Reversible Formation of Alane

A High Hydrogen Density Material for Energy Storage

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This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline
- Start: 10/1/06
- End: Continuing
- Percent complete of activities proposed for FY16: 50%

Budget
- FY14 - $400K
- FY15 - $400K
- FY16 - $400K

Barriers
- Low-cost, energy-efficient regeneration
- Dendrite Formation
- Reduced cost for alane synthesis
- Increase conductivity
- Perfect crystallization methods

Collaborators
- Ardica (CRADA Partners)
- SRI
Relevance: Alane as a Hydrogen Storage Material

Overall Objectives

• Develop a low-cost rechargeable hydrogen storage material with cyclic stability, favorable thermodynamics and kinetics with high volumetric gravimetric hydrogen density

Aluminum hydride (Alane - AlH₃), having a gravimetric capacity of 10 wt.% and volumetric capacity of 149 g/L H₂ and a desorption temperature of ~60°C to 175°C (depending on particle size and the addition of catalysts) has excellent potential for application in high energy density devices

Specific Objectives

• Develop cheaper techniques to synthesize alane which avoids the chemical reaction route of AlH₃ that leads to the formation of alkali halide salts such as LiCl or NaCl.
• Utilize efficient electrolytic methods to form AlH₃.
• Develop crystallization methods to produce alane of the appropriate phase, crystal size and stability.
Relevance: Traditional Methods to Form Alane

• Current alane production techniques use AlCl$_3$ and LiAlH$_4$ in a solution based chemical reaction which is costly due LiCl formation which is not easily reversible.

\[
3\text{LiAlH}_4 + \text{AlCl}_3 \Leftrightarrow 4\text{AlH}_3 + 3\text{LiCl}
\]

• AlH$_3$ Adduct consists of AlH$_3$ and etherates (e.g. THF, or Et$_2$O)

• AlH$_3$ Adduct can also consists of AlH$_3$ and amines (e.g. TEA, TMA)

• Depending on conditions different phases can form (e.g. $\alpha$, $\alpha'$, and $\gamma$)

• Only the alpha phase is the most stable

• LiCl is unrecoverable making the chemical rout a costly process

Current price $3,500/kg small scale
Relevance: Advantages of Electrochemical Alane Generation

Generating alane electrochemically allows for the exclusion of halide salts and simple aluminum recycling methods.

\[ \text{LiAlH}_4 \rightleftharpoons \text{AlH}_3 + \frac{1}{2} \text{H}_2 + \text{Li}^+ + e^- \quad E^0 = -2.05 \text{ V vs. SHE} \]

\[ \text{Li}^+ + \frac{1}{2} \text{H}_2 \rightleftharpoons \text{LiH} + e^- \quad E^0 = -2.33 \text{ V vs. SHE} \]

\[ \text{LiH} + \text{Al}^{+\frac{3}{2}} \text{H}_2 \rightleftharpoons \text{LiAlH}_4 \]

Cost Analysis Including Inefficiencies

**Aluminum not recycled**

<table>
<thead>
<tr>
<th>Component</th>
<th>Cost ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Cost in AlH(_3)</td>
<td>$0.428</td>
</tr>
<tr>
<td>Aluminum Cost in AlH(_3)</td>
<td>$1.982</td>
</tr>
<tr>
<td>E-Chem Thermo Cost</td>
<td>$0.103</td>
</tr>
<tr>
<td>E-Chem Kinetics Cost</td>
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</tr>
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<tr>
<td><strong>Total E-Chem Cost from NAH</strong></td>
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Large scale production using electrochemical method expected to reduce cost below $100/kg
Approach: Resolving Issues to Further Lower Cost of Alane

Increasing efficiency and yield by:

A) Recycling materials and additives used in making alane during:
   - Electrochemical process
   - And crystallizations

B) Improve conductivity and explore different adducts:
   - Use THF in the electrochemical cell
   - Use transmutation process to crystal from different adduct

C) Producing alane of high value by producing:
   - Stable alpha alane with Crystal size larger than 5 microns
   - High capacity product that is safe to handled in air and the presence of moisture
Approach: Crystallization and Reagent Recycling for Alane

- Focusing on methods to reduce materials and processing costs of front end synthesis and back end crystallization
- Efforts address both the recycling of solvent and crystallization aids as well as the use of alternative adducts to ether to use feedstock alternatives to LiAlH$_4$
- Improvements to the electrochemical generation of alane are underway to generate LiH at the cathode for electrolyte regeneration

Dow Method Material Costs

- LiAlH$_4$ (53%)
- Crystallization Aids [LiAlH$_4$ + LiBH$_4$] (22%)
- AlCl$_3$ (3%)
- Solvent (22%)
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Current Progress: Cathode Optimization/Electrolyte Regeneration

2015 Results: Dendrites were significantly reduced by utilizing a reverse pulse technique during the electrochemical reaction.

2016 Results: MgNiHx-based cathode reduces/eliminates dendrite formation while capturing Li⁺ for regeneration of LiH.

Reverse Pulse Electrochemical Cell

Dendrites from typical 18 hour reaction (a) and (b) reduction after reverse pulsing.

XRD of cycled MgNi electrode in the presence of H₂ reveals the formation of LiH.
Current Progress: Recovery of LiBH$_4$ and LiAlH$_4$

- LiBH$_4$ and LiAlH$_4$ are costly additives needed to assist the crystallization process
- Alane was washed with ether to dissolve and recover LiBH$_4$ and LiAlH$_4$

99.9 % Recovery

XRD- depicts the recovery of LiAH4 and LiBH4 used in crystalizing alane

TGA shows the dehydrogenation of recovered of LiAH4 and LiBH4 sample used in crystalizing alane
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![Conductivity of Electrolytes Graph]

Courtesy of Ardica/SRI presentation
Current Progress: Alane from TEA Adduct

- Using THF/LiAlH4 or THF/NaAlH4 electrolytes are an order and half of magnitude more conductive than ether/LiAlH4 electrolyte
- However, Alane forms too stable of an adduct which makes it difficult to break into AlH₃ crystals and THF
- We have shown in the past that it is possible to convert alane THF adduct to alane Triethylamine (TEA) adduct and obtain alane*
- Although not to assist in increasing ionic conductivity similar conversion processes was shown by Graetz el.**, using TMA

$$\text{AlH}_3\cdot n\text{THF} + \text{TEA} \rightarrow \text{AlH}_3\cdot \text{TEA} + \text{THF} \uparrow$$

$$\text{AlH}_3\cdot \text{TEA} \rightarrow \text{AlH}_3 (\alpha\text{-Crystals}) + \text{TEA} \uparrow$$

Figure shows the desorption of hydrogen from alane obtained through TEA conversion


Approach: Resolving Issues to Further Lower Cost of Alane

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Current Progress: Different Phases of Alane

Different Cyclization conditions lead to different phases (e.g. α, α’, β and γ)
Not all phases are suitable storage materials due to their instability and high reactivity

- Only α-phase > 5 micron crystal size is proven to keep its capacity for 10th of years
- The surface of α-phase crystals can be passivated and proven not to react with air or moisture

α’ crystals are unstable nano rods
α cubical crystals
Current Progress: Stable $\alpha$-Alane and Passivation Process

In order to obtain stable alane powder:

- Alane is washed with ether to dissolve any LiAlH$_4$ and LiBH$_4$ residues
- LiAlH$_4$ and LiBH$_4$ can be recovered as shown by our group
- 99.9% of LiAlH$_4$ and LiBH$_4$ was recovered from the wash
- Alane surface is passivated using acid and water as it’s been shown by the DOW’s methods
- Unusable and undesired by-products are dissolved and filtered high capacity alane product is obtained

At the beginning of passivation
In order to obtain stable alane powder:

- Alane is washed with ether to dissolve LiAlH₄ and LiBH₄ residues
- LiAlH₄ and LiBH₄ can be recovered as shown by our group
- 99.9% of LiAlH₄ and LiBH₄ was recovered from the wash
- Alane surface is passivated using acid and water as it’s been shown by the DOW’s methods
- Unusable and undesired by-products are dissolved and filtered high capacity alane product is obtained

**Toward the end of passivation**
Current Progress: Improvement of H₂ Content & Crystal Quality

- SRNL has achieved the crystallization of alane etherate adducts that have a 9.8 H₂ wt% at the 15 g scale
- SRNL is working with partners including Ardica, SRI, Albemarle, and other to better understand the crystallization process and enable scale-up of production to meet demand for portable power systems
- Work is ongoing to optimize the yield
- Utilizing process analytical to understand and control formation kinetics and thermodynamics

Graphs and images showing TGA/RGA data, SEM image, and XRD confirming α-alane formation.
Collaborations and Team members

**SRNL**
- Ragaiy Zidan
- Scott McWhorter
- Rob Lascola
- Joseph Teprovich
- Patrick Ward
- Scott Greenway
- Ted Motyka

**Ardica**
- Dick Martin

**and SRI**
- Robert Wilson
- Mark Petrie
- Steve Crouch-Baker
Remaining Challenges and Barriers

- Identify additives to further improve the conductivity of the electrolyte solution to increase the rate of alane production

- Develop improved understanding of crystallization processes for improved thermal control and processing kinetics

- Optimize the crystallization parameters for the large scale production of alpha alane

- Obtain high yield from alternative adduct
On-Going and Future work

- Using THF as solvent in electrolyte to increase conductivity

- Establishing efficient methods for crystallization of alane from different adducts such as TEA or TMA to enable the use of THF in the electrolyte

- Exploring using additives to the electrochemical cell which can increase the conductivity further

- Using *in-situ* spectroscopy (e.g. Raman) to identify the crystallization mechanisms

- Establishing advanced process analytical techniques that enable a continuous large-scale alane production operation
Summary

• Identified and addressed the most significant costs for the production of $\alpha$-alane

• Demonstrated recovery techniques for the expensive crystallization additives to reduce cost of alane production

• Demonstrated the formation of LiH during the electrochemical production of alane that further reduces dendrite formation

• Demonstrated a route to crystallize the alternative adduct produced by a transamination reaction from the THF adduct that enables the use of high ionic conductivity electrolyte

• Demonstrated production of high hydrogen content alane (9.8 wt%) at 15 g scale with high improved crystal quality