
Electrochemical Reversible Formation of Alane

Ragaiy Zidan (PI)

Brenda Garcia, Andrew Harter, Ashley Stowe, Josh Gray

Savannah River National Laboratory

June 13, 2008

Project ID STP19

Timeline

- Start: 10/01/2006
- End: In Progress
- Percent Complete: 20%

Budget

- 250K Funding received in FY07
- 400 K Funding for FY08

Barriers

- Store hydrogen required for conventional driving range (greater than 300)
- The weight, volume and cost of these systems

Technical Targets

- System Gravimetric Capacity > 6 %
- Storage System Cost < 30 % of hydrogen cost

Partners

- Brookhaven National Laboratory
- University of Hawaii

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: $\sim 60^\circ\text{C}$ to 175°C (depending on particle size) meets the 2010 DOE targets for desorption

➤ Specific Objectives

- Avoid the impractical high pressure needed to form AlH_3 by utilizing electrolytic potential to increase hydrogen activity and/ or drive chemical reactions to recharge AlH_3
- The process used is based on Gibbs free energy and Faraday's equation

Key Milestone

Quantify formation reaction yield, determine energy requirements and demonstrate feasibility of electrolytically charging/forming alane

Specific Milestones:

- Design/build Ambient Pressure Cell (APC) Test Matrix
 - Complete APC 2nd Test Matrix
 - Complete Elevated Pressure Cell (EPC) 1st Test Matrix
- Go/NoGo** Decision on SRNL Charging Process

Following FY07 activities a **GO** decision was made and determined that the potential of this material and process to meet > 8 wt% hydrogen capacity under reasonable operating conditions should be further investigated. Additional work in FY08-09 will include optimization of both the process and the material purity as well as examinations into coatings to improve material handling and safety.

AlH_3 Electrochemical Recharging

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



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

$$\Delta G = -nFE \qquad E = -\frac{RT}{nF} \ln(f)$$

Concern: Because Al and AlH_3 will be oxidized in an aqueous environment, protection of the Al surface from water/oxygen must be achieved by either using coating such as Pd, or using non-aqueous solvents:

- **Ambient Pressure Non-Aqueous Electrochemical Cell**
- **Elevated Pressure Non-Aqueous Electrochemical Cell**

Thermodynamic Bases for Regeneration

(Avoiding Thermodynamic Sink)

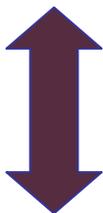
Electrochemical synthesis is analogous to direct chemical means...

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

(Gibb's Equation)

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

(van't hoff Equation)



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

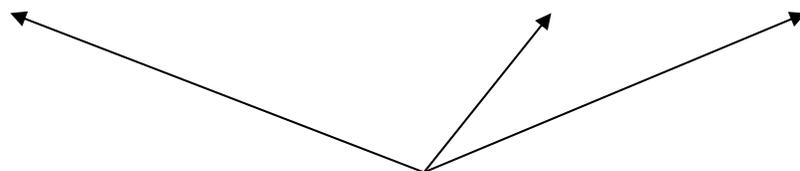
$$RT \ln P = -nFE$$

(Electrochemical Analogue)

We know there are at least 3 phases 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.

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



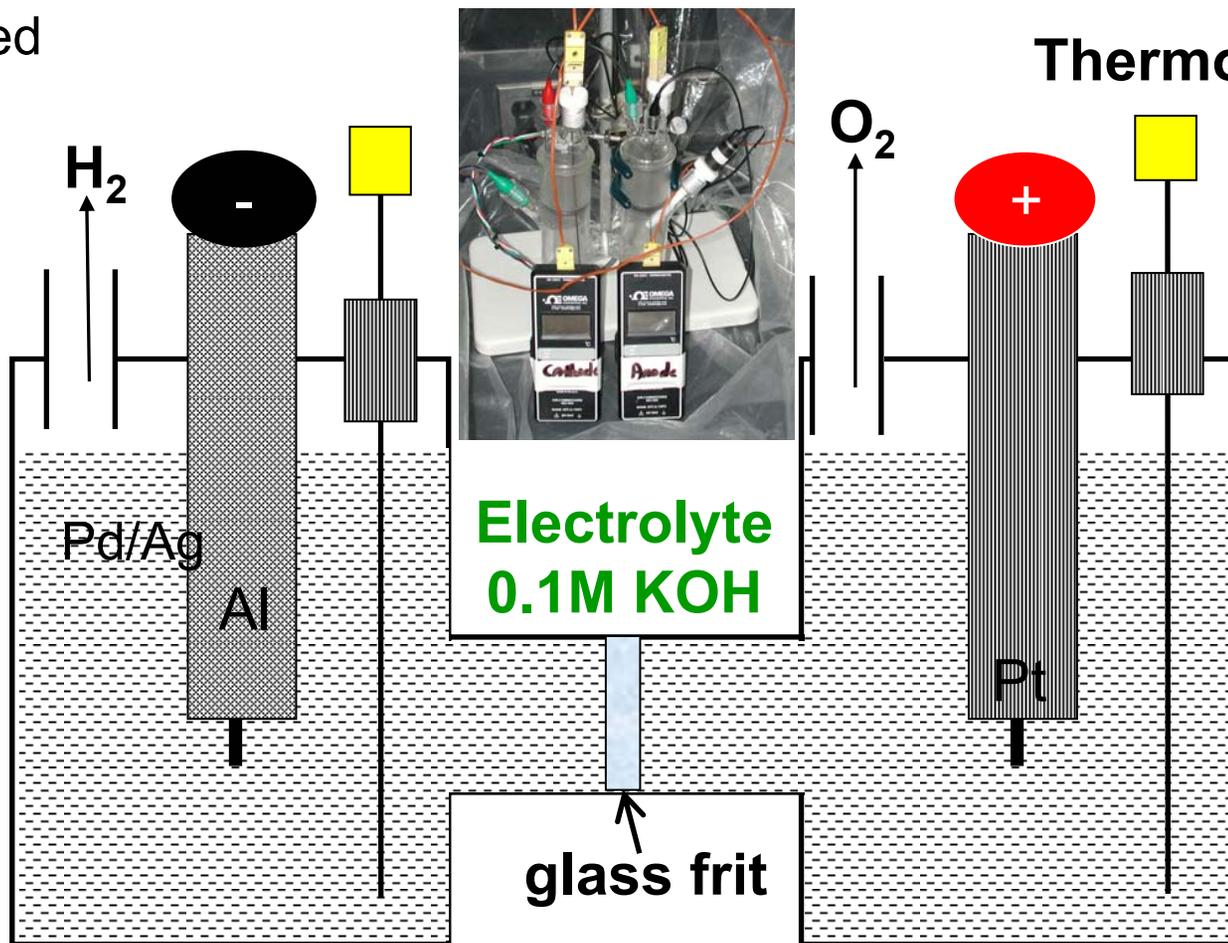
Direct link between E (electrochemical potential), T (temperature) and the ΔH of the formation.

Ambient Pressure Aqueous Cell

current

- Load Pd/Ag tube with dehydrated AlH_3
- 5 volts (Max)
- 50 mA (Max)
- 5 hr

H_2 bubbles were Observed at cathode

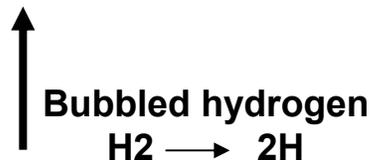
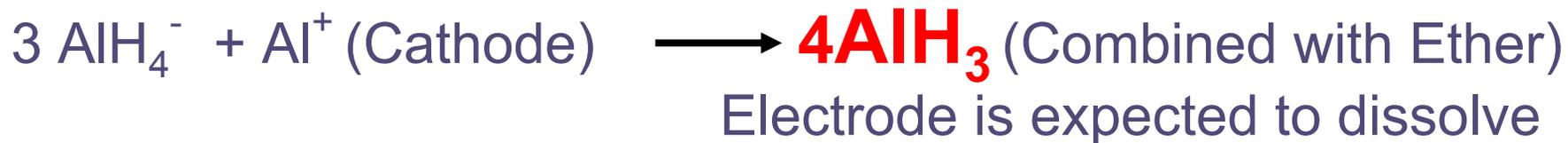


AlH_3 was NOT detected

Non-Aqueous Ionic Solution system 1

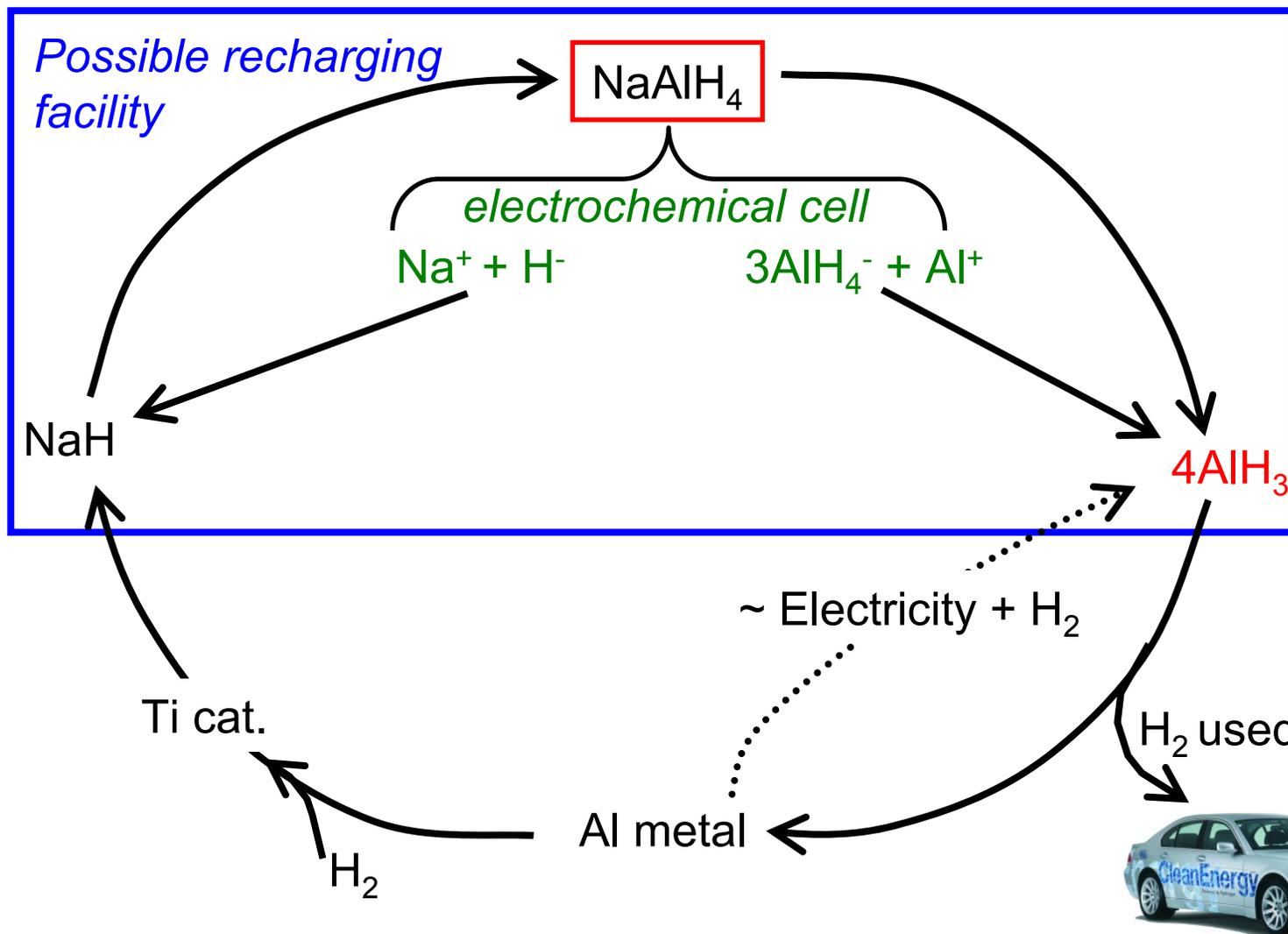
Utilizing Polar Conductive Solution (LiAlH_4 , NaAlH_4 , KAlH_4) in THF or Ether

Example:



Non-Aqueous Solution system 1

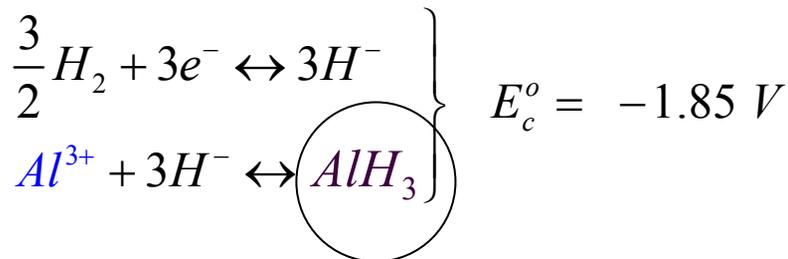
(LiAlH₄, NaAlH₄, KAlH₄)/THF or Ether



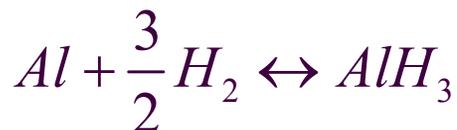
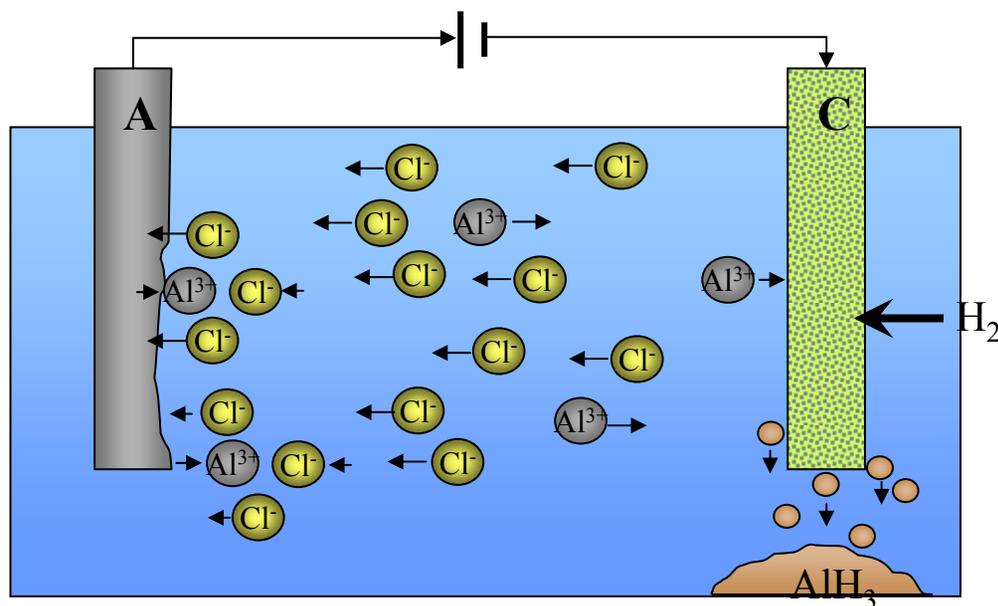
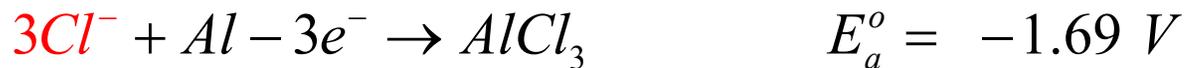
Non-Aqueous Ionic Solution system 2



Cathode



Anode



$$E_{cell}^{\circ} = -0.16 V \quad (\Delta G_{cell}^{\circ} = 46.5 kJ)$$

3/2007 → Present

Status at 3/2007:

- Built facility
- Established electrochemical approach (Non Aqueous Electrolyte, Elevated Pressure Cell)
- Seen initial AlH_3 in early experiments

Since 3/2007:

- Modified electrochemical cell design and materials to achieve larger quantities of AlH_3
- Demonstrated feasibility of electrolytically forming AlH_3 (larger quantities)
- Devise and conduct experiments to understand the mechanism of any reactions taking place and show theoretical production capability
- Characterized reaction products with XRD and other methods
- Quantified yield and efficiencies of recharging reaction

Go Decision on SRNL Charging Process was made at the end of FY 2007, based on charging efficiencies, product yield, process conditions

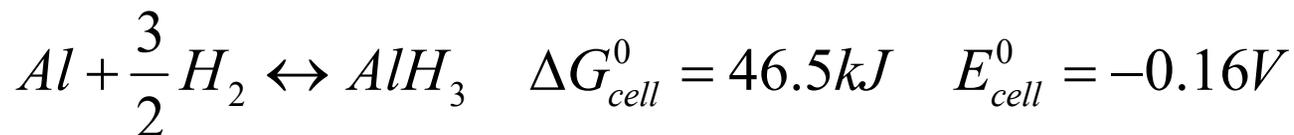
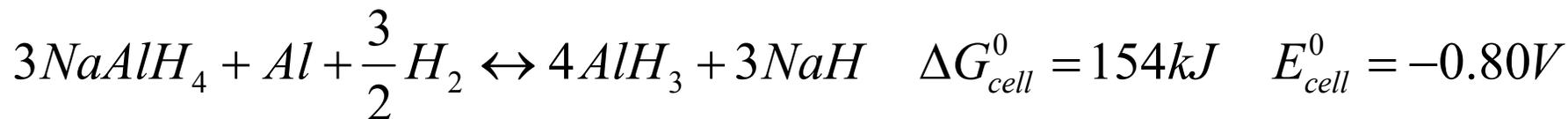
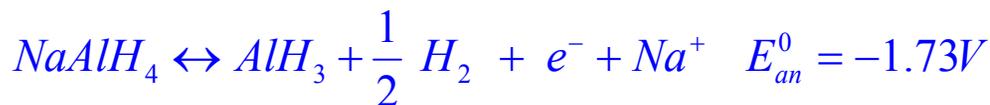
Cell Thermodynamics

Translating Chemical Energy
into Electrical energy

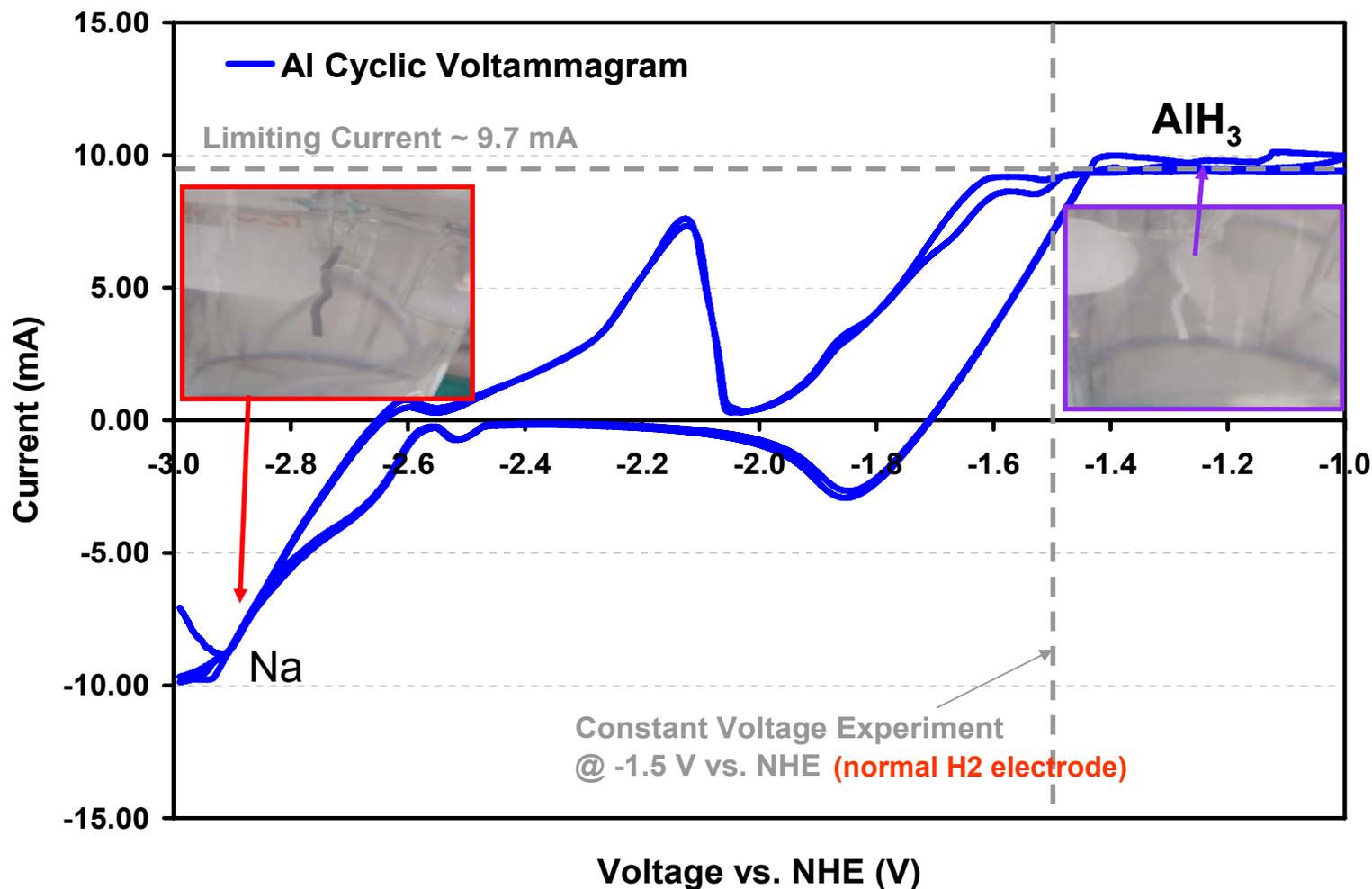
$$E_{cell}^0 = -\frac{\Delta G_{cell}^0}{nF}$$

$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0$$

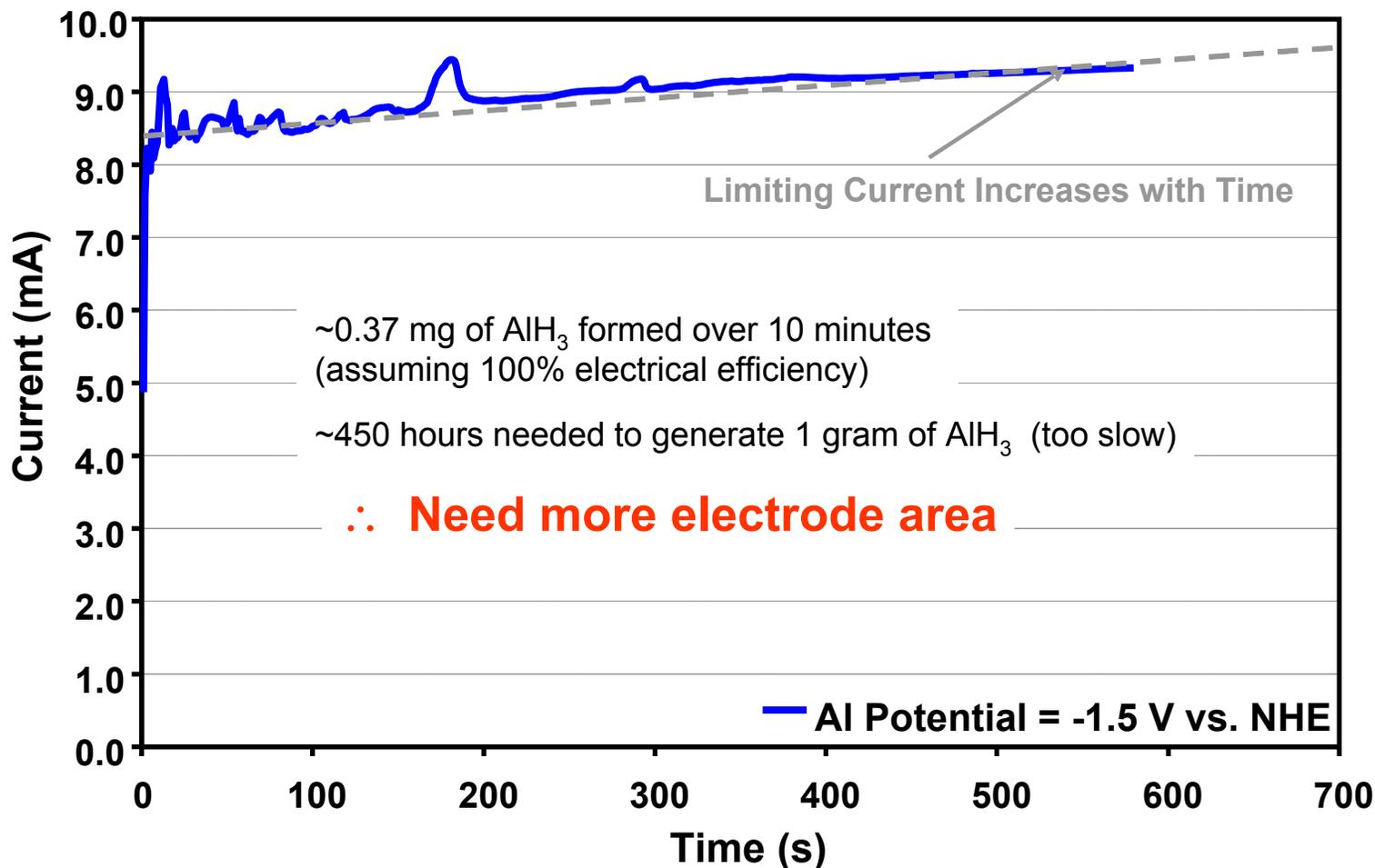
Cell Potential



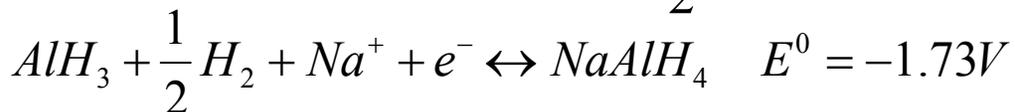
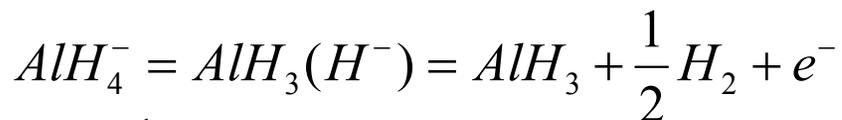
Alane Production Cyclic Voltammetry (CV)



Bulk Electrolysis for AlH_3 Production



Alane Conversion



$$nF = 96500 \text{ C / mol } AlH_3$$

Original Solution

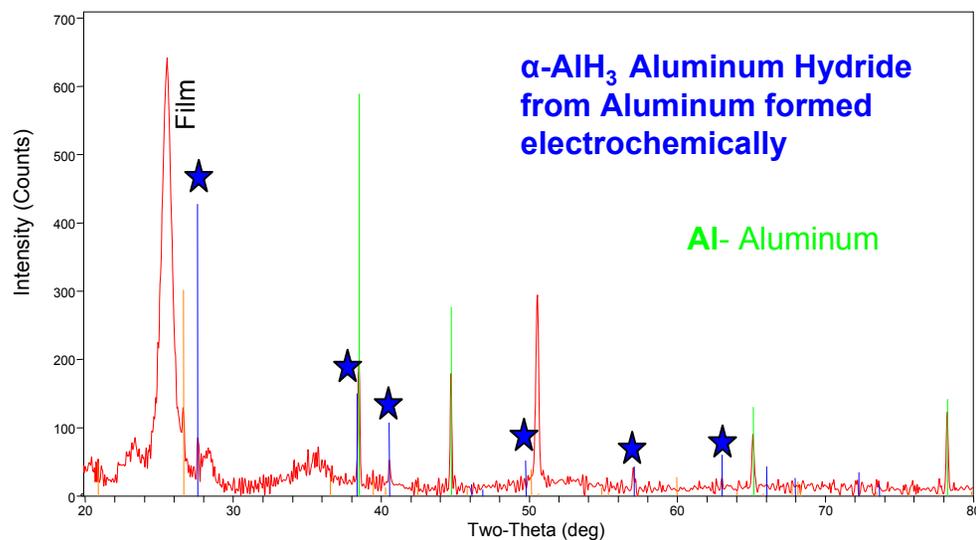
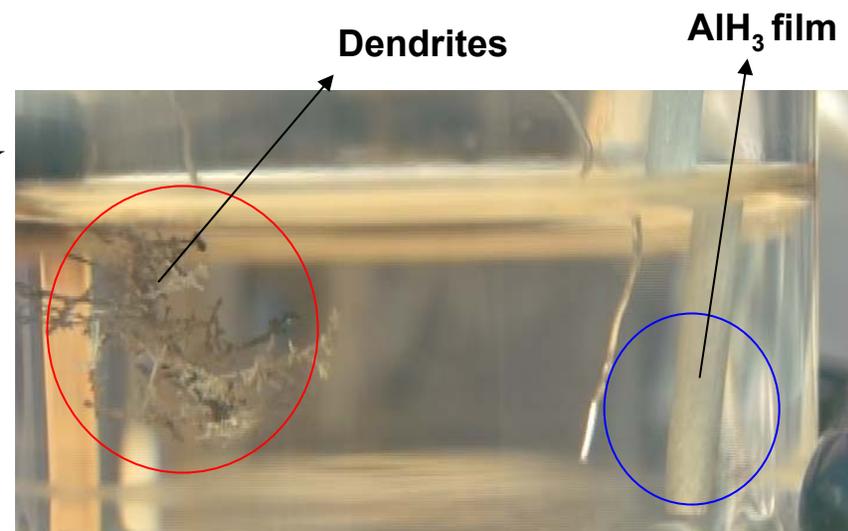
$$85 \text{ mL} \cdot 0.5 \text{ M} = 42.5 \text{ mmol } NaAlH_4$$

Results

For 59.8 C of charge passed during reaction

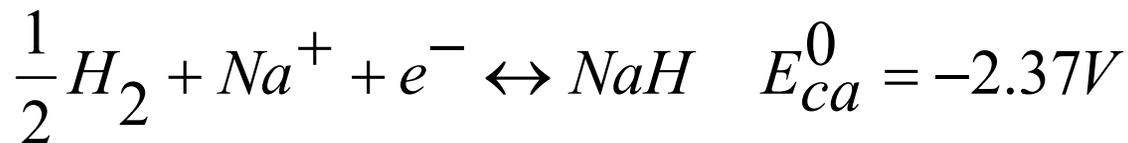
$$\frac{59.8}{96,500} = 0.62 \text{ mmol } AlH_3$$

$$\frac{0.62}{42.5} = 1.4\% \text{ conversion}$$

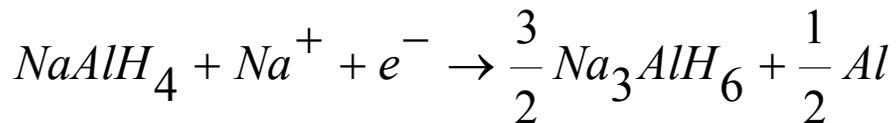
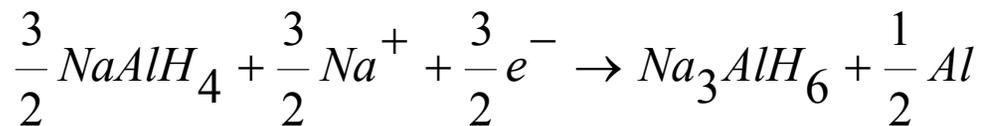


Dendrites Formation in Cell

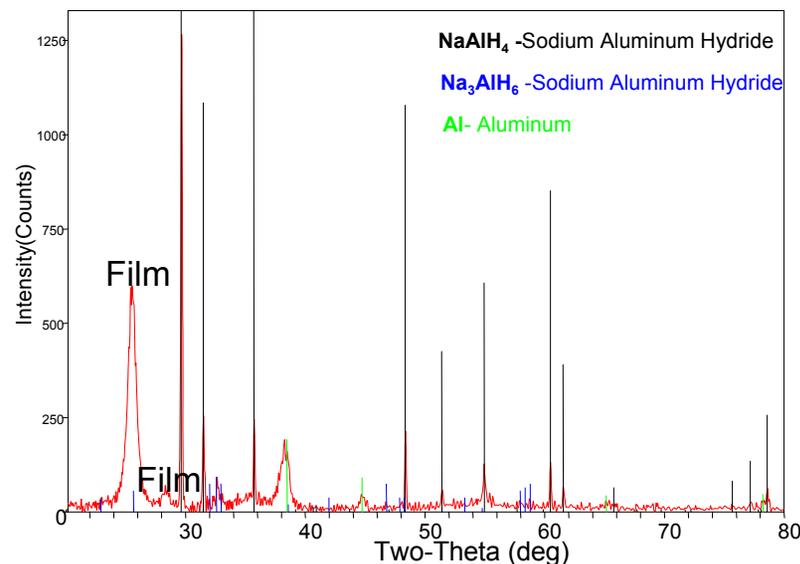
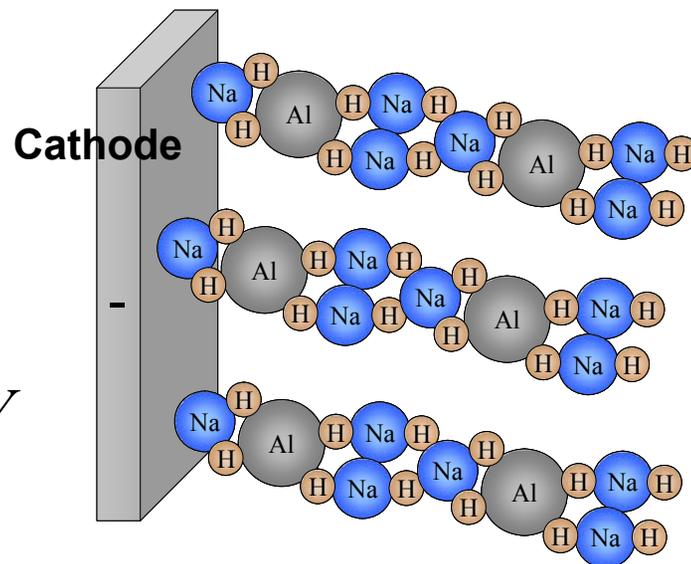
Desired Reaction



Fraction Charge/Molar and Formation of Dendrites



Dendrites composition is consistent with our theory based on x-ray measurements



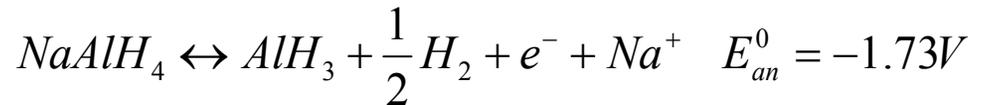
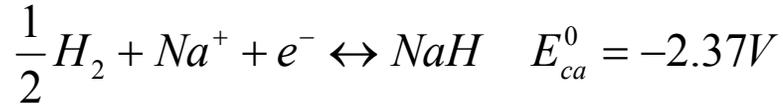
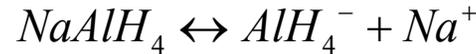
Electrochemical Alane Formation Energy-1

$$\text{Work} = Q \cdot V$$

$$nF = 289,000 \text{ C / mol AlH}_3$$

$$nF \cdot E^\circ_{\text{cell}} = 61.2 \text{ kJ / mol AlH}_3$$

(ideal)



Basis

$$1 \text{ kg H}_2 = 10 \text{ kg AlH}_3$$

or

$$333 \text{ mol AlH}_3$$



$$5.66 \text{ kWh}_e / \text{kg H}_2$$

Comparison

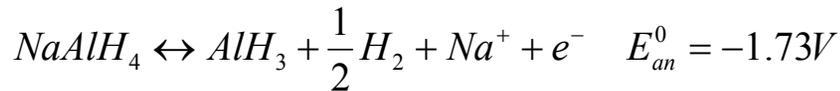
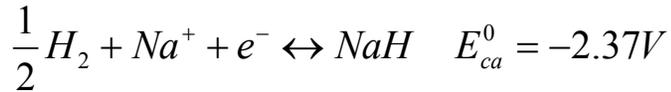
*H₂ Liquefaction: 12.5 – 15 kWh_e / kg H₂

*H₂ Compression: 2.6 – 3.6 kWh_e / kg H₂
(7000 psig)

*Source: PraxAir 2003

@ \$0.05 / kWh = \$0.28 / kg H₂ (ideal case)

Electrochemical Alane Formation Energy-2



$$Work = Q \cdot V$$

$$nF = 289,000 \frac{C}{mol AlH_3}$$

$$E_{cell} = E_{cell}^0 + \eta$$

$$Ideal: \quad W_{Ideal} = (nF)E_{cell}^0 = 61.2 \frac{kJ}{mol AlH_3}$$

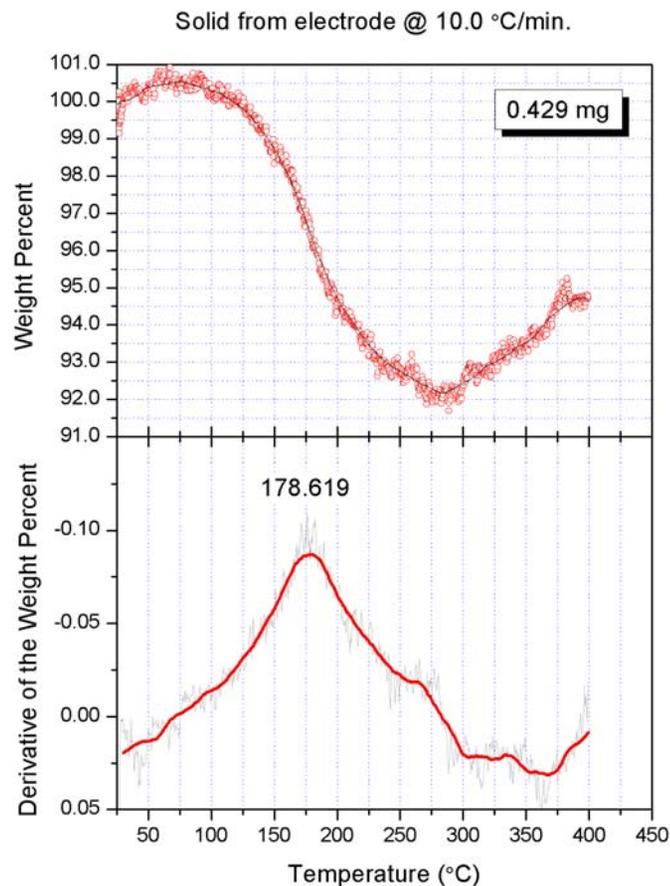
$$Ideal Cost = \frac{61.2 kJ}{mol AlH_3} \left| \frac{33.3 mol AlH_3}{kg AlH_3} \right| \left| \frac{10 kg AlH_3}{kg H_2} \right| \left| \frac{1 kWh}{3,600 kJ} \right| = 5.66 \frac{kWh}{kg H_2} \Rightarrow @ \frac{\$0.05}{kWh} = \frac{\$0.28}{kg H_2}$$

$$\eta = 0.3 V: \quad W_{Real} = (nF)E_{cell} = 90.7 \frac{kJ}{mol AlH_3}$$

$$Real Cost = \frac{90.7 kJ}{mol AlH_3} \left| \frac{33.3 mol AlH_3}{kg AlH_3} \right| \left| \frac{10 kg AlH_3}{kg H_2} \right| \left| \frac{1 kWh}{3,600 kJ} \right| = 8.40 \frac{kWh}{kg H_2} \Rightarrow @ \frac{\$0.05}{kWh} = \frac{\$0.42}{kg H_2}$$

$$Alane Formation Efficiency = \frac{W_{Ideal}}{W_{Real}} = \frac{61.2}{90.7} = 67\%$$

@ \$0.05 / kWh = \$0.42 / kg H₂

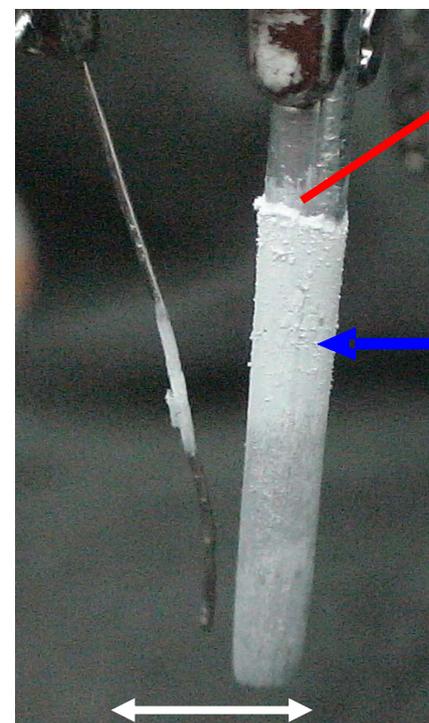


Hydrogen desorption (TGA), showing almost 9% by weight hydrogen capacity, consistent with alane capacity of 10wt%

Gas being H₂ was verified, using RGA



Electrochemical Cell

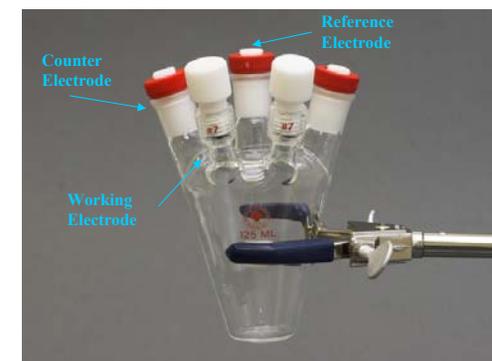
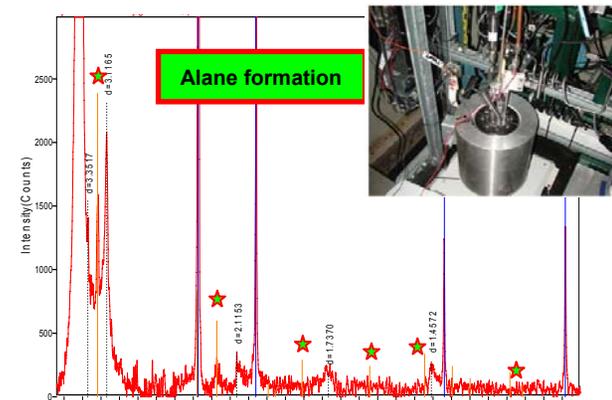
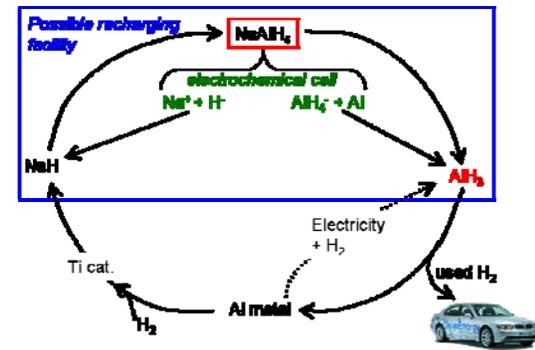


Aluminum Electrode

Alane Film + NaAlH₄

0.25 inch

- A novel electrochemical methods were developed to reversibly form Alane (AlH_3)
- Bulk AlH_3 formed in electrochemical regeneration
- Aluminum electrode dissolved as expected
- The needed energy was found not to exceed 30% of the cost of H_2 stored
- 0.37 mg of AlH_3 were formed in 10 minutes
- At this reaction rate and using the bench size cell, ~ 450 hours of reaction time would be needed to form 1 g of alane



Electrochemical Cell Glassware

Comparison of H₂ Storage Methods

Storage Method	ΔG_{cell}° (kJ)	E_{cell}° (V)	Storage Density (kg H ₂ /m ³)	Storage Energy Cost (kWh _e /kg H ₂)	Storage Cost @ \$0.05/kWh (\$/kg H ₂)
$NaAlH_4 \approx AlH_3 + NaH$	61.2	-0.64	150	<i>Ideal</i> : 5.66	0.28
				$\eta = 0.3 V$: 8.40	0.42
$Al^{3+} / 3Cl^{-}$ solution $Al + \frac{3}{2} H_2 \leftrightarrow AlH_3$	46.5	-0.16	150	<i>Ideal</i> : 4.28	0.21
				$\eta = 0.3 V$: 12.33	0.62
Wet Synthesis	---	---	150	<i>Ideal</i> : 107	5.3
H ₂ Liquefaction	---	---	70	12.5 - 15	0.63 – 0.75
H ₂ Compression (7000 psig)	---	---	79.8	2.6 - 3.6	0.13 – 0.18

FY08

- Upgrade the Electrochemical Cell with larger surface area working (Al) and counter electrodes and focus effort on using alanate solutions
- Examine the use of catalysts (Ti) in accelerating the electrochemical regeneration
- Use other techniques (e.g. NMR and Raman) to quantify and characterize AlH_3
- Work closely with other AlH_3 partners BNL and Hawaii

FY09

- Optimize all parameters needed for producing several grams of AlH_3 efficiently
- Design and construct a larger Electrochemical Cell (EC) capable of producing larger quantities of AlH_3
- Develop efficient methods of extracting AlH_3 from (EC)
- Work closely with other AlH_3 partners BNL and Hawaii