Aluminum Hydride:

the organometallic approach

J. Wegrzyn, Chengbao Ni, and W.M. Zhou

Brookhaven National Laboratory

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Project ID #
ST 034

Overview

Timeline

- Project start date: FY10
- Project end date: FY14

Barriers

MYPP Section 3.3.4.2.1 Hydrogen Storage Barriers:

- A: Weight & Volume
- B: Cost
- C: Efficiency
- D: Durability/Operability
- E: Charge/Discharge Rates

Budget

- FY13 DOE Funding: $150K
- FY14 DOE Funding: $50K
- Total Project Value: $750K

Target

Material development for meeting the packaging, safety, cost and DOE performance targets for delivering hydrogen to the PEM fuel cell for portable power.

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Aluminum hydride (alane, AlH_3):

$$AlH_3 \longrightarrow Al + \frac{3}{2} H_2$$

- High capacity: **10.1 wt%** and **1.48 g/L**;
- Low decomposition enthalpy:
  $\Delta H \approx$ 7 kJ/mol H_2 ($\approx$ 1/5 ΔH_{NaAlH4})
- Rapid H_2 evolution rates at low T:
  meets DOE target (0.02 gH_2/s) at < 100ºC
- High purity H_2:
  no side reaction for the decomposition reaction
- Decomposition rates can be tuned by:
  temperature, catalyst & surface coatings

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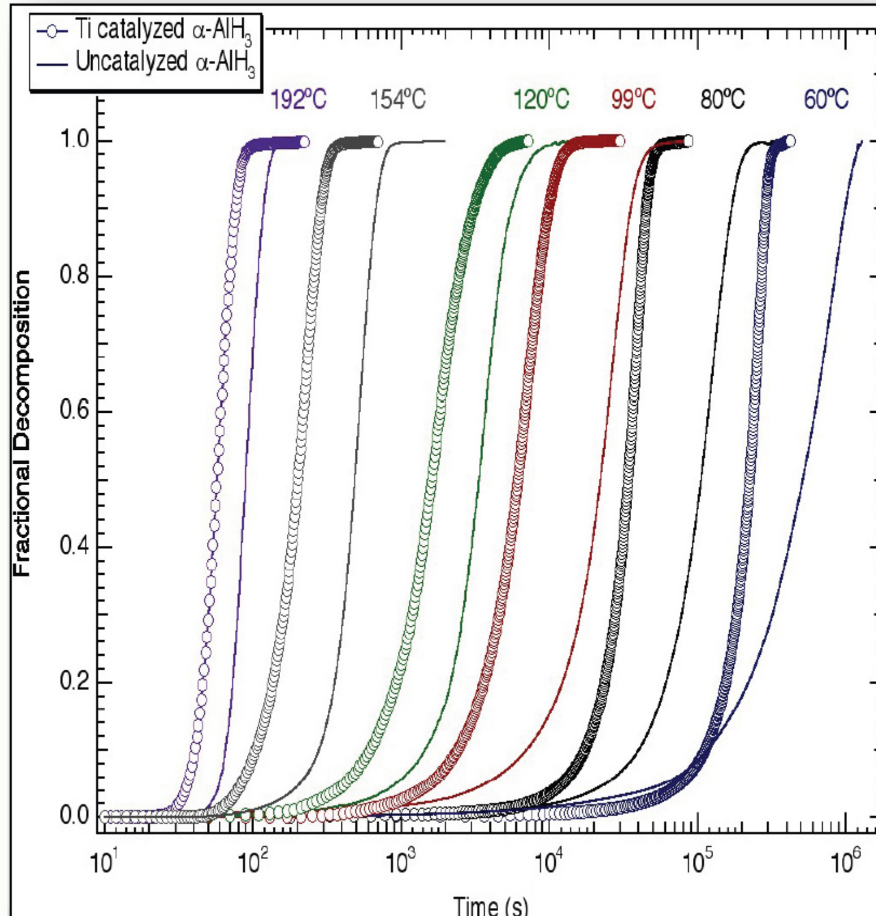


- Ti lowers the activation energy of the decomposition reaction;
- AlH_3 is completely unstable at Ti concentrations $\geq$ 0.1 mol%.

Conventional Synthesis of AlH_3:

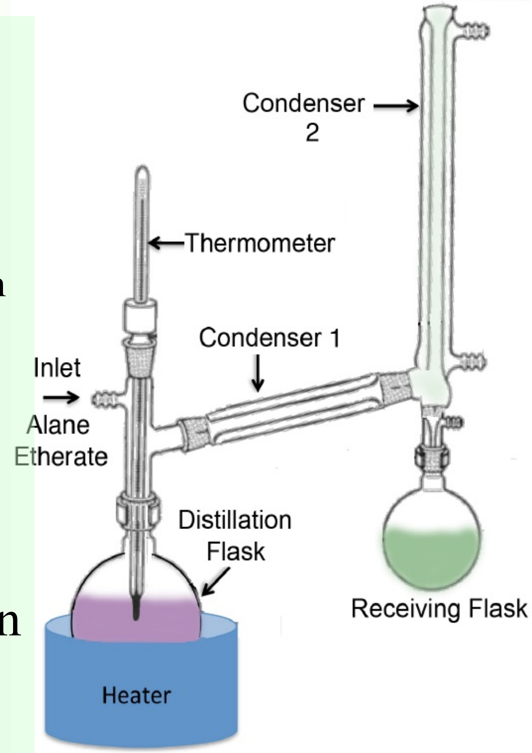
Conventional synthesis:

$$3\ LiAlH_4 + AlCl_3 \xrightarrow{Et_2O} 3\ LiCl + 4\ AlH_3(Et_2O)_n$$

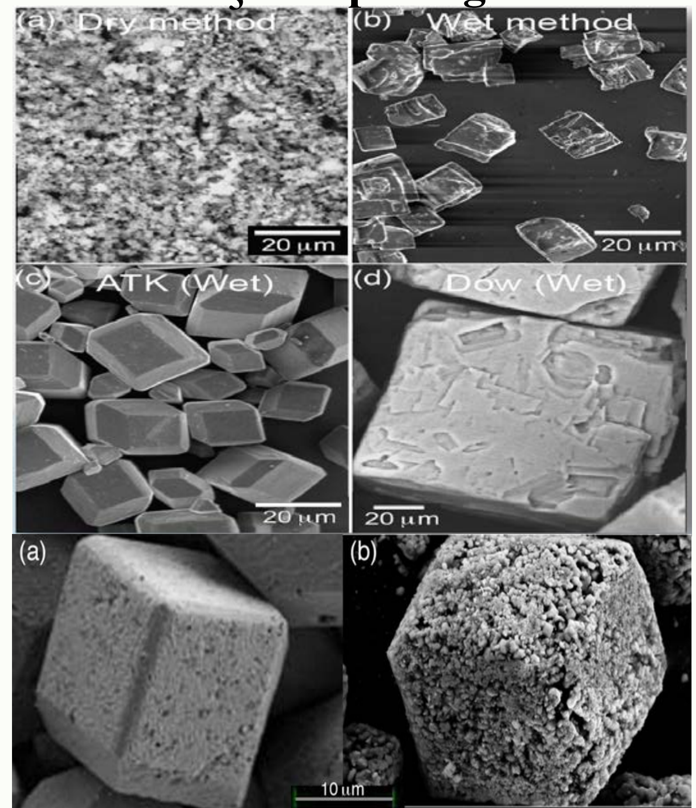
$$\xrightarrow{\text{filtration}} \mathbf{AlH_3(Et_2O)_n}$$

$$\xrightarrow{\text{desolvation/ crystallization}} \mathbf{AlH_3}\ \text{polymorph}$$

Crystallization:



AlH_3 Morphologies:



AlH_3 **Spent AlH_3**

Direct hydrogenation: $Al + \frac{3}{2} H_2 \xrightarrow{?} AlH_3$

- $\Delta H_f = -9.9 \pm 0.6$ kJ/mol AlH_3;
- $\Delta G_{f\,(298K)} = 48.5 \pm 0.6$ kJ/mol AlH_3
- **$P_{298K} \approx 10^5$ atm** (***too high*** for practical applications).
- AlH_3 only formed ***on the surface*** of Al metal;

The hydrogenation synthesis of spent $AlH_3 \longrightarrow AlH_3$ is too costly for vehicular application

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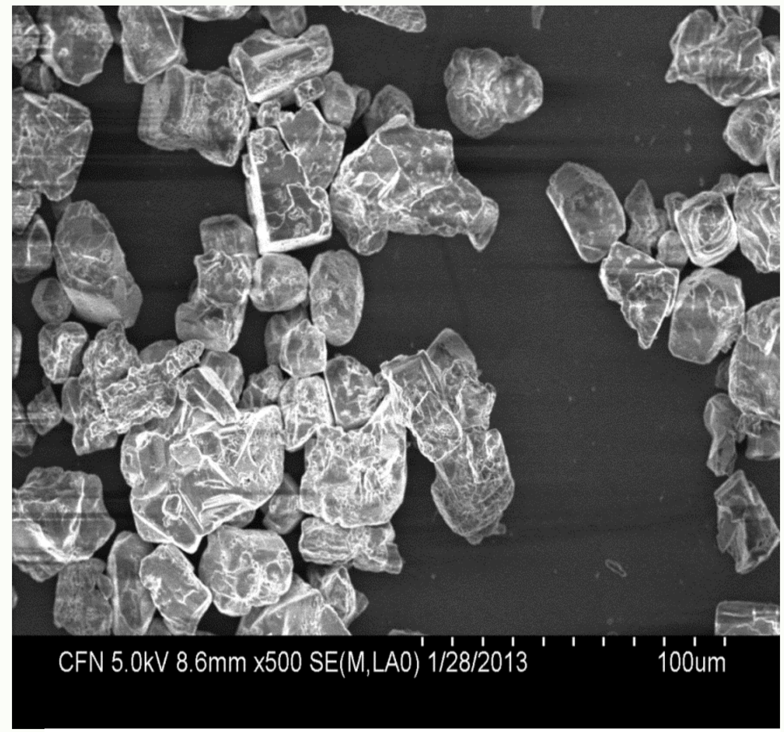
Alane Synthesis by Crystalline Growth Method

Alane-Etherate: $AlCl_3 + 3LiAlH_4{:}Et_2O \rightarrow 4AlH_3{:}Et_2O + 3LiCl$

Crystal Growth & Ether Separation: $AlH_3{:}Et_2O + \text{Toluene} \rightarrow \alpha\text{-}AlH_3 + Et_2O\uparrow$

Alane-Amine: $AlH_3{:}Et_2O + \text{Amine} \rightarrow AlH_3{:}\text{Amine} + Et_2O\uparrow$

Crystal Growth & Alane Separation: $AlH_3{:}\ \text{Amine} + \text{Toluene} \rightarrow \alpha\text{-}AlH_3 + \text{Amine}\uparrow$



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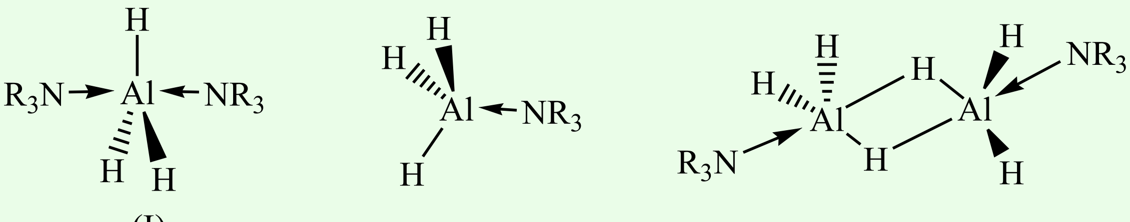
The organometallic previous approach:

- **Common amine·alane structural types:**



(I) (II) (III)

NR_3 is an amine.

- **The 3-step regeneration process:**

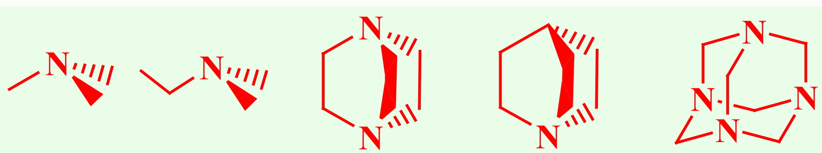
Hydrogenation: $$Al + 2\ \textbf{amine}^{1} + \frac{3}{2} H_2 \xrightarrow{\text{catalyst}} (\textbf{amine}^{1})_2 \cdot AlH_3 \quad (1)$$

Transamination: $$(\textbf{amine}^{1})_2 \cdot AlH_3 + \textbf{amine}^{2} \xrightarrow[\text{heat}]{\text{vacuum}} \textbf{amine}^{2} \cdot AlH_3 + 2\ \textbf{amine}^{1}\uparrow \quad (2)$$

Decomposition: $$\textbf{amine}^{2} \cdot AlH_3 \xrightarrow[\text{heat}]{\text{vacuum}} \textbf{AlH}_3 + \textbf{amine}^{2}\uparrow \quad (3)$$

- **The "Paradox" and challenges:**

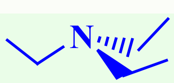
Amine[1]:



TMA **DMEA** **TEDA** **quinuclidine** **hexamine**

- Strong amines, type I structure;
- Facilitate hydrogenation;
- Decomposition to Al metal directly.

Amine[2]:



TEA

- Weak amines, type II or III structures;
- Decomposes to AlH_3 (with Al contamination;
- **Does not** facilitate hydrogenation.

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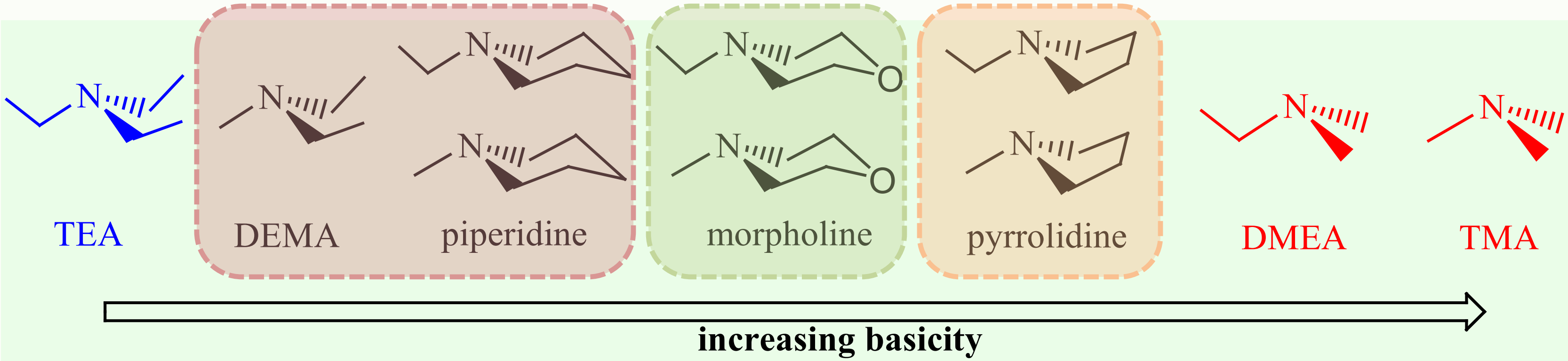
Recent approaches to the project:

➢ Tune the Lewis Basicity of amines:



➢ Objectives:

1. Search for an amine that facilitate both hydrogenation and decomposition:

$$\mathrm{Al} + 2\,\mathbf{amine}^{1} + \frac{3}{2}\mathrm{H_2} \xrightarrow{\text{catalyst}} (\mathbf{amine}^{1})_2\cdot\mathrm{AlH_3} \xrightarrow[\text{heat}]{\text{vacuum}} \mathbf{AlH_3} + 2\,\mathbf{amine}^{1}\uparrow$$

   - Reduce energy input and chemical costs
   - Increase the efficiency of the process

2. Optimize the transamination and thermal decomposition steps:

$$\mathbf{Al + TEA + H_2} \xleftarrow[\text{heat}]{\text{vacuum}} \mathbf{TEA}\cdot\mathrm{AlH_3} \xrightarrow[\text{heat}]{\text{vacuum}} \mathbf{AlH_3} + \mathbf{TEA}\uparrow$$

$$\textbf{Evaporation} \xleftarrow[\text{heat}]{\text{vacuum}} \mathbf{TEA}\cdot\mathrm{AlH_3}$$

   - Suppress Al formation and alane evaporation
   - Increase the yield and purity of AlH_3

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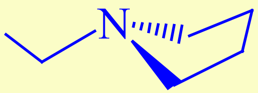
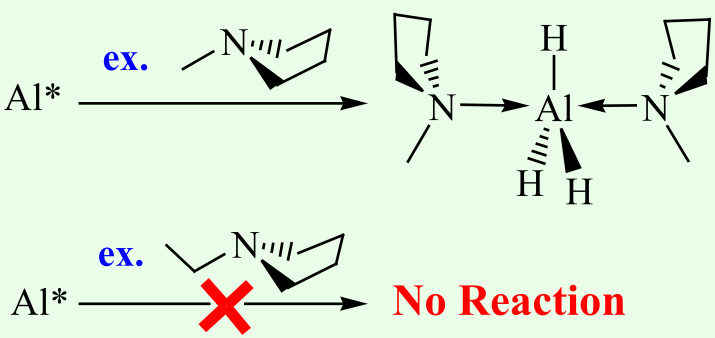
Synthesis of alane adducts from spent Aluminum:

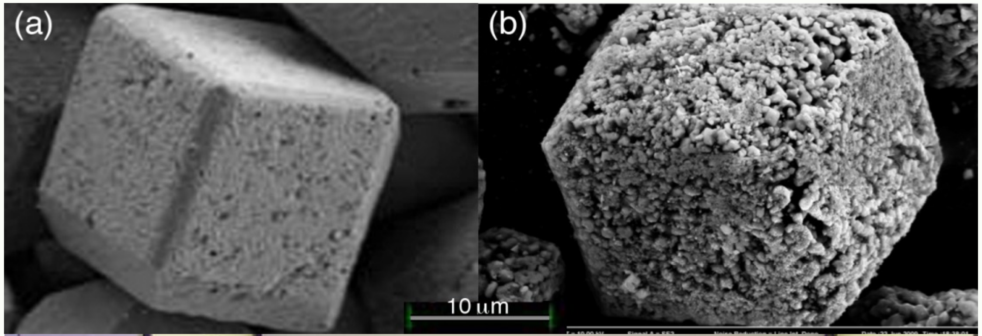
N-methylpyrrolidine
(NMPy)



N-ethylpyrrolidine
(NEPy)

Hydrogenation:





- Reactor set-up:
- H_2 pressure: ~ 1000 psi;
- Temperature: 0 ~ 25 °C;
- Chemicals: Et_2O (80 mL) & amine (20 mL);
- Al*: Ti doped Al metal, ~ 2.0 g.

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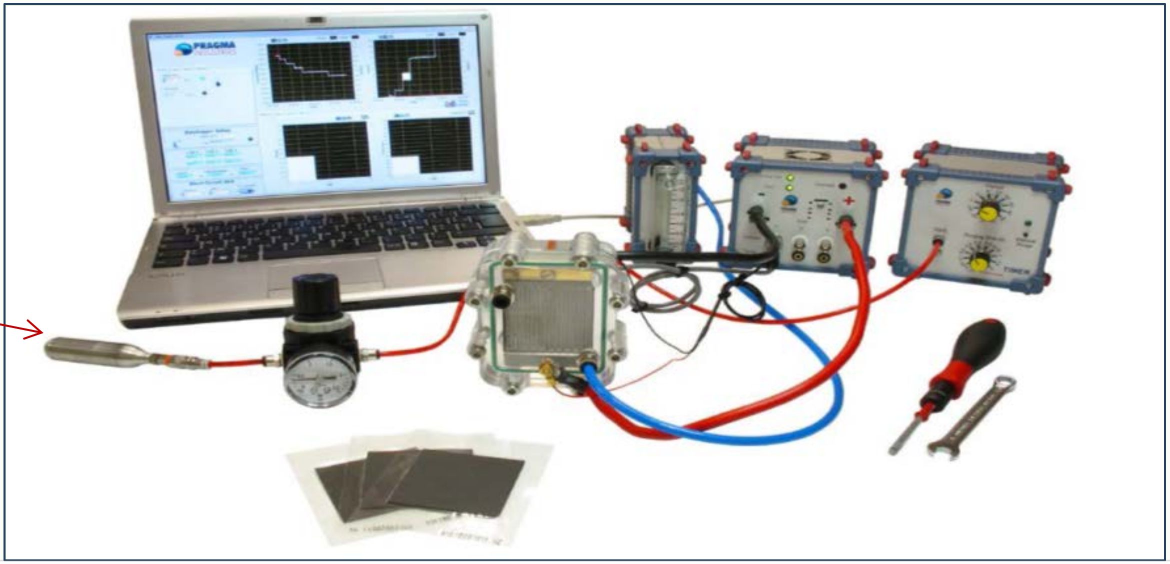
Change in Scope of Work from Onboard Hydrogen Storage to AlH_3 Replacing Battery and Metal Hydride for Portable Power

Portable Power Systems and the energy benefits of AlH_3/fuel cell

Energy Source	Specific Energy (Wh/kg)	Energy Density (Wh/L)
AlH_3/fuel cell	840	568
Li polymer	150	100
Ni-Metal hydride	65	150
Ni-Cd	80	45
Pb-acid	30	70

AB_5 tank 10NL H_2 capacity



PRAGMA Industries 7 Watt Fuel Cell Pack with electronic load, control software and AB_5 metal hydride

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Accomplishments, Future Work and Cost Targets

FY 2014 Accomplishments

Benefits in AlH_3 synthesis of replacing toluene solvent with diphenyl-methane
Benefits in AlH_3 synthesis of replacing diethyl ether solvent with methyl-THF

Future Work

Demonstration test showing that an ambient temperature 10 g AlH_3 storage system operates a 7 Watt PEMFC for 90 minutes

Costs Targets

Near term goal: AlH_3 synthesis from LiH for meeting $300/kg cost target
Stretch goal: AlH_3 synthesis from H_2 and Al for target cost less than $100/kg

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