Electrochemical Reversible Formation of Alane

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Project ID STP19

Program Overview

Timeline

- Start: 10/01/2006

- End: In Progress

- Percent Complete: 20%

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

Budget

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

Partners

- Brookhaven National Laboratory

- University of Hawaii

Objectives

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) 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

Milestones

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.*

$$Al + 3/2 \, H_2 \rightarrow AlH_3$$

Approach:

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

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

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*

Approach

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)

$$RT\ln P = \Delta H - T\Delta S$$
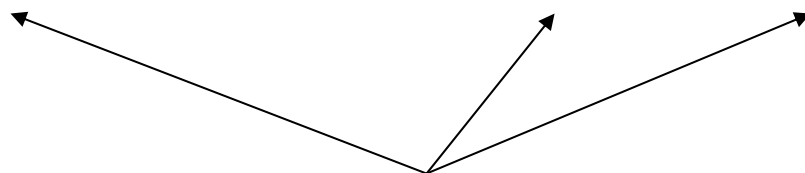(van't hoff Equation)

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

$$RT\ln P = -nFE$$
(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.

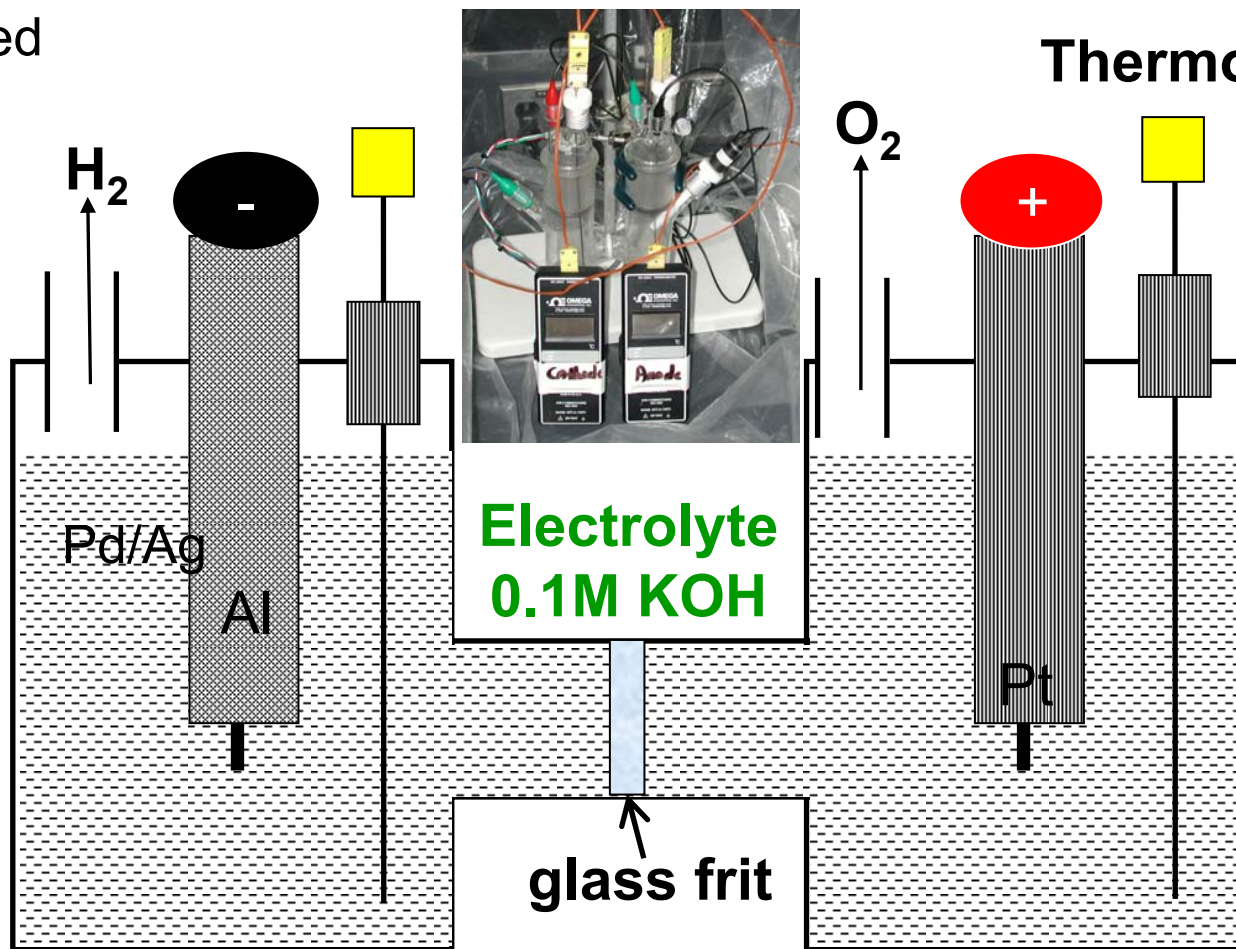$$\Delta H = \Delta G + T\Delta S = -nFE + nFT\,(\partial E/\partial T)_P$$

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

Approach

Ambient Pressure Aqueous Cell

current

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

H_2 bubbles were Observed at cathode

Thermocouple

H_2

O_2

−

+

Pd/Ag

Al

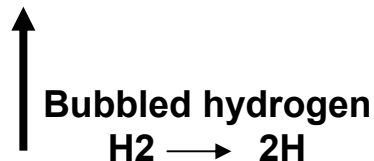**Electrolyte 0.1M KOH**

Pt

glass frit

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
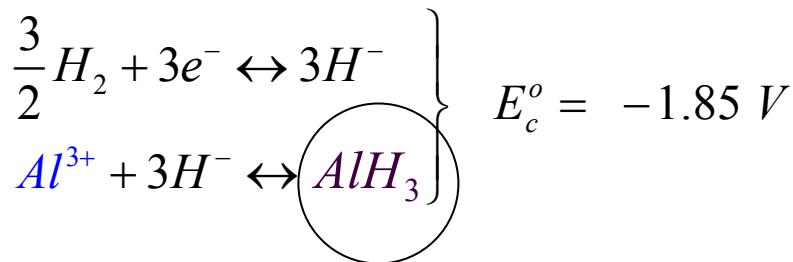
Example:

$$NaAlH4/THF \longleftrightarrow Na^+/AlH_4^-/THF$$

$$3\ AlH_4^-\ + Al^+\ (Cathode) \longrightarrow \textbf{4AlH}_3\ (Combined\ with\ Ether)$$

Electrode is expected to dissolve

$$Na^+ + H^-/\ Pt\ (Anode) \longrightarrow NaH$$

Bubbled hydrogen
$$H2 \longrightarrow 2H$$

Approach

Non-Aqueous Solution system 1

(LiAlH$_4$, NaAlH$_4$,KAlH$_4$)/THF or Ether
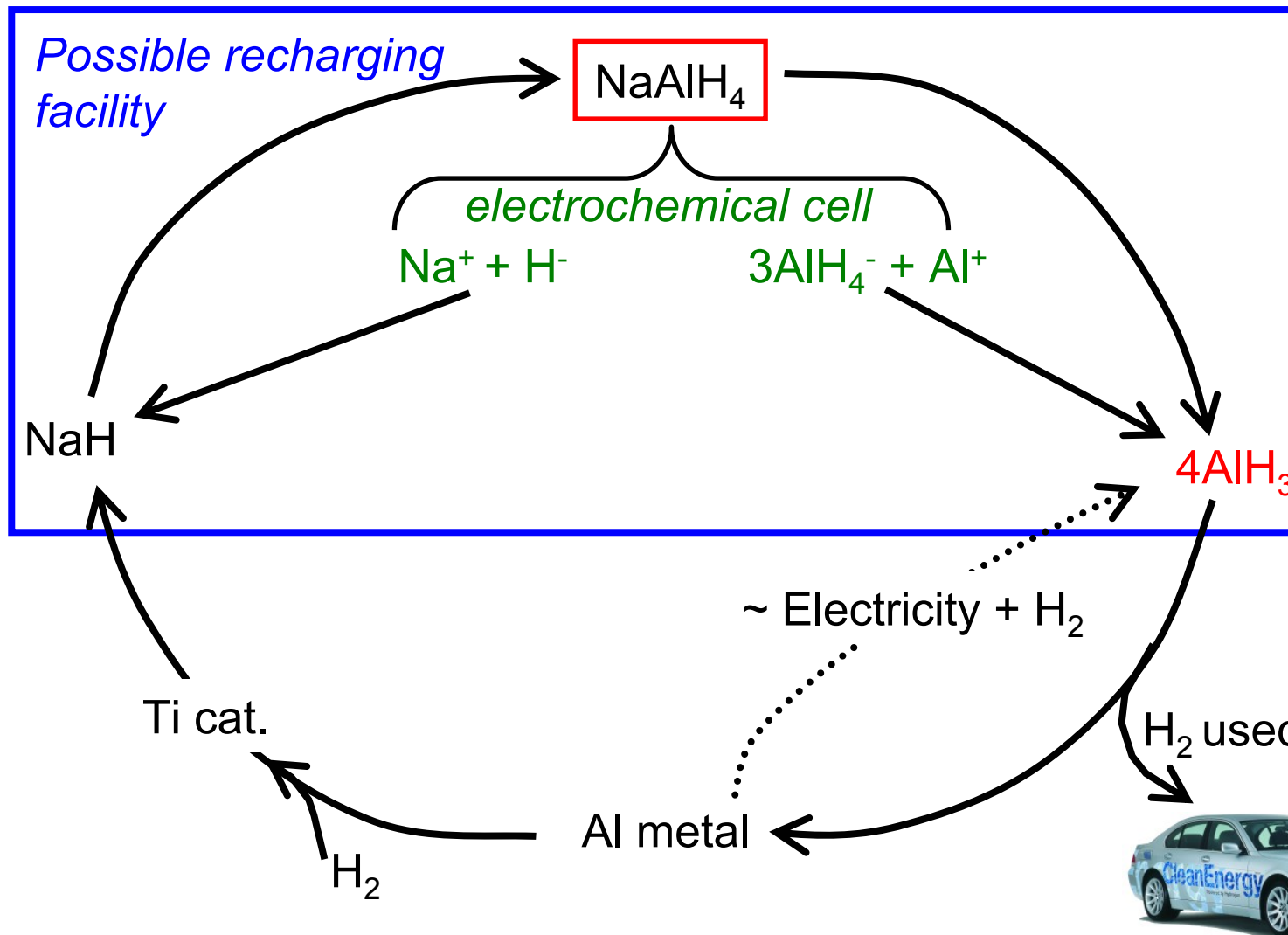
Possible recharging facility

NaAlH$_4$

electrochemical cell

Na$^+$ + H$^-$ 3AlH$_4^-$ + Al$^+$

NaH   4AlH$_3$

~ Electricity + H$_2$

H$_2$ used

Ti cat.

H$_2$

Al metal

Non-Aqueous Ionic Solution system 2

$$AlCl_3 \xleftarrow{\quad Solution(THF) \quad} Al^{3+} / 3Cl^-$$

Cathode

$$\frac{3}{2}H_2 + 3e^- \leftrightarrow 3H^-$$

$$Al^{3+} + 3H^- \leftrightarrow \boxed{AlH_3}$$

$$E_c^o = -1.85\ V$$

A

C

H_2

AlH_3

Anode

$$3Cl^- + Al - 3e^- \rightarrow AlCl_3 \qquad E_a^o = -1.69\ V$$

-- --

$$Al + \frac{3}{2}H_2 \leftrightarrow AlH_3 \qquad\qquad E_{cell}^o = -0.16\ V\ \left(\Delta G_{cell}^o = 46.5\ kJ \right)$$
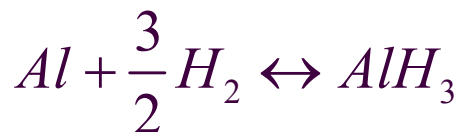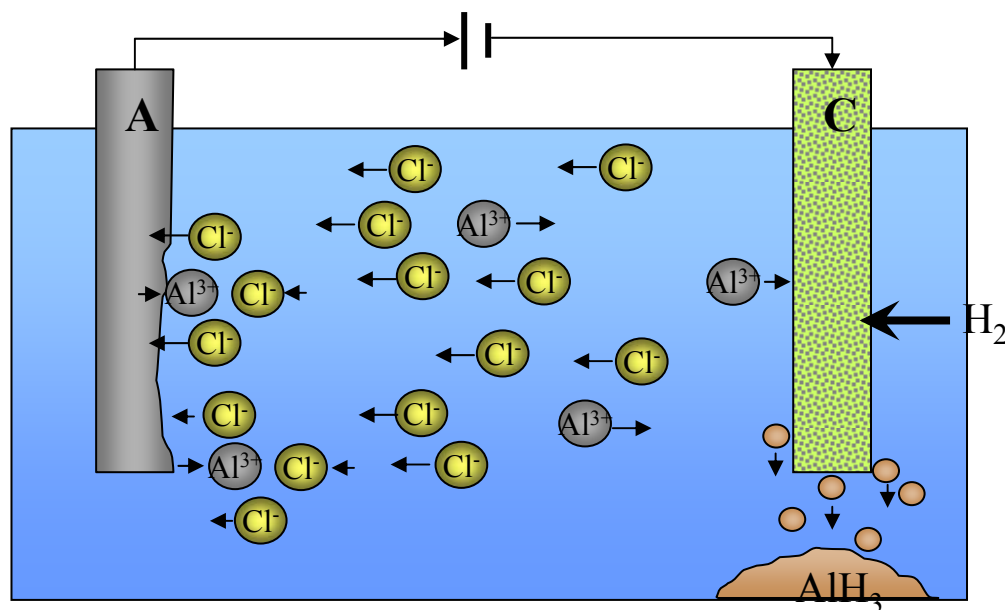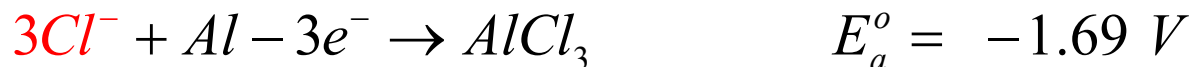
Status at 3/2007:

➢ 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
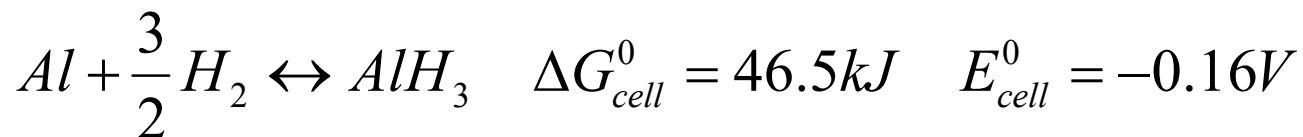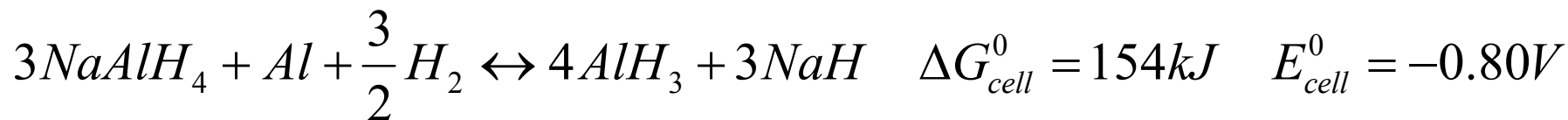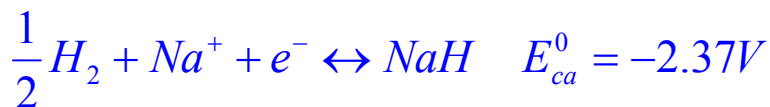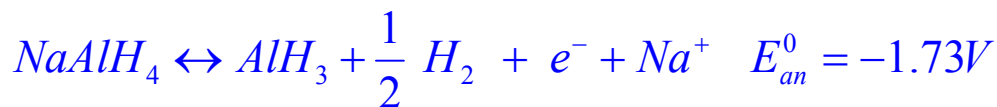
Cell Thermodynamics

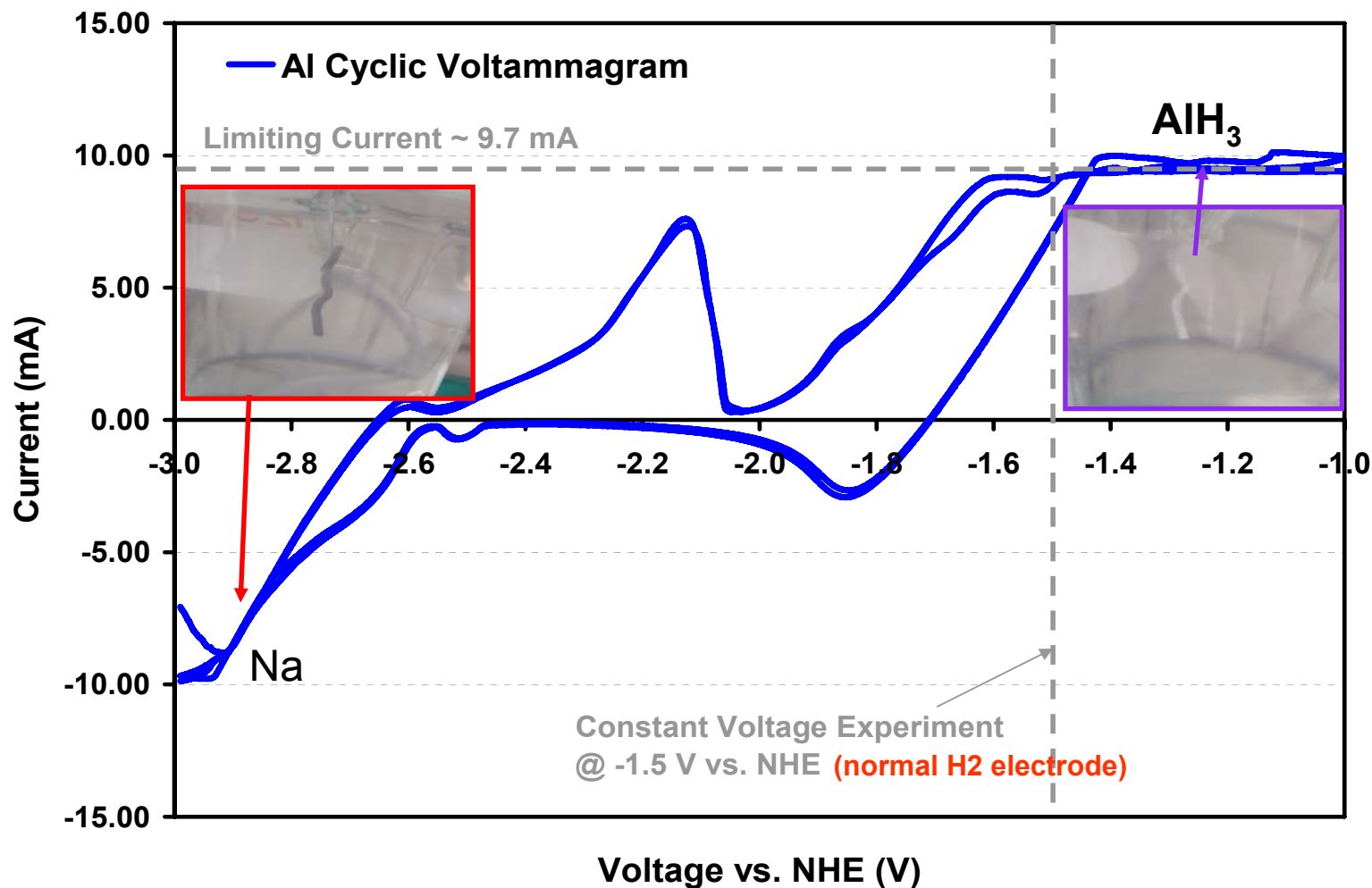**Translating Chemical Energy into Electrical energy**

$$E^0_{cell} = -\frac{\Delta G^0_{cell}}{nF}$$
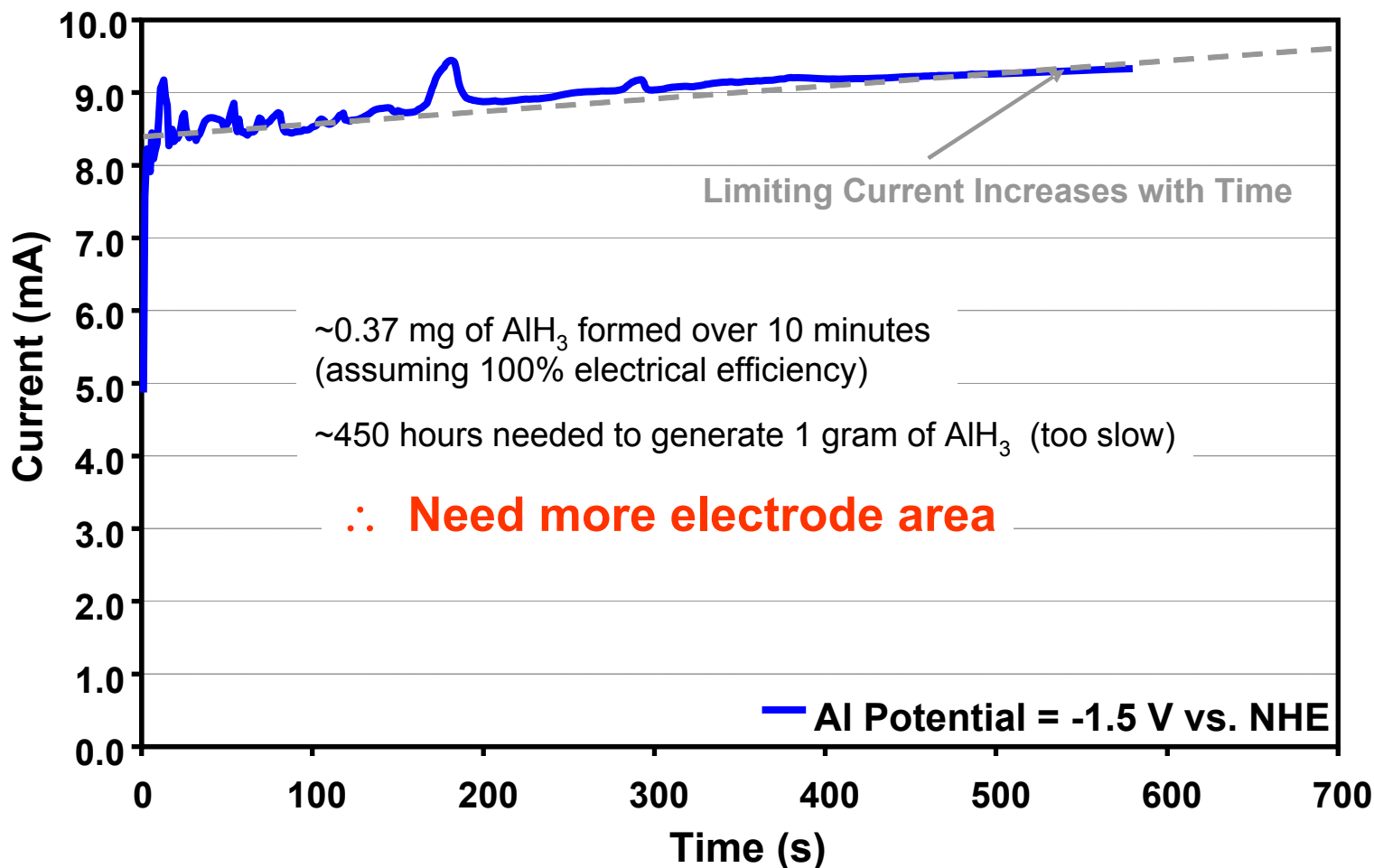
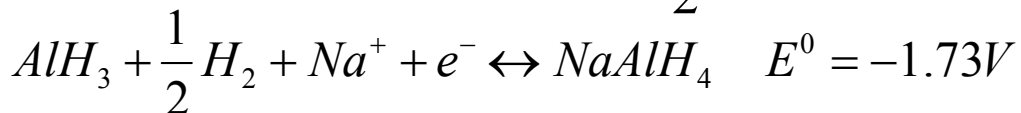$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

Cell Potential

$$NaAlH_4 \leftrightarrow (AlH_4^- + Na^+)/\text{Solution}$$

$$NaAlH_4 \leftrightarrow AlH_3(H)^- + Na^+$$

$$NaAlH_4 \leftrightarrow AlH_3 + \frac{1}{2}H_2 + e^- + Na^+ \quad E^0_{an} = -1.73V$$

$$\frac{1}{2}H_2 + Na^+ + e^- \leftrightarrow NaH \quad E^0_{ca} = -2.37V$$

$$NaAlH_4 \approx AlH_3 + NaH \quad \Delta G^0_{cell} = 61.2kJ \quad E^0_{cell} = -0.64V$$

$$3NaAlH_4 + Al + \frac{3}{2}H_2 \leftrightarrow 4AlH_3 + 3NaH \quad \Delta G^0_{cell} = 154kJ \quad E^0_{cell} = -0.80V$$

$$Al + \frac{3}{2}H_2 \leftrightarrow AlH_3 \quad \Delta G^0_{cell} = 46.5kJ \quad E^0_{cell} = -0.16V$$

Alane Production Cyclic Voltammetry (CV)

Bulk Electrolysis for AlH_3 Production

Limiting Current Increases with Time

~0.37 mg of AlH_3 formed over 10 minutes (assuming 100% electrical efficiency)

~450 hours needed to generate 1 gram of AlH_3 (too slow)

∴ **Need more electrode area**

Al Potential = -1.5 V vs. NHE

Current (mA) vs. Time (s)

Alane Conversion

$$AlH_4^- = AlH_3(H^-) = AlH_3 + \frac{1}{2}H_2 + e^-$$

$$AlH_3 + \frac{1}{2}H_2 + Na^+ + e^- \leftrightarrow NaAlH_4 \quad E^0 = -1.73V$$
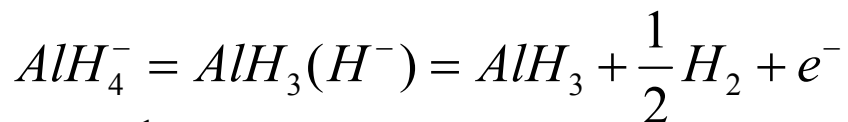
nF = 96500 C / mol AlH$_3$

Original Solution

85 mL · 0.5 M = 42.5 mmol NaAlH$_4$

Results

For 59.8 C of charge passed during reaction
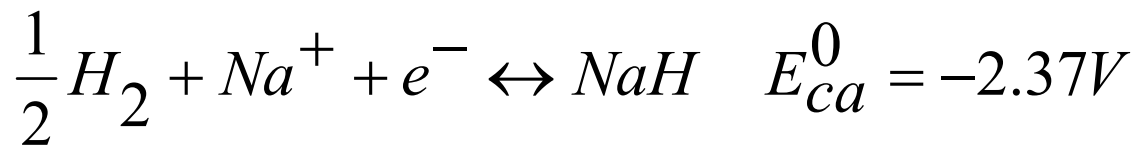
$$\frac{59.8}{96,500} = 0.62 \text{ mmol AlH}_3$$
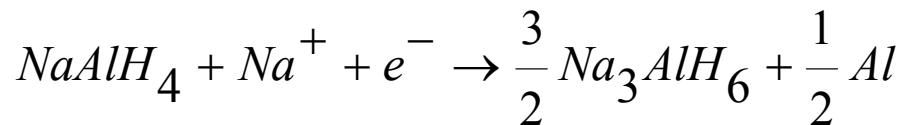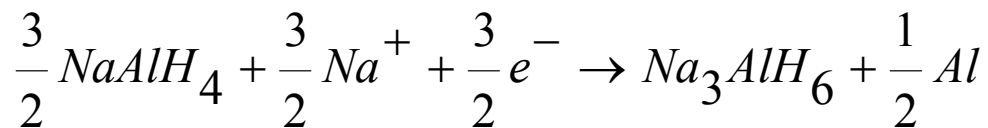
$$\frac{0.62}{42.5} = 1.4\% \text{ conversion}$$

Dendrites

AlH$_3$ film

α-AlH$_3$ Aluminum Hydride from Aluminum formed electrochemically

Al- Aluminum

Intensity (Counts)

Film

Two-Theta (deg)
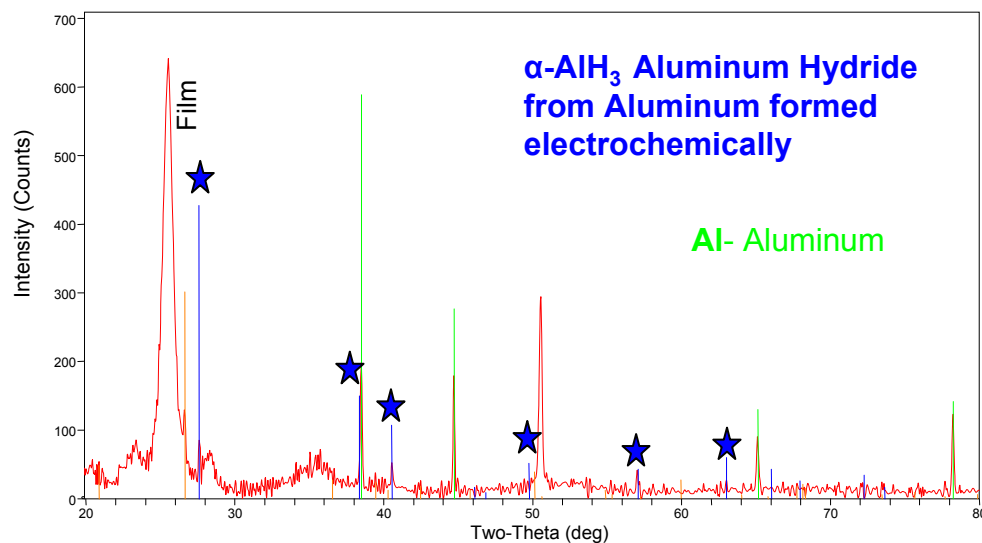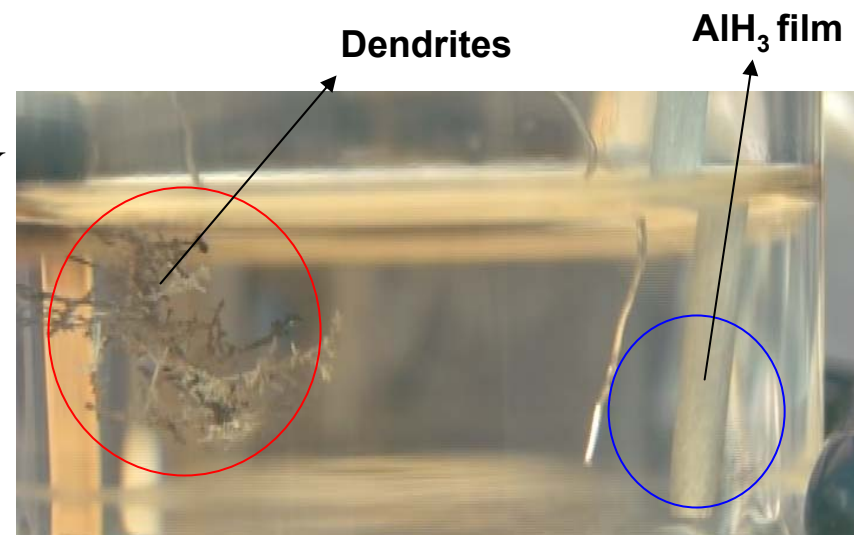
Dendrites Formation in Cell

Cathode

Desired Reaction

$$\frac{1}{2}H_2 + Na^+ + e^- \leftrightarrow NaH \quad E^0_{ca} = -2.37V$$

Fraction Charge/Molar and Formation of Dendrites

$$\frac{3}{2}NaAlH_4 + \frac{3}{2}Na^+ + \frac{3}{2}e^- \rightarrow Na_3AlH_6 + \frac{1}{2}Al$$

$$NaAlH_4 + Na^+ + e^- \rightarrow \frac{3}{2}Na_3AlH_6 + \frac{1}{2}Al$$

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

NaAlH$_4$ -Sodium Aluminum Hydride

Na$_3$AlH$_6$ -Sodium Aluminum Hydride

Al- Aluminum

Film

Film

Intensity(Counts)

Two-Theta (deg)
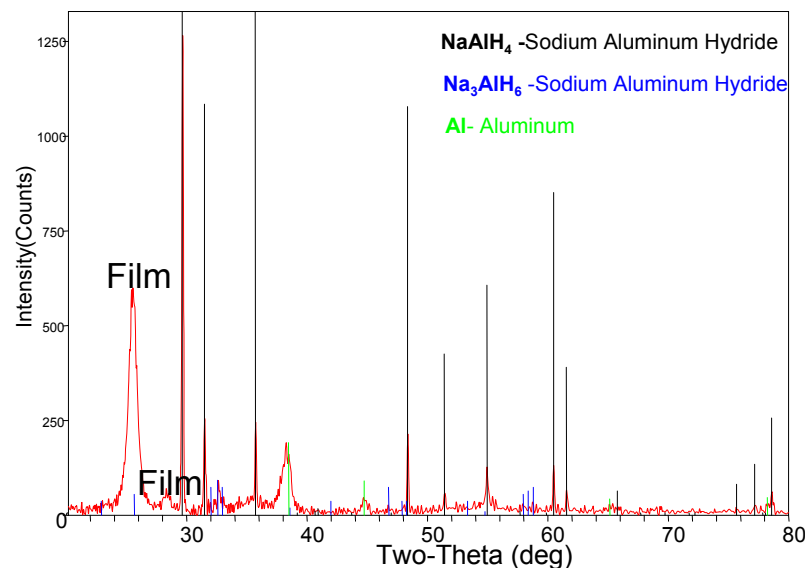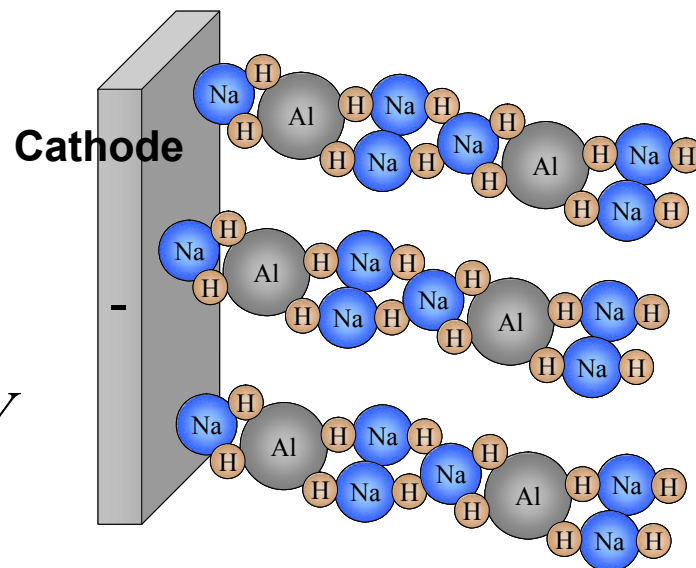
Electrochemical Alane Formation Energy-1

Work = Q · V

nF = 289,000 C / mol AlH$_3$

nF · E°$_{cell}$ = 61.2 kJ / mol AlH$_3$

(ideal)

$$NaAlH_4 \leftrightarrow AlH_4^- + Na^+$$

$$\frac{1}{2}H_2 + Na^+ + e^- \leftrightarrow NaH \quad E_{ca}^0 = -2.37V$$

$$NaAlH_4 \leftrightarrow AlH_3 + \frac{1}{2}H_2 + e^- + Na^+ \quad E_{an}^0 = -1.73V$$

$$NaAlH_4 \approx AlH_3 + NaH \quad \Delta G_{cell}^0 = 61.2kJ \quad E_{cell}^0 = -0.64V$$
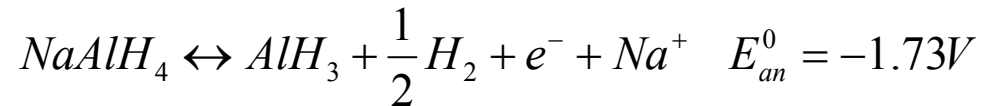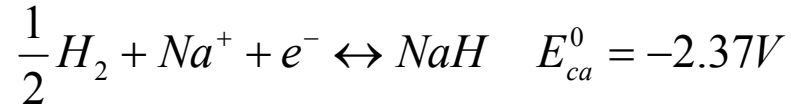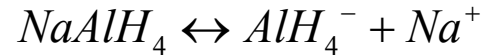
Basis

1 kg H$_2$ = 10 kg AlH$_3$
or
333 mol AlH$_3$

↓

5.66 kWh$_e$ / kg H$_2$

Comparison

*H$_2$ Liquefaction: 12.5 – 15 kWh$_e$ / kg H$_2$

***H$_2$ Compression: 2.6 – 3.6 kWh$_e$ / kg H$_2$
(7000 psig)**

*Source: PraxAir 2003

@ $0.05 / kWh = $0.28 / kg H$_2$ (ideal case)

Electrochemical Alane Formation Energy-2

$$\frac{1}{2}H_2 + Na^+ + e^- \leftrightarrow NaH \quad E_{ca}^0 = -2.37V$$

$$NaAlH_4 \leftrightarrow AlH_3 + \frac{1}{2}H_2 + Na^+ + e^- \quad E_{an}^0 = -1.73V$$

$$\overline{NaAlH_4 \approx AlH_3 + NaH \quad \Delta G_{cell}^0 = 61.2kJ \quad E_{cell}^0 = -0.64V}$$
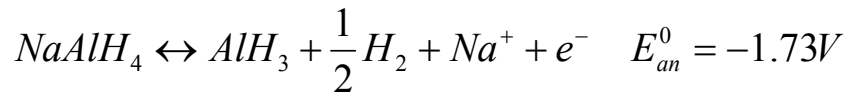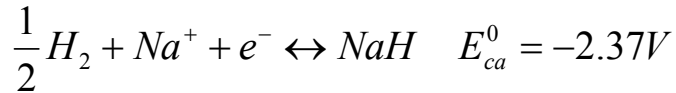
$$Work = Q \cdot V$$

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

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

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

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

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

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

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

@ $0.05 / kWh = $0.42 / kg H$_2$

Solid from electrode @ 10.0 °C/min.
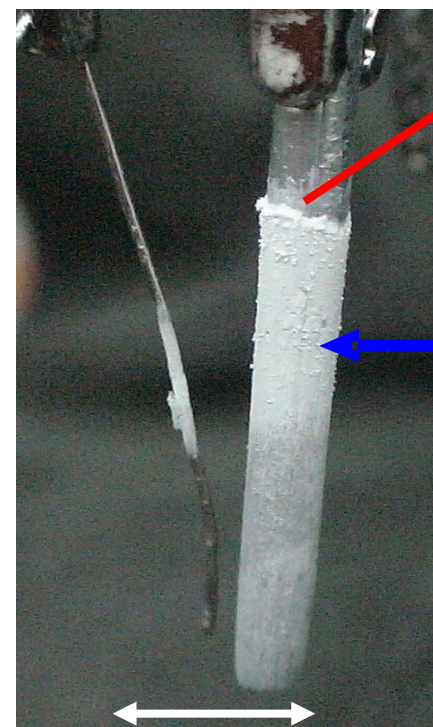
0.429 mg

178.619
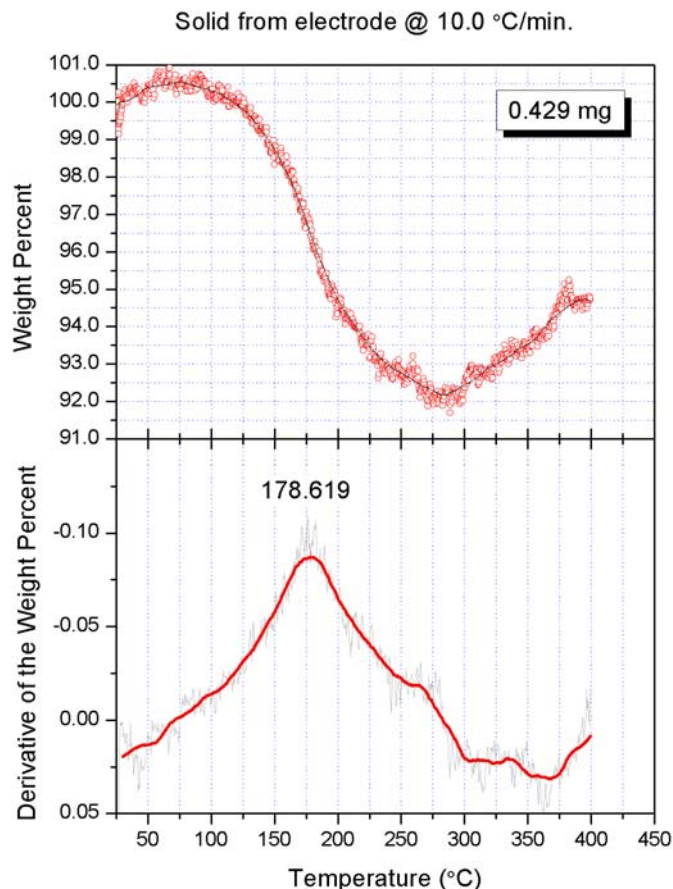
Hydrogen desorption (TGA), showing almost 9% by weight hydrogen capacity, consistent with alane capacity of 10wt%

Gas being H_2 was verified, using RGA
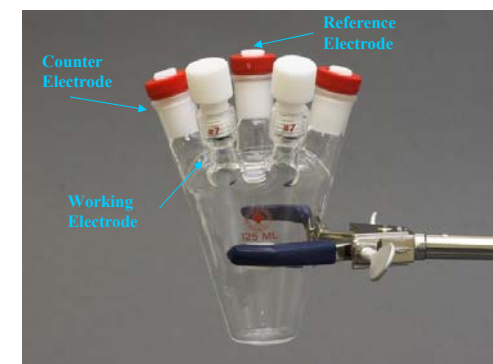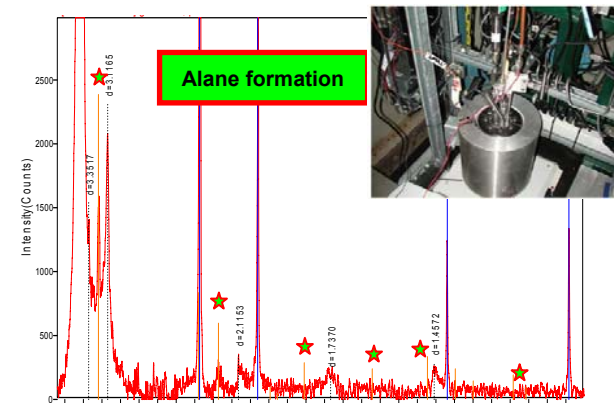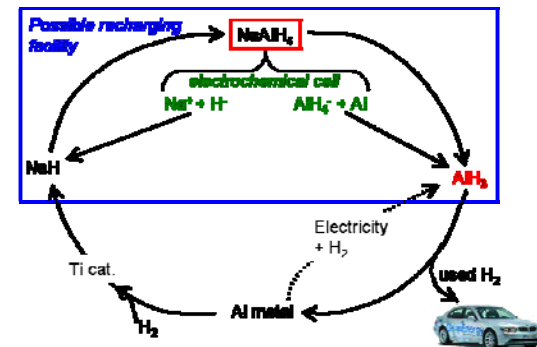

Electrochemical Cell

Aluminum Electrode

Alane Film +$NaAlH_4$

0.25 inch

Summary

- 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

Alane formation

Electrochemical Cell Glassware

Comparison of H$_2$ Storage Methods

Storage Method	ΔG^o_{cell} (kJ)	E^o_{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	*Ideal:* 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	*Ideal:* 4.28	0.21
				$\eta = 0.3\ V$: 12.33	**0.62**
Wet Synthesis	---	---	150	*Ideal:* 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

Future Work

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 lager 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