Electrochemical Reversible Formation of Alane

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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

$3\ Na^{+}/AlH4^{-} + Al^{3+}/(Cl^{-})_3$

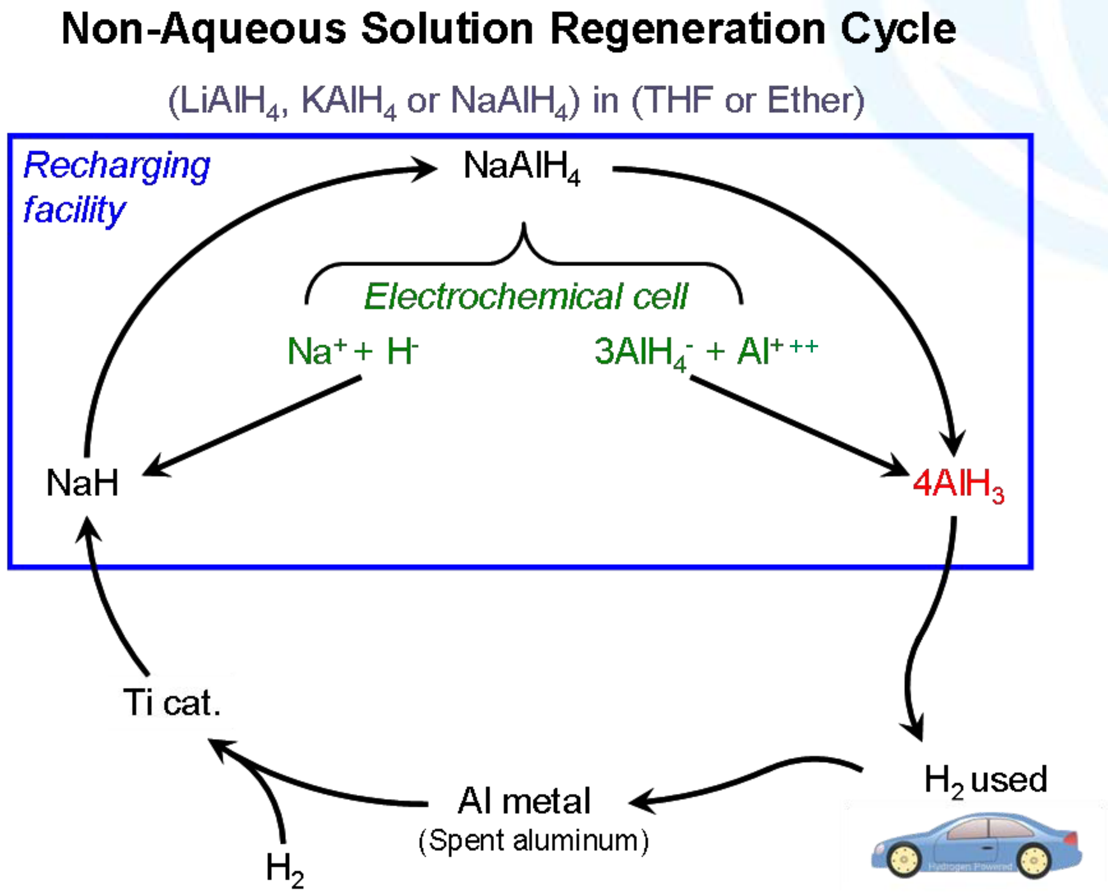
$4\ AlH_3$

$3\ LiCl$

Develop a method to avoid forming Halides

~~LiCl~~

Approach



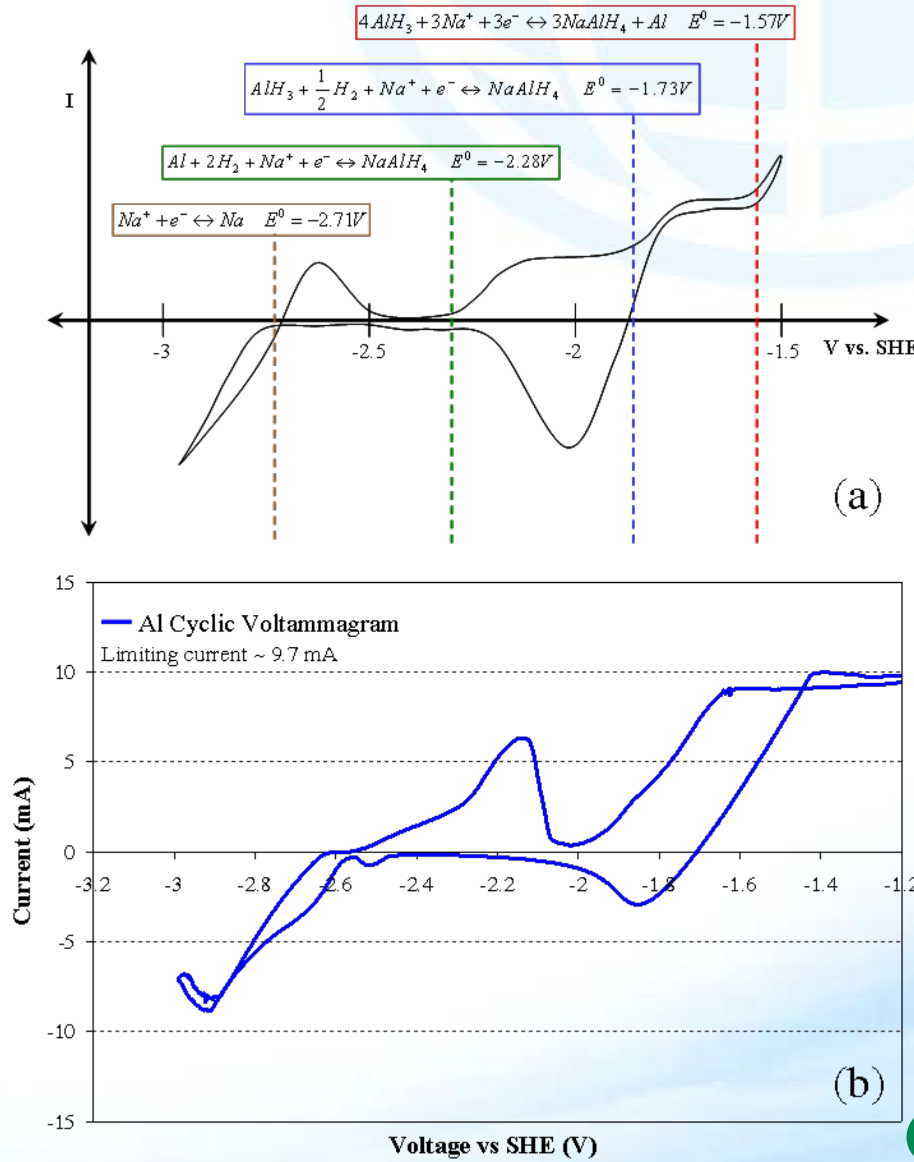
Proposed reversible cycle for alane. All components of the electrochemical process can be recycled to continually afford a viable solid-state storage material

Technical Accomplishments and Progress

Theoretical and Experimental cyclic voltammagrams for the electrochemical formation of alane

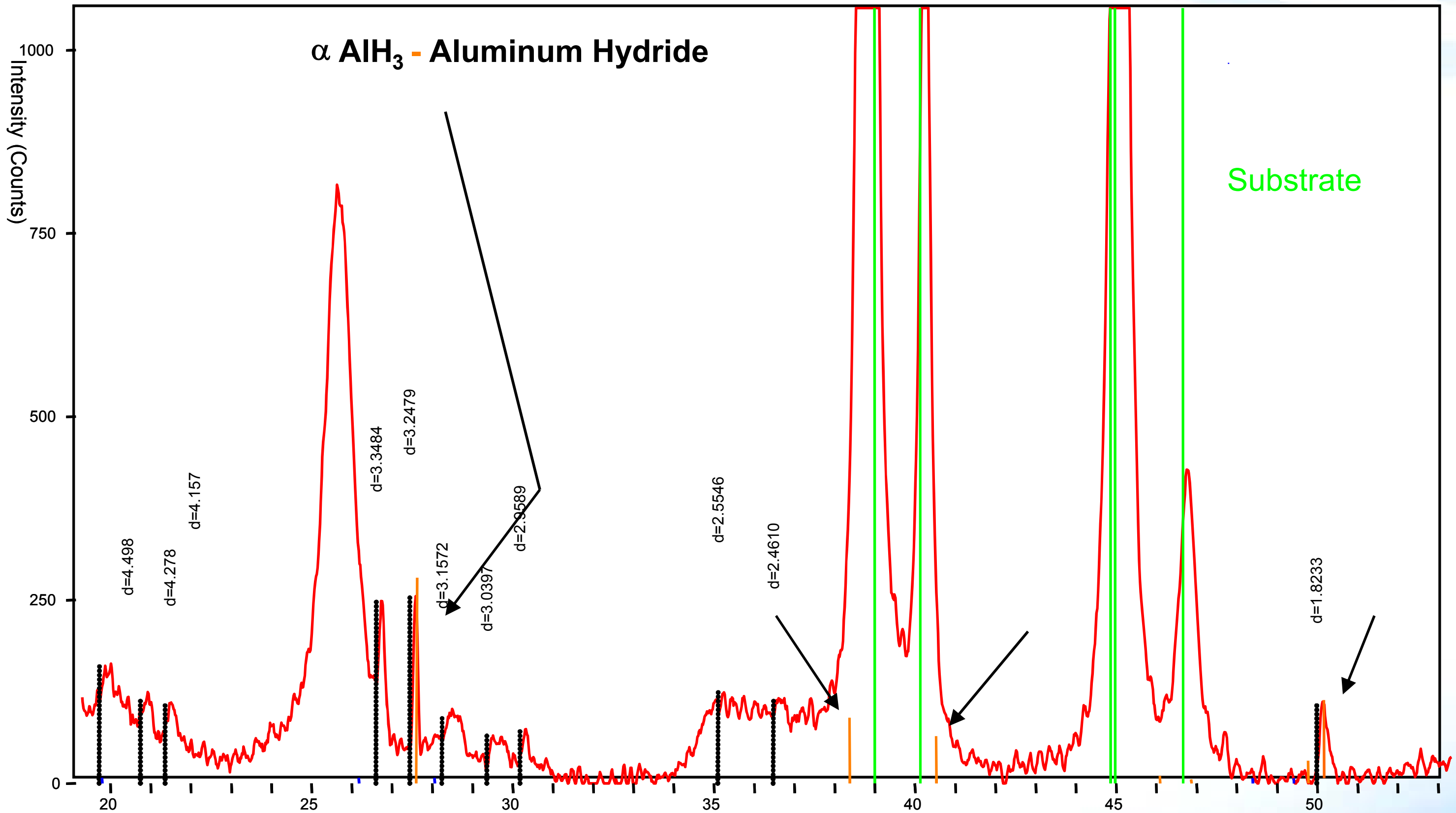
(a) A hypothetical cyclic voltammagram was formulated from the equilibrium potential data for <u>possible reactions and the anticipated state of each species generated</u>

(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



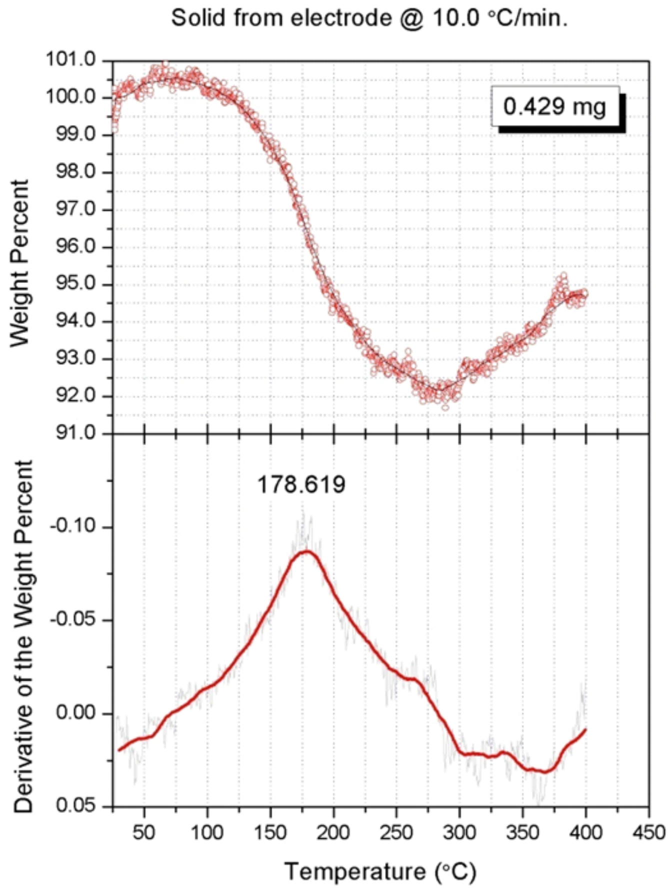
First Evidence of α-AlH_3 Generated Electrochemically

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

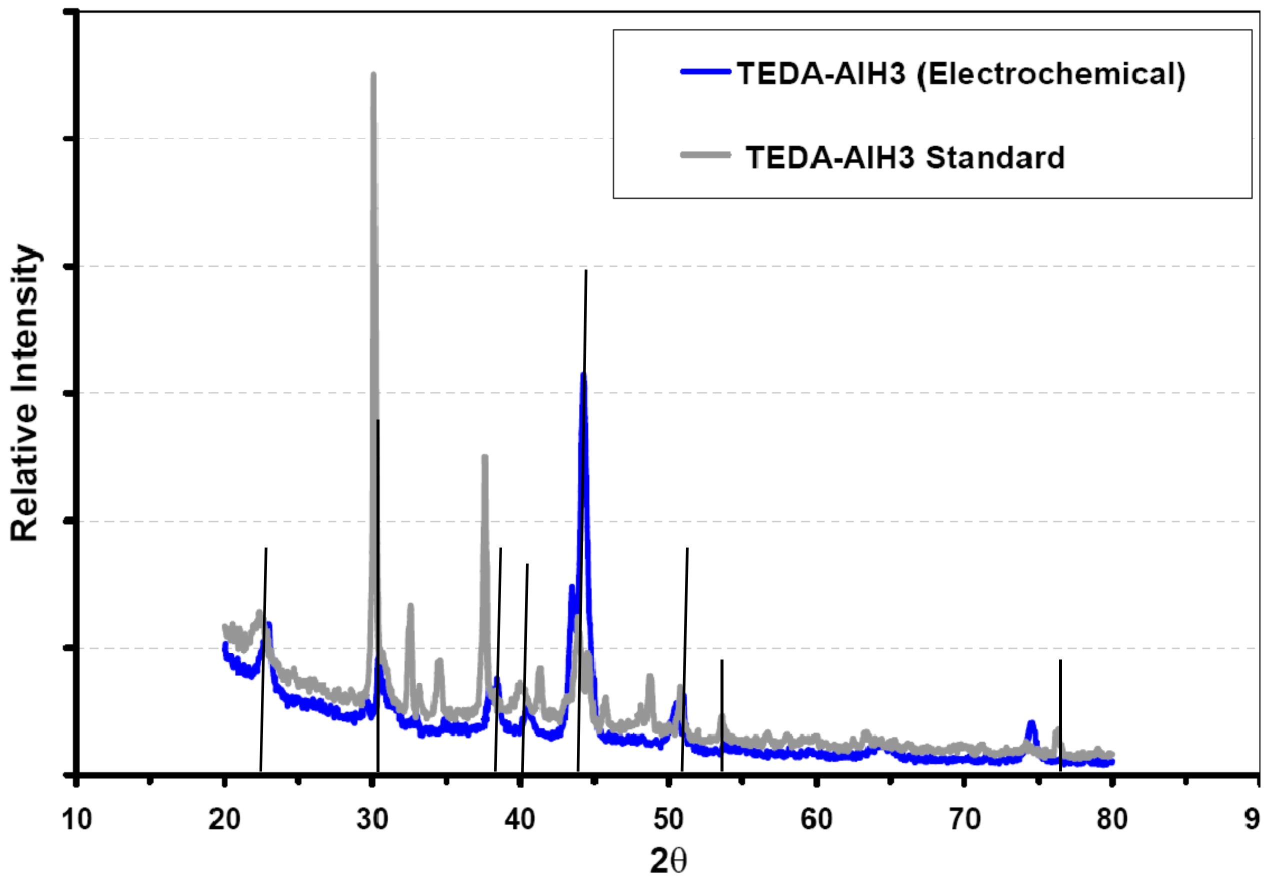
Technical Accomplishments and Progress

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

Feasibility of Electrochemical Synthesis of Alane

$$\mathit{Ideal}: \quad \mathit{Energy\ Input} = (nF)E^{o}_{cell} = 61.2\frac{\mathrm{kJ}}{\mathrm{mol\ AlH_3}}$$

$$\mathit{Ideal\ Cost} = \frac{61.2\ \mathrm{kJ}}{\mathrm{mol\ AlH_3}}\left|\frac{33.3\ \mathrm{mol\ AlH_3}}{\mathrm{kg\ AlH_3}}\right|\frac{10\ \mathrm{kg\ AlH_3}}{\mathrm{kg\ H_2}}\left|\frac{1\ \mathrm{kWh}}{3{,}600\ \mathrm{kJ}}\right. = 5.66\frac{\mathrm{kWh}}{\mathrm{kg\ H_2}}$$

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

$$\mathit{Actual}: \quad \mathit{Energy\ Input} = 5.66\frac{\mathrm{kWh}}{\mathrm{kg\ H_2}}\left|\frac{1}{68\%}\right| = 8.32\frac{\mathrm{kWh}}{\mathrm{kg\ H_2}}$$

68% is based on overpotential value

Energy Consumption

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

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

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

$3\ Na^+/AlH4^- + Al^{3+}/(Cl^-)_3$

$4\ AlH_3$

$3\ LiCl$

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

-Recycling AlH_3 by splitting LiCl requires a <u>minimum</u> of 0.7J for every 1J of fuel

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

–Recycling AlH_3 by splitting LiCl is <u>NOT</u> feasible

Technical Accomplishments and Progress

Possible Reactions : When AlH_3 Generated in Closed Material Cycle

Utilizing Polar Conductive Solution $NaAlH_4$ in THF

$NaAlH_4/THF \longleftrightarrow Na^+/AlH_4^-/THF$

Anode

$AlH_4^- \longrightarrow$ **AlH_3** (combined with THF) + ½ $H_2\uparrow$ +e^-

Or

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

Electrode is expected to dissolve

Cathode

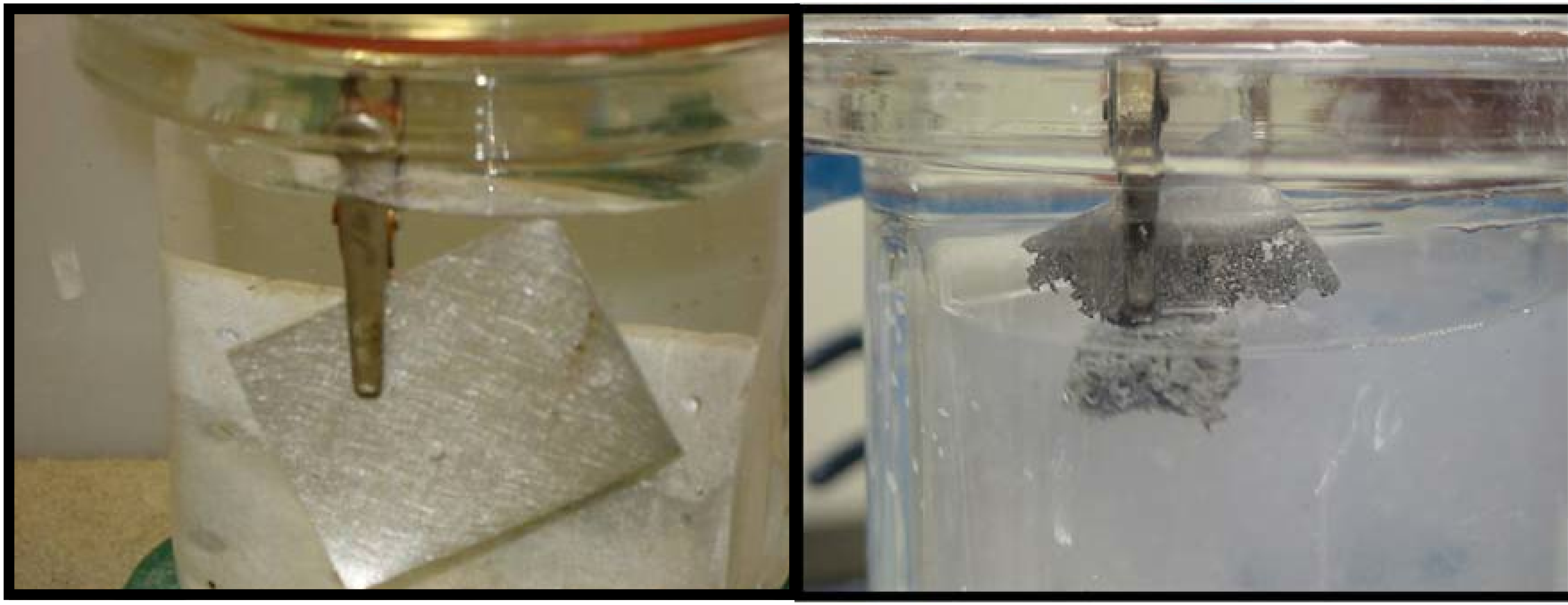
Na+ + ½ H2 $\xrightarrow{Pt^-}$ **NaH**

Regeneration NaH +Al +H_2 $\longrightarrow$ $NaAlH_4$

Technical Accomplishments and Progress

Before

After, Electrode Dissolved



Aluminum electrode before and after an electrochemical run

Technical Accomplishments and Progress

AlH_3 Recovery

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

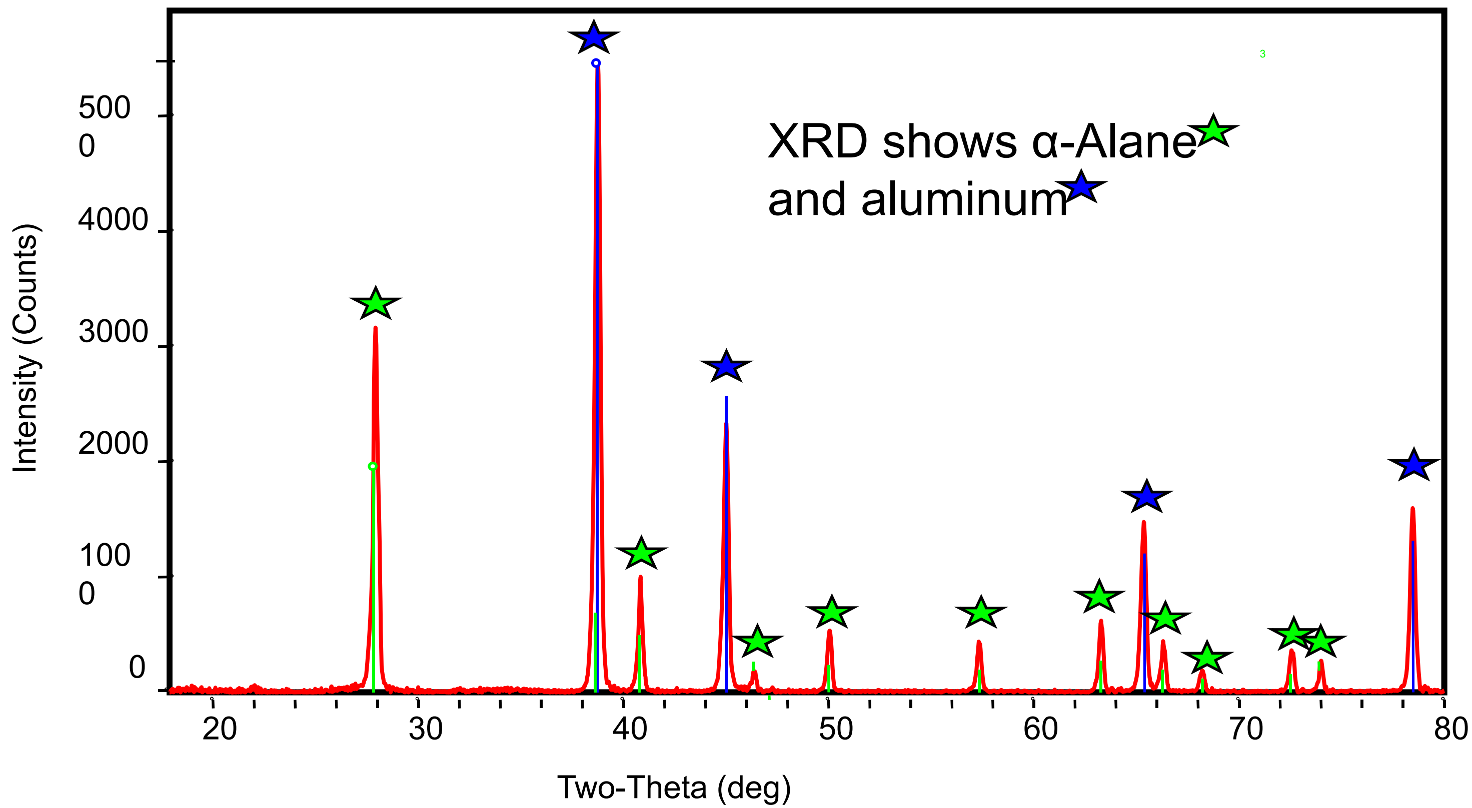
Two Recovery Methods:

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

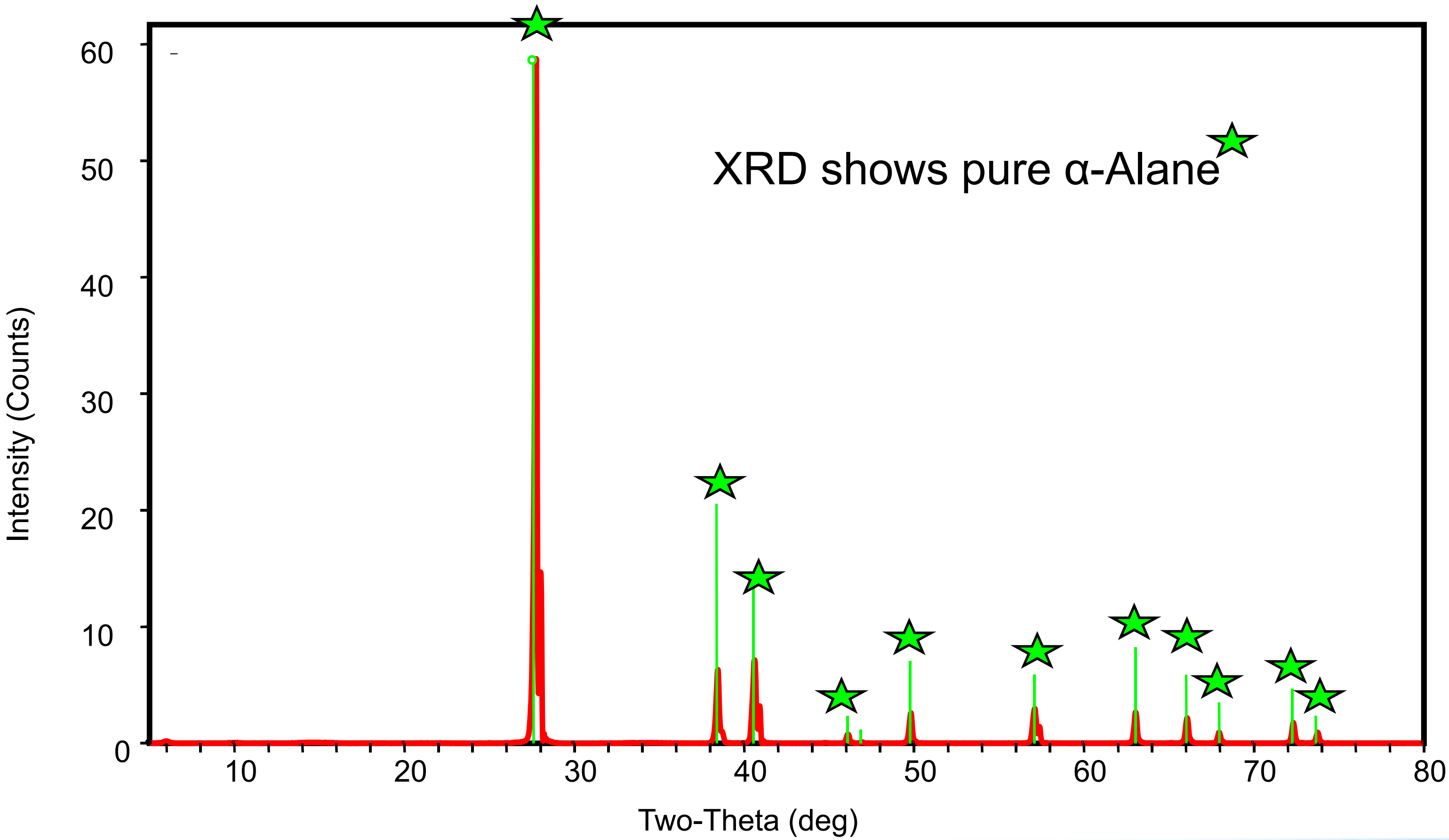


XRD shows generation of α-AlH_3

Technical Accomplishments and Progress

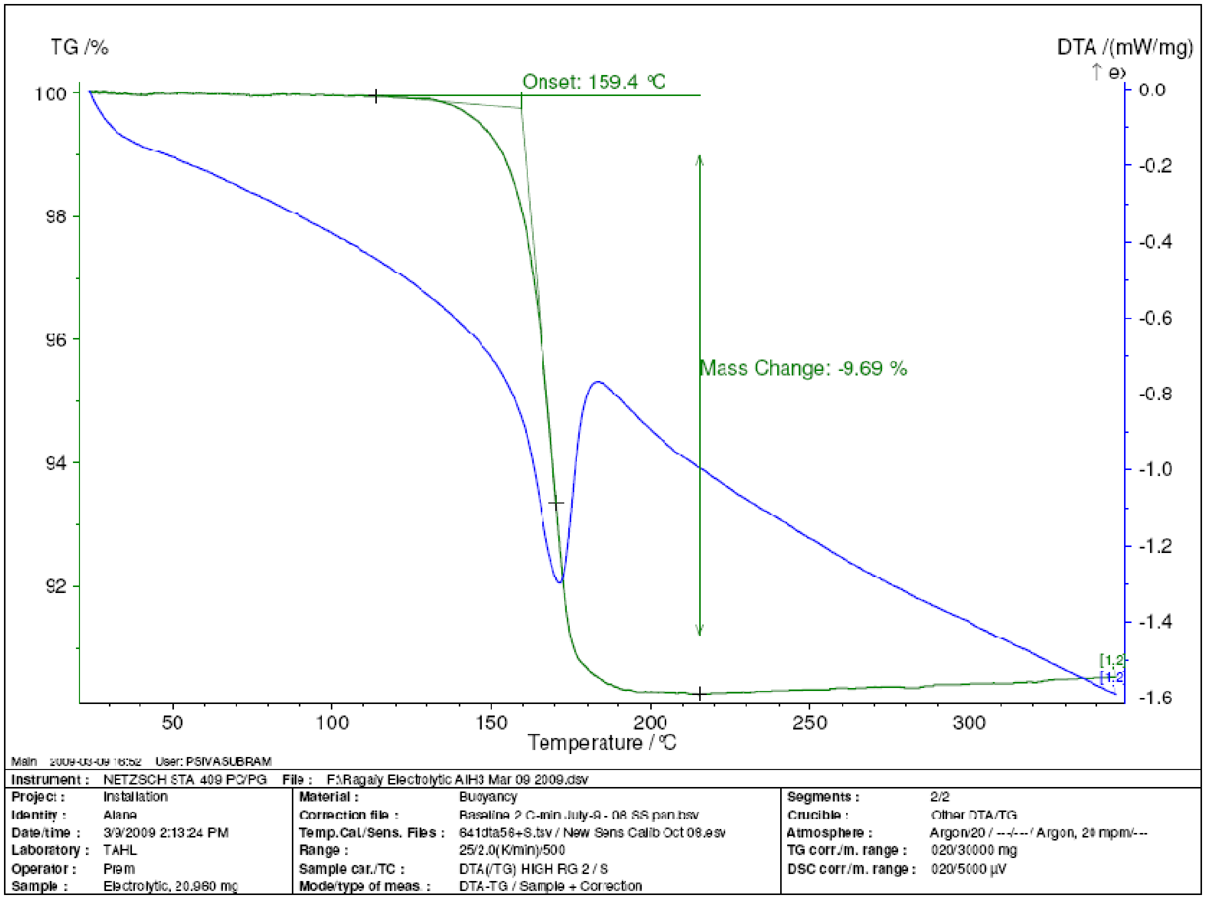
Recovery using different Adduct: Yield is Pure AlH_3

(method 2)



XRD shows generation of pure α-AlH_3

Technical Accomplishments and Progress



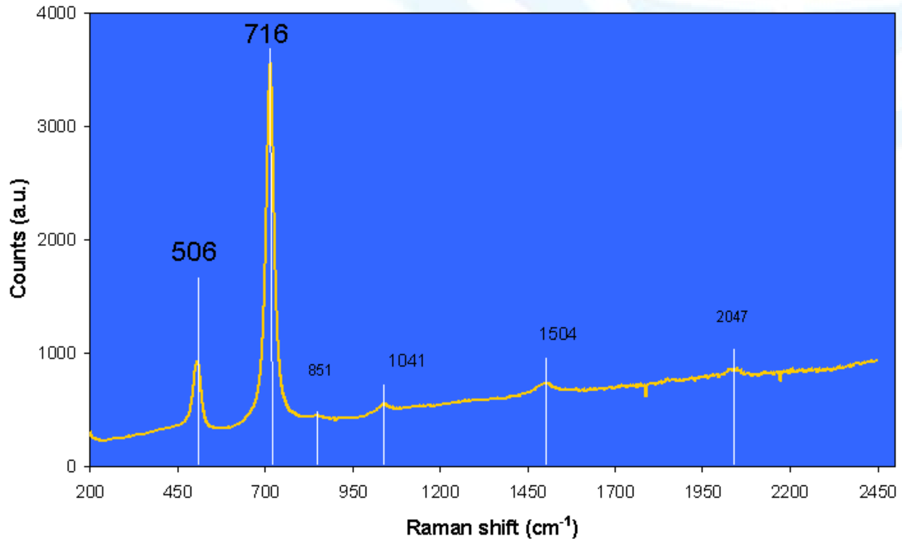
Two grams of AlH_3, alane, electrochemically generated

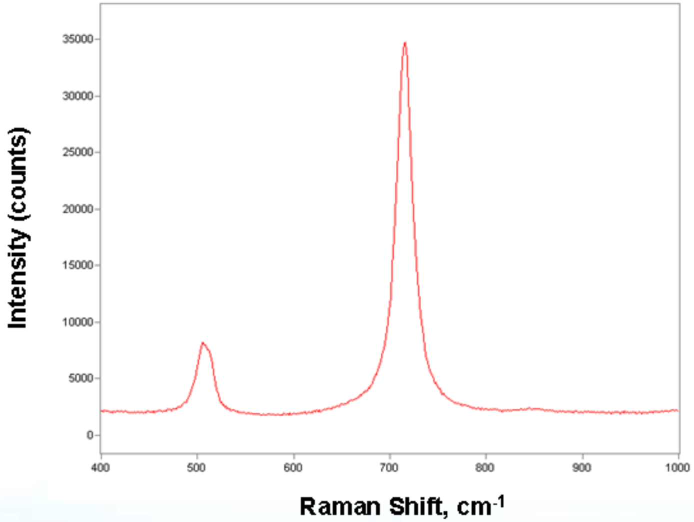
TGA decomposition electrochemically generated alane, shown in photo, releases almost full H_2 capacity expected in AlH_3

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"

Acknowledgements: Co-workers and Collaborators

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Metal Hydride Center of Excellence

DOE Office of Energy Efficiency and Renewable Energy

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