Synthesis and Characterization of Alanes for Automotive Applications

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Part of the DOE Metal Hydride Center of Excellence

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Overview

Timeline
• Project start date: FY05
• Project end date: FY10
• 40 % complete

Budget
• Expected total project funding:
  – $3.00M (DOE)
• Funding received in FY06
  – $400K (DOE)
• Funding for FY07:
  – $925K (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
  - JPL, U. Hawaii, ORNL, SRNL, SNL
• Chemical Hydride Center
• IPHE and IEA collaborations
  - IFE (Norway), Polish Academy of Sciences, Russian Academy of Sciences, Academy of Sciences of Ukraine
Challenges and Objectives

Goal: Develop and demonstrate a hydrogen storage system that meets DOE targets using aluminum hydride as a hydrogen fuel source.

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)
   2. The key issue is regeneration (hydrogenation of Al metal)
      - Multiple regeneration pathways are being investigated

Objectives:
   1. Produce aluminum hydride with 9 wt. % H$_2$ and 0.13 kg H$_2$/L
   2. Develop practical and economical process for the regeneration of AlH$_3$ from the decomposed Al.
   3. Assist in the design for an onboard fuel tank delivery system
BNL Approach

**Task 1: Synthesis**
Synthesize $\alpha$-AlH$_3$ and vary particle size (0.1-50 $\mu$m) & surface coating

**Task 2: Properties**
Decomposition rates for $\alpha$-AlH$_3$ as a function of particle size & morphology

**Task 3: Regeneration**
- Recycling: adapt synthesis to reduce/reuse byproducts
- Organometallic: Direct Al hydrogenation in organic solvents

**Task 4: Tank Study**
Refueling strategy - off-board (transfer of liquid/powder, tank swap, etc.)

**Task 5: Management**
- Coordinate MHCoE Alane subgroup
- Partnerships and reporting: supplying partners with samples (e.g. AlH$_3$)
- Materials characterization at unique BNL facilities (e.g. NSLS and CFN)
Why AlH$_3$?

– Large gravimetric & volumetric capacity
  10.1 wt% (2010 S-Target = 6.0)
  149 g/L (2010 S-Target = 45)

– Low decomposition enthalpy
  $\Delta H_{\alpha AlH_3} \approx 7 \text{ kJ/mol } H_2$ ($\approx 1/5 \Delta H_{NaAlH_4}$)

– Rapid H$_2$ evolution rates at low T
  Meets DOE target (50 kW FC) at 115°C with 45% FC efficiency
  (120kW at 100%)

– Decomposition rates tuned through particle size and coatings

– High purity H$_2$ - AlH$_3$ decomposes to Al and H$_2$ (no side reactions)

– Cyclability - Offboard regeneration may reduce cycling problems

– Regeneration will be challenging, but intrinsic energy costs are low
Progress on Regeneration

- **FY06: Background studies** - regeneration requires a basic understanding of physics/chemistry of AlH₃
  - Crystallographic Structures of AlH₃
  - Thermodynamics
  - $P-T$ phase diagram for $\alpha$-AlH₃
  - Literature Review (selected organometallic route for exp. study)
  - Preliminary experimental design and safety review

- **Program Review Feedback** - focus on regeneration

- **FY07 - Multiple approaches to regeneration**
  - Recycling route studies (e.g. LiCl splitting)
  - Organometallic route - Experimental progress to date:
    - Retrofit 200 bar Parr reactor and purchased 340 bar PPI reactor
    - Preliminary studies on AlH₃-TEDA in THF and dodecane
    - Reduced hydrogenation pressure using activated Al powder
  - Electrochemical route being investigated at SRNL
  - Supercritical fluid route being investigated at UH (proposal submitted)
Synthesis of AlH$_3$

- Regeneration rate and efficiency will likely be a function of crystallite size and surface condition
- Different AlH$_3$ morphologies easily prepared in conventional procedure

$$3\text{LiAlH}_4 + \text{AlCl}_3 + \text{ether} \rightarrow 3\text{LiCl} \downarrow + 4\text{AlH}_3\cdot1.2[(\text{C}_2\text{H}_5)_2\text{O}] + \text{ether}$$

Desolvation

Batch/Continuous Reactions

Microcrystallization Reaction

- Surface coatings (e.g. oxides) introduced through alcohol wash
Which Structure of AlH₃ is Most Stable?

– Regeneration requires better understanding of phases and stability
– 2005 Ke et al. identified two structures of AlH₃ (orthorhombic Cmcm and cubic Fd-3m) more stable than α-AlH₃ (hexagonal) using DFT
– 2006 IFE group solved the structure of α’-AlH₃ (orthorhombic, Cmcm)
– 2006 Collaboration UH, BNL and IFE synthesized and solved structures of β-AlH₃ (cubic, Fd-3m) and γ-AlH₃ (tetragonal, Pnnm)
– All three phases less stable than α-AlH₃ at temperatures ≥ 300K

Formation of $\alpha$-AlH$_3$ From the H$_2$ and Al

- Does $\alpha$-AlH$_3$ transform to a more stable phase at high pressure?
- What does the $\alpha$-AlH$_3$ phase diagram look like?

Structural studies of $\alpha$-AlH$_3$ show no first-order phase transition at high pressure*

DFT results based on exp. lattice suggest structure is destabilized at pressure**

No hydrogenation below 573K - low T region of phase diagram calculated from $\Delta G$

AlH$_3$ formation limited by thermodynamics and low temperature kinetics

*Performed by synchrotron x-ray diffraction (funded through BES)

**Funded through BES
Regeneration Energy Requirements and
BNL Targets

In an effort to concentrate on the most promising pathways we have established two regeneration targets:

(1) Energy required for regeneration will not exceed 30% of the fuel energy
   - One mole of $\text{AlH}_3$ contains 360 kJ of fuel energy based on the lower heating value $LHV_{H_2}=120$ kJ/g = 240 kJ/mol $H_2$. Therefore, 30% energy target equivalent to $\Delta E_{\text{regen}} \leq 73$ kJ/mol $H_2$
   - Direct hydrogenation of Al to form $\text{AlH}_3$ (298K) requires a minimum of 0.13 J for every 1.0 J of fuel energy (13% of fuel energy needed for regeneration)

(2) Regeneration process will produce $\text{AlH}_3$ with at least 90% purity
   - Offboard hydrogenation will utilize spent Al
Recycling Route - LiCl splitting

**Synthesis:** $\text{AlCl}_3 + 3\text{LiH} \rightarrow \text{AlH}_3 + 3\text{LiCl}$

- Recycling byproducts (LiCl and Al) requires splitting $3\text{LiCl}$ per $\text{AlH}_3$:

**Recycling:** $\text{Al} + 3\text{LiCl} + 3/2\text{H}_2 \rightarrow \text{AlCl}_3 + 3\text{LiH}$

- With perfect efficiency ($\text{AlCl}_3$ & LiH formation energy not wasted):

$$\Delta E_{\text{recycle}} \geq 167 \text{ kJ/mol H}_2$$

- Recycling $\text{AlH}_3$ by splitting LiCl ($298K$) requires a minimum of $0.7J$ for every $1J$ of fuel (**70% of fuel energy required for regeneration**)

- Recycling $\text{AlH}_3$ by splitting LiCl will not be investigated further
Liquid Organometallic Route - Overview

– Form AlH₃ complexes from Al and H₂ in organic solvents (THF, Et₂O)
– Reduce $P_{eq}$ by forming a more stable intermediate phase
– Reaction between Al, H₂ and triethylenediamine (TEDA = C₆H₁₂N₂)

\[
\text{Al} + \text{H}_2 + \text{TEDA} \rightarrow \text{AlH}_3
\]

– **FY07 Milestone**: Improve hydrogenation kinetics & reduce required pressure
– Second step required to extract TEDA and recover pure AlH₃:

\[
\text{AlH}_3 \rightarrow \text{Al} + \text{H}_2 + \text{TEDA}
\]

– Another route under investigation is a reversible metal-organic hydride:

\[
\text{Al} + \text{H}_2 + \text{TEDA} \leftrightarrow \text{AlH}_3
\]

2.1 wt % H₂ (theoretical)
Liquid Organometallic Route - Results

Organometallic hydrogenation of aluminum

Hydrogenation of activated Al (Al*) at 300K occurred at much lower pressures than expected (no reaction with non-activated Al up to 110 bar)

Reaction is reversible: TEDA + Al* + H₂ ↔ TEDA-AlH₃ (theor. 2.1 wt% H₂)

Drop in hydrogen pressure indicates hydrogenation (~2 wt% total)
Liquid Organometallic Route - XRD Analysis

- Powder XRD confirms 100% of Al consumed in reaction (yield near 100%)
- No evidence of any phase other than TEDA-AlH₃ (no side reactions)

standard of AlH₃-TEDA prepared from AlH₃ and TEDA in THF
Product: TEDA-AlH₃
No trace of Al or TEDA

Starting materials:
- TEDA (solid)
- Al powder (solid)
- THF solvent (liquid)
- H₂ (gas)
Liquid Organometallic Route - FTIR Analysis

- Reaction works equally well in polar (THF) and nonpolar (dodecane) solvents.

No change in solvent (dodecane) after multiple hydrogenation cycles:
- no trace of AlH₃ in solution
- no solvent deterioration

- Solvent before hydrogenation
- Solvent after hydrogenation

No Al-H signal
Energy required to form TEDA-AlH$_3$ is small, but how much energy is required to break AlH$_3$ from TEDA to recover pure AlH$_3$?

From these values we can approximate the heat required to release AlH$_3$:

- TEDA-AlH$_3$ → TEDA + Al + 3/2H$_2$
  \[ \Delta H_{TEDA-AlH_3} = 53 \text{ kJ/mol H}_2 \]
- AlH$_3$ → Al + 3/2H$_2$
  \[ \Delta H_{AlH_3} = 7 \text{ kJ/mol H}_2 \]
- TEDA-AlH$_3$ → TEDA + AlH$_3$
  \[ \Delta H \approx 46 \text{ kJ/mol H}_2 \]

- Regeneration will require a minimum of 20% of the AlH$_3$ fuel energy
- Although energy requirement is not prohibitive the challenge will be extracting AlH$_3$ without decomposition
Path Forward - Regeneration

Preliminary Studies:
- Crystal structures and phase stabilities (complete)
- Reproduce Ashby’s reaction (complete)
- Reduce hydrogenation pressure and temperature (complete)
- Explore Activated Al powder (ongoing)

Regressive Routes To Be Investigated:
Preparation of pure AlH$_3$ by isolating from alane-adduct

\[
\text{AlH}_3 + \text{amine/adduct} \rightarrow \text{AlH}_3 + \text{amine/adduct}
\]

- Examine amine/adduct substitutions that form less stable compounds
- Evaluate energy requirements

Reversible metal organic hydrides:

\[
\text{Al} + \text{H}_2 + \text{amine/adduct} \leftrightarrow \text{AlH}_3
\]

- Examine solvent and adduct substitutions to determine if capacity can be improved
- Evaluate thermodynamics
Path Forward - Regeneration

Collaborations:

MHCoE Theory Group - Identify possible adduct substitutions; Search for lighter adducts that accommodate multiple AlH₃ units; amine-alane chemistry

Chemical Hydride Center of Excellence - Information exchange; Synergisms between amine-borane and amine-alane investigations

IPHE/IEA - Fundamental high pressure studies; high pressure hydrogenation; decomposition kinetics, in situ synchrotron XRD

Decisions and Milestones:

- FY07 Milestone: Hydrogenate Al at low temp and pressure (P<70 bar)
- FY08 Go/no-go: Regeneration using organometallic approach
- FY09: Overall objective to regenerate AlH₃ with energy penalty \( \leq 73 \text{ kJ/H}_2 \) and a yield of \( \geq 90\% \) and (2) Determine mass/energy balance over 100 cycles on 5g samples
Project Summary

Goal: Develop and demonstrate a hydrogen storage system that meets DOE targets using aluminum hydride as a hydrogen fuel source.

Significant accomplishment: **Direct hydrogenation of activated Al powder at P<35 bar (ten-fold reduction in pressure) with a yield near 100%**

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2010 System Target</th>
<th>FY07 materials*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric Capacity</td>
<td>kWh/kg, wt. % H₂</td>
<td>2.0, 6.0</td>
<td>3.17(3), 9.5(1)</td>
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<tr>
<td>Volumetric Capacity</td>
<td>kWh/L, Kg H₂/L</td>
<td>1.5, 0.045</td>
<td>4.75(4)x, 0.143(2)</td>
</tr>
<tr>
<td>Desorption Temperature</td>
<td>ºC</td>
<td>85</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Rate**(114 ºC)</td>
<td>g/s/kW</td>
<td>1.0**</td>
<td>0.14(1) / 1.0(1)</td>
</tr>
<tr>
<td>BNL Regeneration Target</td>
<td>kJ/mol H₂</td>
<td>73</td>
<td>—</td>
</tr>
</tbody>
</table>

* Data is based on material only, not system value; ** Based on 50kW FC with 45% efficiency for 100kg AlH₃; x Does not account for packing density (a conservative estimate for packing density is 50%)