# Electrochemical Reversible Formation of Alane


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2009 DOE Hydrogen Program Review

**Project ID: st_06_zidan**

# Other Contributors

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# Overview

## Timeline

Start: 10/01/2006

End: In Progress

Percent Complete: 30%

## Barriers

A. System Weight and Volume

B. System Cost

C. Efficiency

R. Regeneration Processes

## Budget

400K Funding received in FY08

500 K Funding planned for FY09

## Partners

Brookhaven National Laboratory

University of Hawaii

University of New Brunswick

Argonne National Laboratory

# Relevance

**Develop a low-cost rechargeable hydrogen storage material with cyclic stability and favorable thermodynamics and kinetics fulfilling the DOE onboard hydrogen transportation goals**

**Aluminum hydride (Alane- $AlH_3$), having a gravimetric capacity of 10wt% and volumetric capacity of 149 g/L $H_2$ and desorption temperature: ~60° C to 175° C (depending on particle size and the addition of catalysts) meets the 2010 DOE targets for desorption**

## ➢ Specific Objectives

- **Avoid the impractical high pressure needed to form $AlH_3$**
- **Avoid chemical reaction route of $AlH_3$ that leads to the formation of alkali halide salts such as LiCl.**
- **Utilize electrolytic potential to translate chemical potential into electrochemical potential and drive chemical reactions to form $AlH_3$**

# Approach

*Motivation: Electrochemical recharging represents a very different, promising and complementary approach to $AlH_3$ recharging.*

*Technique:* Utilize electrolytic potential, E, to drive chemical reactions to form $AlH_3$
Based on Gibbs free energy and Faraday equation:

$$\Delta G = -nFE$$

Concern: Al and $AlH_3$ will be oxidized in aqueous environment. This requires using non-aqueous approaches. We use Non-Aqueous electrolytes in Electrochemical Cell

Specific Milestones:

- ✓ Design/build Ambient Cell (APC)
- ✓ Complete APC Test
- ✓ Obtain Gram quantities of pure alane
- Complete Elevated Pressure Cell (EPC)

Go/NoGo Decision:

Following FY07 activities a **GO** decision was made based on preliminary results obtained and the potential of this material and the process to meet the DOE

# Approach

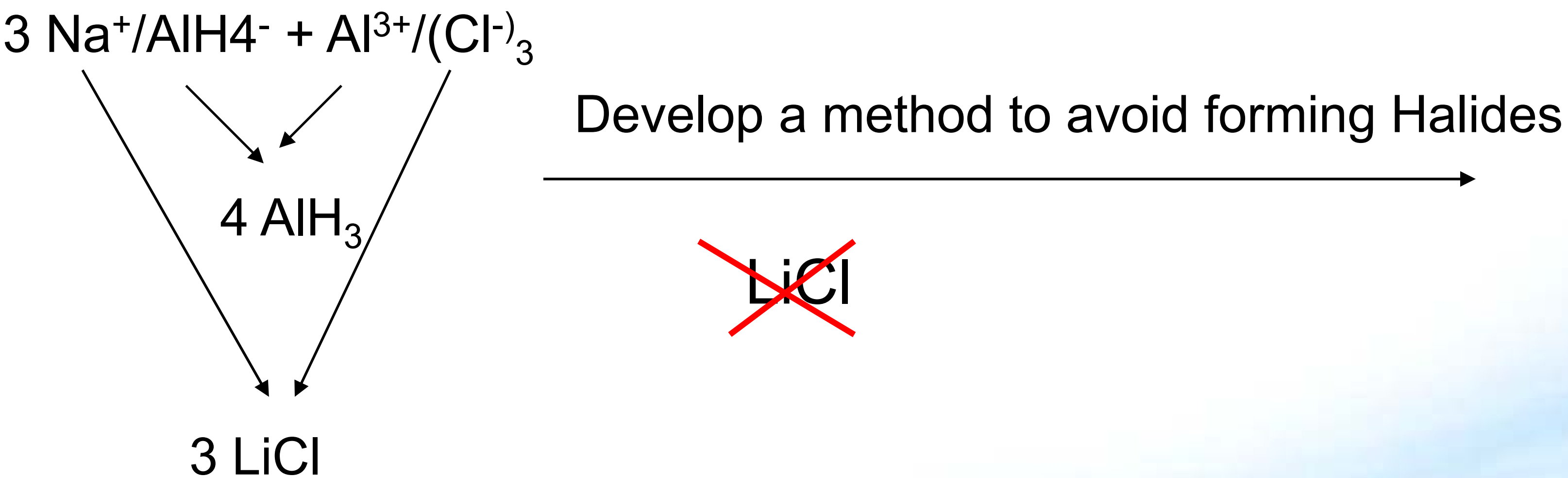
## Traditional method to produce alane:

Chemical Reaction to produce Alane using $NaAlH_4$:

$$3\ LiAlH_4 + AlCl_3 \xrightarrow{THF} 4\ AlH_3 + 3\ LiCl$$

Thermodynamic Sink

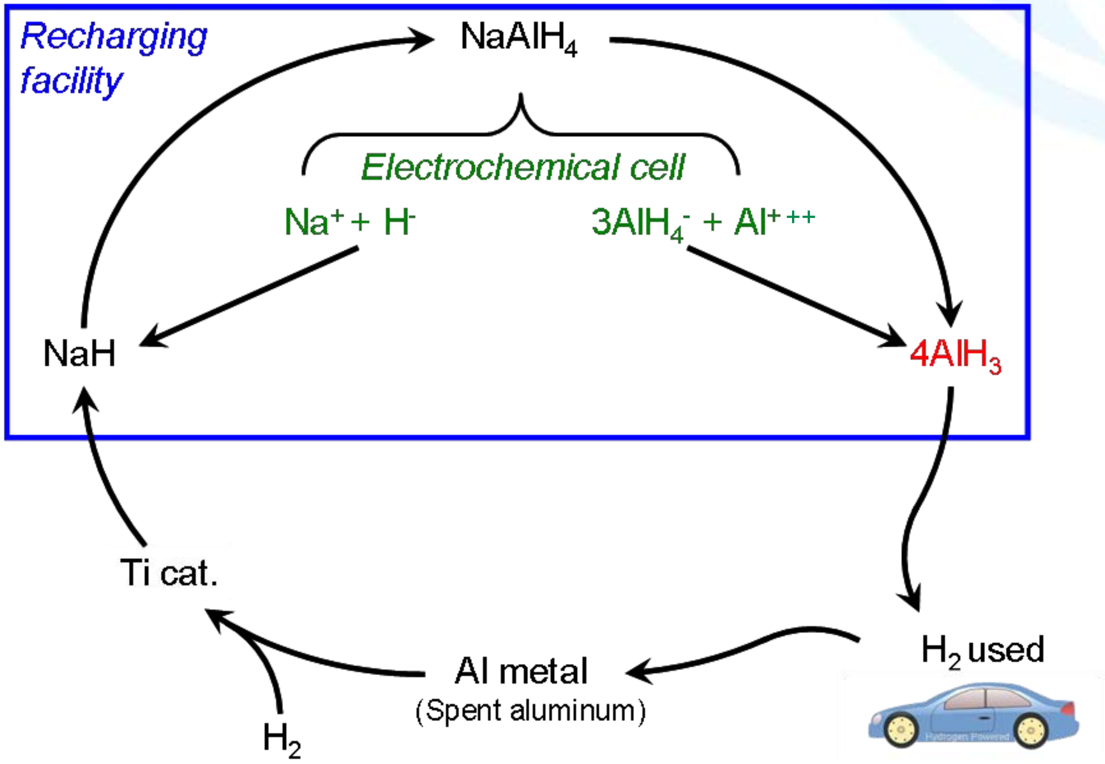
## Chemical Reaction



# Approach

**Non-Aqueous Solution Regeneration Cycle**

($LiAlH_4$, $KAlH_4$ or $NaAlH_4$) in (THF or Ether)



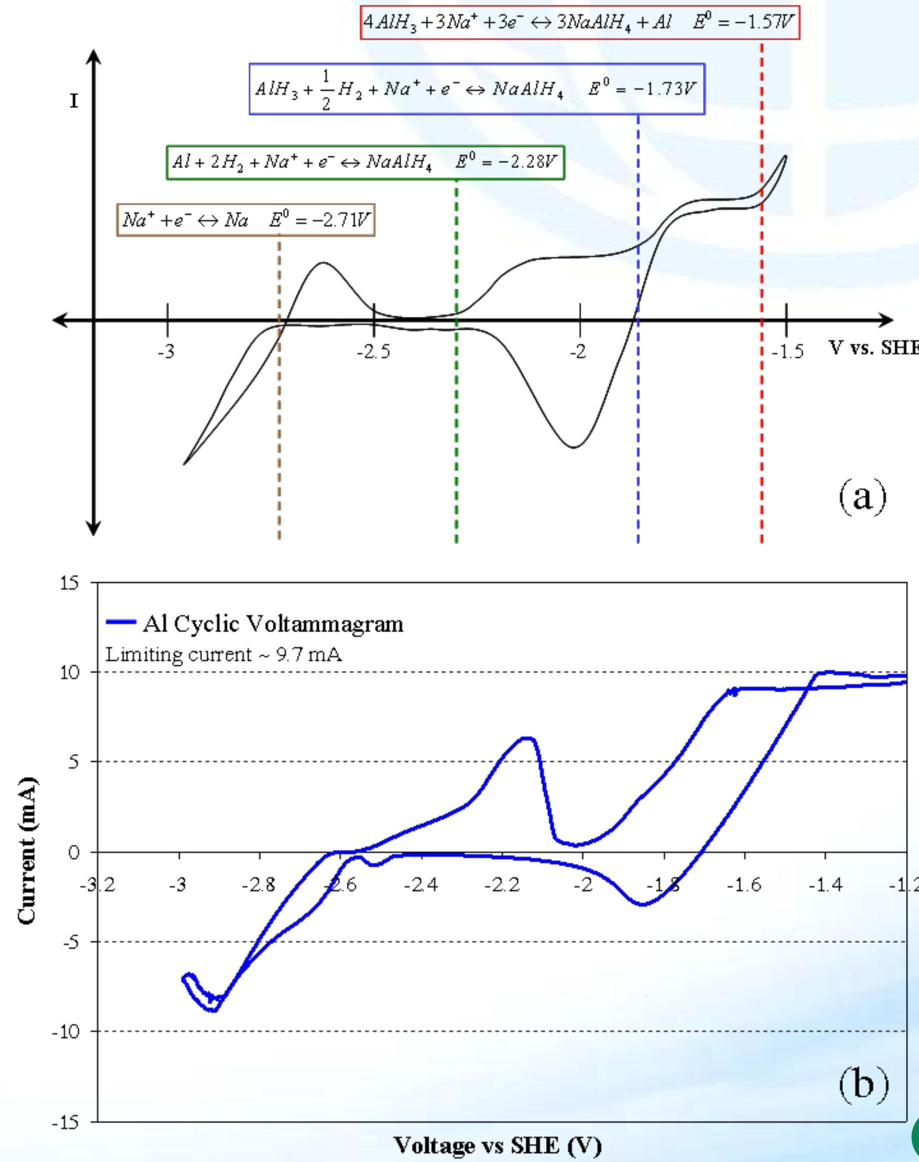

Proposed reversible cycle for alane. All components of the electrochemical process can be recycled to continually afford a viable solid-state storage material

# Technical Accomplishments and Progress

## Theoretical and Experimental cyclic voltammagrams for the electrochemical formation of alane

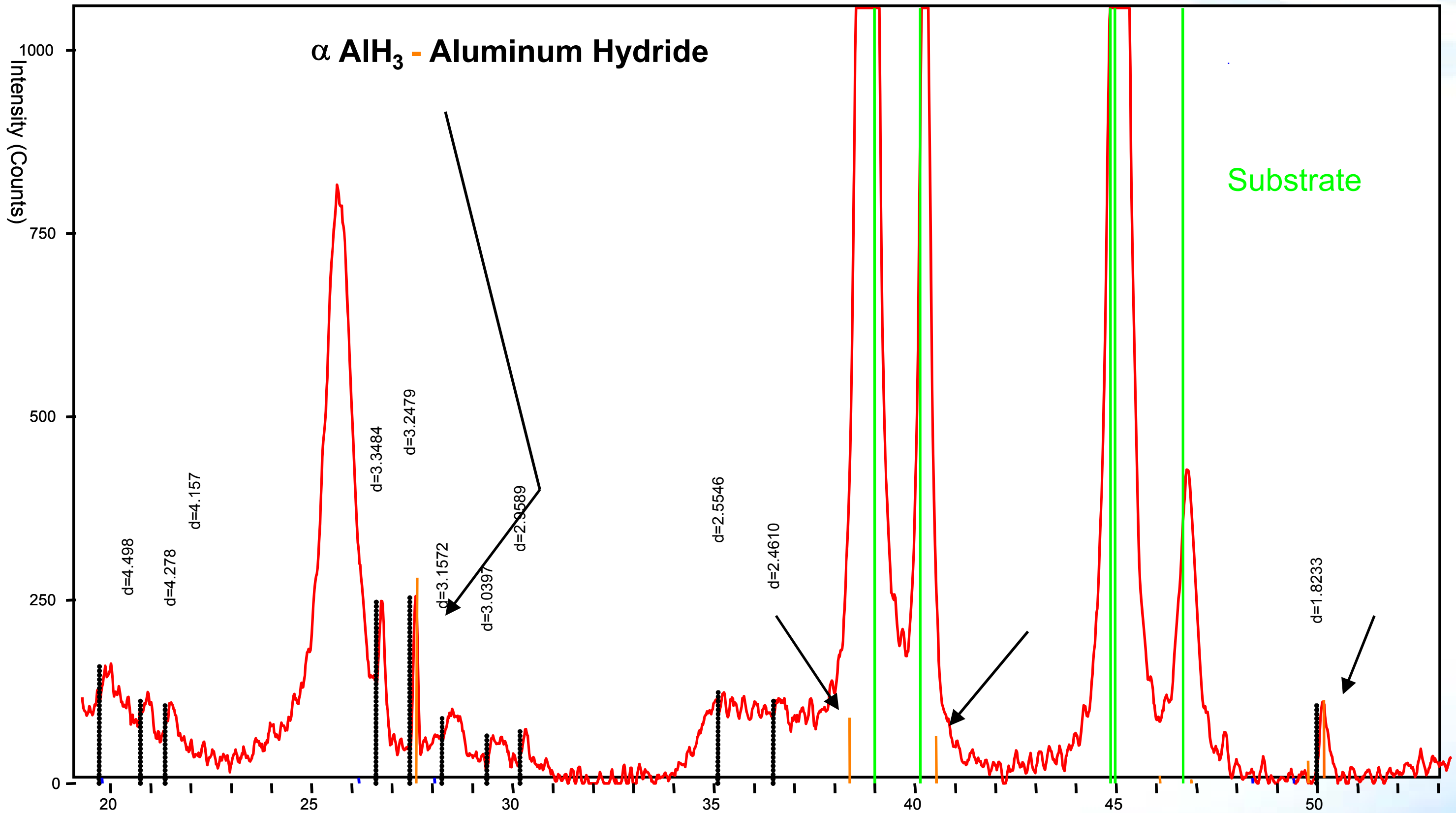
**(a)** **A hypothetical cyclic voltammagram was formulated from the equilibrium potential data for <u>possible reactions and the anticipated state of each species generated</u>**

**(b)** **Bulk electrolysis experiment at an aluminium electrode for a cell containing a 1.0 M solution of $NaAlH_4$ in THF at 25°C**



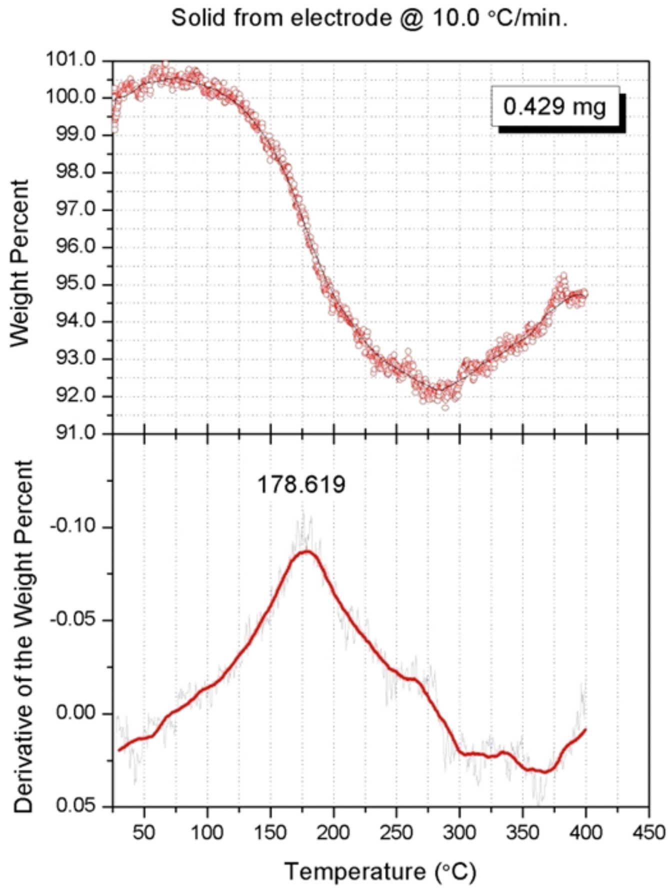
# First Evidence of α-$AlH_3$ Generated Electrochemically

## Past Results (small yield)



# Hydrogen Release from Recovered Powder (small yield)

## Past Results




Hydrogen desorption (TGA), showing almost 9% by weight hydrogen capacity, consistent with alane capacity of 10wt%

The temperature was shifted because the temperature increase rate was 10º C/min

Gas being $H_2$ was verified, using RGA

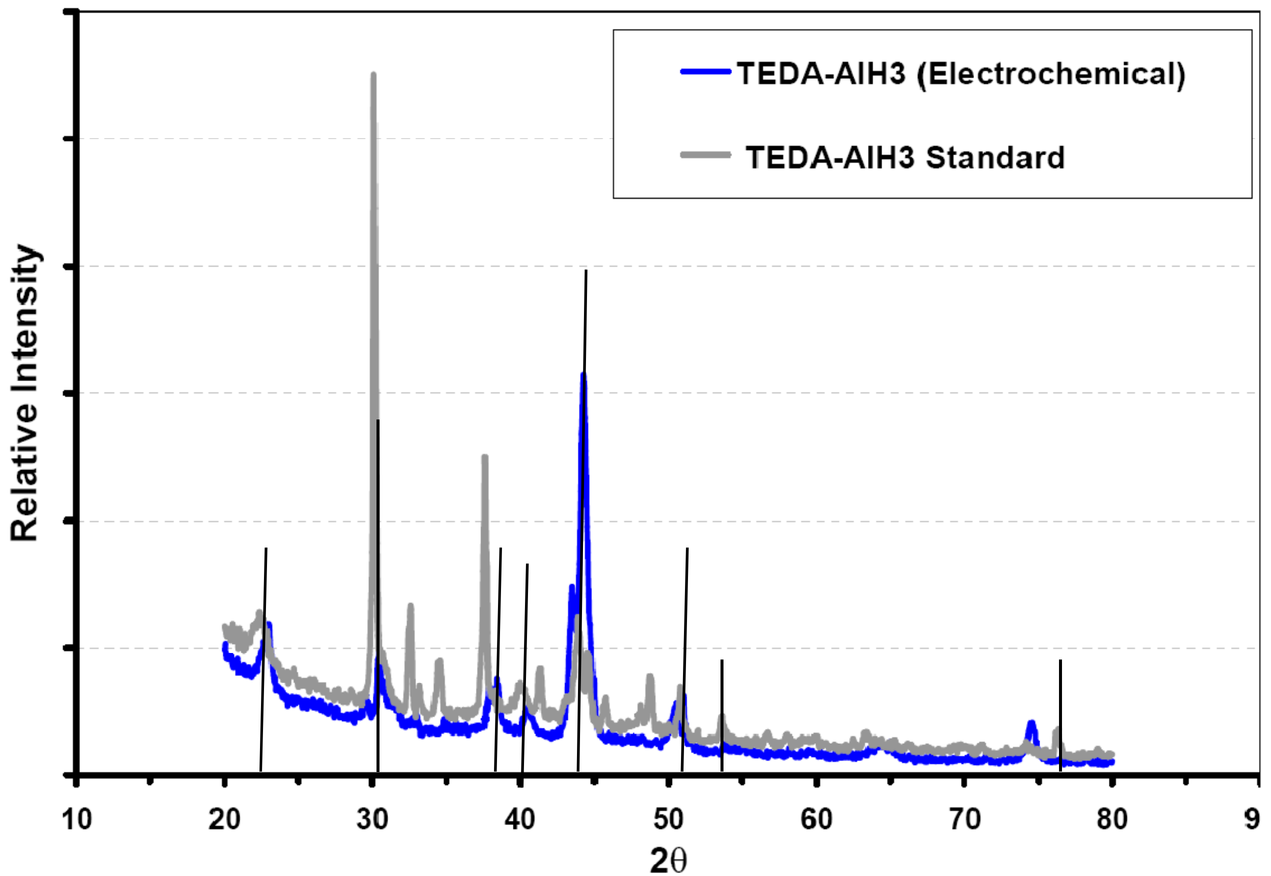
# Technical Accomplishments and Progress

## Based on collaborations with BNL, Alane-TEDA formation was used to confirm the formation of $AlH_3$

TEDA (triethylenediamine) is known to complex with $AlH_3$, appearance of precipitate signals alane molecule formation

Electrochemical Cell Generating $AlH_3$ - TEDA

# Technical Accomplishments and Progress




**XRD Confirms TEDA-$AlH_3$ Production**

# Technical Accomplishments and Progress



## Feasibility of Electrochemical Synthesis of Alane

$$\textit{Ideal}: \quad \textit{Energy Input} = (nF)E^o_{cell} = 61.2\,\frac{\text{kJ}}{\text{mol AlH}_3}$$

$$\textit{Ideal Cost} = \frac{61.2\text{ kJ}}{\text{mol AlH}_3}\left|\frac{33.3\text{ mol AlH}_3}{\text{kg AlH}_3}\right|\frac{10\text{ kg AlH}_3}{\text{kg H}_2}\left|\frac{1\text{ kWh}}{3{,}600\text{ kJ}}\right. = 5.66\,\frac{\text{kWh}}{\text{kg H}_2}$$

### Storage Energy as a Percent of LHV (1 kg basis)

$$\textit{Actual}: \quad \textit{Energy Input} = 5.66\,\frac{\text{kWh}}{\text{kg H}_2}\left|\frac{1}{68\%}\right| = 8.32\,\frac{\text{kWh}}{\text{kg H}_2}$$

68% is based on overpotential value

### Energy Consumption

$$\text{Ideal} = \frac{5.66\text{ kWh}}{33.3\text{ kWh}}x100 = 17\%$$

$$\text{Actual} = \frac{8.32\text{ kWh}}{33.3\text{ kWh}}x100 = 25\%$$

### Efficiency

Ideal = 85%

Actual = 75%

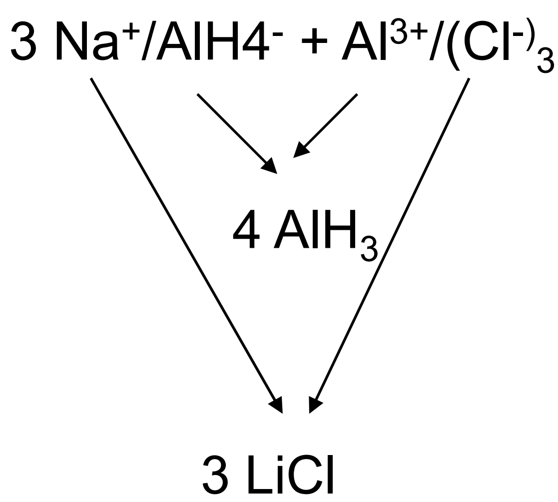
# Comparison to Chemical Methods

Chemical Reaction to produce Alane using $NaAlH_4$:

$$3\ LiAlH_4 + AlCl_3 \xrightarrow{THF} 4\ AlH_3 + 3\ LiCl$$

Thermodynamic Sink

## Chemical Reaction




J. Graetz, J. Wegrzyn, J. Reilly, J. Johnson, WM Zhou:

-Recycling $AlH_3$ by splitting LiCl requires a minimum of 0.7J for every 1J of fuel

(**70% of fuel energy required for regeneration**)

–Recycling $AlH_3$ by splitting LiCl is NOT feasible

# Technical Accomplishments and Progress

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SRNL SAVANNAH RIVER NATIONAL LABORATORY

**Possible Reactions : When $AlH_3$ Generated in Closed Material Cycle**

Utilizing Polar Conductive Solution $NaAlH_4$ in THF

$NaAlH_4$/THF ⟷ $Na^+/AlH_4^-$/THF

Anode

$AlH_4^-$ ⟶ **$AlH_3$** (combined with THF) + ½ $H_2$↑ +$e^-$

Or

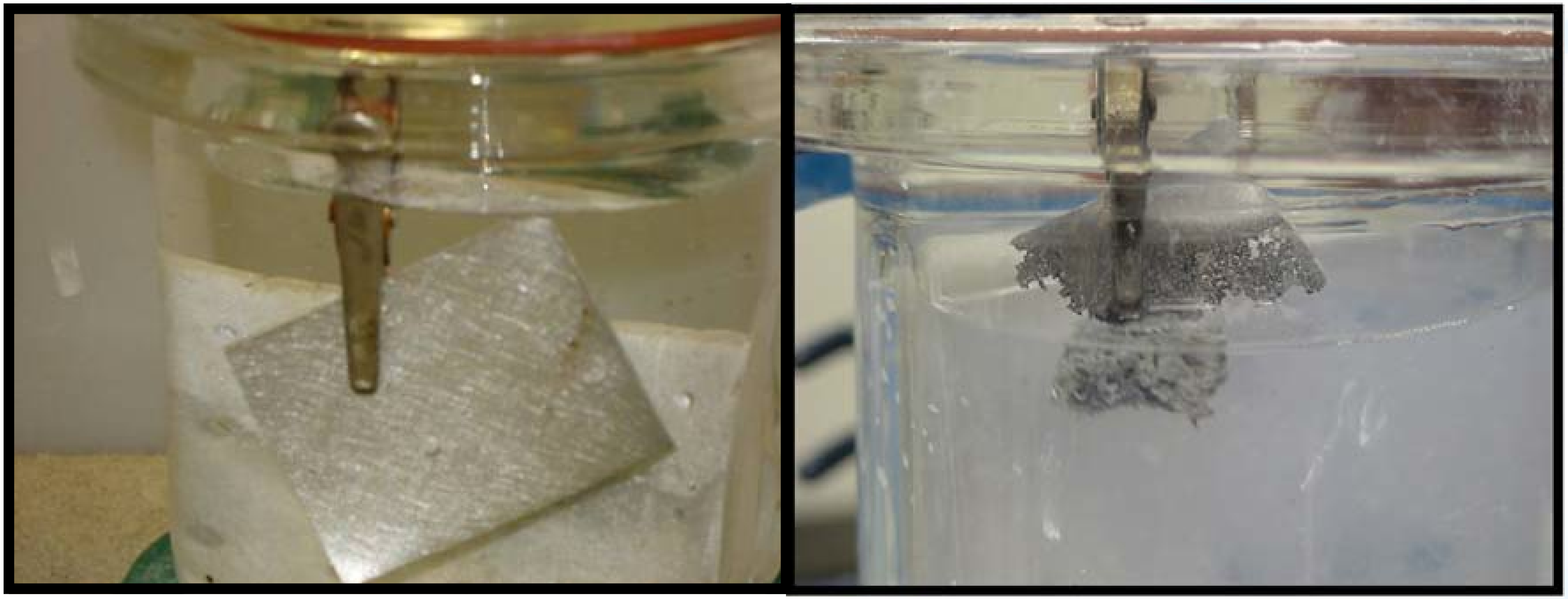
3 $AlH_4^-$ + Al (Anode) ⟶ **4$AlH_3$** (Combined with THF) +3$e^-$

Electrode is expected to dissolve

Na+ + ½ H2 $\xrightarrow{Pt^-}$ **NaH** → Cathode

Regeneration NaH +Al +$H_2$ ⟶ $NaAlH_4$

# Technical Accomplishments and Progress



Before

After, Electrode Dissolved

Aluminum electrode before and after an electrochemical run

## $AlH_3$ Recovery

Once $AlH_3$ is generated in the Electrochemical Cell, it has to be recovered in pure form

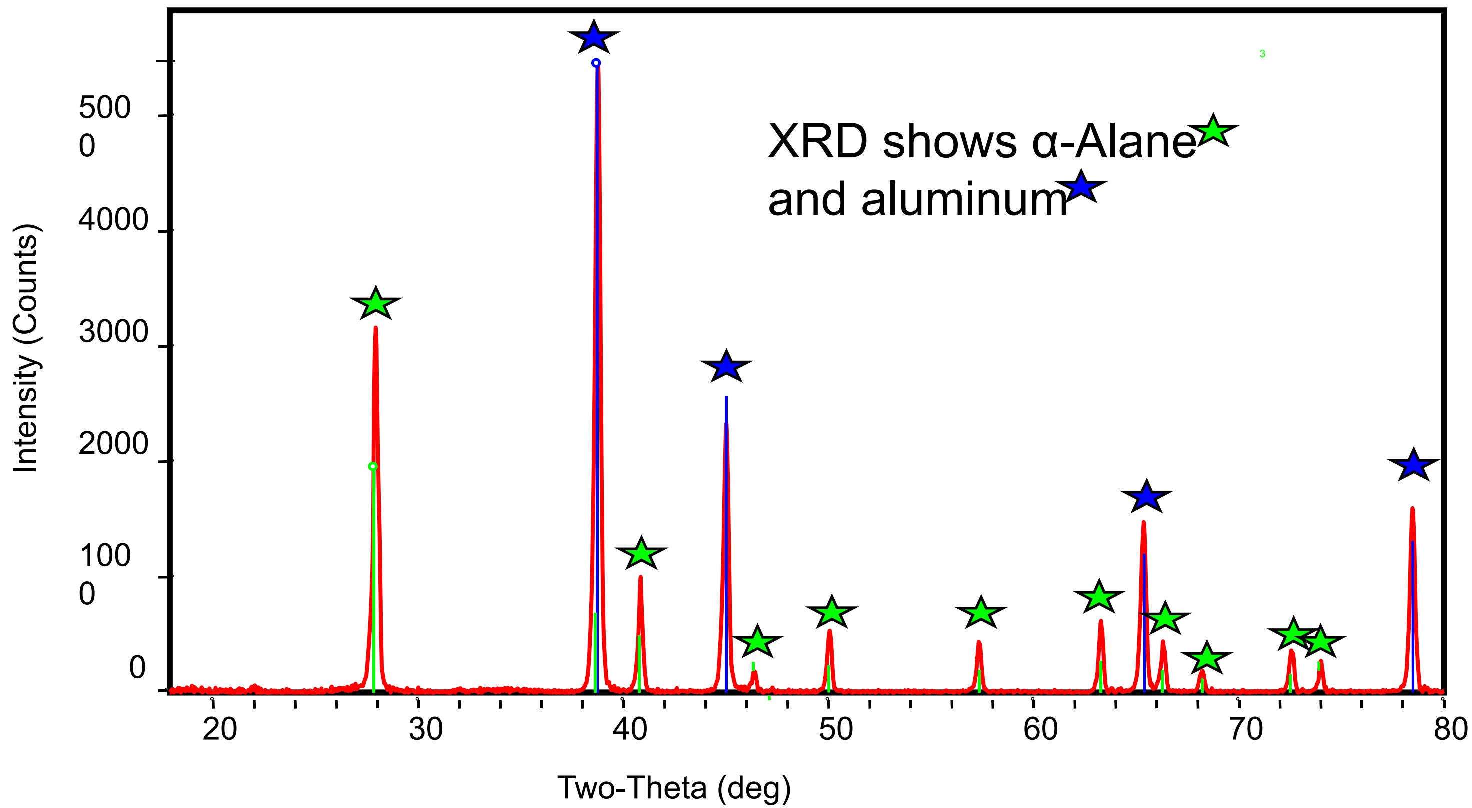
Two Recovery Methods:

**1- Directly from THF-$AlH_3$**

**2- Recovery using different Adducts**

# Technical Accomplishments and Progress

Recovery from THF-$AlH_3$ (method 1) : Yield is a mixture of $AlH_3$ and Al



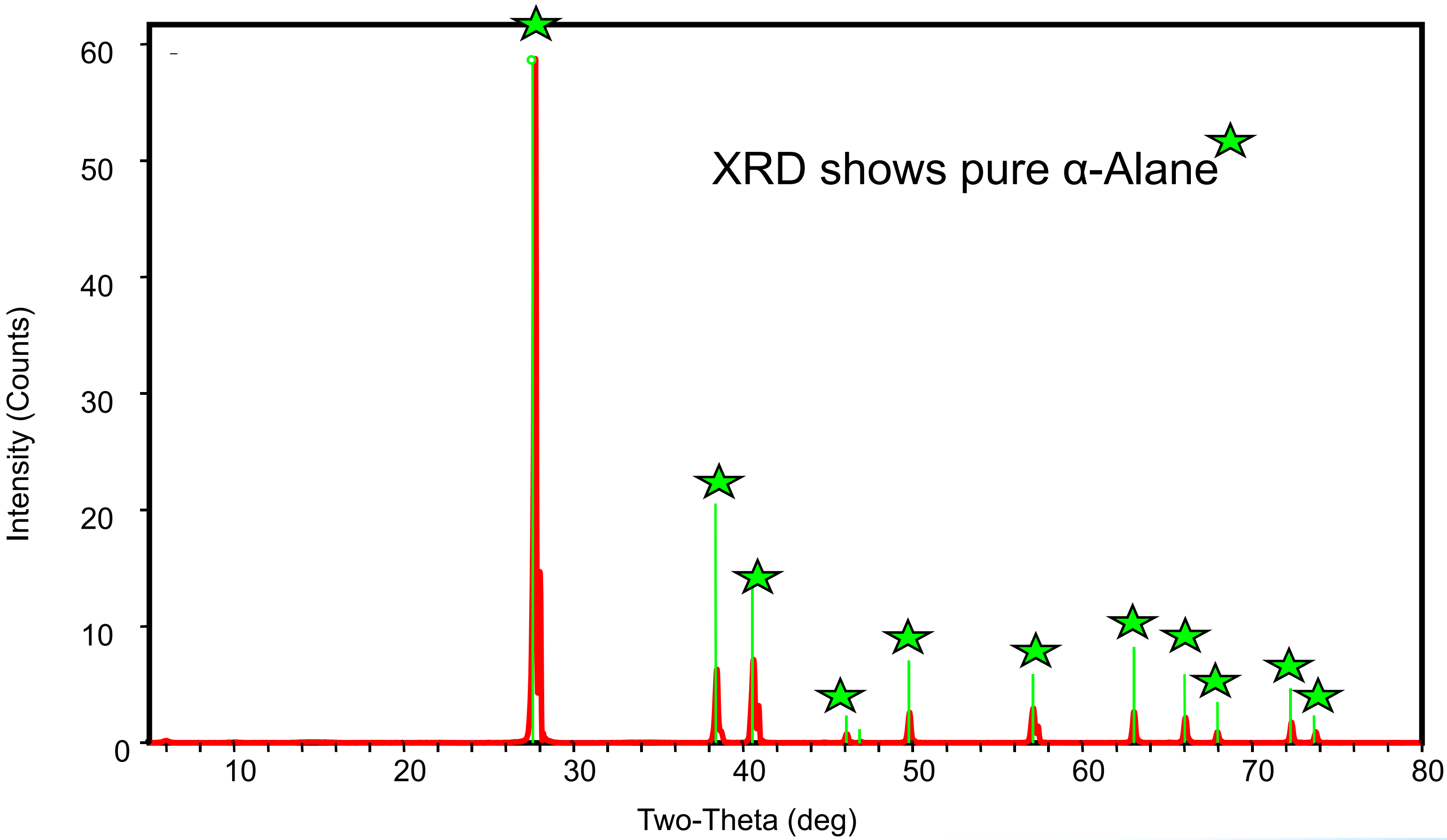

XRD shows generation of α-$AlH_3$

# Technical Accomplishments and Progress



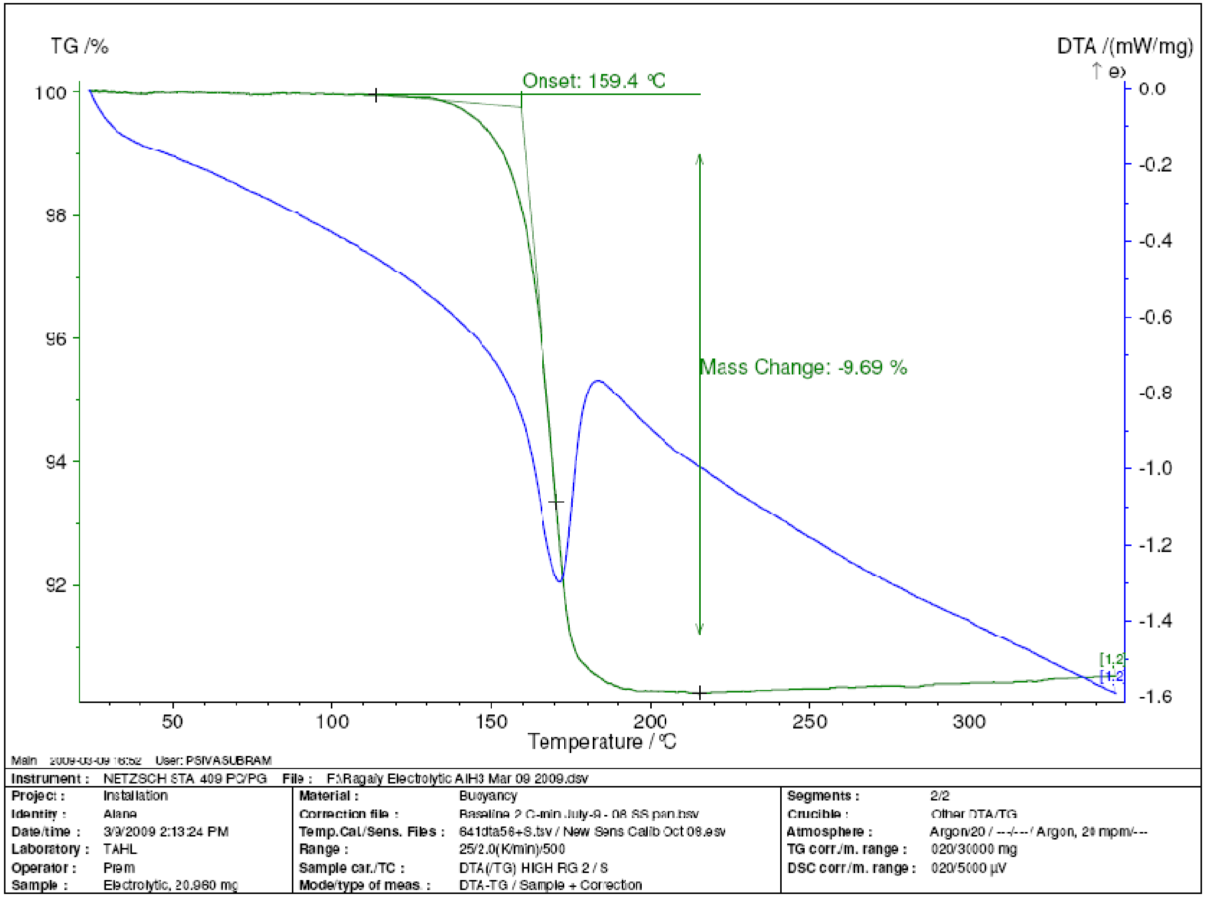
## Recovery using different Adduct: Yield is Pure $AlH_3$

(method 2)




XRD shows generation of pure α-$AlH_3$

# Technical Accomplishments and Progress




**Two grams of $AlH_3$, alane, electrochemically generated**

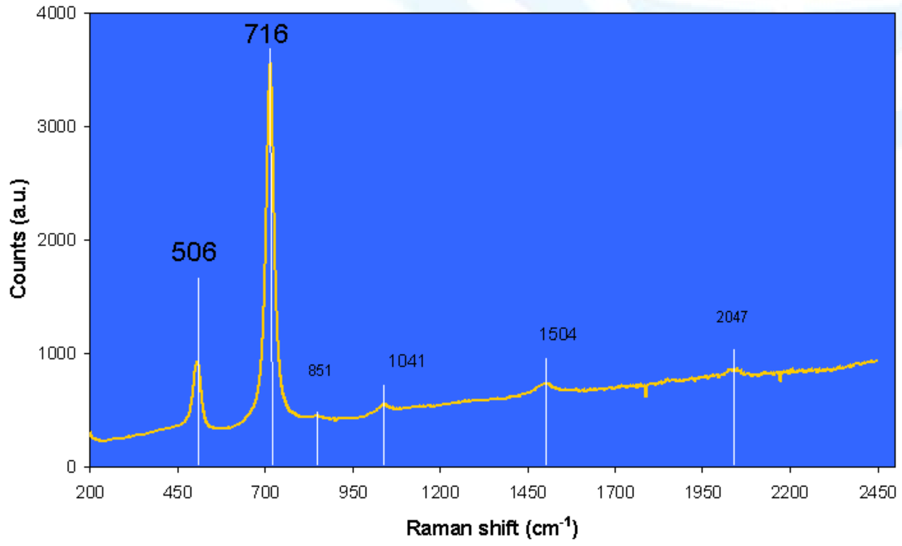
**TGA decomposition electrochemically generated alane, shown in photo, releases almost full $H_2$ capacity expected in $AlH_3$**

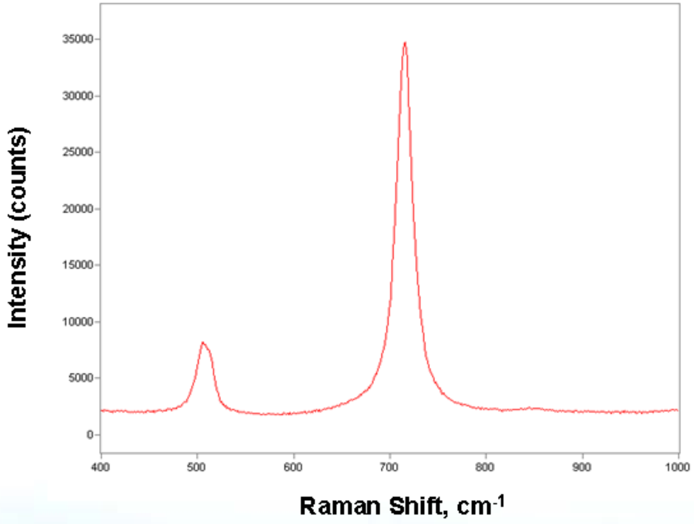
# Technical Accomplishments and Progress



## Raman Confirms Method 2 Gives Pure $AlH_3$

Raman of powder from Method 2




Raman of α –alane (standard)

# Collaborations

- **Jason Graetz, James Wegrzyn and Jim Reilly (BNL)**
  **Alane recovery the formation of adducts (COE)**

- **Craig Jensen (University of Hawaii)**
- **Sean McGrady (University of New Brunswick)**

**Use of novel methods and solvents for more efficient recovery of Alane (COE)**

- **Rajesh Ahluwalia, Thanh Hua (ANL)**
  **Efficiency modeling and optimization of Alane regeneration process (DOE)**

# Proposed Future Work

- Calculations have started with ANL to determine and optimize efficiency and will continue
- Direct collaboration with BNL and SNL to identify better separation solvents
- Promising solvent has been identified with University of Hawaii with promise of higher efficiency
- Other complex hydrides can be regenerated in similar manner

# Summary 3/2008 → Present



## Status at 3/2008:

- 1. Designed and built multiple electrochemical cells for a systematic study

  **(Different electrodes, different electrolytes, resistance measurements)**

- 2. Established Alane Production CV
- 3. Although in a small yield Alane was produced and verified

## Since 3/2008:

- 1. Continued multiple electrochemical cells systematic study
- 2. Developed a methodology to confirm the generation of $AlH_3$ in the cell
- 3. Succeeded in producing large quantities of $AlH_3$-TEDA, electrochemically
- 4. Recovered Alane from Alane-THF adduct
- 5. Developed ways to recover pure alane from solvent
- 6. Produced gram quantities of Alane, electrochemically
- 7. Working on the efficiency aspects of the cycle

# Summary

Although many attempts in the past were made to make alane electrochemically none of these attempts have isolated or characterized alane. These attempts were not directed at hydrogen storage. Our group is the first to show a reversible cycle utilizing electrochemistry and direct hydrogenation, where gram quantities of alane are produced, isolated and characterized

# Summary

**A breakthrough has been achieved in the electrochemical regeneration of $AlH_3$**

$AlH_3$ can now be regenerated :

- Gram quantities have been produce
- High purity (confirmed by Raman, XRD)
- High $H_2$ capacity (confirmed by TGA, XRD)
- A closed material regeneration cycle
- More detailed publication is in press in *ChemComm J.*

Zidan *et. al*, "Aluminum Hydride: A Reversible Material for Hydrogen Storage"

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# Acknowledgements: Co-workers and Collaborators

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**SRNL: Donald Anton, Ted Motyka, Joe Wheeler, and Rob Lasocola**

**Jason Graetz, James Wegrzyn and Jim Reilly (BNL)**

**Craig Jensen (University of Hawaii)**

**Sean McGrady (University of New Brunswick)**

**Rajesh Ahluwalia, Thanh Hua (ANL)**

**Rana Mohtadi and Sivasubramanian, PremKumar** (Toyota)

Metal Hydride Center of Excellence

**DOE Office of Energy Efficiency and Renewable Energy**

# Major Contributors



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