Overview

Timeline

• Project start date: FY05
• Project end date: FY10
• 100 % complete

Budget

• Expected total project funding:
  – $4.00M (DOE)
• Funding received in FY09
  – $1.25M (DOE)
• Planned Funding for FY10
  – $800K (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

MHCoE 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)
Relevance: AlH$_3$

- High capacity: **10.1 wt%** and **149 g/L**
- Low decomposition enthalpy: $\Delta H \approx 7 \text{ kJ/mol H}_2 (\approx 1/5 \Delta H_{NaAlH_4})$
- Rapid H$_2$ evolution rates at low T
- Meets DOE target (0.02 gH$_2$/s) at 104°C (80 kW FC with 45% efficiency & 100 kg AlH$_3$)
- Decomposition rates can be tuned through particle size and coatings
- High purity H$_2$ - AlH$_3$ decomposes to Al and H$_2$ (no side reactions)

**Challenge:** AlH$_3$ not “on-board” reversible

**Objective:** Develop low energy pathway to regenerate AlH$_3$
Approach

Objective: Meet 2010 DOE technical performance targets using kinetically stabilized aluminum-based hydrides (e.g. LiAlH$_4$ and AlH$_3$)

1. Develop low-energy ($\leq$73 kJ/H$_2$ or 30% of fuel energy) regeneration routes to prepare kinetically stabilized hydrides from the spent fuel
2. Assist the engineering design for an off-board system based on a kinetically stabilized hydride

Challenge: These hydrides are thermodynamically unstable at 300K

1. How do we control the H$_2$ evolution? One solution may be a pumpable slurry but how will this impact H$_2$ rates and capacity?
2. Can we regenerate these hydrides from the spent material using a low cost and low energy process?

Two-step approach to regeneration of Al-based hydrides:

**Step I:** Alane stabilization - Form stabilized alane complex by direct hydrogenation of catalyzed Al and complexing agent (e.g. amine)

**Step II:** Remove stabilizing species and recover AlH$_3$
Accomplishments: Previous results

- Demonstrated a low-energy regeneration route for LiAlH₄:
  \[
  \text{LiH} + \text{Al}^{\ast} + \frac{3}{2}\text{H}_2 \xrightarrow{\text{THF}} \text{LiAlH}_4-\text{THF} \xrightarrow{60^\circ C/4\text{hrs}} \text{LiAlH}_4 + \text{THF}^\uparrow
  \]
  
  (spent material)

- Demonstrated the direct formation of AlH₃ from Al* and H₂ under mild conditions using amines:
  \[
  \text{C}_7\text{H}_{13}\text{N} + \text{Al}^{\ast} + \frac{3}{2}\text{H}_2 \rightarrow \text{C}_7\text{H}_{13}\text{N-AlH}_3
  \]

- Preliminary results on H₂ evolution rates from AlH₃ in slurries

- Pressure drop indicates hydrogenation of Al occurs at low pressures

- Al-H stretch in FTIR confirms formation of AlH₃

- Quinuclidine alane \((\text{C}_7\text{H}_{13}\text{N-AlH}_3)\)

- Transmitted intensity

- Product \((\text{C}_7\text{H}_{13}\text{N-AlH}_3)\)

- Al-H stretching modes
Accomplishments: New results
Revised regeneration procedure to incorporate transamimation

Step 1: formation of NR₃-AlH₃ by direct hydrogenation
- Five alane adducts formed by direct hydrogenation under mild conditions (complete - no longer investigating new adducts)
- Alane adducts also formed by reacting amine directly with alane

Step 2: transamination exchange NR₃ for TEA
- Transamination demonstrated starting with DMEA and TMA (complete - may need follow up to decrease time, temp., …)

Step 3: separation of TEA-AlH₃
- Separation of TEA-AlH₃ successful with ~70% AlH₃ recovery (additional optimization is necessary to improve yields)

- Ongoing effort to combine steps 1-3 and optimize yield and efficiency
- Well-to-tank efficiency estimates of 40-55% using this route with TMA (WTT target is 70%)
Step 1: Low pressure AlH₃ formation

**Triethylenediamine (TEDA) alane:**
\[ C₆H₁₂N₂ + Al^* + 3/2H₂ \rightarrow C₆H₁₂N₂-AlH₃ \]
\[ P < 30 \text{ bar} \quad T = 300 \text{ K} \]

**Trimethylamine (TMA) alane:**
\[ 2C₃H₉N + Al^* + 3/2H₂ \rightarrow 2C₃H₉N-AlH₃ \]
\[ P < 230 \text{ bar} \quad T = 300 \text{ K} \]

**Quinuclidine alane:**
\[ 2C₇H₁₃N + Al^* + 3/2H₂ \rightarrow 2C₇H₁₃N-AlH₃ \]
\[ P < 60 \text{ bar} \quad T = 300 \text{ K} \]

**Hexamine alane:**
\[ C₆H₁₂N₄ + Al^* + 3/2H₂ \rightarrow C₆H₁₂N₄-AlH₃ \]
\[ P < 60 \text{ bar} \quad T = 300 \text{ K} \]

**Dimethylethylamine (DMEA) alane:**
\[ C₄H₁₁N + Al^* + 3/2H₂ \rightarrow C₄H₁₁N-AlH₃ \]
\[ P < 60 \text{ bar} \quad T = 300 \text{ K} \]
Step 1: Adduct Formation

- No success retrieving AlH₃ from any of the five alane amines synthesized by direct hydrogenation - adducts decompose upon heating
- Identified only one amine alane, triethylamine alane (TEA-AlH₃), that can be separated to recover pure α-AlH₃

\[
\text{TEA- AlH}_3 \xrightarrow[70\,^\circ\mathrm{C}\,3\,\text{hrs}]{\text{70\,^\circ\mathrm{C}\,3\,\text{hrs}}} \text{AlH}_3 + \text{TEA}
\]

- TEA-AlH₃ cannot be formed by direct hydrogenation only by a direct reaction with AlH₃

\[
\text{C}_6\text{H}_{15}\text{N} + \text{AlH}_3 \rightarrow \text{C}_6\text{H}_{15}\text{N-}\text{AlH}_3
\]

...we found other adducts formed by same method:

**Triethylenediamine alane:** \[\text{C}_6\text{H}_{12}\text{N}_2 + \text{AlH}_3 \rightarrow \text{C}_6\text{H}_{12}\text{N}_2-\text{AlH}_3\]

**Trimethylamine alane:** \[2\text{C}_3\text{H}_9\text{N} + \text{AlH}_3 \rightarrow 2\text{C}_3\text{H}_9\text{N-}\text{AlH}_3\]

**Quinuclidine alane:** \[2\text{C}_7\text{H}_{13}\text{N} + \text{AlH}_3 \rightarrow 2\text{C}_7\text{H}_{13}\text{N-}\text{AlH}_3\]

**Hexamine alane:** \[\text{C}_6\text{H}_{12}\text{N}_4 + \text{AlH}_3 \rightarrow \text{C}_6\text{H}_{12}\text{N}_4-\text{AlH}_3\]

**Dimethylethylamine alane:** \[\text{C}_4\text{H}_{11}\text{N} + \text{AlH}_3 \rightarrow \text{C}_4\text{H}_{11}\text{N-}\text{AlH}_3\]
TEA-alane and transamination

• No success separating any of the five alane amines synthesized by direct hydrogenation - adducts decompose upon heating

• Triethylamine alane (TEA-AlH₃) can be separated to recover AlH₃

$$\text{TEA-AlH}_3 \xrightarrow{70^\circ C, 3\text{hrs}} \text{AlH}_3 + \text{TEA}$$

Since it is the only amine alane that is easily separated, TEA-AlH₃ is a critically important compound for the regeneration process...

...but TEA-AlH₃ does not form by direct hydrogenation (from H₂)

• Can we use an exchange or transamination reaction to form AlH₃-TEA from another amine alane (NR₃-AlH₃) that forms more readily?

• Possibly, but exchange is thermodynamically uphill so we need to maintain a high concentration of TEA and preferentially remove NR₃ to drive reaction

• Fortunately, TEA-AlH₃ has a low vapor pressure so all we need is an amine (NR₃) with a high Vp that forms a stable NR₃-AlH₃ adduct: TMA and DMEA
Step 2: amine exchange (transamination)

Transamination reaction to form TEA-$\text{AlH}_3$ from DMEA-$\text{AlH}_3$

$\text{AlH}_3$-$\text{DMEA} + \text{TEA} \xrightarrow{50^\circ\text{C} \text{ for 3 hrs}} \text{AlH}_3$-$\text{TEA} + \text{DMEA} \uparrow$

DMEA-$\text{AlH}_3$ + 4TEA

$T = 50^\circ\text{C}$

$\Pi_i = 1$ bar

$\Pi_f = 26$ mbar

_time = 4.5 hrs_

Al-H stretch in FTIR used to identify type of adduct:

DMEA-$\text{AlH}_3$: ~1710 cm$^{-1}$

TEA-$\text{AlH}_3$: ~1780 cm$^{-1}$

FTIR confirms final product after transamination is TEA-$\text{AlH}_3$
Step 2: amine exchange (transamination)

Transamination reaction to form TEA-AlH$_3$ from TMA-AlH$_3$

\[ \text{AlH}_3\text{-TMA} + \text{TEA} \xrightarrow{50^\circ\text{C}, 3\text{hrs}} \text{AlH}_3\text{-TEA} + \text{TMA} \uparrow \]

TMA-AlH$_3$ + 4TEA

T = 50ºC
N$_2$ flow (P = 1 bar)
time = 2 hrs

Al-H stretch in FTIR used to identify type of adduct:

\[ \text{TMA-AlH}_3: \sim 1700 \text{ cm}^{-1} \]
\[ \text{TEA-AlH}_3: \sim 1780 \text{ cm}^{-1} \]

FTIR confirms final product after transamination is TEA-AlH$_3$
Step 3: Separation of TEA-AlH\textsubscript{3}

- TEA-AlH\textsubscript{3} successfully separated at 70°C under vacuum (<100 mbar)
- Analysis of recovered AlH\textsubscript{3} (XRD and decomposition) suggests ~70% AlH\textsubscript{3} with 30% Al
Combining step 2 + 3: Separation of DMEA-AlH₃

- DMEA-AlH₃ separated by combining steps 1 & 2
- Analysis of recovered AlH₃ (XRD) suggests ~35% AlH₃ with 65% Al when steps 1 & 2 are combined
- Improvements expected with optimization & washes to remove unwanted material
Energy consumption for AlH$_3$ regeneration (per kg H$_2$ in AlH$_3$)

<table>
<thead>
<tr>
<th>Process (TMA route)</th>
<th>Operating Conditions</th>
<th>Q, MJ</th>
<th>E, kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compress H$_2$ from SMR to 30 bar</td>
<td>70, 30</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Compress circulating H$_2$ to 30 bar</td>
<td>70, 30</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Distill trimethylamine</td>
<td>65, 5, 1.0</td>
<td>28.6</td>
<td></td>
</tr>
<tr>
<td>Distill ether</td>
<td>25, 0.3, 0.3</td>
<td>22.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Decompose triethylamine alane</td>
<td>50, 0.2</td>
<td>20.2</td>
<td>1.4</td>
</tr>
<tr>
<td>Vacuum dry alane product</td>
<td>50, 10$^{-4}$ - 10$^{-1}$</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>71.9</td>
<td>3.6</td>
</tr>
</tbody>
</table>

- Without using wasted heat, well-to-tank (WTT) efficiency is 40.5%
- Using wasted heat for thermal energy increases WTT to 55%
- **Target is 70%** - improvements possible by reducing excess H$_2$, TMA and TEA, switching to gas flow (rather than vacuum) and using DMEA
# Collaborations

**MHCoE Project D - Aluminum hydride** (Lead: Jim Wegrzyn, BNL)

<table>
<thead>
<tr>
<th>BNL (POC)</th>
<th>SRNL</th>
<th>U. Hawaii/UNB</th>
<th>ORNL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid-alane harvesting</td>
<td>Electrochemical</td>
<td>Supercritical fluids</td>
<td>Ionic liquids</td>
</tr>
</tbody>
</table>

- **UC Davis (P. Power)** – sterically crowded ligands to stabilize unusual bonding and geometries
- **ECKA Granules of America** – Preparation of catalyzed Al
- **SNL** – calculations of adduct stability
- **UIUC** – studies of reaction products and catalyst distribution
- **ANL** – Cycle life analysis (not MHCoE)

## Industrial Partnerships

- We submitted a Navy STTR (N10A-T030) with Aspen Products to synthesize and characterize micron-sized AlH₃ particles for marine applications
- **A number of companies are interested in using AlH₃ in portable power systems and have contacted us requesting material or information**
Summary of Accomplishments

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

**Major accomplishments:**

**Step 1:** Five pathways identified to form AlH₃ adducts from H₂ and Al
- Triethylenediamine: \( \text{C}_6\text{H}_{12}\text{N}_2 + \text{Al}^* + \frac{3}{2}\text{H}_2 \rightarrow \text{C}_6\text{H}_{12}\text{N}_2\text{-AlH}_3 \)
- Quinuclidine alane: \( \text{C}_7\text{H}_{13}\text{N} + \text{Al}^* + \frac{3}{2}\text{H}_2 \rightarrow \text{C}_7\text{H}_{13}\text{N}\text{-AlH}_3 \)
- Dimethylethylamine alane: \( \text{C}_4\text{H}_{11}\text{N} + \text{Al}^* + \frac{3}{2}\text{H}_2 \rightarrow \text{C}_7\text{H}_{13}\text{N}\text{-AlH}_3 \)
- Hexamine alane: \( \text{C}_6\text{H}_{12}\text{N}_4 + \text{Al}^* + \frac{3}{2}\text{H}_2 \rightarrow \text{C}_6\text{H}_{12}\text{N}_4\text{-AlH}_3 \)
- Trimethylamine alane: \( 2\text{C}_3\text{H}_9\text{N} + \text{Al}^* + \frac{3}{2}\text{H}_2 \rightarrow 2\text{C}_3\text{H}_9\text{N}\text{-AlH}_3 \)

**Step 2:** Transamination demonstrated with high yields for DMEA and TMA using dynamic vacuum and inert gas sweep methods

**Step 3:** TEA-AlH₃ separated with ~70% recovered AlH₃

• ANL analysis of WTT efficiency suggests 55% possible with TMA route using waste heat
Proposed Future Work

• Improve and optimize regeneration pathways:

  Pathway 1: \( \text{Al} + \text{H}_2 + \text{TMA} \rightarrow \text{AlH}_3\text{-TMA} \xrightarrow{\text{TEA}} \text{AlH}_3\text{-TEA} \rightarrow \text{AlH}_3 \)

  Pathway 2: \( \text{Al} + \text{H}_2 + \text{DMEA} \rightarrow \text{AlH}_3\text{-DMEA} \xrightarrow{\text{TEA}} \text{AlH}_3\text{-TEA} \rightarrow \text{AlH}_3 \)

• Regenerate AlH\(_3\) with \( E \) penalty \( \leq 73 \text{ kJ/H}_2 \) (70% Efficiency)

• Continue work with ANL to determine mass balance & energy cost for revised/improved regeneration method (TMA & DMEA)

• Continue investigation of alane slurries and liquid carriers - develop procedures to tune AlH\(_3\) particle size during regeneration

• Work with partners on safety and engineering of alane system
Supplemental Slides
### Methods and Materials

- Ti catalyzed Al (Al*) prepared by first making AlH$_3$ with TiCl$_3$ in ether and then decomposing the ether adduct

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

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

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

- Reactions performed in solvent medium: THF, Et$_2$O
  - Solvent acts as electron donor and helps stabilize AlH$_x$