Synthesis and Properties of Aluminum Hydride as a Hydrogen Storage Material

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– A Participant in the DOE Metal Hydride Center of Excellence –

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This presentation does not contain any proprietary or confidential information
Overview

Timeline

• Project start date: FY05
• Project end date: FY09
• Percent complete: New Project

Budget

• Expected Total Project Funding:
  5 years: $3.00M
  – DOE Share: $2.60M
  – Contractor Share: $0.40M
Funding for FY05:
$200K (DOE),
$150K (cost share BNL-LDRD)

Barriers

Hydrogen reversibility
Energy penalty of regeneration

Targets

Total system gravimetric: >8%
Total system volumetric: > 0.10 kg H$_2$/L
Tank operating temp: 85/95°C
Tank operating pressure: 2 bar (30 psig)

Partners

• Participant in DOE Metal-Hydride Center of Excellence; collaborations with MHCoE partners on modeling, regeneration and engineer tank design
• Coordinator of sub-team on aluminum hydride for onboard hydrogen storage systems (U. Hawaii, JPL, SRNL, U. Illinois, Carnegie Mellon and SNL)
Mission Statement: To develop and demonstrate a safe and cost-effective light-metal hydride material system that meets or exceeds the DOE goals for on-board hydrogen storage.

Decomposition of AlH₃

\[ \text{AlH}_3 \rightarrow \frac{3}{2} \text{H}_2 + \text{Al} \] (Temp. = 60° – 100° C)

- H-capacity (g) = 10.1 wt% (DOE 2010 Storage-Target = 6.0)
- H-capacity (v) = 149 kg/m³ (DOE 2010 Storage-Target = 45)
- \( \Delta H_{\text{des}} = 7.6 \text{ kJ/mol H}_2 \) (only 20% of NaAlH₄)
Other partners in MHCoE will also contribute in areas of modeling, simulation, and diagnostics.
Baranowski & Tkacz, Z. Phys. Chem. NF, 135 (1983) 27
α-AlH$_3$ TPD Curves vs BM Time & Particle Size

Isothermal Kinetics of \( \alpha\)-AlH\(_3\) (Dow) 20 mol\% LiH

100°C Arrhenius Plot
\[
\text{Rate} = k_0 \exp \left(\frac{-Q}{RT}\right)
\]

- high-rate segment: \( k_0 = 6.5 \times 10^{12} \) and \( Q = 91.3 \text{ kJ/mol H}_2 \)
- lower-rate segment: \( k_0 = 5.4 \times 10^8 \) and \( Q = 68.2 \text{ kJ/mol H}_2 \)

A total of seven AlH$_3$ isomers are known to exist:

- $\alpha$, $\alpha'$, $\beta$, $\delta$, $\varepsilon$, $\gamma$, $\zeta$

With exception of $\alpha$-AlH$_3$, little is known about these polymorphs.

- $\alpha$, $\beta$, and $\gamma$ phases can be grown using an organo-metallic synthesis method.

\[
\begin{align*}
3\text{LiAlH}_4 + \text{AlCl}_3 + \text{ether} \\
\downarrow \quad \text{(filter)} \\
4\text{AlH}_3 + 3\text{LiCl} + \text{ether} \\
\downarrow \quad \text{(remove ether)} \\
4\text{AlH}_3
\end{align*}
\]
AlH₃ Synthesis

• Ethereal reaction of AlCl₃ and LiAlH₄ yields solvated AlH₃
• Solvent removed by adding excess LiAlH₄ and heating at 60-70° C
• Desolvated AlH$_3$ undergoes a number of phase transitions at 60° C

\[
\text{AlH}_3 \text{ etherate} \rightarrow \beta + \gamma \rightarrow \alpha \rightarrow \text{Al}
\]

• Transformations occur with little/no H$_2$ evolution

• AlH$_3$ decomposition note induction period ~10 h at 60° C

\[\gamma-\text{AlH}_3 \text{ and } \beta-\text{AlH}_3 \text{ do not appear to decompose directly to Al and H}_2 \text{ at 60° C, rather, a transformation to a more stable polymorph (}\alpha-\text{AlH}_3\text{) occurs first. } \alpha-\text{AlH}_3 \text{ then undergoes complete decomposition to the elements at 60° C (t~100 h).}\]
Temperature Programmed Decomposition

- $\alpha$AlH$_3$ synthesized by DOW Chem. Co. composed of large crystallites (50 - 100 $\mu$m) aged 25 yrs in air:
  - measure hydrogen capacity 8 wt%
  - onset of rapid H$_2$ evolution occurs at 160° C

- BNL synthesized AlH$_3$
  - measured hydrogen capacity $\sim$10 wt%
  - onset of rapid H$_2$ evolution occurs at 120° C
Reversible AlH₃

• AlH₃ may be regenerated from recovered products after hydrogen fuel is spent

\[
\begin{align*}
\text{AlCl}_3 + \text{NaAlH}_4 & \rightarrow \text{AlH}_3 + \text{NaCl} \\
\text{NaCl electrolysis} & \rightarrow \text{Na} + 3/2\text{H}_2 \\
\text{Al} + 3\text{Cl} & \rightarrow \text{AlCl}_3 \\
\text{Recycled} & \rightarrow \text{H}_2 \\
\text{Fuel} & \rightarrow \text{Al} \text{ recovered after H}_2 \text{ fuel is exhausted}
\end{align*}
\]

Note: system is “reversible” since all products are recovered and reused (except hydrogen).
Onboard Recharging
Problem with Conventional Hydrides

How much heat must be removed during recharging?
DOE 2010 Target = 3 min = 1.67 kg/min (5 kg H₂ tank)
Take as example NaAlH₄ (ΔH = -37 kJ/mol H₂)

\[ \frac{dQ}{dt} = 510 \text{ kw} \text{ or } Q_{\text{total}} = 91.8\text{MJ} \]
⇒ Offboard recharge required
Milestones/Decision Points

Deliverables:
- 10 gm. AlH$_3$ samples to SwRI; 8% or better by wt. @ 150°C; FY 06
- 10 gm. AlH$_3$ samples to SwRI; 9% or better by wt. @ 85/95°C; FY 07
- 1000 gm AlH$_3$ samples to SNL for fuel tank development and testing; FY 08

Decision Points:
- selection of either direct or chemical method of regeneration; FY 06
- selection of additives and optimum particle size for AlH$_3$; FY 07
- selection of tank refueling method; FY 08

Go/No-Go:
- on the direct onboard re-hydriding of spent aluminum powder; FY 06

Milestones
- complete stability and shelve life studies on AlH$_3$; FY 07
- complete thermal management studies on the control release of H$_2$; FY 08
- selection of method for regenerating AlH$_3$; FY 09
### Summary of Program Plans

<table>
<thead>
<tr>
<th>TASK</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
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<tbody>
<tr>
<td><strong>Task 1: AlH₃ Synthesis</strong></td>
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<td>- Particle Size and Additives</td>
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<td>- Regeneration Studies</td>
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**Notes:**
- Milestone
- Down-select
- Regen. method
- Select particle size and additives
- 10 gm samples
- 1000 gm sample
- Go/No-Go direct re-hydride
- Down-select tank refuel
- 1000 gm sample
1. $\text{AlH}_3$ is a promising $\text{H}_2$ fuel source for a PEM fuel cell due to the high gravimetric/volumetric hydrogen capacity and the low heat required to extract $\text{H}_2$ (7.6 kJ/mol $\text{H}_2$).

2. Doping aged $\text{AlH}_3$ (DOW) with LiH, NaH or KH increases low-temperature decomposition kinetics.

3. $\alpha$, $\beta$ and $\gamma$ AlH$_3$ have been synthesized at BNL using organo-metallic methods

4. Hydrogen capacities approaching 10 wt% at $T < 100^\circ$ C have been demonstrated with freshly prepared AlH$_3$

5. Recharging of spent Al back to AlH$_3$ likely to be done with an offboard process yet to be developed.