Aluminum Hydride Regeneration

Jason Graetz, J. Wegrzyn, J. Reilly, J. Johnson, Y. Celebi and WM Zhou
Brookhaven National Laboratory

Project ID
#ST 39

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

Timeline
- Project start date: FY05
- Project end date: FY10
- 60 % complete

Budget
- Expected total project funding:
  - $4.00M (DOE)
- Funding received in FY07
  - $960K (DOE)
- Funding for FY08
  - $1.125M (DOE)

Barriers
- MYPP Section 3.3.4.2.1 On-Board Storage Barriers
  - A. Weight & Volume
  - B. Cost
  - C. Efficiency
  - D. Durability/Operability
  - E. Charge/Discharge Rates
  - R. Regeneration Processes

Partners and Collaborators
- Project D (aluminum hydride) Lead
  - UH-UNB, ORNL, SRNL, SNL
- Other collaborations: JPL, UIUC, ANL
- Chemical Hydride Center
- International Energy Agency (IEA)
Challenges and Objectives

Objective: Develop a material that supports the 2010 DOE technical performance targets using Aluminum Hydride (AlH$_3$), by fully elucidating the nature of hydrogen desorption from AlH$_3$ and developing an efficient regeneration method.

1. Develop new routes to prepare pure crystalline $\alpha$-AlH$_3$ from Al (spent fuel) with minimal energy cost
2. Assist the engineering design for an off-board system based on AlH$_3$

Challenge: AlH$_3$ thermodynamically unstable below 7 kbar (300K)

1. In an AlH$_3$ system H$_2$ evolution controlled by T (rather than P) so the ability to tune decomposition kinetics will be critical - Various routes exist to adjust kinetics (e.g. size, coatings and catalysts)
2. The key issue is regeneration (hydrogenation of Al metal), and multiple regeneration pathways are being investigated
Routes to AlH₃ Regeneration
MHCoE Project D Lead: Jim Wegrzyn, BNL

BNL (POC)
Liquid phase - alane harvesting

SRNL
Electrochemical

U. Hawaii/UNB
Supercritical fluids

ORNL
Ionic liquids

SNL – calculations of adduct stability

UIUC – studies of reaction products and catalyst distribution

ANL - Cycle life analysis (not MHCoE)
BNL Approach to AlH₃ Regeneration

Alane (AlH₃) harvesting

**Step I:** Form molecular AlH₃ by hydrogenating Ti-catalyzed Al and harvest/stabilize AlH₃ as a Lewis Acid/Base adduct

**Step II:** Remove stabilizing species and recover AlH₃

stabilizer ≡ amine (TEDA), alkali hydride (LiH), solvent (THF)
Methods and Materials

- Ti catalyzed Al (Al*) prepared by first making AlH₃ with TiCl₃ in ether and then decomposing the ether adduct

\[3\text{LiAlH}_4 + \text{AlCl}_3 + 0.08\text{TiCl}_3 \xrightarrow{\text{Et}_2\text{O}} 3.24\text{LiCl} \downarrow + 4\text{AlH}_3\cdot\text{Et}_2\text{O} + 0.08\text{Ti}\]

\[4\text{AlH}_3\cdot\text{Et}_2\text{O} + 0.08\text{Ti} \xrightarrow{100^\circ\text{C} \text{ 2 hrs}} 4\text{Al} + 0.08\text{Ti}\]

- Typical catalyst concentration was 2 mol % Ti
  - Recent results suggest reactions will work with much lower catalyst concentration

- Reactions performed in solvent medium: THF, Et₂O
  - Solvent acts as electron donor and helps stabilize AlHₓ
TEM studies of Ti catalyzed Al at UIUC (Ian Robertson and Dennis Graham)

- Al crystals (average grain size 165 nm) show few defects
- Ti well-dispersed throughout Al matrix - no enhancement of Ti at particle edge suggests Ti not just on surface but distributed through the bulk
Proposed reaction: \( \text{Al} + \text{TEDA} + \frac{3}{2}\text{H}_2 \rightarrow \text{AlH}_3\cdot\text{TEDA} \)

- Hydrogenation reaction does not occur without Ti catalyst
- \( \text{AlH}_3\cdot\text{TEDA} \) is reversible in other solvents (THF, dodecane)
- Reversible capacity \(~100\%\) of theoretical (2.1 wt\%)
Theory Guides Choice of Adduct

Accurate Al-N bond dissociation energies (BDE’s) needed to guide optimal choice of adduct for AlH₃ regeneration ...

- Employ “Bond Additivity Correction” to provide accurate Al-N bond dissociation energies (BDE’s)

- BAC values differ from DFT predictions (S. McGrady (UNB) shown in back-up slides), but similar trends

- AlH₃-TEDA exhibits strong Al-N Bond while AlH₃-NEt₃ has a weak Al-N bond

- Pyridine and pyrazine are promising amines with moderate Al-N energies

-1:2 complexes (e.g. (AlH₃)-2pyrazine) are significantly less stable

- Future efforts look at Al-O bond energies

Results from gas-phase calculations:

<table>
<thead>
<tr>
<th>1:1 Complexes</th>
<th>Al-N BDE* (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlH₃--NH₃</td>
<td>142.7</td>
</tr>
<tr>
<td>AlH₃--NMe₃</td>
<td>147.6</td>
</tr>
<tr>
<td>AlH₃--NEt₃</td>
<td>118.6</td>
</tr>
<tr>
<td>AlH₃--TEDA</td>
<td>156.3</td>
</tr>
<tr>
<td>AlH₃--Quinuclidine</td>
<td>159.9</td>
</tr>
<tr>
<td>AlH₃--pyridine</td>
<td>135.2</td>
</tr>
<tr>
<td>AlH₃--pyrazine</td>
<td>125.3</td>
</tr>
<tr>
<td>AlH₃--2TEDA</td>
<td>233.8</td>
</tr>
<tr>
<td>AlH₃--2NEt₃</td>
<td>158.7</td>
</tr>
</tbody>
</table>

BDE = Energy to dissociate to AlH₃+ligands

BAC-MP2 M. Allendorf (Sandia)
Other compounds prepared by “alane harvesting”

Other alane compounds may be useful intermediates to forming AlH₃. Can we make LiAlH₄ from Al*, LiH (stabilizer) and H₂ in THF?

![Graph showing pressure over time for Al (no Ti) and Al + 2% Ti with reaction equations](image)

**YES!** Hydrogenation occurred at low pressure (<13 bar) and low temp (300K) - no hydrogenation without Ti
Reversible Lithium Alanate

LiAlH$_4$ is not normally reversible, yet….

- Reaction is reversible (~90%) at moderate pressure and temperature
- If we can extract THF we have a simple regen. route for LiAlH$_4$
- We may be able to use LiAlH$_4$ as step to $\alpha$-AlH$_3$
Recovering AlH₃ from Adduct

AlH₃ recovered from AlH₃·Et₂O by heating 70°C under vacuum

\[
\text{AlH₃-Et₂O} \xrightarrow{70°C \ 4\text{hrs}} \text{AlH₃} + \text{Et₂O}\uparrow
\]

Similar method used to recover AlH₃ from alane-amine (AlH₃-TEA)

\[
\text{AlH₃-TEA} \xrightarrow{70°C \ 3\text{hrs}} \text{AlH₃} + \text{TEA}\uparrow
\]

No success yet recovering AlH₃ from TEDA

\[
\text{AlH₃} \xrightarrow{} \text{AlH₃} + \text{TEDA}
\]

XRD plot demonstrates AlH₃ can be recovered from alane-amines
LiAlH$_4$ Recovery From LiAlH$_4$·THF

**Procedure:** LiAlH$_4$·THF heated ~60°C under vacuum for ~4hrs

- XRD confirms Ti-catalyzed LiAlH$_4$ recovered from LiAlH$_4$·THF

- Reaction precursors (LiH + Al$^*$)
Multi-Step Pathways

Direct two-step approach is preferred, but a multi-step scheme may have lowest overall energy cost

Direct formation of AlH₃-TMA:

\[
\text{Al} + \frac{3}{2} \text{H}_2 + \text{N(CH}_3\text{)}_3 \rightarrow (\text{AlH}_3) \cdot \text{N(CH}_3\text{)}_3
\]

known reaction

Murib Patent 3,642,853

Amine exchange (transamination):

\[
(\text{AlH}_3) \cdot \text{N(CH}_3\text{)}_3 + \text{NR}_3 \rightarrow \text{AlH}_3 \cdot \text{NR}_3 + \text{N(CH}_3\text{)}_3
\]

known reaction

Direct formation of LiAlH₄-nTHF:

\[
\text{Al} + \frac{3}{2} \text{H}_2 + \text{LiH} + \text{nTHF} \rightarrow \text{LiAlH}_4 \cdot \text{nTHF}
\]

demonstrated reaction

Exchange THF for tertiary amine:

\[
3\text{LiAlH}_4 \cdot \text{nTHF} + \text{NR}_3 \rightarrow \text{Li}_3\text{AlH}_6 + 2\text{AlH}_3 \cdot \text{NR}_3
\]

possible reaction

Decomposition and recovery:

\[
\text{AlH}_3 \cdot \text{NR}_3 \rightarrow \text{AlH}_3 + \text{NR}_3
\]

demonstrated reaction

\[\text{Note: Li}_3\text{AlH}_6 \text{ may be decomposed to LiH + Al or possibly regenerated directly to LiAlH}_4\]

Overall reaction: \[\text{Al} + \frac{3}{2}\text{H}_2 \rightarrow \text{AlH}_3\]
Goal: Develop and demonstrate a storage system that meets DOE targets using aluminum hydride as hydrogen fuel source.

Four major accomplishments:
(1) Developed a simple method to prepare Ti-catalyzed Al for Al hydrogenation reactions, Ti uniformity confirmed by TEM/EDS
(2) Demonstrated reversible hydrogenation of spent Al* and TEDA to form AlH$_3$-TEDA in solution at low P and T
(3) Developed preliminary method based on TEA and Et$_2$O to separate stabilized alanes and recover $\alpha$-AlH$_3$
(4) Demonstrated reversible hydrogenation of spent Al* and LiH to form LiAlH$_4$ in solution at low P and T
Path Forward

**FY08:** Demonstration of complete regeneration cycle

Identify new pathways to $\alpha\text{-AlH}_3$
- direct formation of alane adducts (pyridine, pyrazine, ethers, …)
- recovering hydride from alane-adducts, determine energy penalty

**Continue effort on two existing pathways:**

\[
\text{Al + H}_2 \rightarrow \text{AlH}_3\text{-TMA} \rightarrow \text{AlH}_3 \text{-TEA} \rightarrow \text{AlH}_3
\]

\[
\text{Al + H}_2 + \text{LiH} \rightarrow \text{LiAlH}_4 \rightarrow \text{AlH}_3\text{-TEA} \rightarrow \text{AlH}_3
\]

**Go/no-go** on regeneration using organometallic approach

**Down select** (FY08) type(s) of alane adduct(s) for further study

**FY09:** Regenerate AlH$_3$ with $E$ penalty $\leq$ 73 kJ/H$_2$ (30% of fuel energy)

Work with partners to determine mass balance & energy cost

Begin investigation of alane slurries and liquid carriers

Work with group(s) in Engineering CoE on alane system