Chemical Hydrogen Storage R&D at Los Alamos National Laboratory

Project ID# ST040

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2010 DOE Annual Merit Review

This presentation does not contain any proprietary or confidential information
Overview

Timeline
• Start: FY 05
• End: FY 10
• 100% Complete

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

Budget
• FY 09
  - $2,750 K
• FY 10
  - $2,000 K

Partners
• Chemical Hydrogen Storage Center of Excellence
• IPHE (UK, New Zealand)
• Hiroshima University, Japan
Relevance - Objectives

• Complete demonstration of regen process and provide data for preliminary cost analysis of NEW LANL regen process

• Develop liquid ammonia-borane (AB) fuels and increase rate and extent of hydrogen release

• Develop and demonstrate heterogeneous catalysts and continuous flow reactor operation

• Identify and demonstrate new materials and strategies for near-thermoneutral hydrogen release ($\Delta G^\circ = \text{ideally no less negative than ca. } -0.8 \text{ kcal/mol}$)

• Develop materials and processes to minimize gas-phase impurities, and demonstrate adequate purity of hydrogen stream
### Relevance - Milestones

<table>
<thead>
<tr>
<th></th>
<th>Make recommendations of materials, release and regen processes to DOE</th>
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<tbody>
<tr>
<td></td>
<td>Catalog process details and result in DOE Storage Database</td>
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<td>Preparation to pass final report and associated information along to Engineering Center</td>
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<tr>
<td></td>
<td>Finish analysis of hydrazine regeneration route</td>
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<td></td>
<td>Demonstrate details of ‘one pot’ regeneration</td>
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<td></td>
<td>Complete impurities quantification on most promising systems (solid AB, IL(s) AB)</td>
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</table>
Approach: Los Alamos Technical Contributions

- **Engineering Guided Research**
  - Gas cell analysis of impurities in hydrogen release
  - Completed demonstration of regen process and provided data for preliminary cost analysis of NEW LANL regen process
  - Interfacing with Engineering CoE to transfer relevant materials data

- **New hydrogen storage materials for portfolio**
  - Design and synthesis of near-thermoneutral release materials
  - Design and synthesis of liquid fuel compositions

- **Hydrogen Release**
  - Identify reaction pathways to maximal storage and release rates
  - Design, synthesize, and demonstrate heterogeneous catalysts with high rates at T < 100 °C
  - New Base Metal catalysts

- **Regeneration**
  - Demonstrate all individual steps to ammonia borane from spent fuel and begin process integration
  - Refined stoichiometry, concentrations, separations, substitutions, reaction times, materials properties etc
  - Completed demonstration of regen process and provided data for preliminary cost analysis of NEW LANL regen process
  - Use theory to guide toward most energy efficient matching of regeneration reactions

- **Patents**
  - Published – 8
  - Pending – 8
  - Disclosures – 6
Technical Accomplishments since last review

- A complete **one pot** regen cycle has been proven with overall yield of spent fuel digestion through reduction steps exceeding 90%. This method works for multiple spent fuel forms including spent fuels from ionic liquids giving ammonia borane.

- Cost Analysis on NEW LANL regen process underway in collaboration with DOW. LANL is providing all of the experimental data and conditions.

- Liquid fuel compositions, based upon ionic liquids, have been DOWN SELECTED to continue. Development of new ionic liquid fuel compositions with greater than 10 wt% hydrogen.

- Heterogeneous base metal catalysts for hydrogen release have been prepared and demonstrated to have high rates of release to > 9 wt % $\text{H}_2$

- Hydrogen purity analysis system has been assembled and is operating to identify and quantify impurities in $\text{H}_2$ stream.

- Preliminary analysis of filter requirements begun in collaboration with engineering center of excellence. Data indicates we need to minimize borazine production.
Ammonia Borane 20 wt% H₂ But …

3 Ammonia Borane (H₃N-BH₃) → Spent fuel (B₃N₃H₄) + 7H₂↑  ΔH ≈ -7 kcal/mol

- Good news in that temperature necessary for fast H₂ release can be obtained from heat of reaction
- Bad news in that extra cooling may be required
- Process is too exothermic to consider direct dehydrogenation (off board regeneration needed)
- Side reactions are known and accelerated by overheating (difficult to control in large volumes of solid)
  - Impurities
    * Can lead to loss of material as well as fuel cell poisons
  - Different spent fuel forms possible
    * Can complicate regeneration
Solving the Issues: Kinetics in the laboratory

Solid release rates AMR 2007 St_28
Higher Temperature Preliminary Data

- New gas burette apparatus allows release at higher temperature
- Working to higher temperature to further increase rate and capacity
- Wt% > 16% H₂
- Max rate > 3 g H₂/s/kg AB
- Virtually no induction period observed at higher temperatures

IL release rates AMR 2007 St_27
2007: Proton Sponge Increases H₂-Release from AB Solutions and Avoids the Formation of M⁺BH₄⁻ and NH₃

Catalytic release rates LANL 2009 St_17

Thermal IL release rates AMR 2009 St_16

Technical Accomplishments
2009: Significantly Faster Rates for AB H₂-Release In Ionic Liquids with Only Small Temperature Increases

Hydrogen release kinetics are no longer a major issue
ANL analysis of ionic liquid release system

ANL kinetics model fits experimental thermal release data

\[ \frac{d\alpha_i}{dt} = n_i k_i (1 - \alpha_i) \left[ -\ln(1 - \alpha_i) \right]^{(n_i-1)/n_i} \]

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<th>( \beta )</th>
<th>( n )</th>
<th>( E ) (kJ/mol)</th>
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</table>

Heat rejection and startup/shutdown are key challenges.

ANL dehydrogenation kinetics model and preliminary system analysis indicate that hydrogen release rates will meet the DOE target.
Approach – Materials Development

Materials must meet CHSCoE 2007 down select criteria

- Literature search
- Prescreen materials
  - $H_2$ Wt% must be in excess of 7%
  - Example $W(NH_2BH_3)_6 = 8.3$ wt%
- Materials synthesis

- Hydrogen release profile
- Characterization
- X-ray Structure
- Thermodynamics
- Impurities
- Feedback to discovery

- Exothermic or endothermic?
- Improved release rates?
- Improved release volume?
- Fewer impurities?

\[
\begin{align*}
\text{MgCl}_2 + 2\text{NaNH}_2\text{BH}_3 & \rightarrow \text{Mg}(\text{NH}_2\text{BH}_3)_2 + 2\text{NaCl} \\
\text{MgCl}_2 + \text{NaNH}_2\text{BH}_3 & \rightarrow \text{Mg}(\text{NH}_2\text{BH}_3)\text{Cl} + \text{NaCl} \\
\text{ZnCl}_2 + 2\text{NaNH}_2\text{BH}_3 & \rightarrow \text{Zn}(\text{NH}_2\text{BH}_3)_2 + 2\text{NaCl} \\
\text{TiCl}_4 + 4\text{NaNH}_2\text{BH}_3 & \rightarrow \text{Ti}(\text{NH}_2\text{BH}_3)_4 + 4\text{NaCl} \\
\text{LiNH}_2 + \text{NH}_3\text{BH}_3 & \rightarrow \text{LiNH}_2\text{BH}_3 + \text{NH}_3
\end{align*}
\]
We have been looking at gas impurities for several years.

Impacts from the H₂ Stream on Fuel Cell Operation can be determined.

We can use spectroscopy and spectrometry for determining H₂ purity. But what about effects of very small, perhaps undetectable contaminants over long operating times?

Raw H₂ from thermal treatment of AB contains borazine, which is known to poison Pt fuel cell catalyst.

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

- Future Test hydrogen release systems H₂ purity using long term fuel cell operation.

Collaboration with Rod Borup of the LANL Fuel Cell Durability Team.
Impurities can be detected before major hydrogen release temperatures

- Ammonia \( (963 \text{ cm}^{-1}) \) ~ 70 °C
- Diborane \( (720 \text{ cm}^{-1}) \) ~ 86 °C
- Borazine \( (2550 \text{ cm}^{-1}) \) ~ 86 °C

Pure solid ammonia borane produces large amounts of impurities.
Impurities and Mitigation (solid AB)

- **Experimental Data**
  
  **AB/MC Borazine Production**
  
  $0.2 \text{ mg}_{\text{Borazine}} / \text{ mg}_{\text{AB/MC}}$ Reacted
  
  *Reaction Conditions: 30-200°C @ 5°C/min*

  **Borazine Sorption Capacity**
  
  Activated Carbon (ACN-210-15):
  
  $0.26 \text{ mg}_{\text{Borazine}} / \text{ mg}_{\text{Carbon}}$

- **Carbon Sorbent Scaleup**
  
  - 5kg of H₂ results in 37kg of AB/MC (2.5 moles H₂/mole AB)
  - 6.2 kg of borazine produced per fuel tank
  - 24 kg of carbon per fuel tank

- **Raw Product Stream from AB Thermal Decomposition**

- **Filtered Product Stream from AB Thermal Decomposition**
Center Approaches to hydrogen release: Faster rates, lower temps and cleaner hydrogen

- Additives to solid AB
- Solvents plus AB
- Homogeneous catalyst
- Ionic Liquids
- Heterogeneous catalyst
- Alkyl-AB / AB mixtures for liquids
- New cyclic derivatives
- Metal ammonia
2009 Liquid Fuels based upon alkyllamine boranes

solid at RT, m.p. = 37°C

liquid at RT

liquid at RT

cis/trans cyclohexane-bisAB
pasty solid at RT

Last year sec-butylammine-BH$_3$ has shown the most promise with sec-butylammine-BH$_3$:AB 50:50 wt% mixtures liquid at below room temp.
Gas analysis of thermal profile of secBuNH₂BH₃ indicated significant impurities at temperature greater than 50 C.
No improvements were observed in the rates of hydrogen release possibly due to poisoning from Sec-butylNH₂. Gas phase impurities were significant.

This approach to liquid storage systems has been halted at LANL.
Metal AB materials \( M-(\text{NH}_2\text{BH}_3)_x \)

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Metal-AB derivatives are now known for several metals.
KAB crystal structure
Y. Zhang and C. Wolverton, 2010

Predicted structure nearly degenerate with experimental structure (within 11 meV/f.u.)
Predicted structure also has two symmetrically distinct K positions, in agreement with expt.

<table>
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<tr>
<th>Bond Lengths</th>
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<th>Theory (PEGS+DFT)</th>
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Space group: Pbca
a = 9.35 Å
b = 8.21 Å
c = 17.19 Å
α = 90.00
β = 90.00
γ = 90.00

Space group: P1
a = 5.54 Å
b = 7.52 Å
c = 5.36 Å
α = 103.98
β = 64.25
γ = 104.20

Progress with theory for structure prediction.
Metal AB materials

Great kinetics at low temperatures, no borazine, small amounts of ammonia

All materials currently known show exothermic hydrogen release. It is not possible to regenerate these materials efficiently but these materials are useful for stationary near term applications. Work with these materials should continue with possibility of better thermodynamics in as yet unknown materials.
Hydrogen Release from NH$_3$BH$_3$ in Ionic Liquids (ILs)

Contrasting dehydrogenation at 85 °C

Ionic liquids improve thermal kinetics of hydrogen release


Impurities still present in hydrogen from thermal release, but no diborane!
2010 Ionic liquids and catalyst results in different reaction products

Ethylcyclobutane (ECB) analog

\[ [M] + H_2NBH_2 + 2 AB \rightarrow H_2B_N BH_2N \rightarrow -3 H_2 \rightarrow \text{polyborazylene} \]

Cyclohexane analog

\[ [M] - BH_2 \rightarrow -H_2 \rightarrow \text{polyborazylene} \]

Ethylcyclobutane (ECB) analog

\[ [M] - BH_2 \rightarrow -H_2 \rightarrow \text{polyborazylene} \]

1 equiv. H_2

> 2 equiv. H_2
Properties of IL:AB mixtures look promising

Thermal stability of IL:AB mixtures

50 °C - no change on mass of sample or in gas above sample for over 100 hours

50 °C sample exposed to air - no change on mass of sample or in gas above sample for over 120 hours but water observed in gas. Chloride is hydroscopic

60 °C sample exposed to air - no change on mass of sample for over 120 hours but slight changes in gas above sample

Only ammonia is observed in the gas phase at 70 C for catalyst but long term stability of samples at 60 °C still needs to be addressed
Summary – LANL Down Selects for 2010

Organic solvents currently weight % hydrogen too low - stopped

Alkyl ammonia borane materials do not show enough promise, catalyst poisoning and too much impurities in hydrogen to continue – stopped

Metal ammonia borane materials have potential but no current material is suitable for automotive applications – small scale continued support

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

2007-08 Discovery
- Literature search
- Theory
- Scoping reactions

2008 Demonstration
- Test reactions
- Characterization
- Scaling
- Modeling
- Thermodynamic assessment
- Feedback to discovery

2009-10 Cost Analysis
- Process conceptualization
- Flow sheet development
- Iterate w/experiments
  - separations
  - kinetics
  - yield
- Aspen
- H2A Tool
Off-Board Regeneration Required  
(timeline 2008-2010)

3 Ammonia Borane \((H_3N-BH_3)\) → Spent fuel \((B_3N_3H_4)\) + \(7H_2\uparrow\)  
\[
\Delta H \approx -7 \text{ kcal/mol} 
\]  
(Miranda and Ceder 2007)

Center of Excellence Targets: 60% process efficiency for regeneration  
$2-4$ gallon of gas equivalent for H\(_2\) stored

\[3 \text{Am} \Rightarrow \text{Sp fuel} + 7\text{H}_2\]

2007 – Thiol based digestion of spent fuel first demonstrated

Mid 2007 – Tin hydrides observed to form ammonia borane (AB)

2008 – Digestion/reduction combined into one cycle

Mid 2008 – Feedback from TT, AMR increases emphasis on process analysis, cost; optimization of reactions, reducing unit operations

August 2008 – Center ‘Engineering Summit’ in Philadelphia with R/H

Fall/Winter 2008/2009 – Iterative process modifications with DOW input;

2010 - DOW analysis of hydrazine regeneration

• Fall 2009 hydrazine Regeneration Scheme

• January 2008 Full Scheme

• Work to DOW Baseline Analysis

• Ultimate Goal
Problem: ANL and Dow analysis indicate that SnH reagent too massive and the CO₂ compression was too energy intensive. Significant effort was expended to fix the problems.
Hydrazine is a light hydrogen transfer material that removed over 50% of weight, due to tin, in the regen cycle. But some tin is still required.
2010 Hydrazine also reacts directly with PB

Tin is no longer required but add a amine metathesis step

\[ \text{NH}_3\text{BH}_3 \rightarrow \text{H}_3\text{N-BH}_3 + (\text{H}_4\text{N}_2)-\text{BH}_3 + "\text{B(N}_2\text{H}_3)_3" \]

\[ \text{H}_2\text{NNH}_2 \rightarrow \text{H}_2\text{NNH}_2-\text{BH}_3 + \text{NH}_3\text{BH}_3 \]

- \( \text{NH}_3 \)
- \( \text{N}_2\text{H}_4 \)

\[ \text{H}_3\text{B}-\text{N}-\text{NMe}_2 \]
Complete Regen Cycle 5
LANL 2010

Again theory helps select best amine for metathesis

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<tr>
<th>Reactant</th>
<th>B3LYP ΔΔH (rel BDE)</th>
<th>G3MP2 ΔΔH (rel BDE)</th>
<th>B3LYP BDE absolute rel to CCSD(T) NH2NH2</th>
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THE UNIVERSITY OF ALABAMA

Los Alamos National Laboratory
EST.1943

DOE Chemical Hydrogen Storage Center
At elevated temperature ammonia will directly convert hydrazine borane to ammonia borane
Complete Regen Cycle 7 Demonstrated for several different fuel forms  LANL 2010

Ammonia can be used as the solvent in a one pot direct conversion of spent fuel to ammonia borane
Summary

To date we have demonstrated 7 complete cycles for regeneration

Regeneration of spent ammonia borane **IS POSSIBLE**

More work is required to determine the optimal regeneration process as both catalysts and fuel form evolves

Current hydrazine synthesis relies on the Chloralkali process, requiring in significant separation (distillation, drying etc) and is therefore expensive!

\[ 2\text{NH}_3 + \text{NaClO} \rightarrow \text{N}_2\text{H}_4 + \text{NaCl} + \text{H}_2\text{O} \]

Other processes are known in the chemical literature and some are even used commercially but as hydrazine is not used in very large quantities little effort has gone into alternative (cheaper) synthetic routes.

We need to either improve hydrazine cost or develop yet another regen scheme
## LANL Materials Comparisons and Progress; Selected Results

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- **2007 AB Mixtures**: Metal AB’s
- **2010 Liquid AB**: Metal AB’s
- **2010 Metal AB’s**: Ionic Liquid ABs
- **Platinum catalysts**: NON-Platinum catalysts
- **inline filter required**: $7-8 1st process
CHSCoE Materials Decision Tree

Criteria for materials down selection has been adhered to by LANL

Yellow - marginally acceptable, or secondary issues e.g. impurities
Green - high priority materials of exceptional promise
Collaborations

Chemicals COE

IPHE