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2010 DOE Hydrogen Program Review

Electrochemical Reversible Formation of Alane

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Project ID #: ST063

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Overview

Timeline

Start: 10/1/06

End: In Progress

Percent complete: 90 %

Barriers

- Store hydrogen required for conventional driving range (greater than 300 mi)
- Technical Targets
  - System gravimetric capacity > 6%
  - Storage cost < 30% of hydrogen cost

Budget

- Funding received in FY09
  - $500K
- Funding for FY10
  - $375K

Partners

- Brookhaven National Laboratory
- University of Hawaii
- University of New Brunswick
- Argonne National Laboratory

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 10 wt% and volumetric capacity of 149 g/L H_2 and a desorption temperature of ~60°C to 175°C (depending on particle size and the addition of catalysts) has potential to meet the 2010 DOE onboard system desorption targets.

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 or NaCl.
- Utilize electrolytic potential to translate chemical potential into electrochemical potential and drive chemical reactions to form AlH_3.

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Known Methods to Produce Alane

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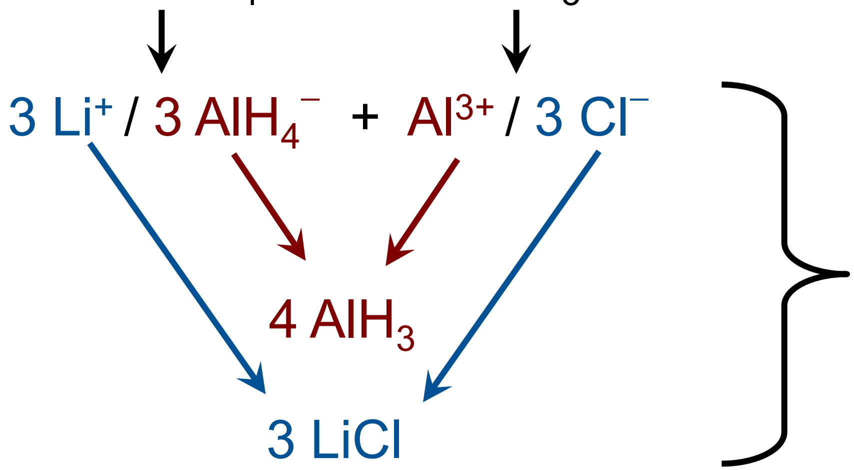
A) Formation of alane from the elements:

$Al + 3/2\ H_2 \rightarrow AlH_3$ at 10^5 bar of H_2 pressure

Thermodynamic sink

B) Traditional chemical method to produce alane:

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



Develop a method to avoid the formation of halides.

~~LiCl~~

innovative methods are needed to avoid both the high hydriding pressure of aluminum or the formation of stable by-products such as LiCl

Electrochemical Synthesis of Alane

Electrolyte

The electrolysis is carried out in an electrochemically stable, aprotic, and polar solvent such as THF or ether. $MAlH_4$ (M = Li, Na) is dissolved in this solvent, forming the ionic solution as shown below which is used as an electrolyte.

$$MAlH_4 / THF \leftrightarrow M^+ / AlH_4^- / THF$$

Though not directed at the regeneration of alane, extensive studies on the electrochemical properties of this type of electrolyte have been reported.[3,4]

Concern: Al and AlH_3 will be oxidized in aqueous environment. This requires using non-aqueous approaches.

3. H. Senoh, T. Kiyobayashi, N. Kuriyama, K. Tatsumi and K. Yasuda, *J. Power Sources*, 2007, 164, 94–99.
4. H. Senoh, T. Kiyobayashi and N. Kuriyama, *Int. J. Hydrogen Energy*, 2008, 33, 3178–3181.

Previous Attempts

Although many attempts in the past were made to make alane electrochemically[1,2] 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.

Our regeneration method is based on a complete cycle that uses electrolysis and catalytic hydrogenation of spent Al(s)

1. N. M. Alpatova, T. N. Dymova, Y. M. Kessler and O. R. Osipov, *Russ. Chem. Rev.*, 1968, 37, 99–114.
2. H. Clasen, Ger. Pat., 1141 623, 1962.

Electrochemical Synthesis of Alane

Possible Reactions When AlH_3 is Generated in a Closed Material Cycle

Anode:

Reaction 1: $AlH_4^- \rightarrow \mathbf{AlH_3 \cdot} n\mathrm{THF} + \frac{1}{2} H_2\uparrow + e^-$

Hydrogen bubbles at the anode

Reaction 2: $3AlH_4^- + Al\ (Anode) \rightarrow \mathbf{4AlH_3 \cdot} n\mathrm{THF} + 3e^-$

Electrode is expected to dissolve

Cathode:

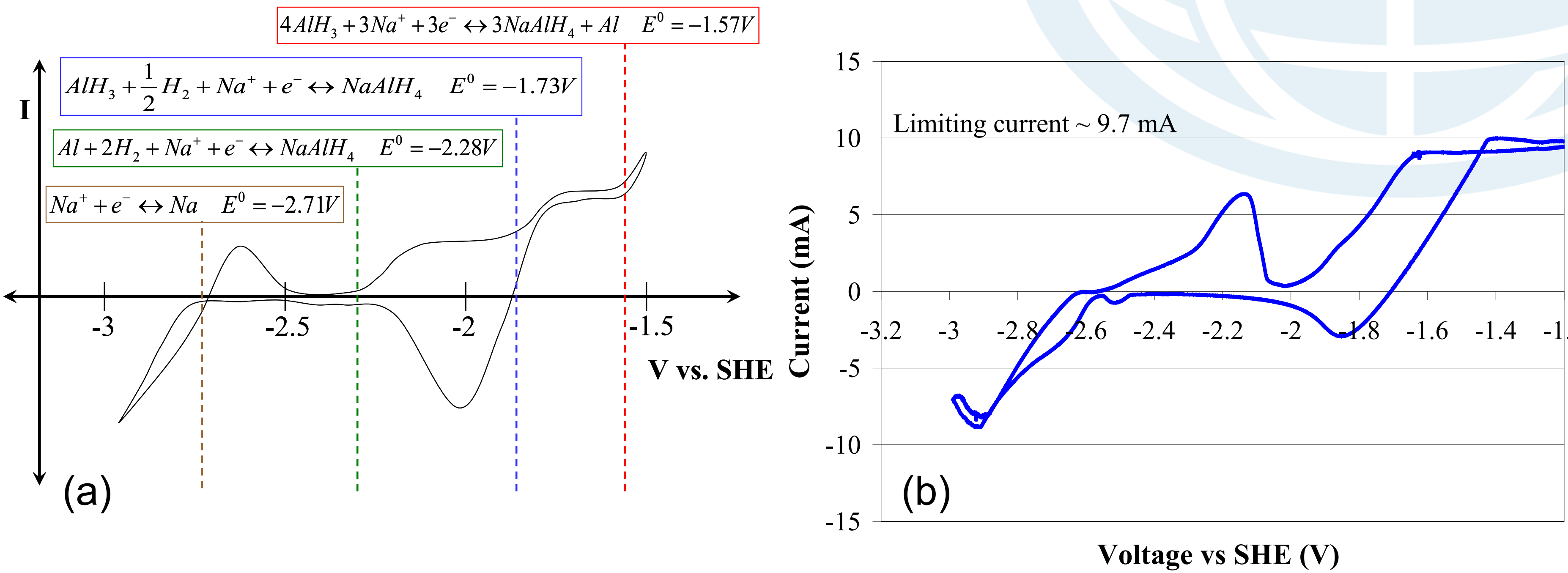
Reaction 1: $M^+ + \frac{1}{2} H_2 + e^- \xrightarrow{Pt} \mathbf{MH}$

Reaction 2: $M^+ + PdH\ (Cathode) + e^- \rightarrow \mathbf{MH} + Pd$

Regeneration: $2\ MH + 2\ Al + 3H_2 \rightarrow \mathbf{2\ MAlH_4}$

Electrochemically Generated AlH_3

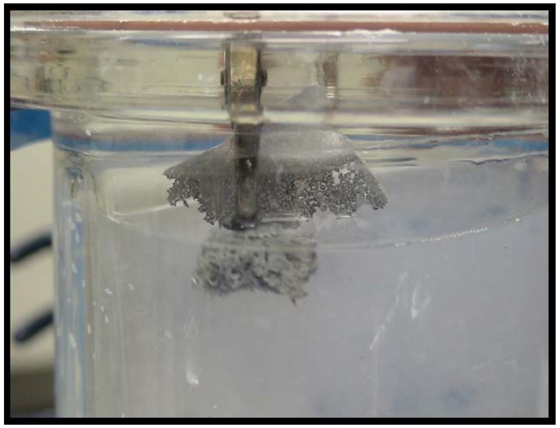
Cyclic Voltammograms (CV)



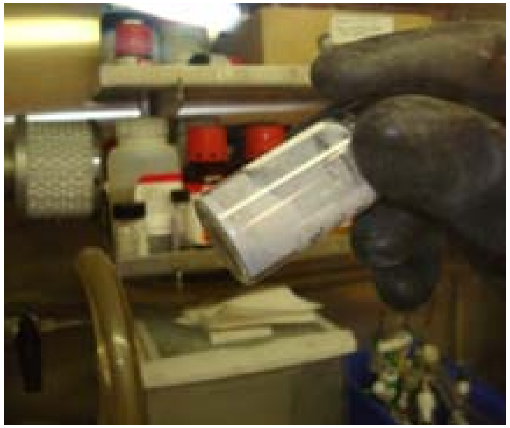
Experimental and hypothetical cyclic voltammograms for the electrochemical formation of alane. (a) A hypothetical cyclic voltammogram was formulated from the equilibrium potential data for possible reactions and the anticipated state of each species generated. (b) Bulk electrolysis experiment at an aluminum wire electrode for a cell containing a 1.0 M solution of NaAlH4 in THF at 25°C.[5]

5. Zidan *et. al*, "Aluminum Hydride: A Reversible Material for Hydrogen Storage" *Chem. Commun.*, 2009, 3717–3719

Electrochemically Generated AlH_3



Aluminum electrode dissolved after an electrochemical run as expected when AlH_3 is formed.[5]



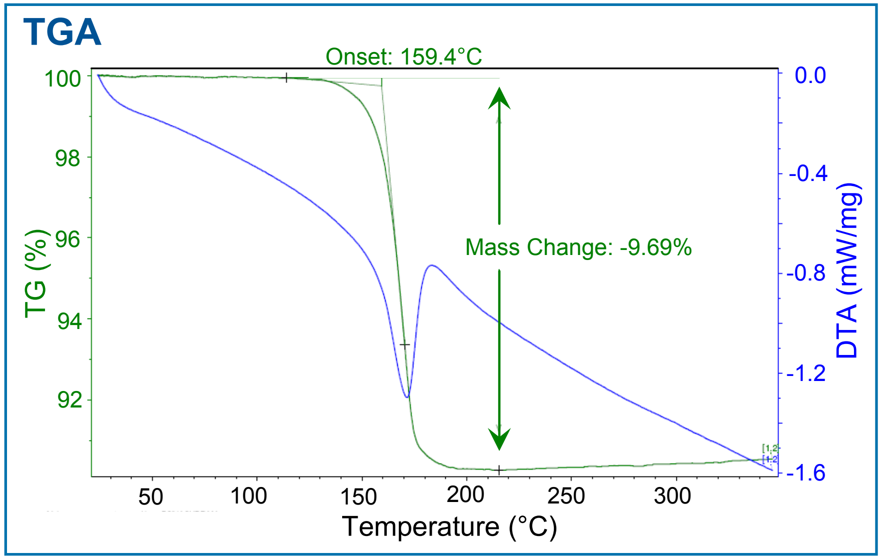
Two grams of AlH_3 electrochemically generated.

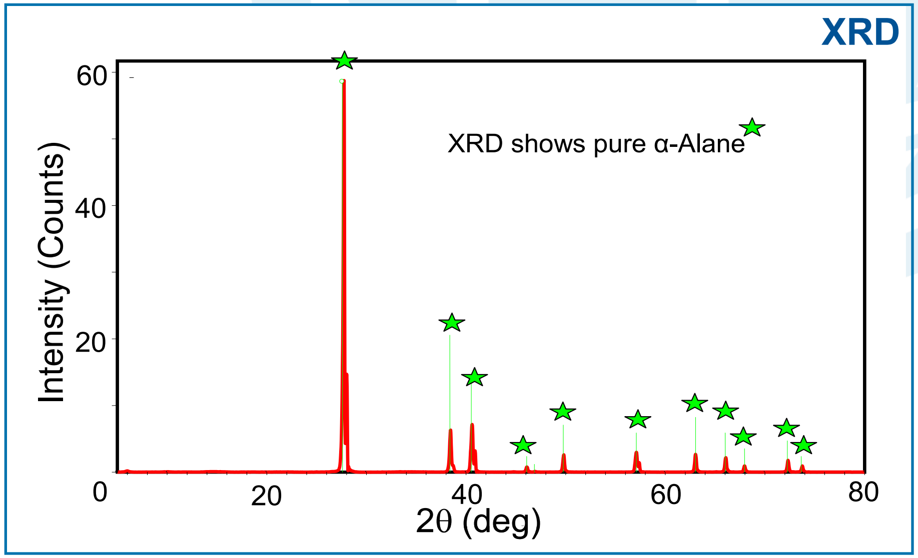
Electrochemically generated AlH_3-TEDA

Methods have been developed to extract alane from THF. These methods involve the heating and vacuum distillation of THF adducted alane solutions with subsequent crystallization of alane in toluene or other non coordinating solvents.

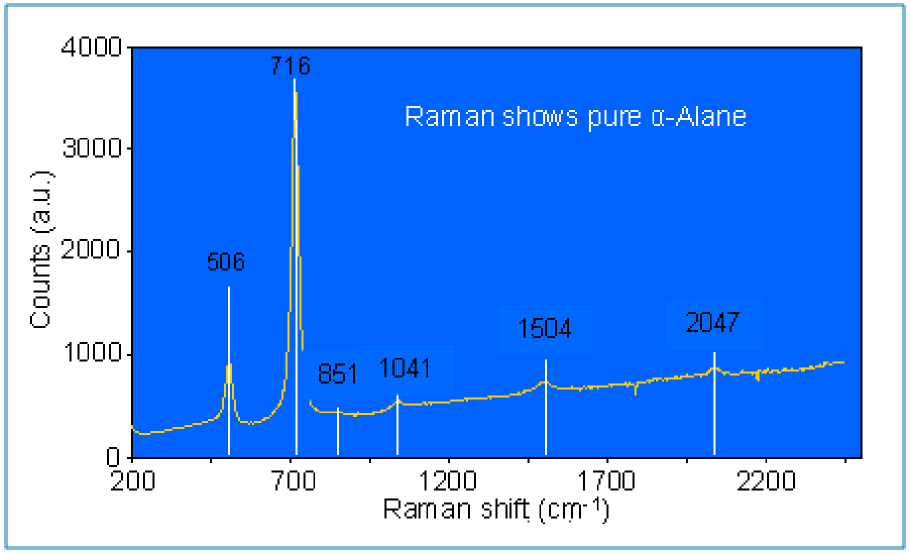
5. Zidan *et. al,* "Aluminum Hydride: A Reversible Material for Hydrogen Storage" *Chem. Commun.,* 2009, 3717–3719

Electrochemically Generated AlH_3



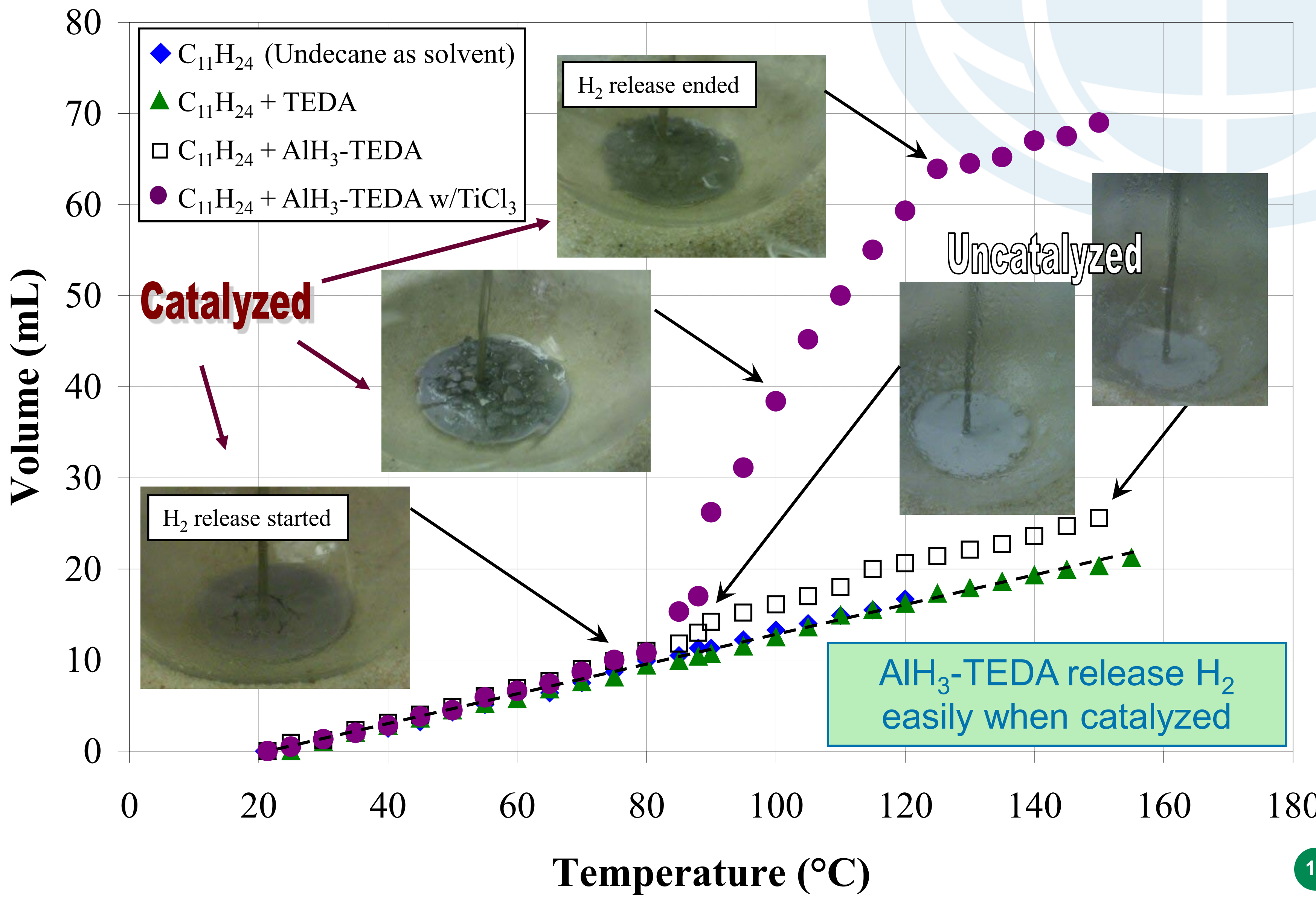


TGA decomposition of electrochemically generated alane releases almost full H_2 capacity expected in AlH_3.



TGA, XRD, Raman confirm the product is high purity AlH3, alane.

H_2 Release from Electrochemically Formed AlH_3-TEDA Catalyzed with Ti



AlH_3-TEDA release H_2 easily when catalyzed

Feasibility of Electrochemical Synthesis of Alane

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

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

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

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

68% is based on overpotential value

Energy Consumption Relative to Energy Stored

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

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

Efficiency

Ideal = 83%

Actual = 75%

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Efficiency and Energy losses

Energy Consumption Relative to Energy Stored

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

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

Efficiency

Ideal = 83%

Actual = 75%

- **The above relative energy consumption is only the energy consumed by the electrochemical cell (dos not include AlH_3 separation via heating and vacuuming)**

- **Goal is for energy consumption relative to energy stored not to exceed 30% (narrow margin)**

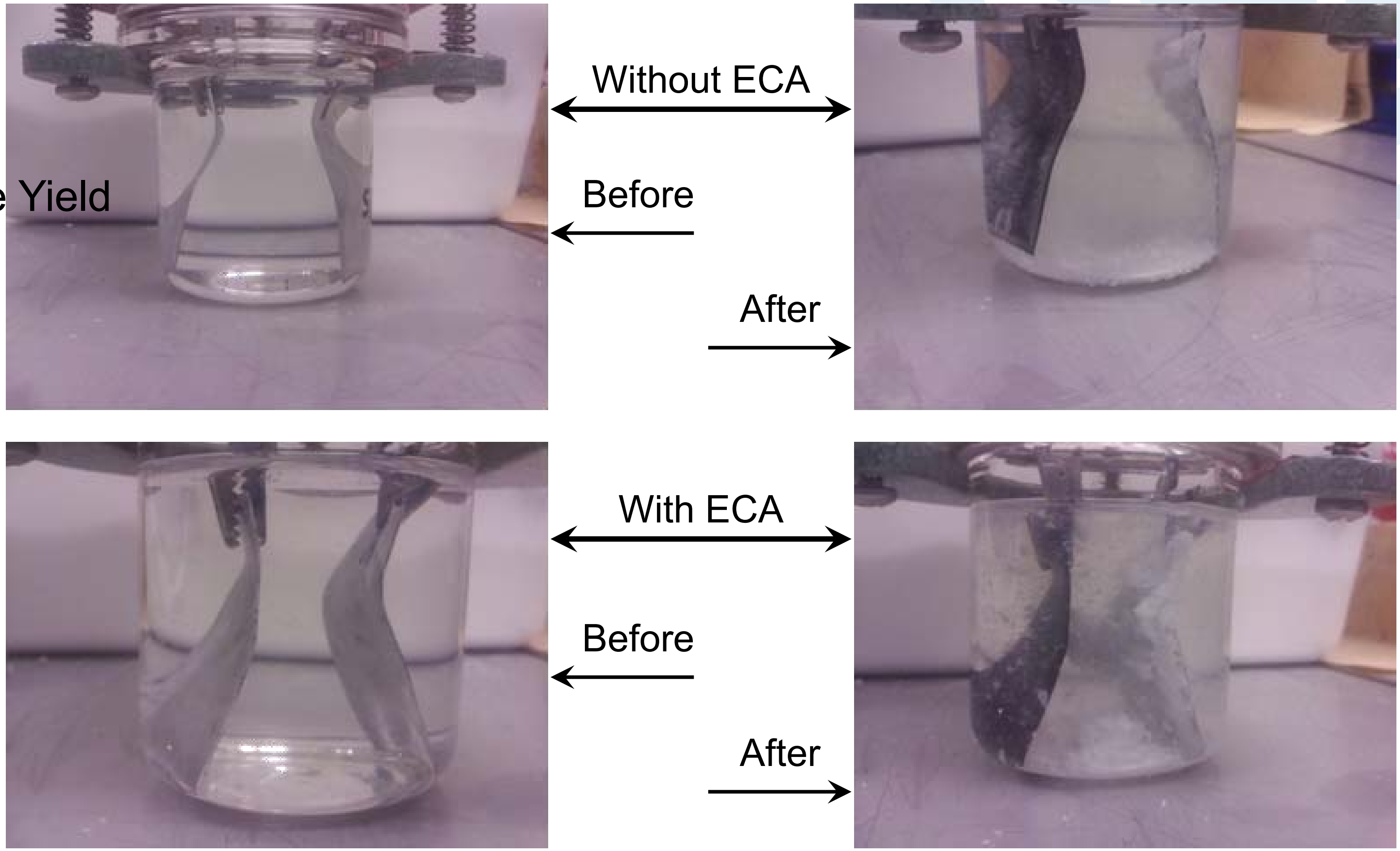
- **Higher efficiency is sought for all possible steps of the process (electrochemical cell, yield and AlH_3 separation)**

Achieving higher efficiencies in every step of the regeneration is ongoing effort

Electro-Catalytic Additive (ECA) to Increase Yield

Visual Observation of Higher Yield

Increase Yield



Electrochemical cells producing AlH_3 with and without ECA. Also very small amount of dendrites.

The use of the ECA increased the amount of AlH_3 produced in the cell.

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Effect of ECA on the Production of Alane

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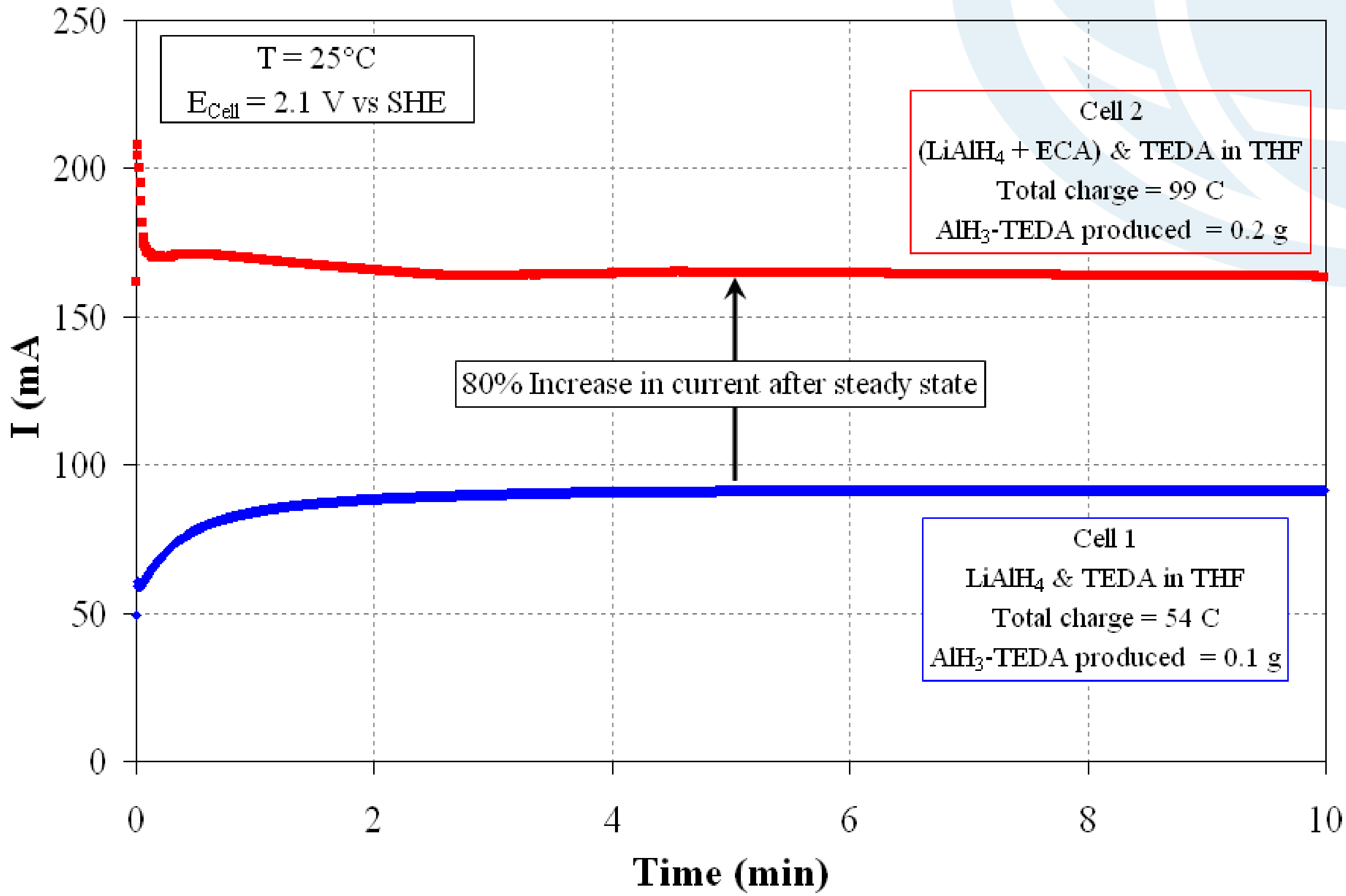
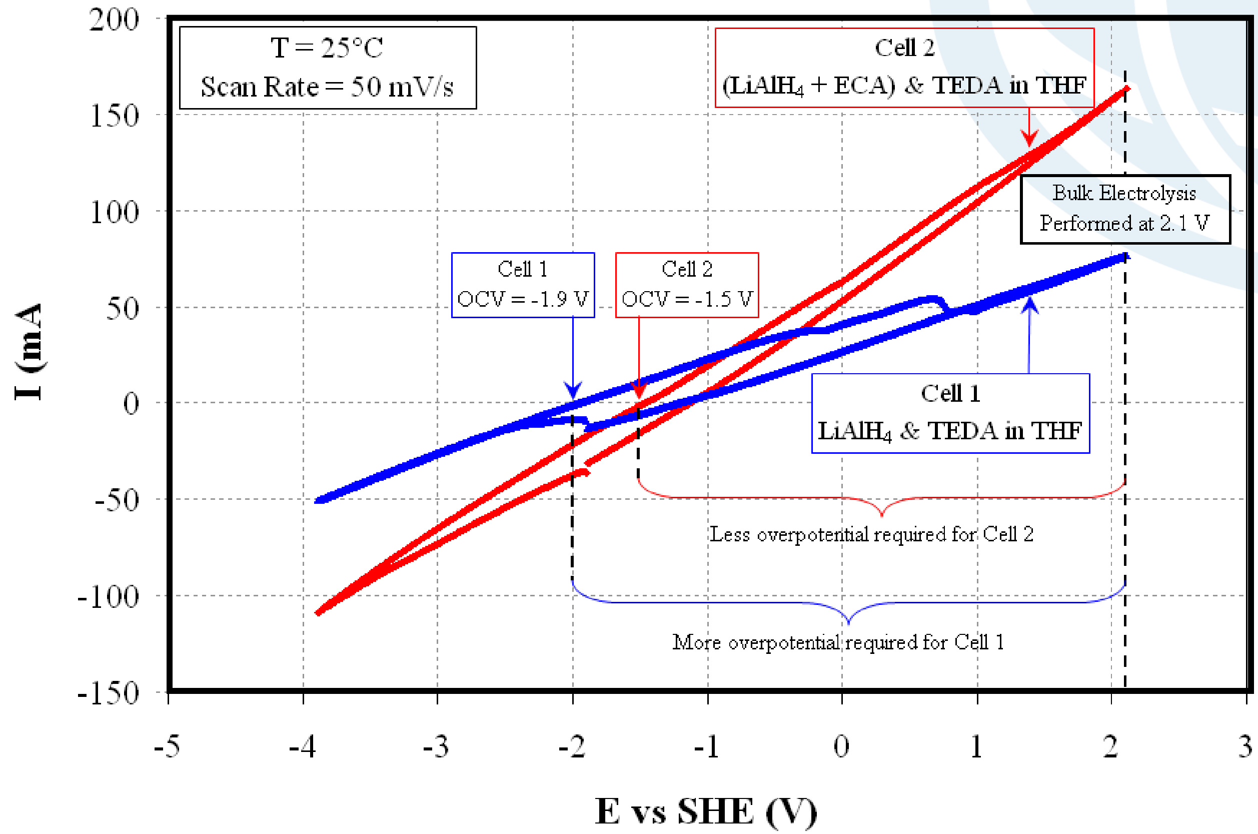


The bulk electrolysis to produce alane show that cell 2 has almost two times of the total charge and the amount of AlH_3-TEDA as compared to cell 1. An 80% increase in current was observed after the current is steady.

ECA increased current and alane yield

CVs Showing Effect of ECA



The open circuit voltage (OCV) for cell 2 is shifted to -1.5 V from the original cell 1 (OCV = -1.9). This means that the overpotential required for cell 2 is less when performing the electrolysis at 2.1 V. Consequently, lower energy is required for cell 2 to produce AlH_3, which implies that cell 2 is more efficient because it has more current with less voltage input.

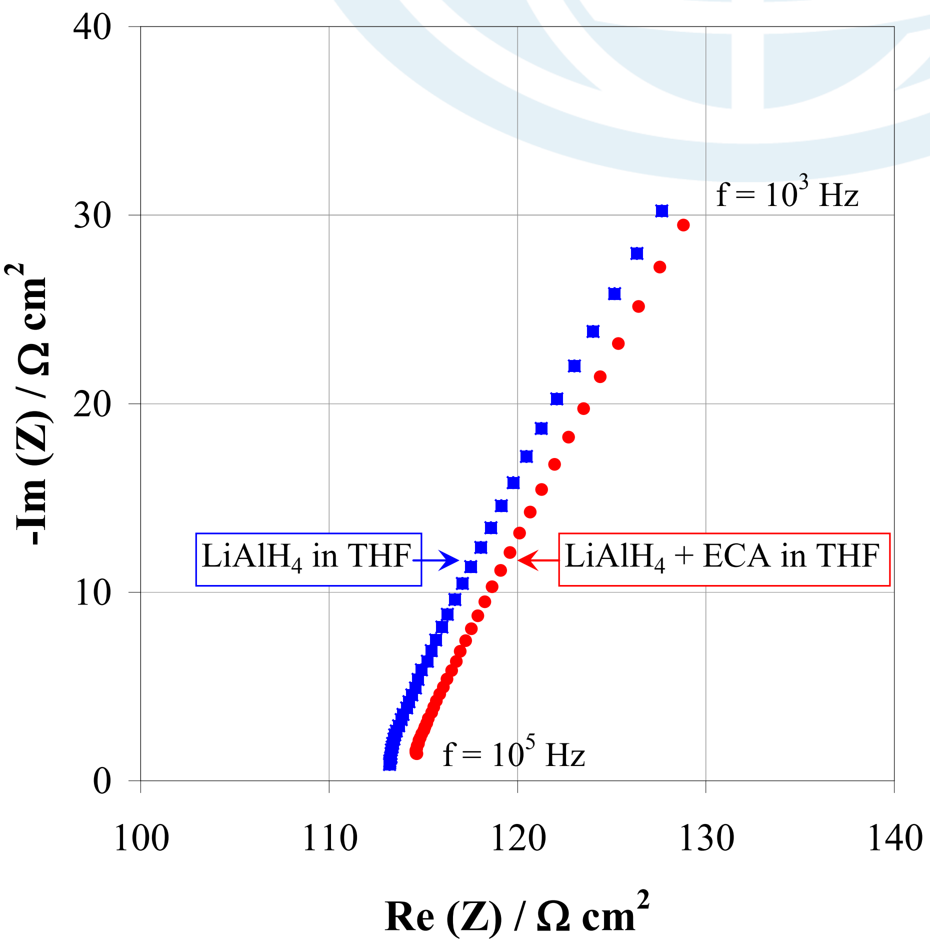
ECA improves cell efficiency.

Without ECA	75%
With ECA	78%

Impedance Showing Effect of ECA

ECA Function:

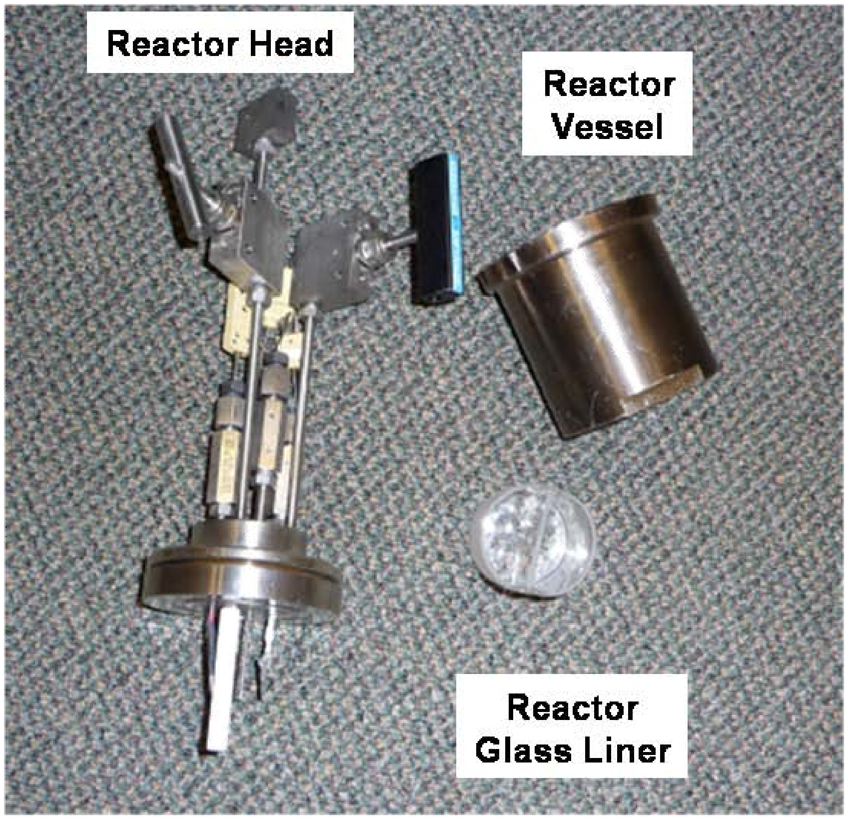
Electrochemical impedance spectroscopy (EIS) was performed on the cells with and without the ECA. The resistance for both cells is ~112 Ωcm^2. This shows that the ECA does not have a significant effect in the resistance (or conductivity) of the solution. That is, the ECA is not acting as an electrolyte. Consequently, the increase in current and efficiency shown previously are an electro-catalytic effect of the added species.



Results indicate that the ECA does not act as an electrolyte but rather as a catalyst

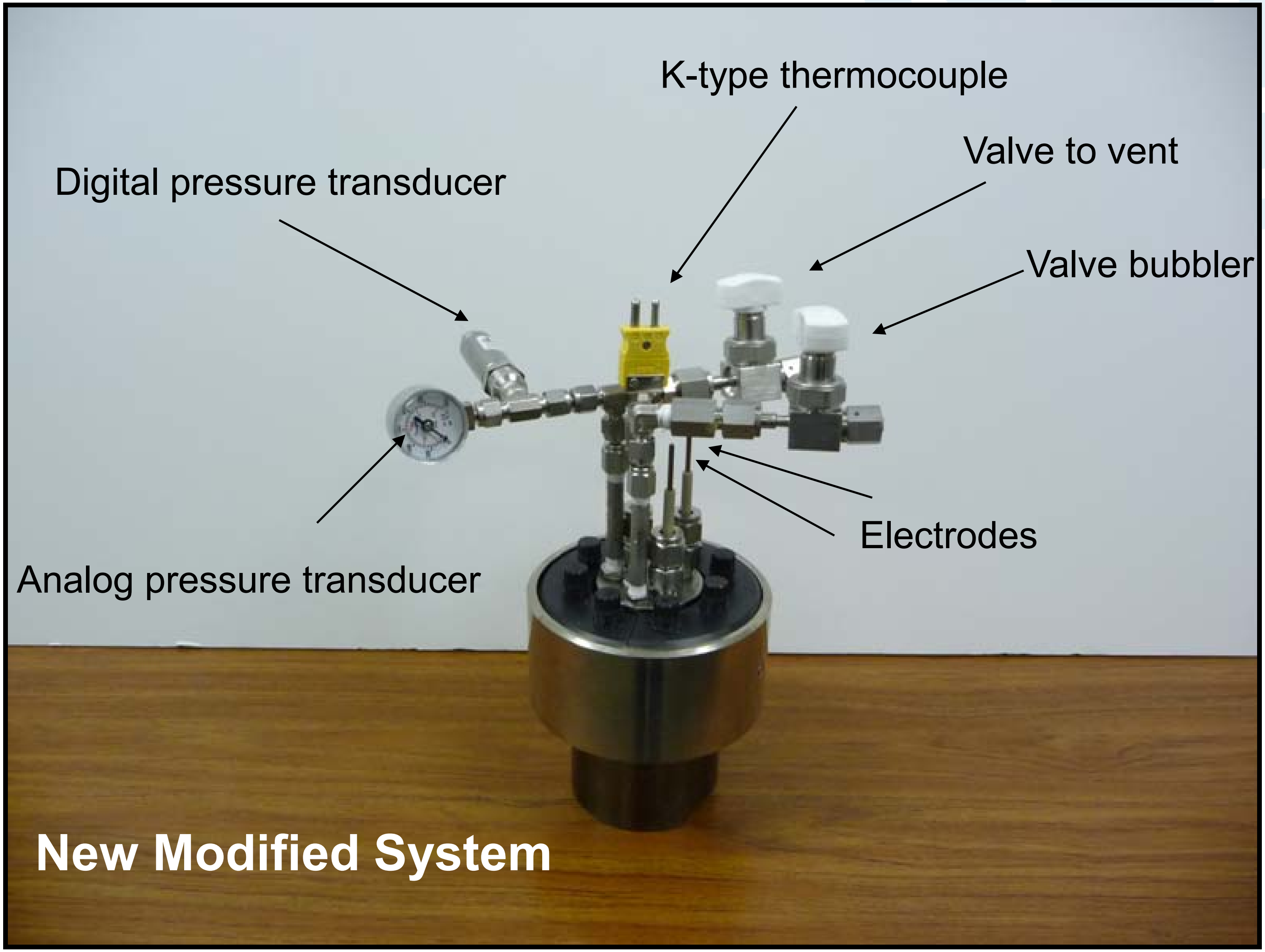
Higher Efficiency AlH_3 Separation

H_2 Pressurized Electrochemical Cell



Electrodes

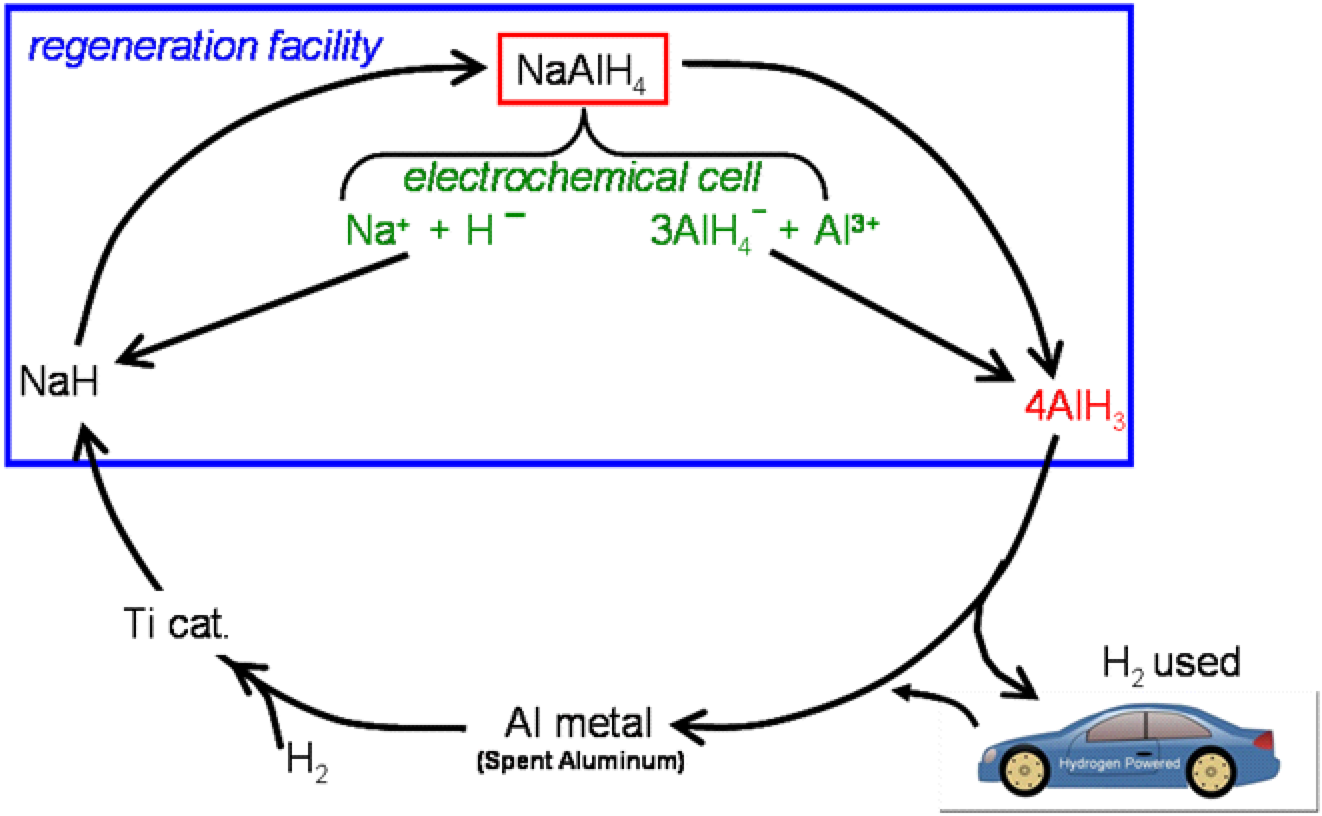
Higher Efficiency AlH_3 Separation Cell



Alane Generation Reversible Cycle

Non-Aqueous Solution Electrochemical System

($NaAlH_4$, $KAlH_4$ or $LiAlH_4$)/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.

Summary

- Continued to produce gram quantities of alane with high purity.
- $LiAlH_4$ was also used to produce alane and shows higher efficiency
- An electro-catalytic additive was discovered and found to greatly enhance the process.
- Started Improving efficiencies in every step of the regeneration method and achieved success
- Yield was increased and higher electrochemical cell efficiency was achieved
- A pressurized ECC is being constructed for close material regeneration cycle and the use of more efficient separation.
- Very small amount of dendrites.

Proposed Future Work

- Examine catalysts in accelerating formation and regeneration- **Started**
- Advanced Analytical Methods
  - Use other techniques (e.g. NMR, Prompt Gamma Activation Analysis (PGAA, In Situ neutron and Raman) to quantify and characterize AlH_3- **On going**
- Optimization and Scale-Up Electrolytic Cell
  - Develop closed and efficient AlH_3 extracting system based on new solvents-**Started**
  - Optimize all parameters needed for producing several grams of AlH_3 efficiently-**On going**
  - Explore, reversibly, forming other high capacity complex hydrides such as Mg and Ca based complex hydrides using electrochemical methods
  - Design and construct a lager electrochemical cell capable of producing larger quantities of AlH_3

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