

Alane Electrochemical Recharging



SRNLTM
SAVANNAH RIVER NATIONAL LABORATORY

We Put Science To Work

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Hydrogen Technology Group

Presentation does not contain any confidential, proprietary or otherwise sensitive information

Review Meeting May 2007

- Program Overview
- AlH_3 Background
- Approach
- Technical Accomplishments
 - New cell design with reference electrode
 - Experimental Matrix
 - Representative Experiments
 - Conclusions
 - High Pressure Electrochemistry
- Future Work
- Energy Cost
- Relevance of Work to DOE Goals
- Reviewer Comments
- Technology Transfer / Collaborations
- Presentations / Patents

Timeline:

- Start: 10/01/2006
- End: 09/30/2008
- Percent Complete: 20%

Barriers Addressed:

- System Gravimetric Capacity
- System Volumetric Capacity
- Storage System Cost

Budget:

- Funding received in FY '06:
\$300,000
- Funding received in FY '07:
\$300,000

Partners:

- Brookhaven National
Laboratory
- University of Hawaii

Alane Formation

- Alane formation, from the elements, has been reported to occur under **very high** pressure conditions
- Or plasma Conditions
- Or by non-economical chemical reactions (thermodynamic sinks)
- Competing reaction can lead to unstable phases

Different methods are needed!

α -AlH₃ Physical Properties

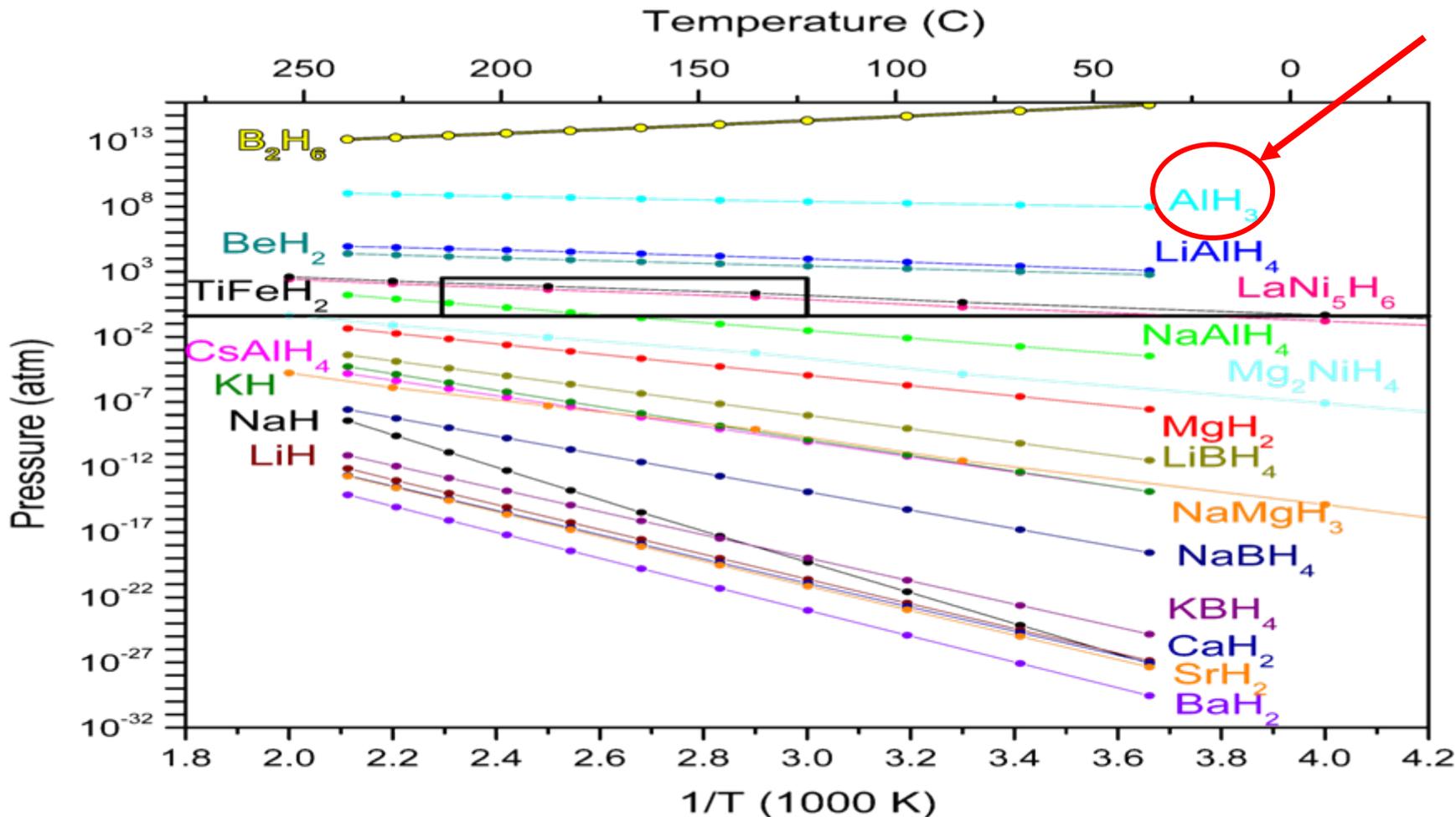
- Molecular weight: 30.00532 g/mol
- Density: 1.48 g/mL (1.48 kg/L)*
- Desorption Start Temperature: ~100°C to 175°C (depends on particle size)**
- This gives (assuming 10 wt. % α -AlH₃ and 100% H₂ capture):
 - 0.1008 kg H₂ per kg AlH₃ (System Gravimetric Capacity)
 - 0.1491 kg H₂ per liter AlH₃ (System Volumetric Capacity)
- These values exceed the 2010 DOE targets, even assuming energy loss to the process.

*Turley, J.W.; Rinn, H.W.; *Inorganic Chemistry*, Vol. 8, Pg. 18, 1969.

**Sandrock, G.; Reilly, J.; Graetz, J.; Zhou, W.-M.; Johnson, J.; Wegrzyn, J.; *Applied Physics A*, Vol. 80, Pg. 687, 2005.

Usable Hydrides

Reversible Compounds: $\Delta G^\circ=0$ in the range of 60-160°C and 1-100 atm.
(i.e. must be a reversible reaction within reasonable temperatures and pressures)



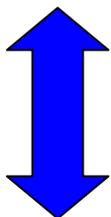
Thermodynamic Bases for Regeneration

Electrochemical synthesis is analogous to direct chemical means...

$$\Delta G = \Delta H - T \Delta S$$

$$RT \ln P = \Delta H - T \Delta S$$

(van't Hoff Equation)



$$RT \ln P = -nFE$$

(electrochemical analogue)

We know there are at least 3 phase of AlH_3 with different enthalpies of formation. We want the α phase, the most usable phase.

To select for the enthalpy of the α phase, we need to control T (mostly), and E.

$$\Delta H = \Delta G + T \Delta S = -nFE + nFT \left(\frac{\partial E}{\partial T} \right)_P$$

**Direct link between
E (electrochemical potential)
and the ΔH of the formation.**

AlH₃ Electrochemical Recharging

Motivation: Electrochemical recharging represents a very different, promising and complementary approach to AlH₃ recharging.



Utilize electrolytic potential, E, to increase hydrogen activity to hydrogenate Al. Based on Gibbs free energy and Faraday equation:

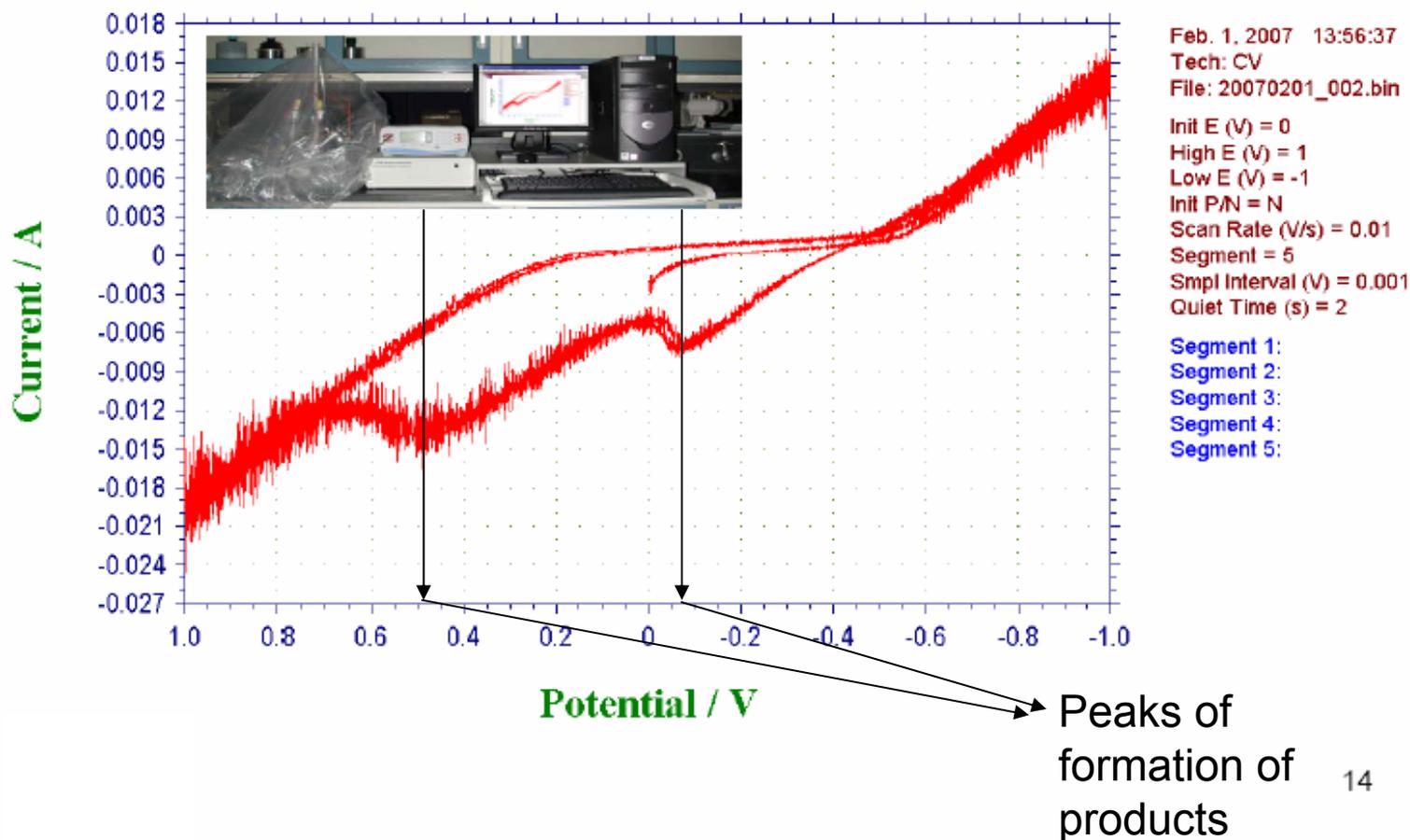
$$\Delta G = -nFE \qquad E = -\frac{RT}{2\mathfrak{F}} \ln(P_{\text{H}_2})$$

Concern: Al and AlH₃ will be oxidized in aqueous environment. This requires protecting the Al metal from water with either a Pd coating, or using non-aqueous approaches (without Pd):

- **Ambient Pressure Aqueous Electrochemical Cell (with Pd coating)**
- **Ambient Pressure Non-Aqueous Electrochemical Cell**
- **High Pressure Non-Aqueous Electrochemical Cell**

Identifying Regions of Reaction

Approach: Sweep the potential, E , and look for regions where reactions occur. Charge AI at those potentials and measure production rate vs current.



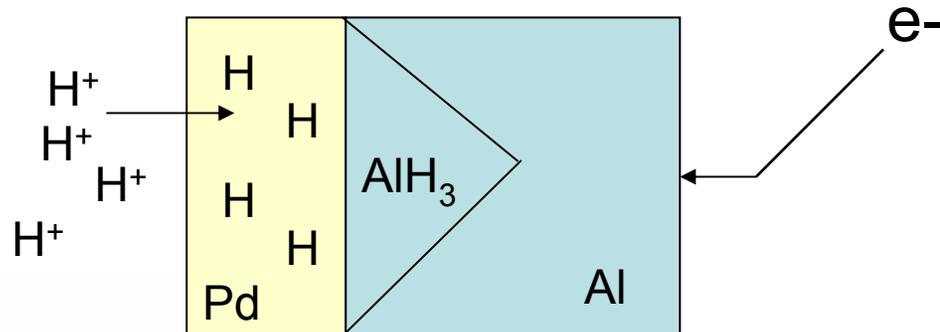
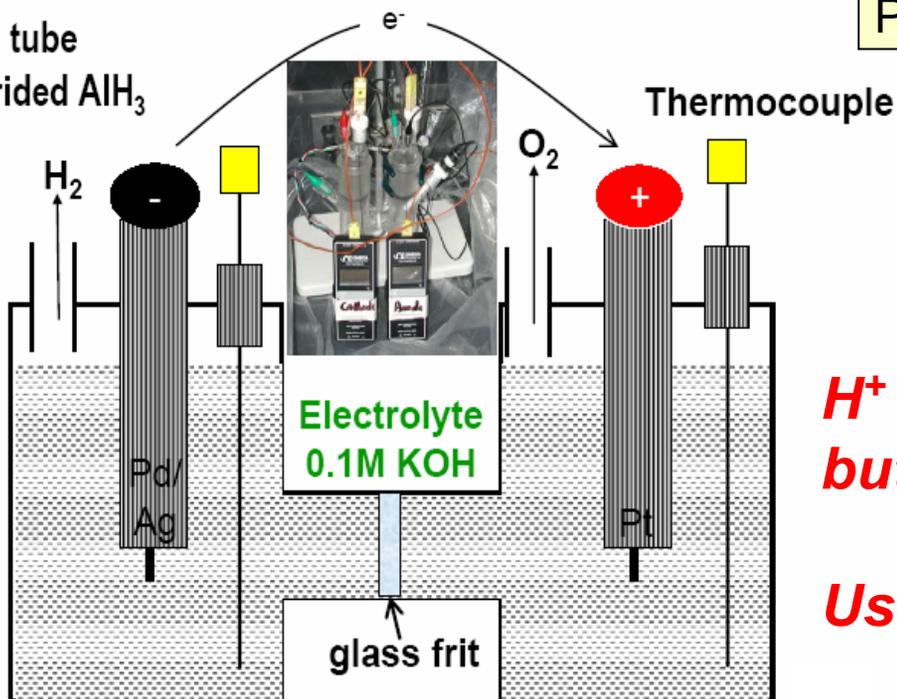
Aqueous Cell

First Attempt: Use aqueous solution with Pd coating on Al

Place Pd-coated Al inside Pd/Ag tube:

- Load Pd/Ag tube with dehydrated AlH_3
- 80 °C
- 15 V
- 50 mA
- 5 hr

Observed H_2 bubbles on cathode



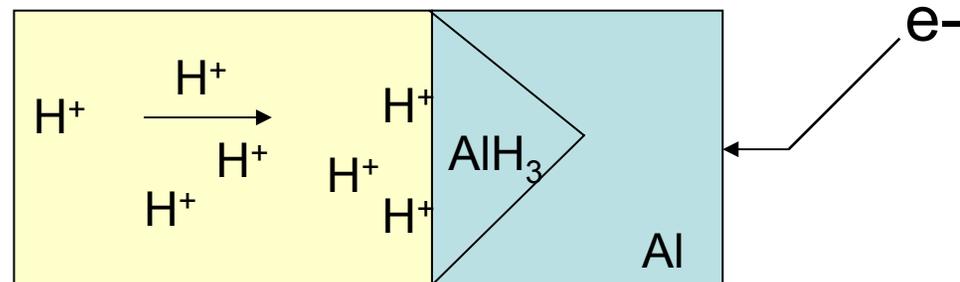
H⁺ reduction, but no AlH₃ observed

Use other approaches

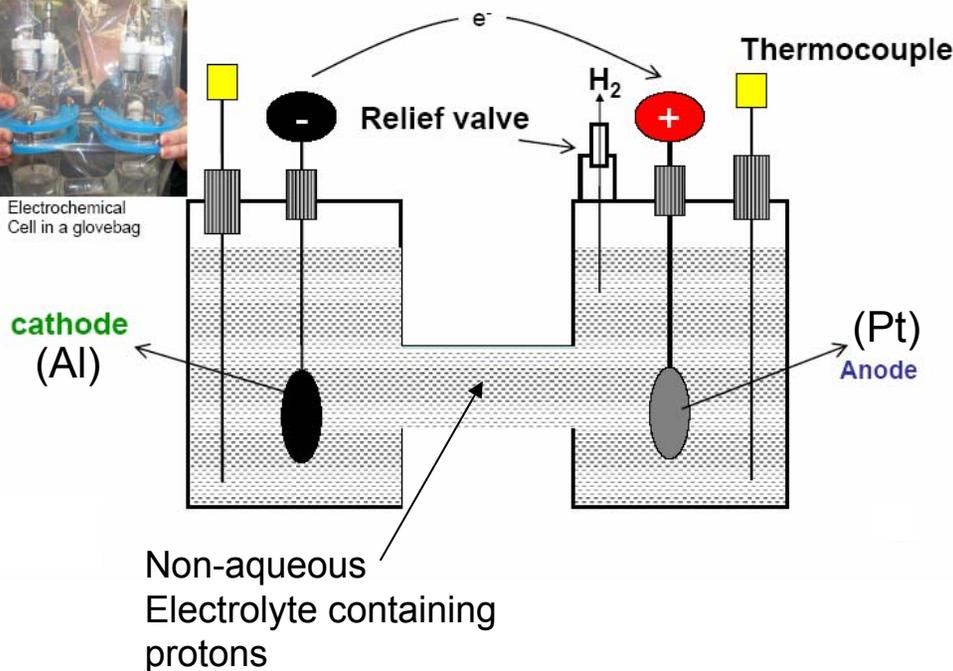
Non-Aqueous Cell

*Second Attempt:
Reduce protons directly from
non-aqueous electrolyte*

Electrolyte w/protons



Electrochemical Cell in a glovebag

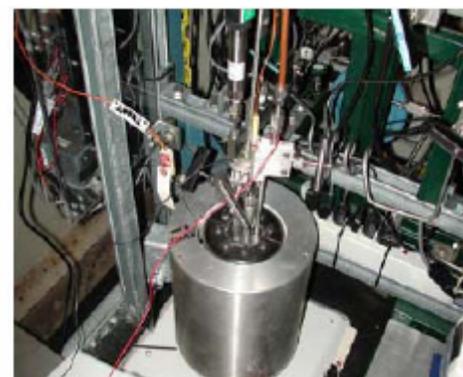
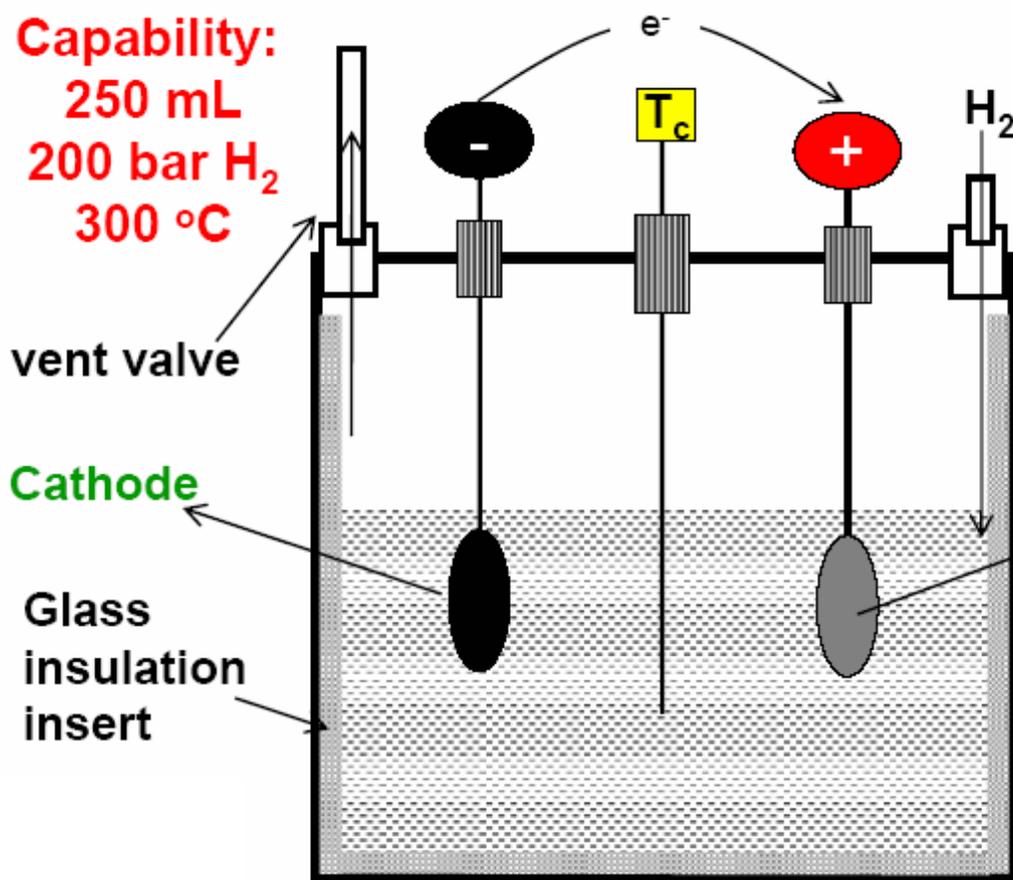


H^+ reduction seen, and AlH_3 formed

Higher pressure Cell

High P Electrochemical Cell to Control Thermodynamic Parameters

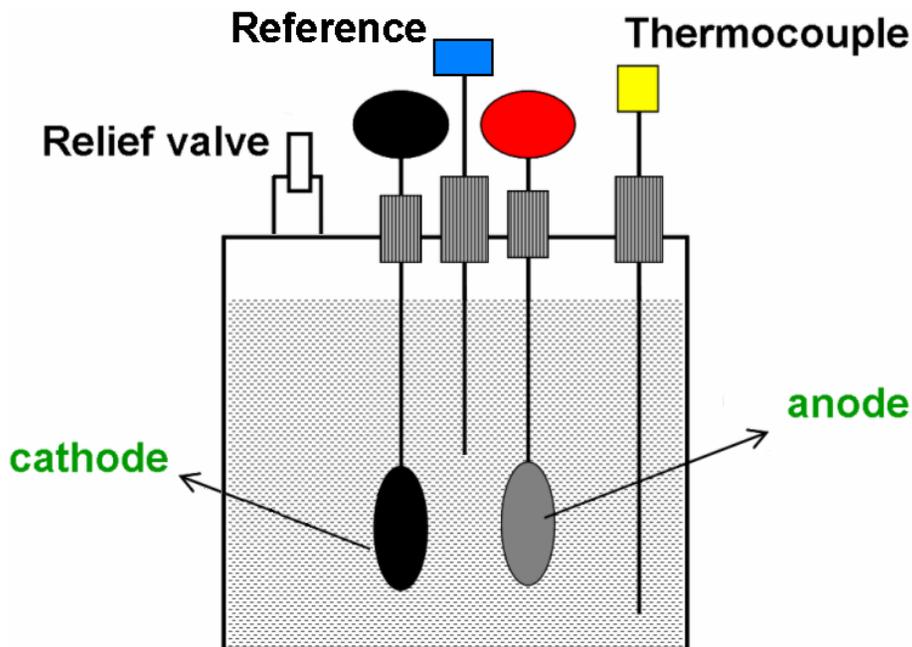
Capability:
250 mL
200 bar H₂
300 °C



Summary

- Mechanical:
 - Redesigned the non-aqueous electrochemical cell to provide better reaction kinetics.
 - Working towards relocating the non-aqueous cell to a Schlenk line where elevated temperatures, up to the boiling point of the electrolyte, can be achieved.
- Experimental (non-aqueous cell):
 - Experimental Focus
 - Experimental Matrix: Met and exceeded.
 - Electrode Evaluation: Reproduced the **formation of alane** and gas formation with different electrode configurations.
 - Alane Formation: Multiple techniques have to be used to characterize the consistency of the formation of alane and to also identify the barrier of the formation of AlH_3 .

Non-Aqueous Cell Design



- The configuration of the electrochemical cell was adapted to obtain better ionic conduction in Electrolyte.
- New cells are in design for Schlenk line work, enabling better control of physical properties.

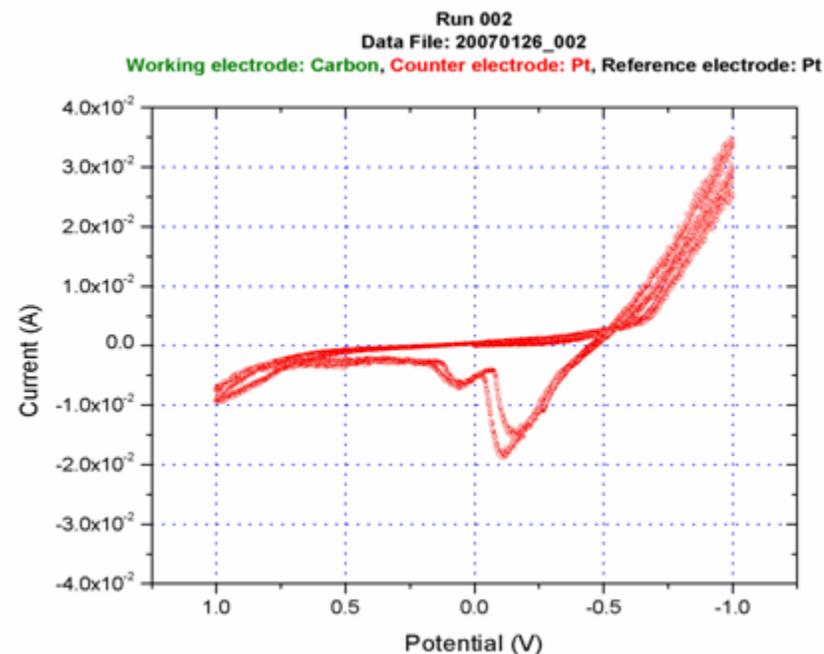
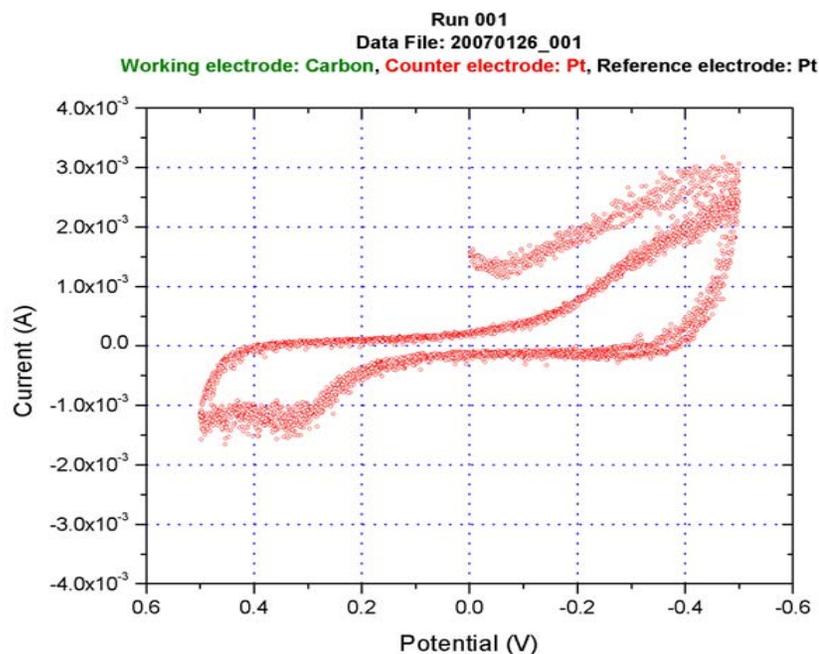
Non-Aqueous Cell Experimental Focus

-  1. Repeat previous experiments while changing conditions to improve upon cell design and assure reproducibility
-  2. Experiment with different electrodes/counter-electrodes (CV's) to search for the best combination
-  3. Once an electrode pair is chosen, investigate those electrodes for reduction/oxidation reactions
-  4. Devise and conduct experiments to understand the mechanism of any reactions taking place
-  5. Determine the feasibility of the production of larger quantities alone based on previous work

Representative Experiment – CV

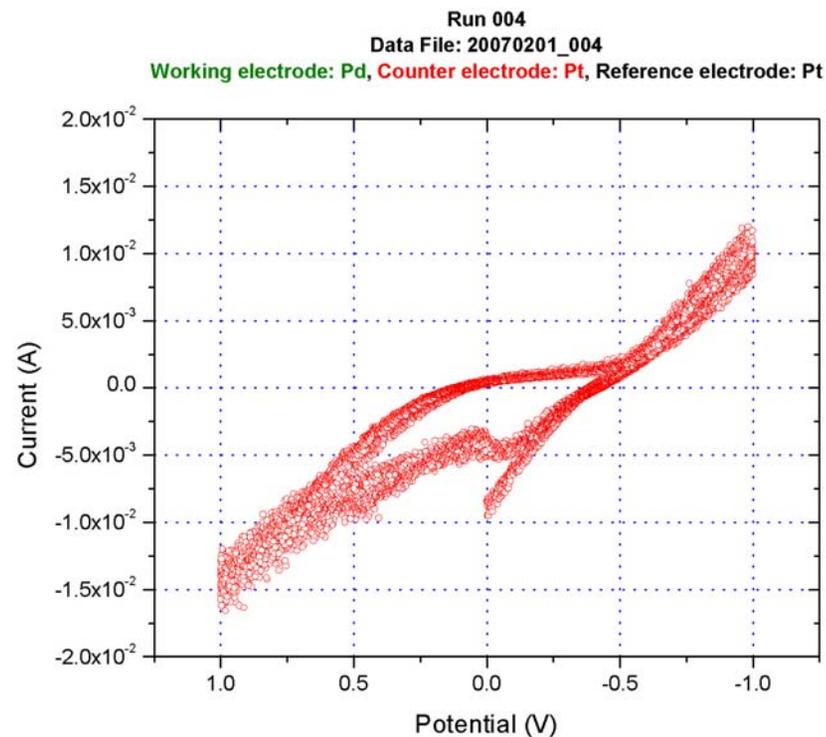
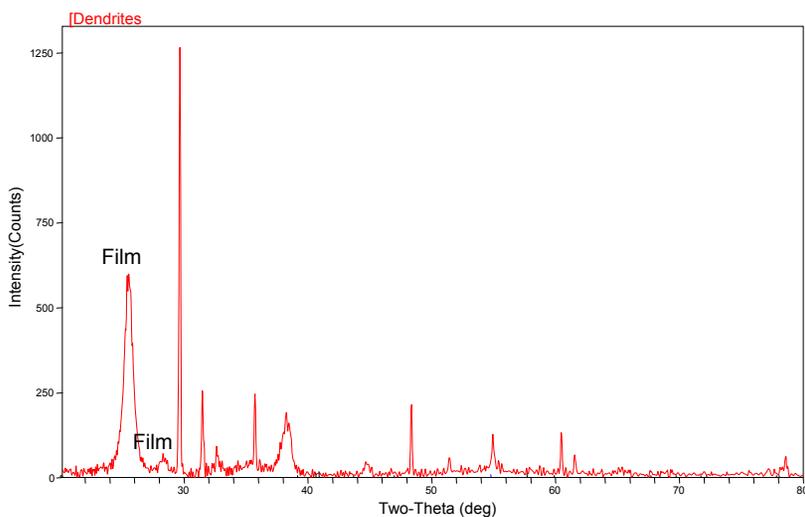
Electrode and electrolyte investigation:

- Carbon / Pt Electrodes with a Pt reference electrode.
- Reductions are present.
- Established reproducibility with the reference electrode and new cell design..



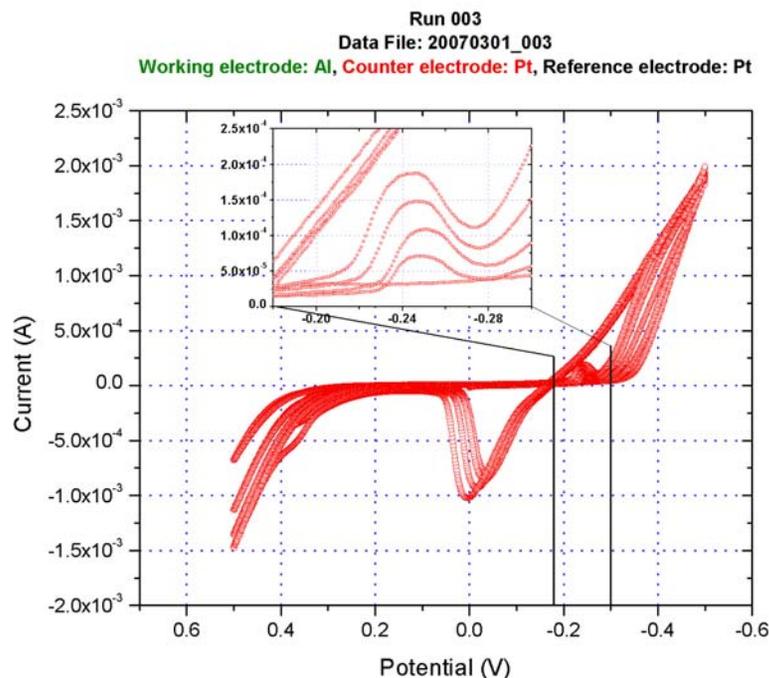
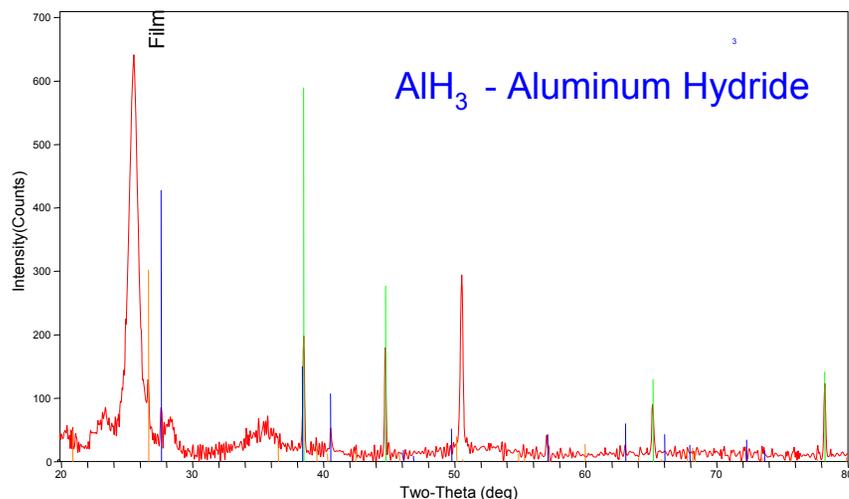
Representative Experiment – CV

- Pd / Pt Electrodes with a Pt reference electrode.
- Again, reductions are present along with gas formation
- First real evidence of hydrogen charging
- PdH formation, showing that protons are mobile in solution.



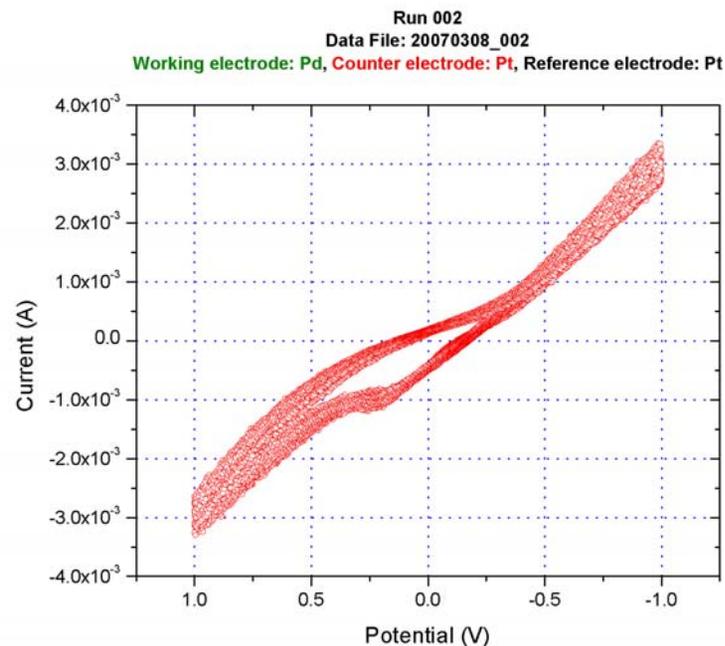
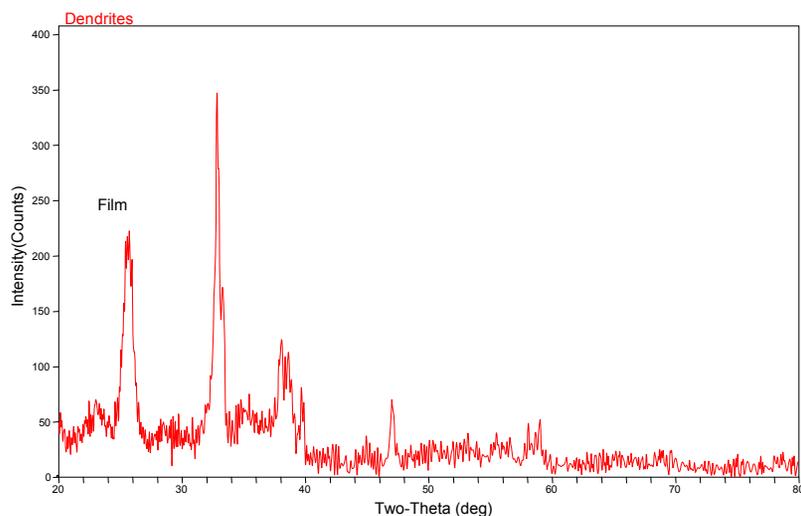
Representative Experiment – CV and Constant Voltage

- Al / Pt Electrodes with a Pt reference electrode.
- Red/ox are present along with dendrite and gas formation. Red/ox peaks grow with each cycle. Also performed a constant voltage experiment at +0.9V.
- X-ray shows the possibility of production of alane. Further tests needed to confirm this result.
- Possible problems: Removal of the oxidation layer present on the Al electrode. Identify the broad peaks in the X-ray. Need multiple technique analysis.



Representative Experiment – CV and Constant Voltage

- Pd / Pt Electrodes with a Pt reference electrode.
- Red/ox are present along with gas formation. Constant voltage experiment at +0.84V.
- Decision: Go with Al / Pt electrode pair because of the possibility that alane was formed. Need to determine the mechanism of dendrite formation before proceeding.**

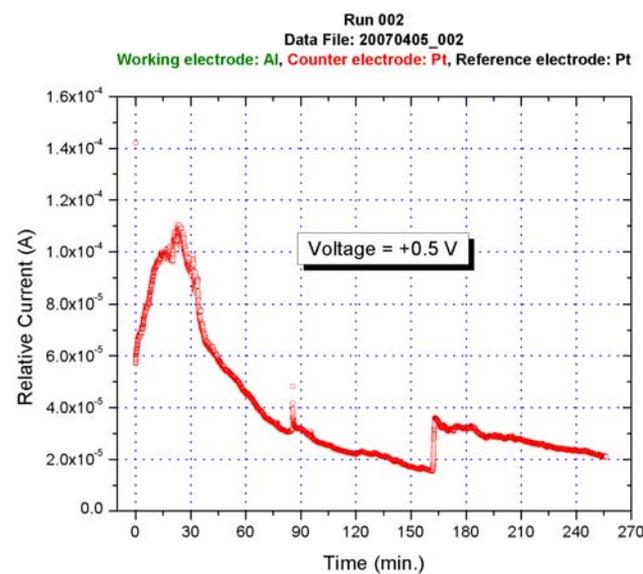
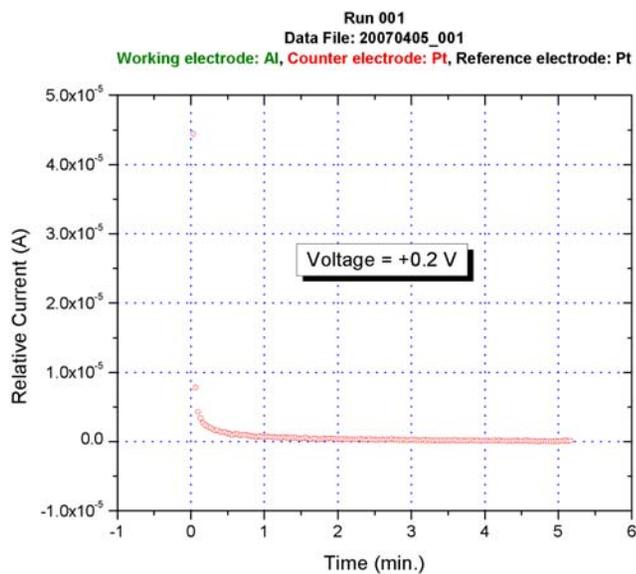


ICP / NMR

- Determination the makes up of the dendrites is necessary to determine an appropriate mechanism of formation
- The dendrites were dissolved in distilled water, and then ICP was run to give a ratio of metal ions
- Presence of aluminum was confirmed
- NMR has also been conducted to determine the nature of the electrolyte mixture
- Further analysis, to include more NMR, IR, and Raman are planned

Representative Experiments – Constant Voltage

- Al / Pt Electrodes with a Pt reference electrode.
- Constant voltage experiments at +0.2V and +0.5V. No CV experiments run.
- The relative current decreases to 0 quickly at +0.2V, indicating that no conductivity in electrolyte. The voltage was then increased to +0.5V. Immediately dendrite formation occurs and the relative current jumps.
- **Decision: Step up the voltage from +0.1V until current flow begins, this will be where the dendrite formation starts. From there, theoretical calculations can proceed as to the pressure associated with that voltage, leading to alane formation.**



Conclusions

1. We reproduced previous experiments and affirmed the formation of alane
2. A new cell and electrode configuration were designed based on results from those previous experiments
3. The new setup led to the ability to easily reproduce results
4. Further techniques are required to determine mechanism and identify intermediate steps
5. We are proceeding with the Al / Pt electrode system as it gave the most promising result
6. Experiments are currently under way to determine the optimum voltage and current needed for alane formation
7. The state of the surface of the aluminum is essential to the reproducibility of alane formation
8. Gas formation occurs at every electrode.

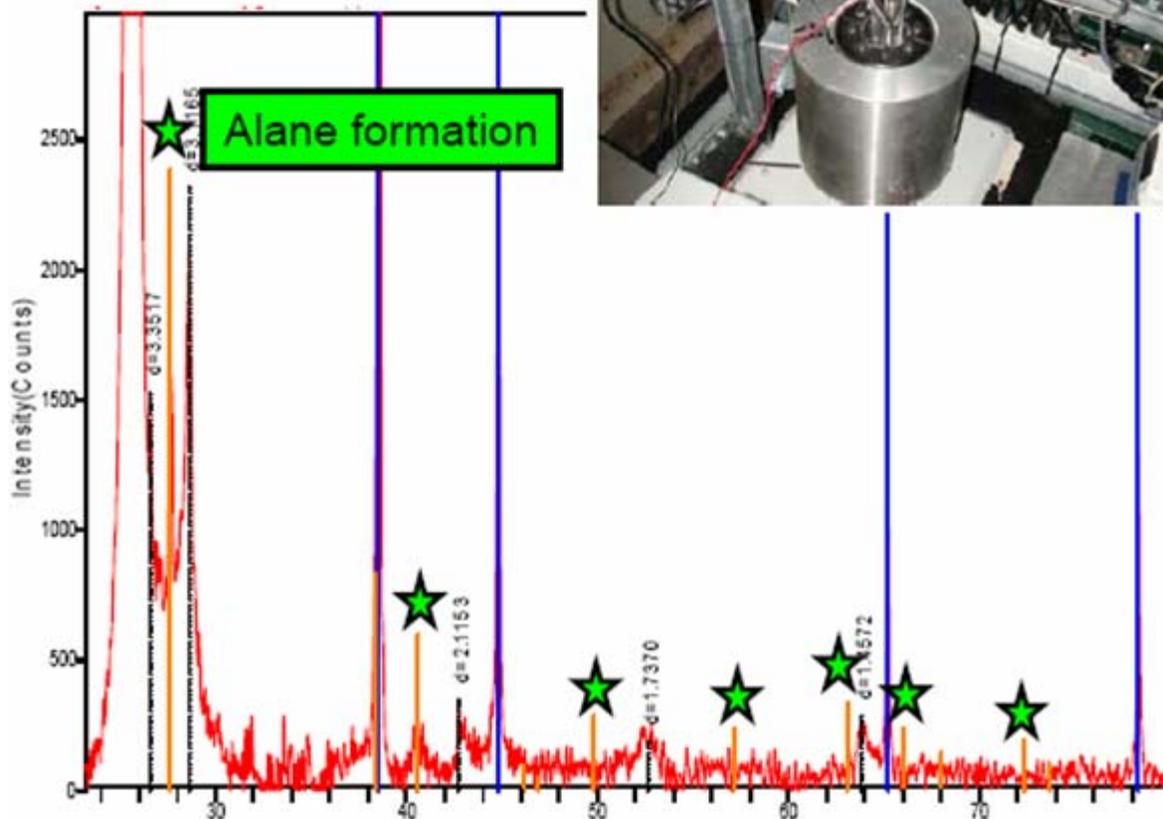
Higher Pressure Electrochemistry Cell

- Elevated H₂ pressure will provide more hydrogen content for recharging.
 - Increased hydrogen activity at anode
 - Establish H₂ equilibrium between electrolyte and H₂ gas
- Elevated temperatures can be used since electrolyte evaporation is not a concern in pressurized system.
 - Improved kinetics
- Optimization of thermodynamic parameters can be better controlled.

Note: Multiple ambient pressure (non aqueous) cells are being used for quick screening

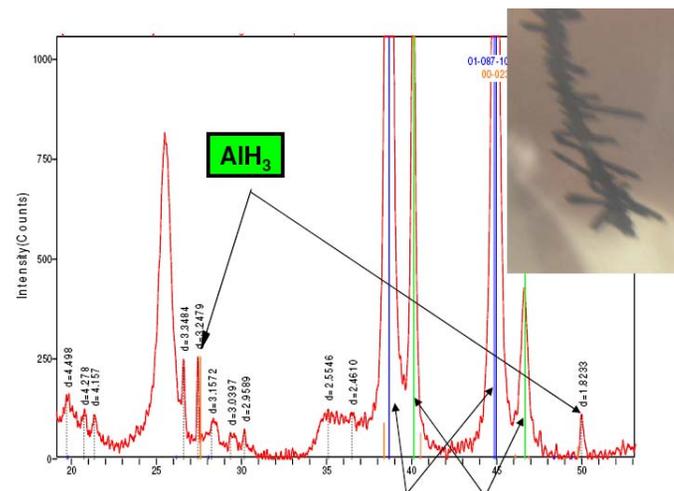
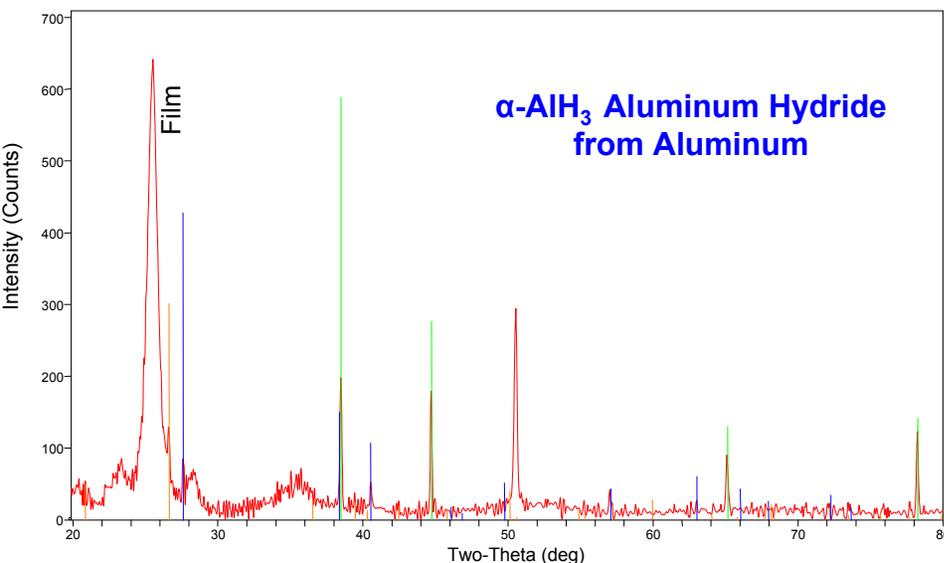
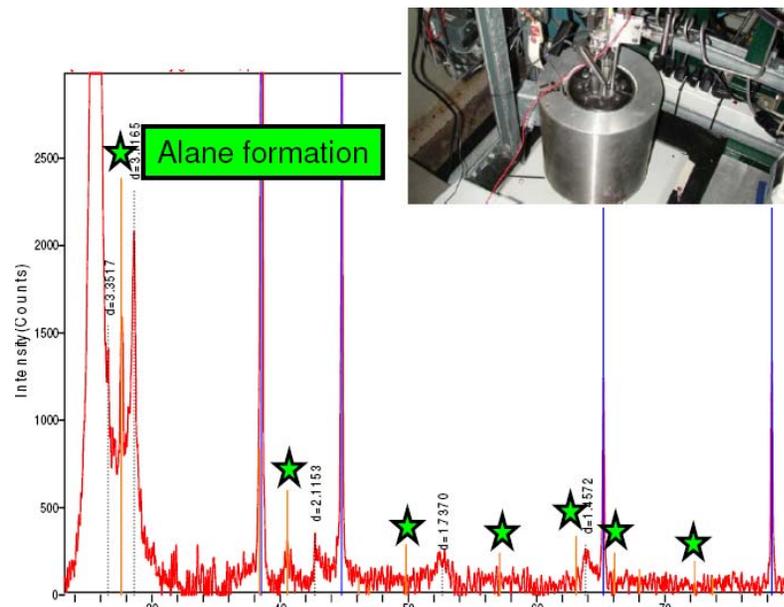
High Pressure Electrochemistry Cell

- Electrochemical charging under elevated hydrogen pressure.
- 500 psi H₂
- 60 °C
- 10 V
- 2 hours
- Process needs to be optimized to increase yield from mg to grams.



Summary of All Electrochemical Cells

Non-Aqueous Cell



Path Forward / Questions to Answer

1. Determine the mechanism of proton transfer in the electrochemical cell
2. Determine how the state of the surface can hinder the formation of alane.
3. Based on the previous two answers, determine quantitatively the theoretical yield of alane production through electrochemical synthesis
4. Important side projects:
 - Determine the amount of hydrogen gas being produced at electrodes
 - Investigate how the change of temperature affects the formation of different phases of Alane
 - Determine if mixed electrolyte systems provide different electrochemical reactions
 - Keep the surface of the aluminum electrode fresh by removing formed alane layer (either mechanically or chemically) to obtain continuous flow of electrons

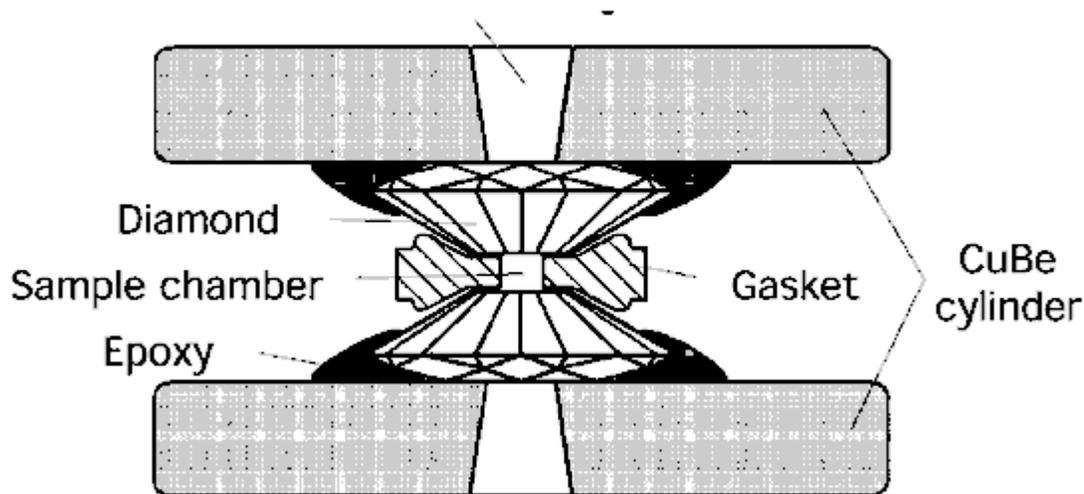
Path Forward / Questions to Answer

1. Demonstrate feasibility of electrolytically charging AlH_3 (larger quantities).
2. Quantify yield and efficiencies of recharging reaction.
3. Optimize cell performance to achieve efficient AlH_3 yield.
 - Evaluate electrode design and materials
 - Electrolyte and composition need to be selected to avoid electrolytic or thermal breakdown during operation
4. Modify electrolytic charging parameters to yield AlH_3 having discharge kinetics sufficient to meet DoE 2010 targets (via obtaining the optimum particle size)

Note: Go/NoGo Decision on SRNL Charging Process at end of FY 2007, based on charging efficiencies, product yield, process conditions

Path Forward / Questions to Answer

1. Diamond Anvil Cell (DAC) work has been conducted at Florida International University.
2. Charging of Al under high H_2 pressure (PRESSURE RANGE) will be investigated to determine the thermodynamic bases of Alane formation



Criteria for Down-Select and **go/no-go** Decisions

- Can AlH_3 be formed electrochemically?
- Which conditions for electrochemical cell(s) work best?
- What are the recharge efficiencies & kinetics?
- Cost of producing AlH_3 from Al metal should not exceed 30% of the value of stored hydrogen

Wet Synthesis vs. Electrochemical Synthesis

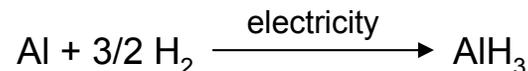
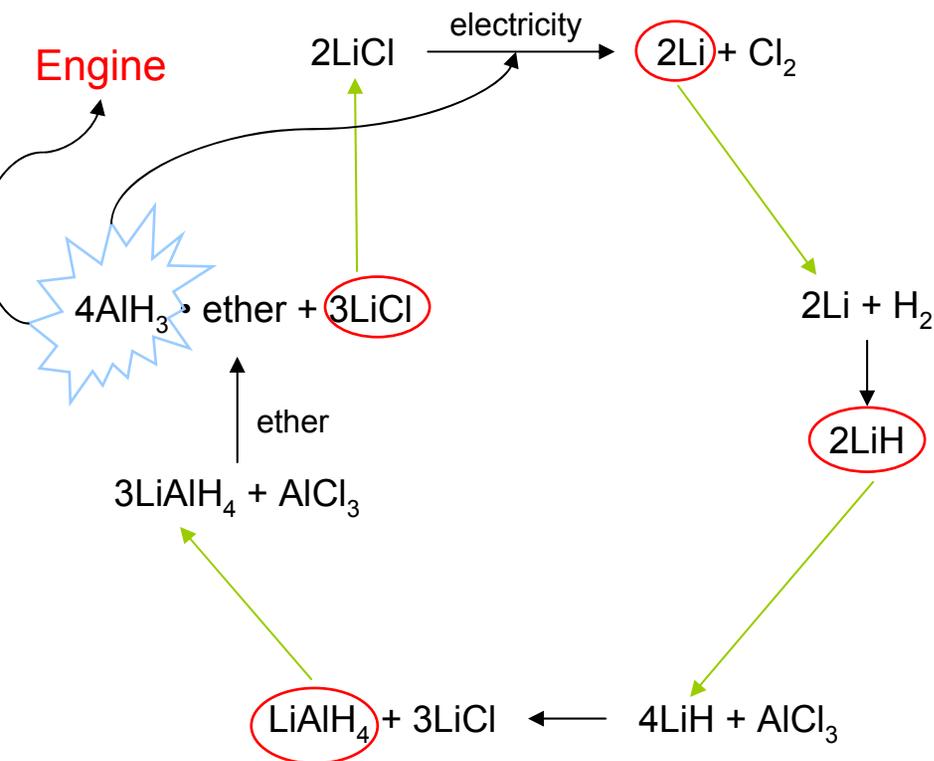
$$\Delta H_f^\circ \text{LiCl} = -408.3 \text{ kJ/mol}$$

$$\Delta_{\text{fus}} H^\circ \text{LiCl} = 19.8 \text{ kJ/mol}$$

Energy required reach melting temperature = 22.7 kJ/mol

$$\Delta H_f^\circ \text{AlH}_3 = -11.4 \text{ kJ/mol}^*$$

$$\Delta G_f^\circ \text{AlH}_3 = 46.5 \text{ kJ/mol}^*$$



- Potentiostat Max voltage: 10 V
- Potentiostat Max current: 250 mA
- With the current and voltage level known, the amount of power consumed by the chemical reaction can be calculated.
- Charging energy then depends on understanding and then optimizing the kinetics of the chemical reaction.

Wet Synthesis vs. Electrochemical Synthesis

- Assume production of Li metal takes ~400 kJ/mol energy to recover.
- One mole of AlH_3 contains 360 kJ of fuel energy (based on LHV of H_2 = 120 kJ/g).*
- It takes ~110% of the energy from AlH_3 to produce Li metal through electrochemical means.
- Using electricity will drive the reaction.
- Direct charging of Al requires a at least 0.1J for every 1J of fuel energy.*
- Goal is to achieve less than 20% consumption to the process of the AlH_3 energy: 72 kJ/mol

- The overall relevance of this project is quite straight forward as we attempt to directly charge and recharge Alane taking into account a low cost/high yield method for forming this material. If accomplished, we will have exceeded the DOE 2010 goals for System Gravimetric Capacity (0.06 kg H₂/kg material) and System Volumetric Capacity (0.045 kg H₂/L). The Storage System Cost is still to be determined with future results.
- Molecular weight: 30.00532 g/mol
- Density: 1.48 g/mL (1.48 kg/L)*
- Desorption Start Temperature: ~100°C to 175°C (depends on particle size)**
- This gives (assuming 10 wt. % α-AlH₃ and 100% H₂ capture):
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- These values exceed the 2010 DOE targets, even assuming energy loss to the process.