# Aluminum Hydride Regeneration

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METAL HYDRIDE CENTER OF EXCELLENCE

BROOKHAVEN NATIONAL LABORATORY

Project ID # ST 034

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# 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:

$$\Delta H \approx 7\ \mathbf{kJ/mol\ H_2}\ (\approx\ 1/5\ \Delta H_{NaAlH4})$$

– Rapid $H_2$ evolution rates at low T

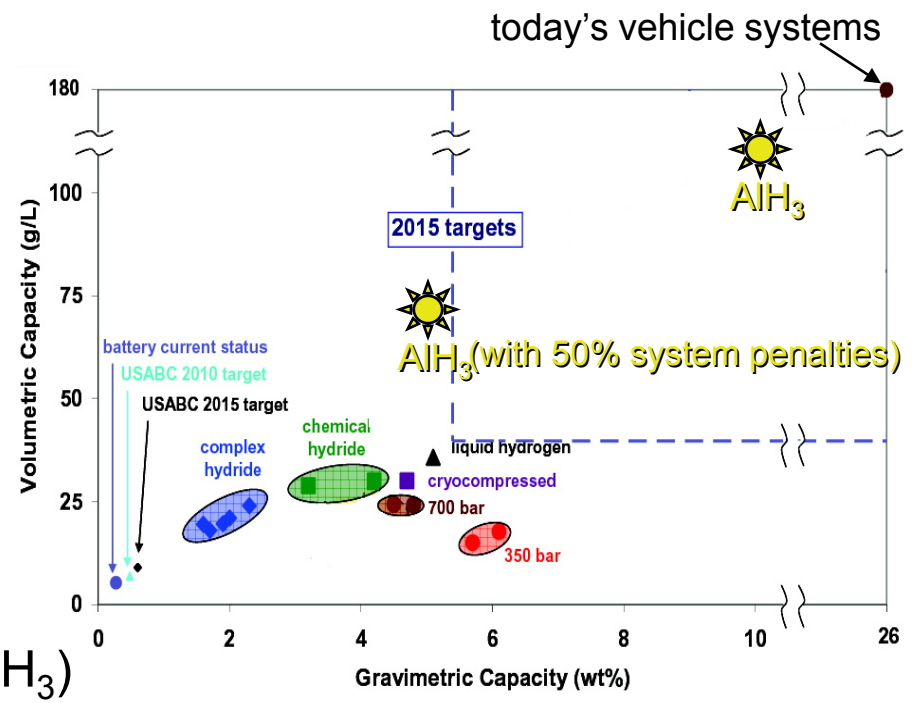
Meets DOE target (0.02 $gH_2/s$) at 104°C (80 kW FC with 45% efficiency & 100 kg $AlH_3$)

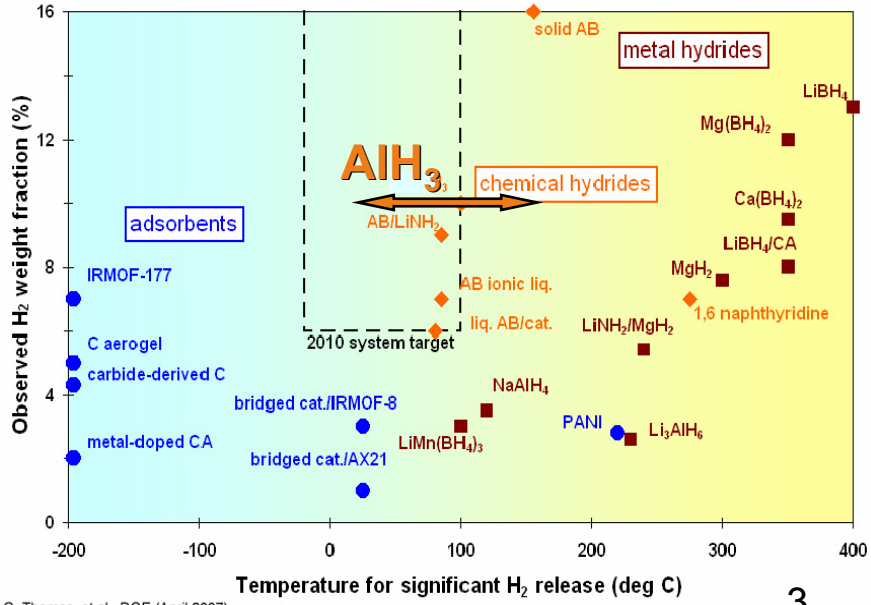
– Decomposition rates can be tuned through particle size and coatings

– 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 $AlH_3$




G. Thomas, et al., DOE (April 2007)

# Approach

**Objective**: M*eet 2010 DOE technical performance targets using kinetically stabilized aluminum-based hydrides (e.g. $LiAlH_4$ and $AlH_3$)*

1. Develop low-energy (≤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)

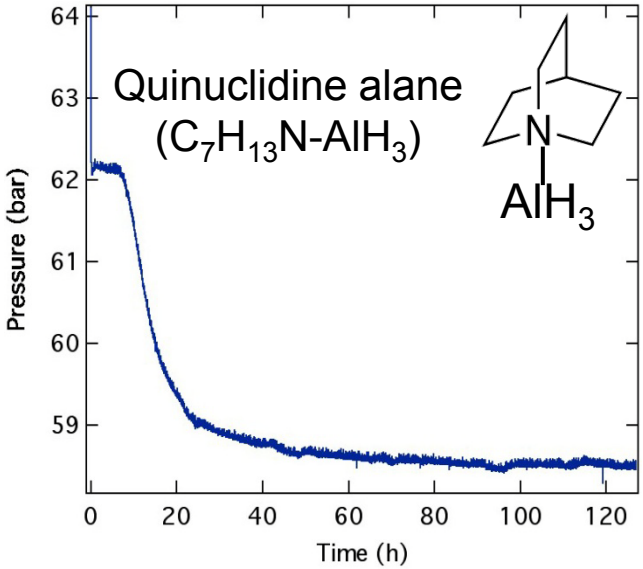
**Step II**: Remove stabilizing species and recover $AlH_3$

# Accomplishments: Previous results

- Demonstrated a low-energy regeneration route for $LiAlH_4$:

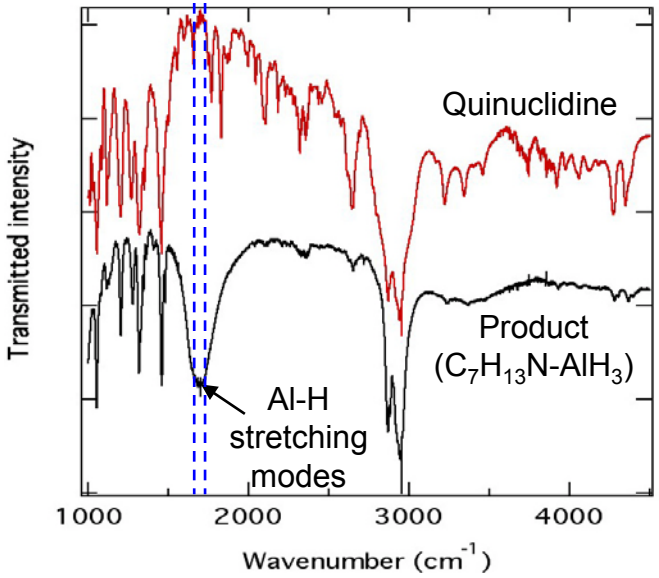
$$\underset{\text{(spent material)}}{LiH + Al^{*} + 3/2H_2} \xrightarrow{THF} LiAlH_4\text{-}THF \xrightarrow[4hrs]{60^{o}C} LiAlH_4 + THF\uparrow$$

- Demonstrated the direct formation of $AlH_3$ from Al* and $H_2$ under mild conditions using amines: $C_7H_{13}N + Al^{*} + 3/2H_2 \rightarrow C_7H_{13}N\text{-}AlH_3$




Pressure drop indicates hydrogenation of Al occurs at low pressures

Al-H stretch in FTIR confirms formation of $AlH_3$




- Preliminary results on $H_2$ evolution rates from $AlH_3$ in slurries

# Accomplishments: New results

**Revised regeneration procedure to incorporate transamination**

**Step 1: formation of $NR_3$-$AlH_3$ 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 $NR_3$ for TEA**

- Transamination demonstrated starting with DMEA and TMA (**complete** - may need follow up to decrease time, temp., …)

**Step 3: separation of TEA-$AlH_3$**

- Separation of TEA-$AlH_3$ successful with ~70% $AlH_3$ 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 $AlH_3$ formation

**Triethylenediamine (TEDA) alane**:

$C_6H_{12}N_2 + Al^* + 3/2H_2 \rightarrow C_6H_{12}N_2\text{-}\mathbf{AlH_3}$

$P < 30$ bar $T = 300$ K

**Trimethylamine (TMA) alane**:

$2C_3H_9N + Al^* + 3/2H_2 \rightarrow 2C_3H_9N\text{-}\mathbf{AlH_3}$

$P < 230$ bar $T = 300$ K

**Quinuclidine alane**:

$2C_7H_{13}N + Al^* + 3/2H_2 \rightarrow 2C_7H_{13}N\text{-}\mathbf{AlH_3}$

$P < 60$ bar $T = 300$ K

**Hexamine alane**:

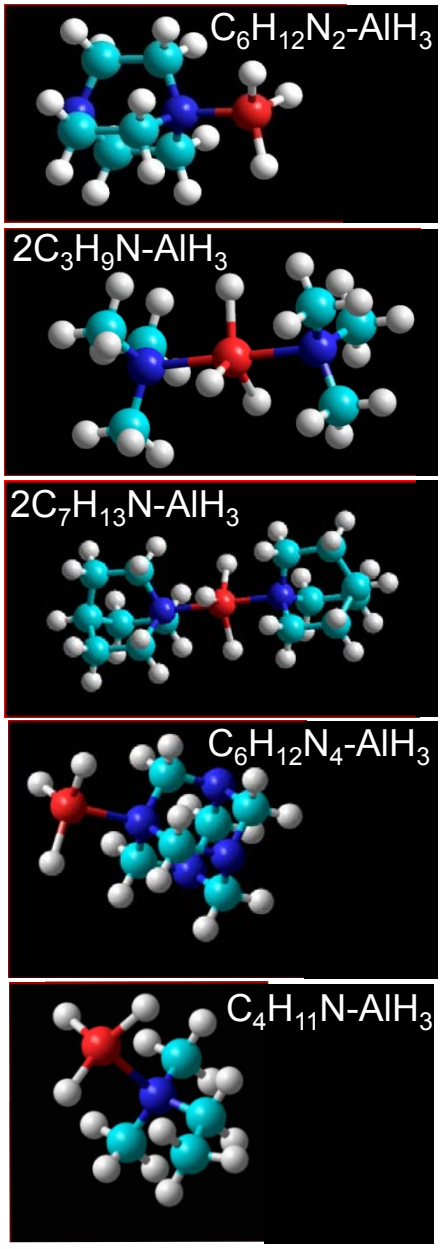
$C_6H_{12}N_4 + Al^* + 3/2H_2 \rightarrow C_6H_{12}N_4\text{-}\mathbf{AlH_3}$

$P < 60$ bar $T = 300$ K

**Dimethylethylamine (DMEA) alane**:

$C_4H_{11}N + Al^* + 3/2H_2 \rightarrow C_4H_{11}N\text{-}\mathbf{AlH_3}$

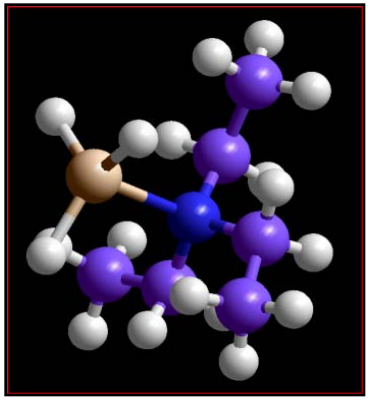
$P < 60$ bar $T = 300$ K



# **Step 1**: Adduct Formation

- No success retrieving $AlH_3$ from any of the five alane amines synthesized by direct hydrogenation - adducts decompose upon heating
- Identified only one amine alane, triethylamine alane (TEA-$AlH_3$), that can be separated to recover pure $\alpha$-$AlH_3$

$$\textbf{TEA-}\textbf{AlH}_3 \xrightarrow[\textbf{3hrs}]{\textbf{70°C}} \textbf{AlH}_3 + \textbf{TEA}\uparrow$$



- TEA-$AlH_3$ cannot be formed by direct hydrogenation only by a direct reaction with $AlH_3$

$$C_6H_{15}N + AlH_3 \rightarrow C_6H_{15}N\text{-}\mathbf{AlH_3}$$

…we found other adducts formed by same method:

**Triethylenediamine alane**: $C_6H_{12}N_2 + AlH_3 \rightarrow C_6H_{12}N_2\text{-}\mathbf{AlH_3}$

**Trimethylamine alane**: $2C_3H_9N + AlH_3 \rightarrow 2C_3H_9N\text{-}\mathbf{AlH_3}$

**Quinuclidine alane**: $2C_7H_{13}N + AlH_3 \rightarrow 2C_7H_{13}N\text{-}\mathbf{AlH_3}$

**Hexamine alane**: $C_6H_{12}N_4 + AlH_3 \rightarrow C_6H_{12}N_4\text{-}\mathbf{AlH_3}$

**Dimethylethylamine alane**: $C_4H_{11}N + AlH_3 \rightarrow C_4H_{11}N\text{-}\mathbf{AlH_3}$

# TEA-alane and transamination

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

- Triethylamine alane (TEA-$AlH_3$) can be separated to recover $AlH_3$

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

**Since it is the only amine alane that is easily separated, TEA-$AlH_3$ is a critically important compound for the regeneration process…**

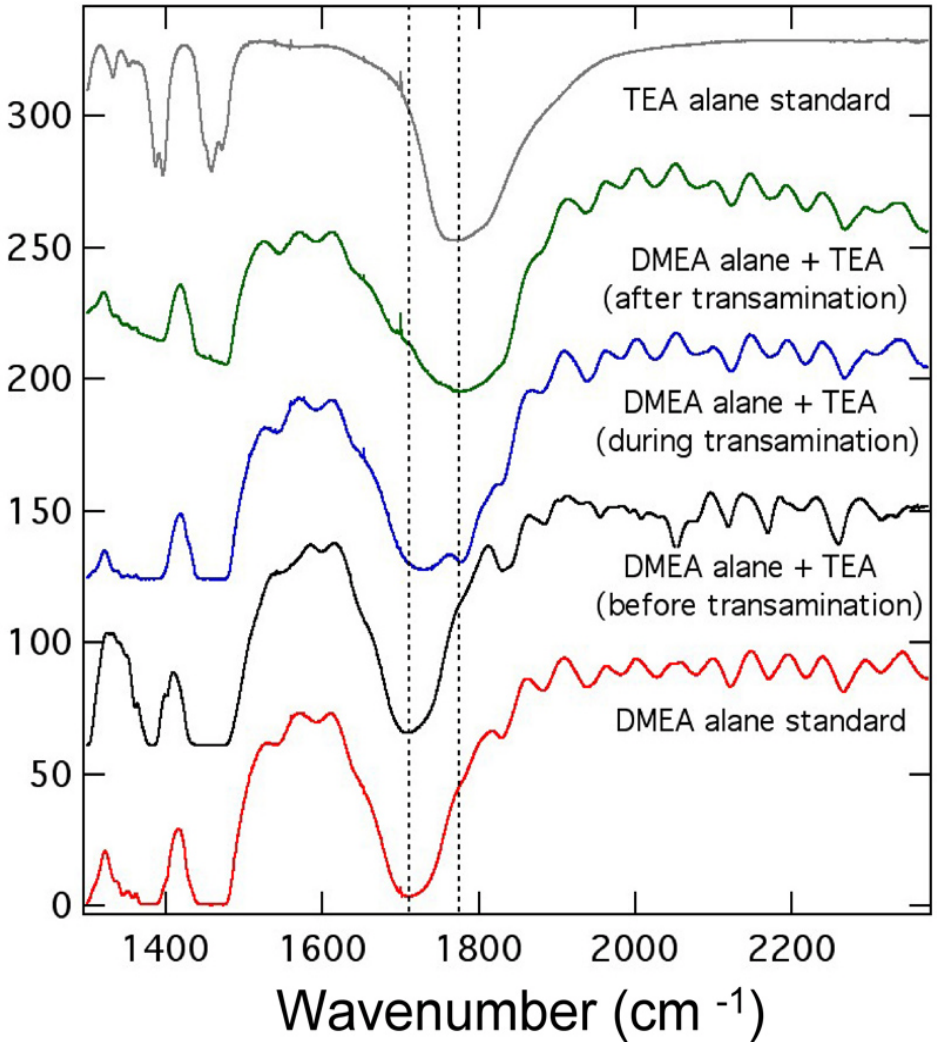
**…but TEA-$AlH_3$ does not form by direct hydrogenation (from $H_2$)**

- Can we use an exchange or **transamination** reaction to form $AlH_3$-TEA from another amine alane ($NR_3$-$AlH_3$) that forms more readily?

- Possibly, but exchange is thermodynamically uphill so we need to maintain a high concentration of TEA and preferentially remove $NR_3$ to drive reaction

- Fortunately, TEA-$AlH_3$ has a low vapor pressure so all we need is an amine ($NR_3$) with a high *Vp* that forms a stable $NR_3$-$AlH_3$ adduct: **TMA and DMEA**

# **Step 2**: amine exchange (transamination)




**Transamination** reaction to form TEA- $AlH_3$ from DMEA-$AlH_3$

$$AlH_3\text{-DMEA} + TEA \xrightarrow[3hrs]{50^{\circ}C} AlH_3\text{-TEA} + DMEA\uparrow$$

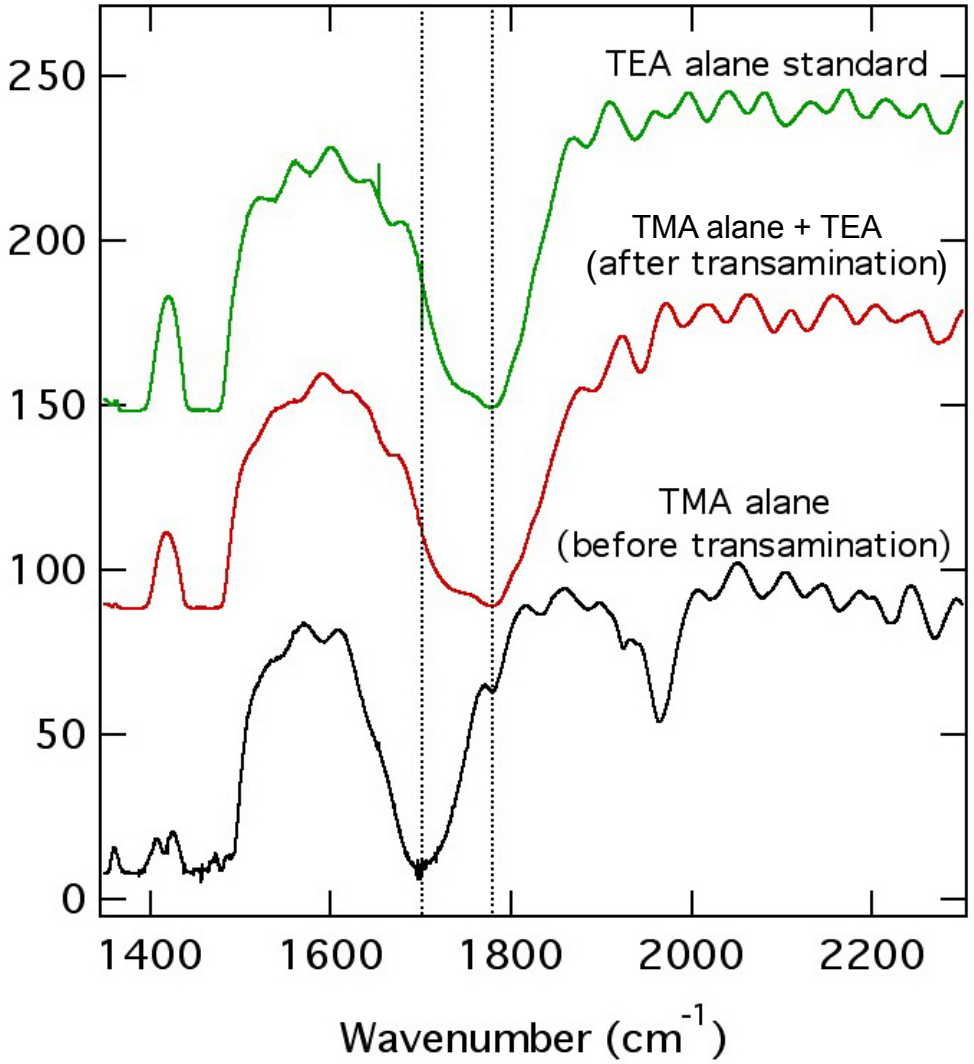
**$DMEA\text{-}AlH_3$ + 4TEA**
**T = 50ºC**
**Pi = 1 bar**
**Pf = 26 mbar**
**time = 4.5 hrs**

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

DMEA-$AlH_3$: ~1710 $cm^{-1}$
TEA-$AlH_3$: ~1780 $cm^{-1}$

**FTIR confirms final product after transamination is TEA-$AlH_3$**

# **Step 2**: amine exchange (transamination)




**Transamination** reaction to form TEA- $AlH_3$ from TMA-$AlH_3$

$$AlH_3\text{-TMA} + TEA \xrightarrow[3hrs]{50^\circ C} AlH_3\text{-TEA} + TMA\uparrow$$

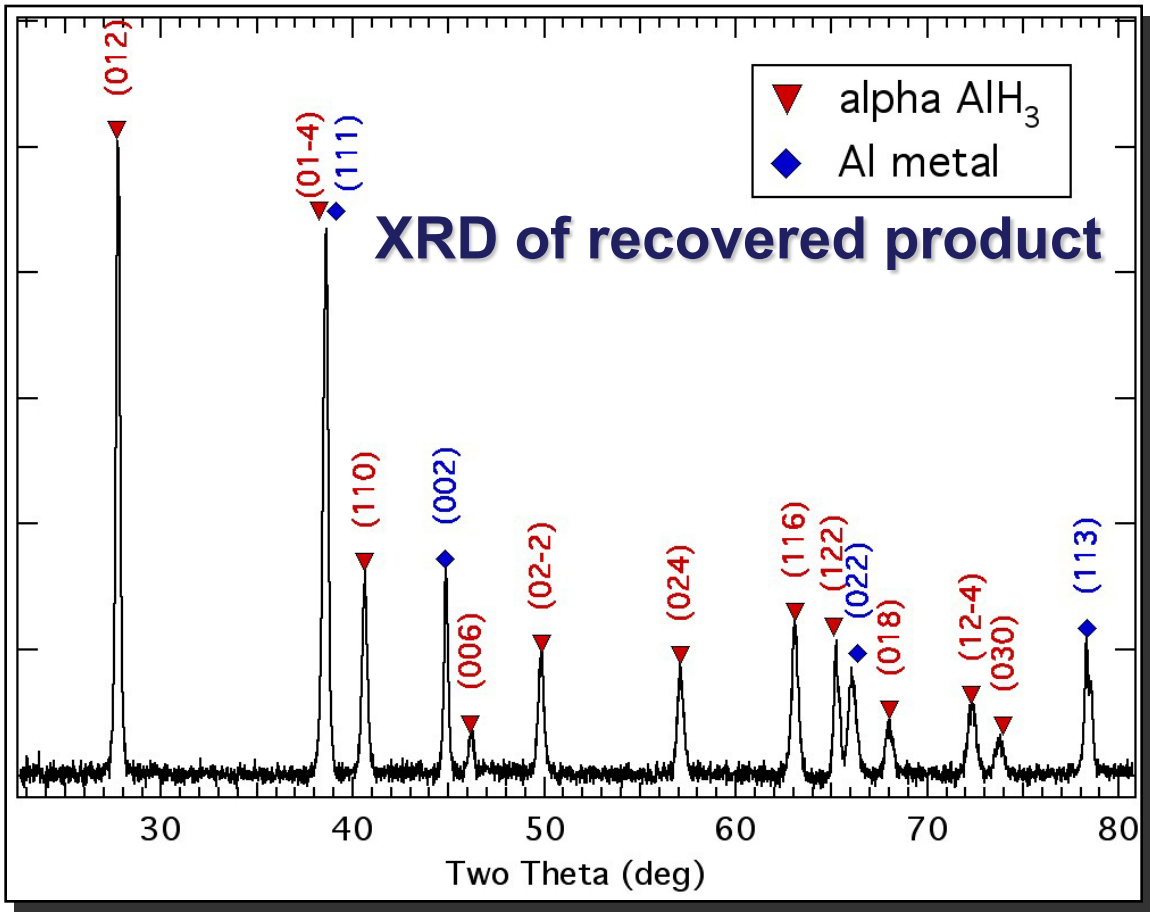
**$TMA\text{-}AlH_3$ + 4TEA**
**T = 50ºC**
**$N_2$ flow (P = 1 bar)**
**time = 2 hrs**

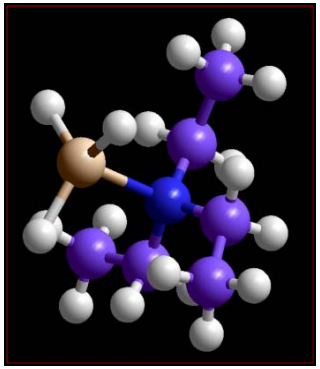
Al-H stretch in FTIR used to identify type of adduct:

$TMA\text{-}AlH_3$: ~1700 $cm^{-1}$
$TEA\text{-}AlH_3$: ~1780 $cm^{-1}$

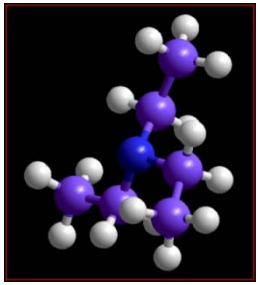
**FTIR confirms final product after transamination is TEA-$AlH_3$**

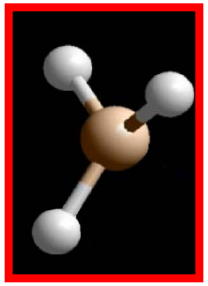
# **Step 3**: Separation of TEA-$AlH_3$



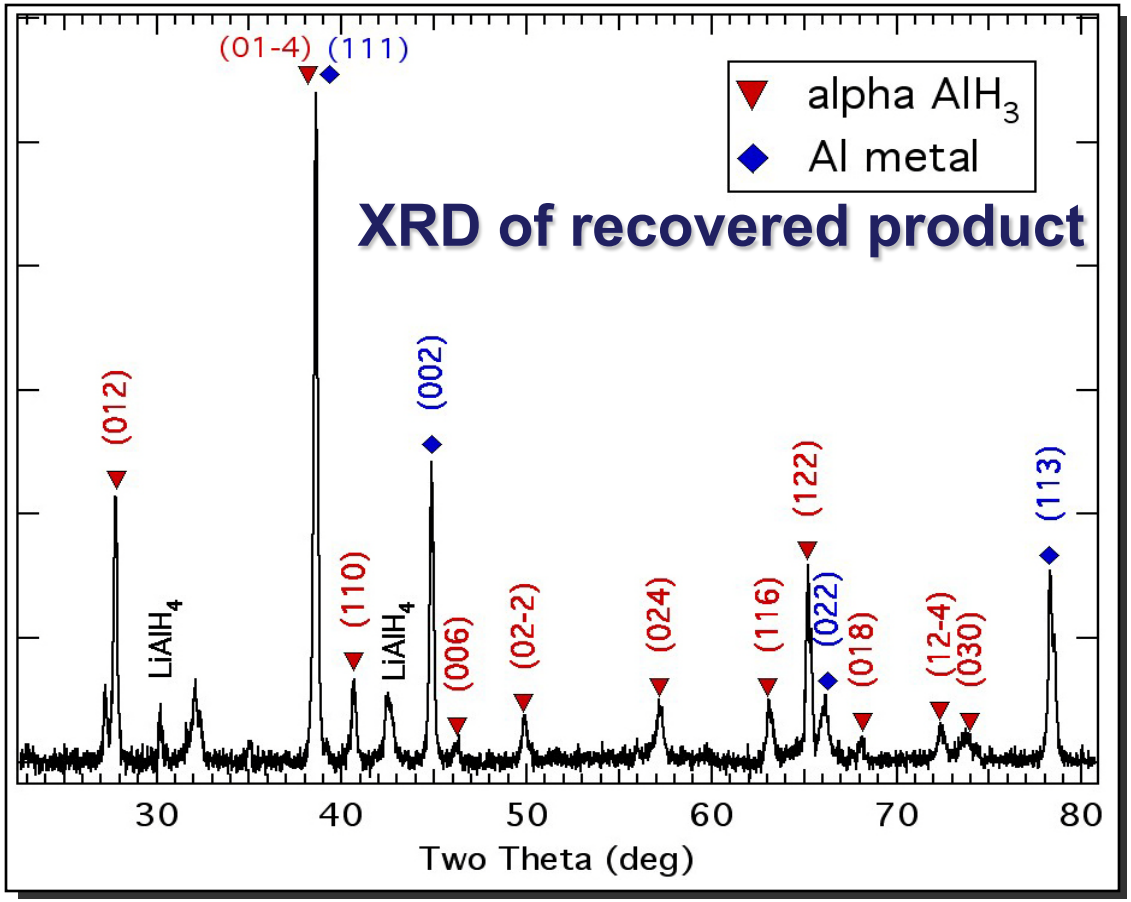
T = 70ºC
$P_{initial}$ = 100 mbar
$P_{final}$ = 15 mbar
time = 3 hrs

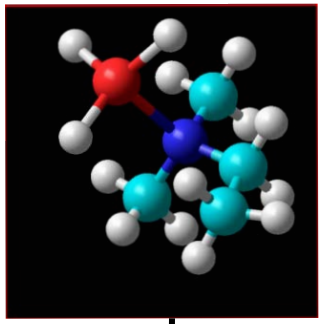




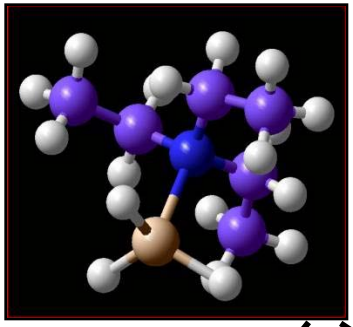
- TEA-$AlH_3$ successfully separated at 70ºC under vacuum (<100 mbar)
- Analysis of recovered $AlH_3$ (XRD and decomposition) suggests ~70% $AlH_3$ with 30% Al

# **Combining step 2 + 3**: Separation of DMEA-$AlH_3$

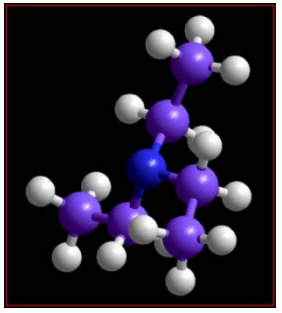


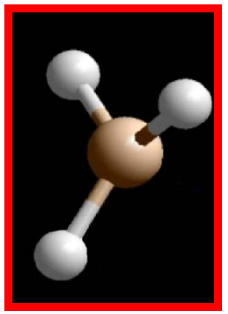



T = 50ºC
$P_{initial}$= 270 mbar
$P_{final}$ = 26 mbar
time = 2 hrs



T = 75ºC
$P_{initial}$= 220 mbar
$P_{final}$ = 5 mbar
time = 4.5 hrs





- DMEA-$AlH_3$ separated by combining steps 1 & 2
- Analysis of recovered $AlH_3$ (XRD) suggests ~35% $AlH_3$ 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 $AlH_3$)

| Process (TMA route) | Operating Conditions | | | Q, MJ | E, kWh |
|---|---|---|---|---|---|
| | T, °C | P, bar | Reflux ratio | | |
| Compress $H_2$ from SMR to 30 bar | 70 | 30 | | | 0.3 |
| Compress circulating $H_2$ to 30 bar | 70 | 30 | | | 0.6 |
| Distill trimethylamine | 65 | 5 | 1.0 | 28.6 | |
| Distill ether | 25 | 0.3 | 0.3 | 22.9 | 1.1 |
| Decompose triethylamine alane | 50 | 0.2 | | 20.2 | 1.4 |
| Vacuum dry alane product | 50 | $10^{-4}$ - $10^{-1}$ | | 0.2 | 0.2 |
| **Total** | | | | **71.9** | **3.6** |

- 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)

| BNL (POC) | SRNL | U. Hawaii/UNB | ORNL |
|---|---|---|---|
| Liquid-alane harvesting | Electrochemical | Supercritical fluids | Ionic liquids |

**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 $AlH_3$ particles for marine applications
- **A number of companies are interested in using $AlH_3$** 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 $AlH_3$ adducts from $H_2$ and Al

- Triethylenediamine: $C_6H_{12}N_2 + Al^* + 3/2H_2 \rightarrow C_6H_{12}N_2\text{-}\mathbf{AlH_3}$
- Quinuclidine alane: $C_7H_{13}N + Al^* + 3/2H_2 \rightarrow C_7H_{13}N\text{-}\mathbf{AlH_3}$
- Dimethylethylamine alane: $C_4H_{11}N + Al^* + 3/2H_2 \rightarrow C_7H_{13}N\text{-}\mathbf{AlH_3}$ ← Most promising
- Hexamine alane: $C_6H_{12}N_4 + Al^* + 3/2H_2 \rightarrow C_6H_{12}N_4\text{-}\mathbf{AlH_3}$
- Trimethylamine alane: $2C_3H_9N + Al^* + 3/2H_2 \rightarrow 2C_3H_9N\text{-}\mathbf{AlH_3}$ ← Most promising

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

**Step 3**: TEA-$AlH_3$ separated with ~70% recovered $AlH_3$

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

# Proposed Future Work

- Improve and optimize regeneration pathways:

**Pathway 1:** $\mathbf{Al + H_2 + TMA \rightarrow AlH_3\text{-}TMA \xrightarrow{TEA} AlH_3 - TEA \rightarrow AlH_3}$

**Pathway 2:** $\mathbf{Al + H_2 + DMEA \rightarrow AlH_3\text{-}DMEA \xrightarrow{TEA} AlH_3\text{-}TEA \rightarrow AlH_3}$

- Regenerate $AlH_3$ with *E* penalty ≤73 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

$$3LiAlH_4 + AlCl_3 + 0.08TiCl_3 \xrightarrow{Et_2O} 3.24LiCl\downarrow + 4AlH_3 \bullet Et_2O + 0.08Ti$$

$$4AlH_3 \bullet Et_2O + 0.08Ti \xrightarrow[2\ hrs]{100\,^{\circ}C} 4Al + 0.08Ti$$

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

- Reactions performed in solvent medium: THF, $Et_2O$
  - Solvent acts as electron donor and helps stabilize $AlH_x$