂/L)</td>
<td>0.090, 4h</td>
<td>0.021 0.039</td>
</tr>
<tr>
<td></td>
<td>System .037</td>
<td>.048</td>
</tr>
<tr>
<td></td>
<td>0.083</td>
<td>.047</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.059</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.060</td>
</tr>
<tr>
<td>H₂ Flow Rate (g/s) per kg</td>
<td>0.0042, 4h</td>
<td>1 (max rate) 1.8 (max)</td>
</tr>
<tr>
<td></td>
<td>System 0.024</td>
<td>.84 (1 H₂) 0.22 (2+ H₂)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>.0055</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0064</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0060</td>
</tr>
<tr>
<td>Kg of Mat. for 0.8 mol/s</td>
<td>377, 4h (halted work)</td>
<td>2 (max) 1 (max rate) 0.8 (max rate)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>295</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250</td>
</tr>
<tr>
<td></td>
<td></td>
<td>267</td>
</tr>
</tbody>
</table>

DOE System Targets for Hydrogen Storage Systems
Gravimetric Density (wt%)

Volumetric Density (Kg-H₂/L)
0.036 (2007), 0.045 (2010), 0.081 (2015)
## Tier II: Materials Comparisons and Progress

### Selected Results

<table>
<thead>
<tr>
<th>Metrics</th>
<th>Catalysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grav. density (Mat. wt%)</td>
<td>UW Ir, AB w/solvent, 23 °C</td>
</tr>
<tr>
<td></td>
<td>LANL Ni, MeAB/AB (neat) 80 °C</td>
</tr>
<tr>
<td></td>
<td>1:1 MeAB/AB Theoretical, 2 equivalents H₂</td>
</tr>
<tr>
<td></td>
<td>LANL Ni cat 2% AB, in solvent 80 °C</td>
</tr>
<tr>
<td></td>
<td>Extrapolated Ni AB, saturated sol’n</td>
</tr>
<tr>
<td></td>
<td>LANL Ru cat, 2% AB in solvent 80 °C</td>
</tr>
<tr>
<td></td>
<td>LANL Bronsted Acid; 20 wt % AB, 60 °C 18 hr</td>
</tr>
<tr>
<td>Grav. density (Mat. wt%)</td>
<td>0.4 (4.9 - no solvent)</td>
</tr>
<tr>
<td></td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>.015</td>
</tr>
<tr>
<td></td>
<td>10.8 - no solvent</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>13.5 - ns</td>
</tr>
<tr>
<td>Vol. density (Kg-H₂/L Mat.)</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>0.00015</td>
</tr>
<tr>
<td></td>
<td>.08 - ns</td>
</tr>
<tr>
<td></td>
<td>.03</td>
</tr>
<tr>
<td></td>
<td>.00019</td>
</tr>
<tr>
<td></td>
<td>.1 - ns</td>
</tr>
<tr>
<td>H₂ Flow Rate (g/s) per kg Mat.</td>
<td>0.068</td>
</tr>
<tr>
<td></td>
<td>0.82 - ns</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.00002</td>
</tr>
<tr>
<td></td>
<td>.016 - ns</td>
</tr>
<tr>
<td></td>
<td>.004</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>.01 - ns</td>
</tr>
<tr>
<td>Kg of Mat. for 0.8 mol/s</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>2 - ns</td>
</tr>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>70,000</td>
</tr>
<tr>
<td></td>
<td>98 - ns</td>
</tr>
<tr>
<td></td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>16,000</td>
</tr>
<tr>
<td></td>
<td>160 - ns</td>
</tr>
</tbody>
</table>

[ns -- no solvent included in calculation]

---

**DOE System Targets for Hydrogen Storage Systems**

**Gravimetric Density (wt%)**
- 4.5 *(2007)*, 6.0 *(2010)*, 9.0 *(2015)*

**Volumetric Density (Kg-H₂/L)**
- 0.036 *(2007)*, 0.045 *(2010)*, 0.081 *(2015)*
Tier III: Advanced Concepts

- **Organics** - contain appreciable hydrogen for release
  - Demonstrated 1,1-elimination of hydrogen to make carbene
    - Currently 2 wt% of possible 7.2 wt%
  - Demonstrated hydrolysis of carbenes
  - 1,5-Elimination to diimidazolium rings

- **Nanoparticles**
  - UC Davis demonstrated hydrogen release from Si nanoparticles (TG/MS); not reversible
  - Terminated nanoparticle work at LANL

- **Coupled Reactions**
  - Goal is to develop concepts with > 1 H/carbon or hetero atom
  - Developed 25 well reactor for catalyst screening and hydrogen quantification (Center capability)

- **IPHE** - new start Winter, 06
  - Metal amine boranes - potential up to 11.9 wt % H₂; reversible?
  - Patent application
Tier III Advanced Concepts

Organic materials

1. Grubbs cat., CH2Cl2
2. LiAlH4, dioxane
3. HBF4
4. I2, TEA, EtOAc

KH, THF

Prepared precursor to 7.2% polymer

Nanomaterials

TG/MS showing ~3 wt % H2 between 200-350°C.

~5 nm diameter Si nanoparticles

IPHE materials

Ball milled MgH2 + NH3BH3

TG/MS showing ~3 wt % H2 between 200-350°C.

~5 nm diameter Si nanoparticles

Rapid Throughput

- Two 25-well plate batch reactors fabricated
- H2 quantification by gas chromatography

7.2 % H2 quantified by GC
## Tier III: Materials Comparisons and Progress

Selected Results

<table>
<thead>
<tr>
<th>Metrics</th>
<th>Organic Hydrides Theory</th>
<th>Coupled Reactions Theory</th>
<th>IPHE Theory</th>
<th>Nano Theory</th>
<th>Washington /Alabama BNHC’s Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grav. density (Mat. wt%)</td>
<td>[0.9 -- 2006(^a)]</td>
<td>[4.4-2006(^b)]</td>
<td>Measured 7.2</td>
<td>4.5(^d)</td>
<td>7-8%</td>
</tr>
<tr>
<td></td>
<td>2(^b)</td>
<td>8-9</td>
<td>Max 10 - 11.9</td>
<td>8-11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.2</td>
<td></td>
<td>Opt. 8-10.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vol. density (Kg-H(_2)/L Mat.)</td>
<td>[’06--.015]]</td>
<td>0.04</td>
<td>Measured 0.072</td>
<td>.1</td>
<td>tbd</td>
</tr>
<tr>
<td></td>
<td>0.045</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2) Flow Rate (g/s) per kg Mat.</td>
<td>tbd</td>
<td>.008</td>
<td>Measured 0.02</td>
<td>tbd</td>
<td>tbd</td>
</tr>
<tr>
<td>Kg of Mat. for 0.8 mol/sec</td>
<td>tbd</td>
<td>195</td>
<td>Measured 80</td>
<td>tbd</td>
<td>tbd</td>
</tr>
</tbody>
</table>

---

**DOE System Targets for Hydrogen Storage Systems**

**Gravimetric Density (wt%)**

**Volumetric Density (Kg-H\(_2\)/L)**
- 0.036 (2007), 0.045 (2010), 0.081 (2015)

---

\(a\). benzimidizole, terminated; \(b\). U. Alabama carbenes proposed; \(c\). 2007 work focused on IPHE, rapid screening; \(d\). preliminary results on 4 nm particles.
Engineering Assessment & Coordination (PNNL, Lead)

- Analysis: Rohm & Haas (lead), Millennium Cell, PNNL, LANL
- Fuel Stability: PNNL (lead), Rohm & Haas, NAU
- Hydrolysis Systems: Millennium Cell (lead), PNNL
- New Process Concepts: PNNL, LANL, Rohm & Haas, Millennium Cell
- AB Regeneration: LANL, Rohm & Haas, PNNL
- Catalysis: LANL, PNNL

Coordination between engineering and scientific advances critical to Center success
Functional Schematic of an Onboard Storage System - Engineering Research Needs

- **Products of Hydrogen Release:**
  - Separation requirements
  - Hydrogen purification

- **Fuel Storage:**
  - Fuel formulation
  - Fuel stability
  - Storage geometry for volumetric capacity

- **Fuel Cell System Integration:**
  - Match Hydrogen flow to fuel cell requirements over the drive cycle

- **Reactor/Heat Exchange:**
  - Catalyst & structure
  - Catalyst kinetics
  - Heat exchange requirements & thermal integration with the fuel cell

Components identified separately, but could be integrated
Engineering Approach

Developing the tools - modeling, experimental apparatus, and experiments - to move from batch processes to continuous flow processes

Phase 1
- Kinetic Analyses
- Catalyst Synthesis
- Catalyst Screening
- Material Chemistry/Thermodynamics

Phase 2
- Process/Reactor Modeling
- Reactor Engineering
- Process Design
- Scaled Prototypes

Batch Process → Continuous Flow Process
Engineering Assessment Tier II/III: Key Results

- Bed void volume limits capacity to achieve goals
- Solvents limit capacity to achieve goals
- ‘Breadboard’ approach to rapid prototyping for continuous processing
- Accelerated rate calorimeter used to define solid AB fuel stability from number of vendors
Summary

• Engineering analysis and regeneration pathway selection completed for SBH and Go/No-Go milestones developed
• Polyhedralboranes hydrolysis tied to SBH Go/No-Go
• Demonstrated potential of liquid fuel amine boranes; high capacity release from solid AB, high rate catalysts and high capacity catalysts for amine borane H₂ release
• Demonstrated two distinct regeneration chemistries of spent fuel AB, efficiencies calculated approaching or exceeding the target
• Theory and modeling continue to play an integral role in guiding and interpreting experiments
• New solid materials being developed with promising preliminary results
• New heteroatom-substituted organics and hybrid organic amine boranes being developed
• Engineering assessments guiding experiments; leading toward down selection criteria and prototype processes
Future Work

- Continue to innovate and to develop many promising materials and regeneration options to maintain a ‘pipeline’ of candidates
  - High capacity materials with high rates of $\text{H}_2$ release
  - $\geq 2$ H released / element; $\text{AB} = 2^+$; more candidates needed
  - Innovate on release from organics $\geq 2\text{H/C}$
  - Search for materials regenerable with $\text{H}_2$
  - Hybrid materials - e.g. IPHE project

- Improve efficiency of existing AB regeneration schemes
  - Novel digestion agents
  - Improved, efficient recycle of hydride transfer agents
  - Continue to search for liquid fuel compositions
  - Enhance rates, extent of release through catalyst design

- Continue to use quarterly reporting matrix to guide offramp decisions; re-direct resources where needed

- Engineering - move from batch to continuous processes
Center Management and Communication

- Established IP agreement that allows free exchange of ideas and materials among Center partners
- Tiers are coordinated through single LANL point of contact; Coordinating Council (slide 40)
- Projects within Tiers have single POCs, e.g. AB regen, BO to BH e-chem, etc.
- Regular tier and sub-tier conference calls and meetings, frequent one-on-one phone calls, site visits to exchange information in real time
  - eg. AB regen meeting, electrochem conf. calls, IPHE meetings, integration of theory/modeling, engineering conference call, etc.
- Quarterly tracking of Partner’s progress toward DOE target capacities, rates, regeneration efficiencies, etc.
- Develop materials down selection criteria and recommends down selection, revision of workscope decisions with Coordinating Council input; input to Phase 1 to 2 transition
- Hydrogen Storage Centers conference calls with DOE to foster cross-Center information exchange with Carbon- and Metal Hydride Storage Centers
- Biannual Center meetings coincident with Tech Team and Annual Review
- Participation in Storage Systems Analysis Working Group: cross-Center engineering issues
- Organize Annual Review, Tech Team Review
Key Impacts of Center Communications

• Mid-year Center Coordination meeting (Denver)
  – ID Center Capabilities and Gaps
    • Re-directed Center resources to regeneration: UC Davis chemistry expertise to work on M-X to M-H recycle
    • Brought more focus to Engineering Assessment, added LANL expertise to the team
  – Developed Center-wide quarterly reporting matrix for chemical hydrogen storage materials (release capacity, rates, conditions, etc.)
  – Identified gap in Center capability - rapid throughput for homogeneous H₂ release catalysts

• Tier and Subtier Conference calls
  – E-chem conf. call -- LANL assists Penn State e-chem effort with synthetic chemistry support
  – Coordinated NAUs MeAB/AB work to rapidly get samples to other partners for testing
  – Decision to suspend LANL Bronsted acid-catalysed AB H₂ release, LANL nanoparticle work
  – SBH Go/No-Go milestones developed via Tier I meetings, conference calls
  – Tied polyhedral boranes materials down selection to SBH Go/No-Go
  – Tier II/III Center-wide equipment needs -- developed Center prioritization for DOE
  – Sharing of samples for further characterization
  – Feedback mechanisms to increase rate of progress, Center-wide

• Coordinate personnel exchange
  – Bowden (IRL) to PNNL&LANL; LANL staff to Oxford (collaborations with IPHE)
  – Grad students use of equipment for data collection at National Labs
Self Assessment

Results from Chemical Center of Excellence Respondents

- University: Efficacy of applying work breakdown structures to university work
- Protection of IP across the CoE
- Protection of IP between CoE partners
- Communication of safety-related issues
- Value-added performance of DOE HQ
- Communication with partners "within subject area or major concentration area" in the Center of Excellence
- Level of communication across the Center of Excellence
- Level of communication within subject area
- Value-added performance of DOE Golden
- Value-added performance of subject area coordinators
- Accessibility of subject area coordinators
- Accessibility of DOE HQ
- Opinion of value of CoE meetings
- Accessibility of DOE Golden
- Value-added performance of lead national center coordinators
- Accessibility of lead national lab center coordinators
- Usefulness of partner interactions and collaborations in the Center of Excellence vs. an independent project

Average Scores:
- 2.2
- 3.6
- 4.1
- 4.3
- 4.3
- 4.4
- 4.4
- 4.5
- 4.5
- 4.6
- 4.6
- 4.7
- 4.7
- 4.7
- 4.8
- 4.8
- 4.8

Key points/issues from assessment:
- Milestone driven research and academic cultures
- IP procedures across complex Center structure still improving
- Communication across Center/DOE is very good
- Integrated Center adds value vs. independent projects