

# 2010 DOE Hydrogen Program Review

# Electrochemical Reversible Formation of Alane

Ragaiy Zidan, Brenda García-Díaz,  
Michael Martínez-Rodríguez, Joseph Teprovich

Energy Security Directorate  
Savannah River National Laboratory

*Project ID #: ST063*

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## Timeline

Start: 10/1/06

End: In Progress

Percent complete: 90 %

## Budget

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

## Barriers

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

## Partners

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

- 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 -  $\text{AlH}_3$ ), having a gravimetric capacity of 10 wt% and volumetric capacity of 149 g/L  $\text{H}_2$  and a desorption temperature of  $\sim 60^\circ\text{C}$  to  $175^\circ\text{C}$  (depending on particle size and the addition of catalysts) has potential to meet the 2010 DOE onboard system desorption targets.

### Specific Objectives

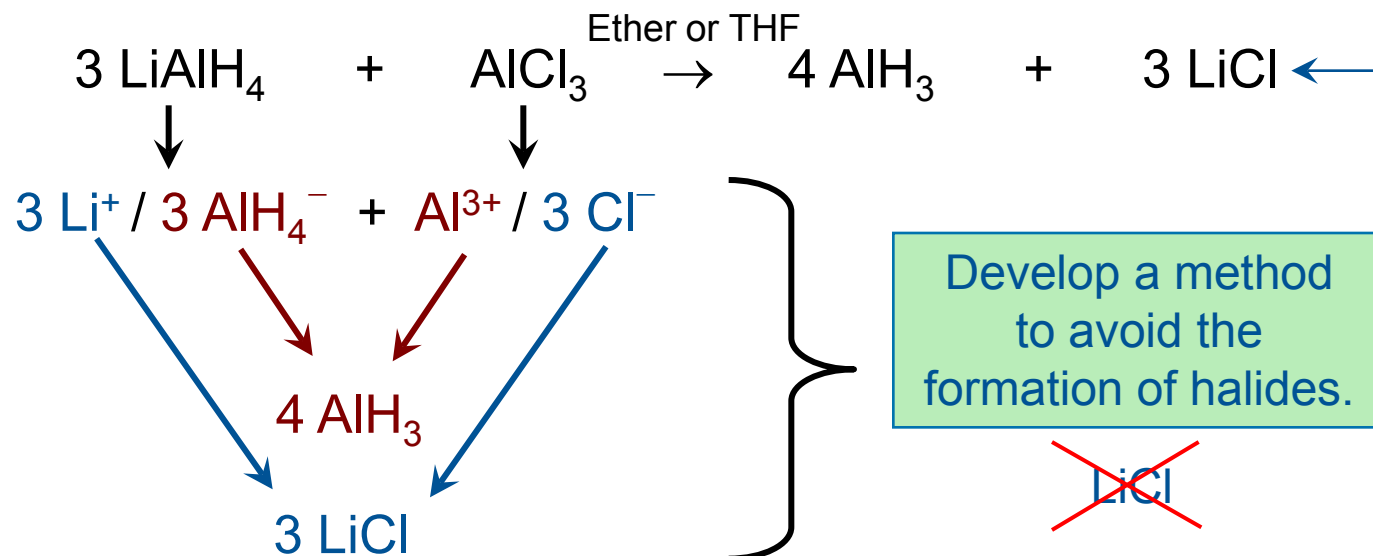
- Avoid the impractical high pressure needed to form  $\text{AlH}_3$ .
- Avoid chemical reaction route of  $\text{AlH}_3$  that leads to the formation of alkali halide salts such as  $\text{LiCl}$  or  $\text{NaCl}$ .
- Utilize electrolytic potential to translate chemical potential into electrochemical potential and drive chemical reactions to form  $\text{AlH}_3$ .

# Known Methods to Produce Alane

A) Formation of alane from the elements:



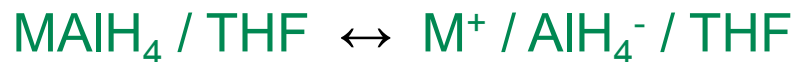
B) Traditional chemical method to produce alane:



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

## Electrolyte

The electrolysis is carried out in an electrochemically stable, aprotic, and polar solvent such as THF or ether.  $\text{MAIH}_4$  ( $\text{M} = \text{Li}, \text{Na}$ ) is dissolved in this solvent, forming the ionic solution as shown below which is used as an electrolyte.



Though not directed at the regeneration of alane, extensive studies on the electrochemical properties of this type of electrolyte have been reported.<sup>3,4</sup>

**Concern:** Al and  $\text{AlH}_3$  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<sup>1,2</sup> 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.

## Possible Reactions When $\text{AlH}_3$ is Generated in a Closed Material Cycle

Anode:

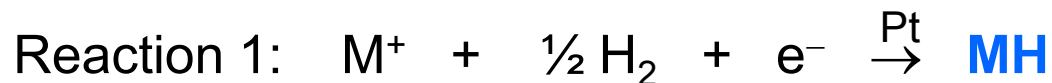


Hydrogen bubbles at the anode

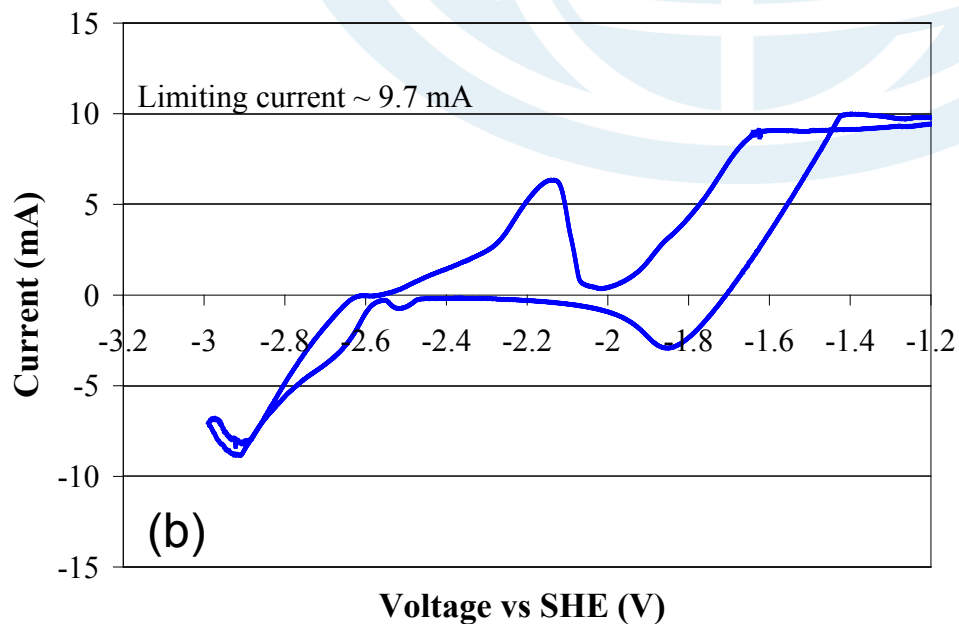
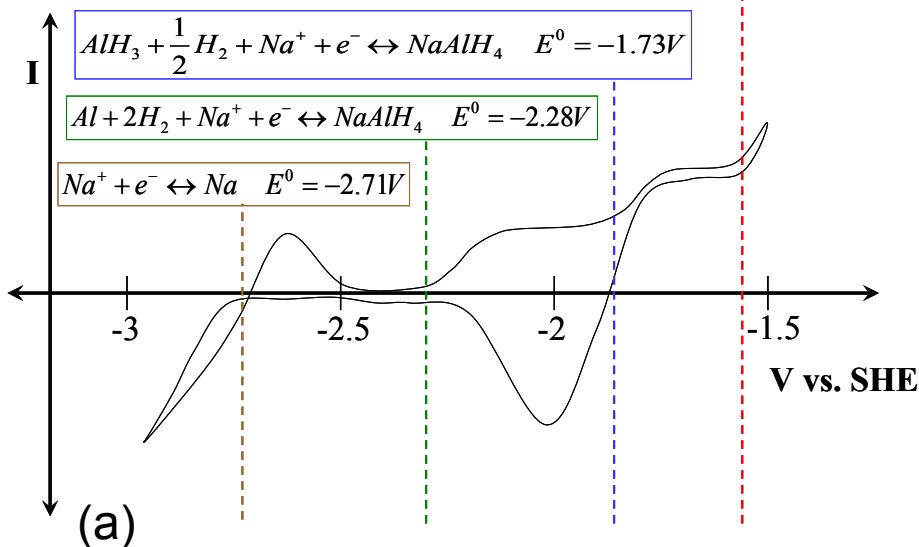
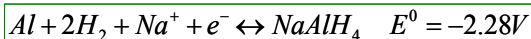
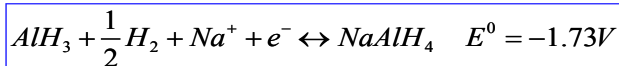
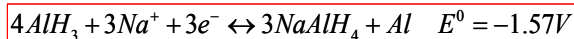


Electrode is expected to dissolve

Cathode:



### 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  $\text{NaAlH}_4$  in THF at  $25^\circ\text{C}$ .<sup>5</sup>

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





Aluminum electrode dissolved after an electrochemical run as expected when  $\text{AlH}_3$  is formed.<sup>5</sup>



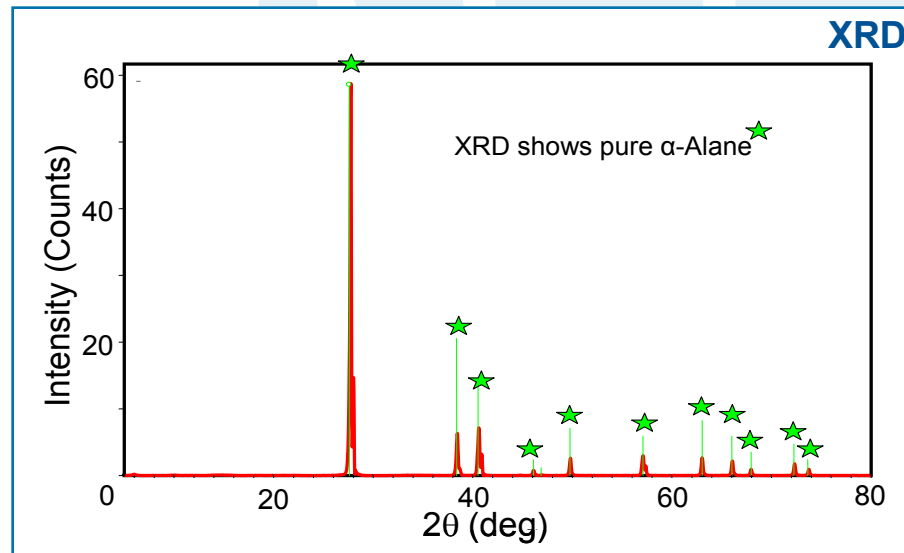
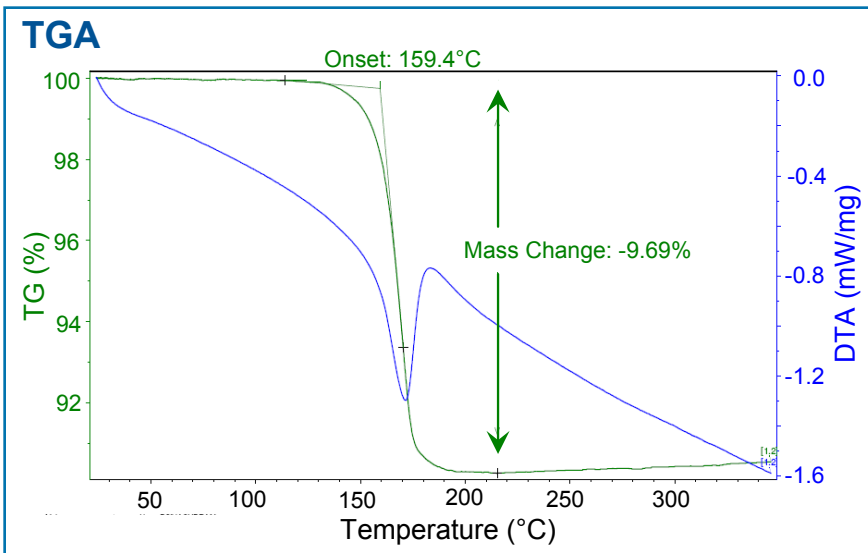
Two grams of  $\text{AlH}_3$  electrochemically generated.



Electrochemically generated  $\text{AlH}_3$ -TEDA

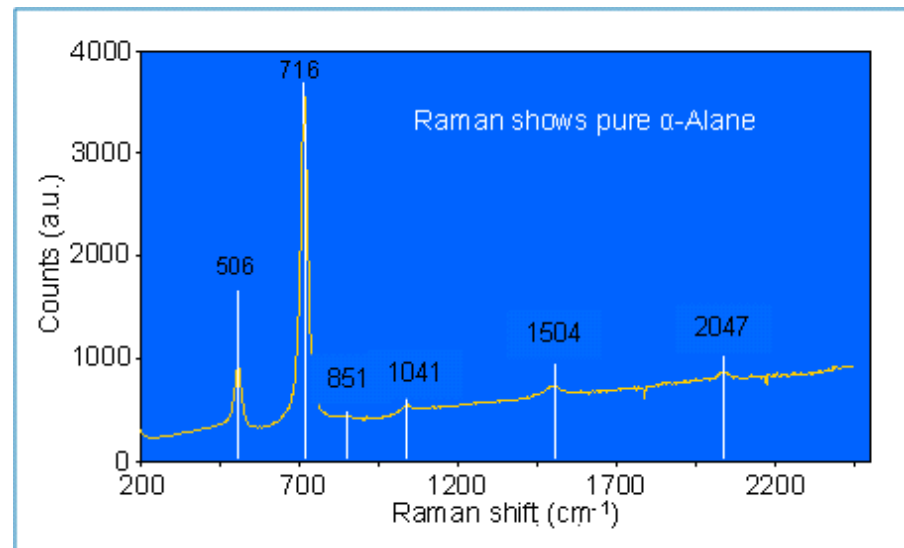
Methods have been developed to extract alane from THF. These methods involve the heating and vacuum distillation of THF adducted alane solutions with subsequent crystallization of alane in toluene or other non coordinating solvents.

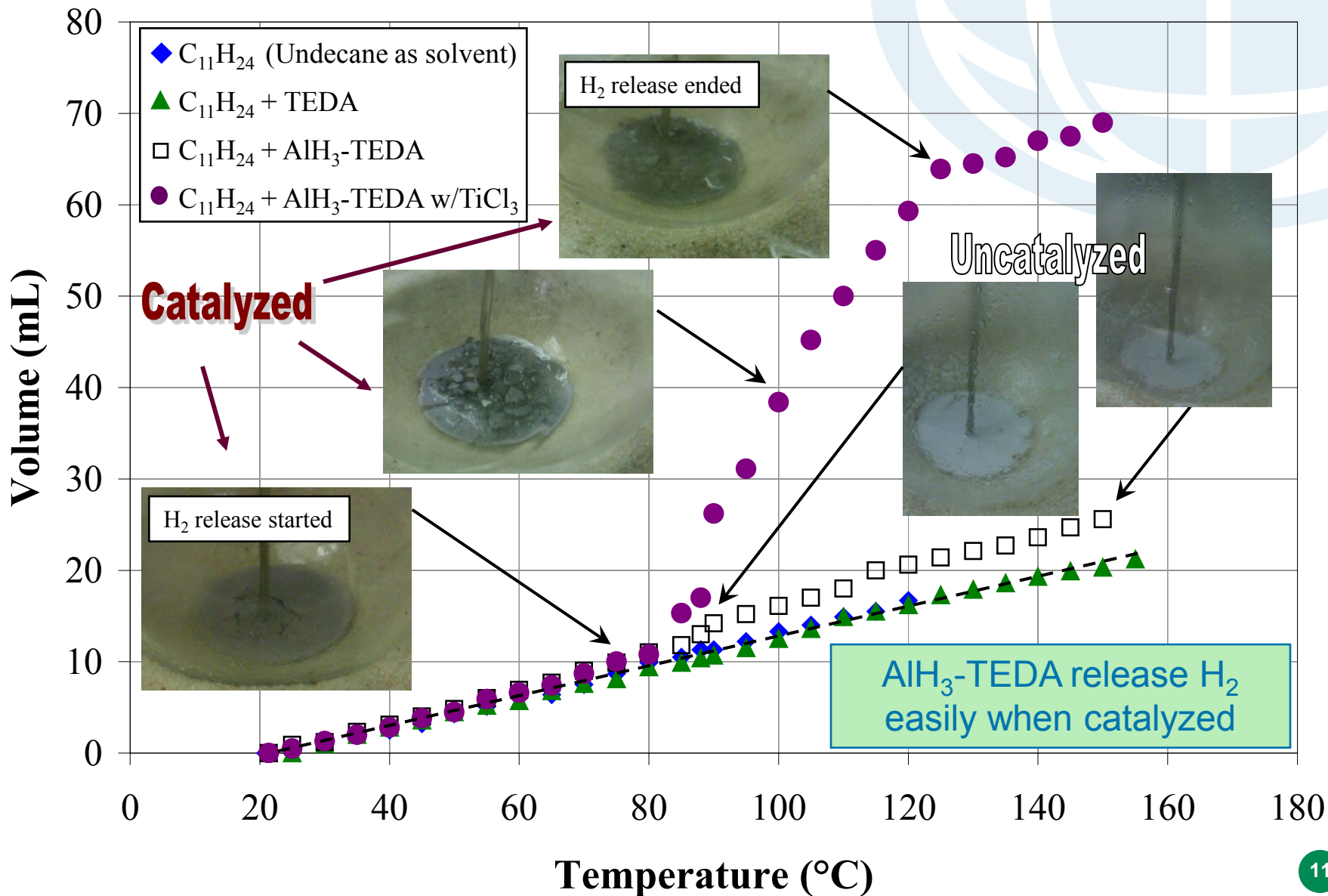
5. Zidan *et. al*, "Aluminum Hydride: A Reversible Material for Hydrogen Storage" *Chem. Commun.*, 2009, 3717–3719



TGA decomposition of electrochemically generated alane releases almost full  $\text{H}_2$  capacity expected in  $\text{AlH}_3$ .

TGA, XRD, Raman confirm the product is high purity  $\text{AlH}_3$ , alane.





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

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

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

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

### Energy Consumption Relative to Energy Stored

$$\textit{Ideal} = \frac{5.66 \text{ kWh}}{33.3 \text{ kWh}} \times 100 = 17\%$$

$$\textit{Actual} = \frac{8.32 \text{ kWh}}{33.3 \text{ kWh}} \times 100 = 25\%$$

### Efficiency

$$\textit{Ideal} = 83\%$$

$$\textit{Actual} = 75\%$$

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## Efficiency

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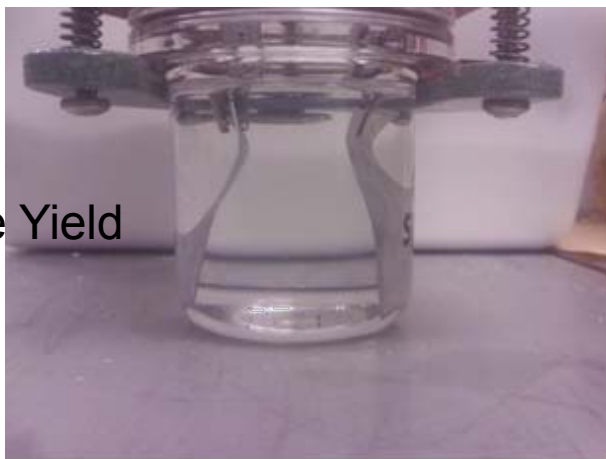
$$\text{Actual} = 75\%$$

- The above relative energy consumption is only the energy consumed by the electrochemical cell (does not include  $\text{AlH}_3$  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  $\text{AlH}_3$  separation)

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

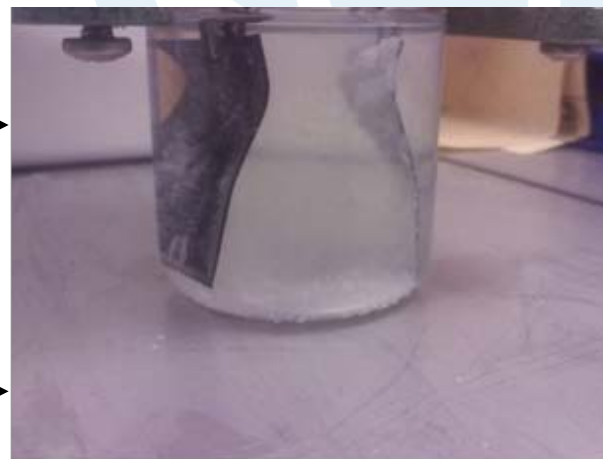
Visual Observation of Higher Yield

Increase Yield



Without ECA

Before



After



With ECA

Before

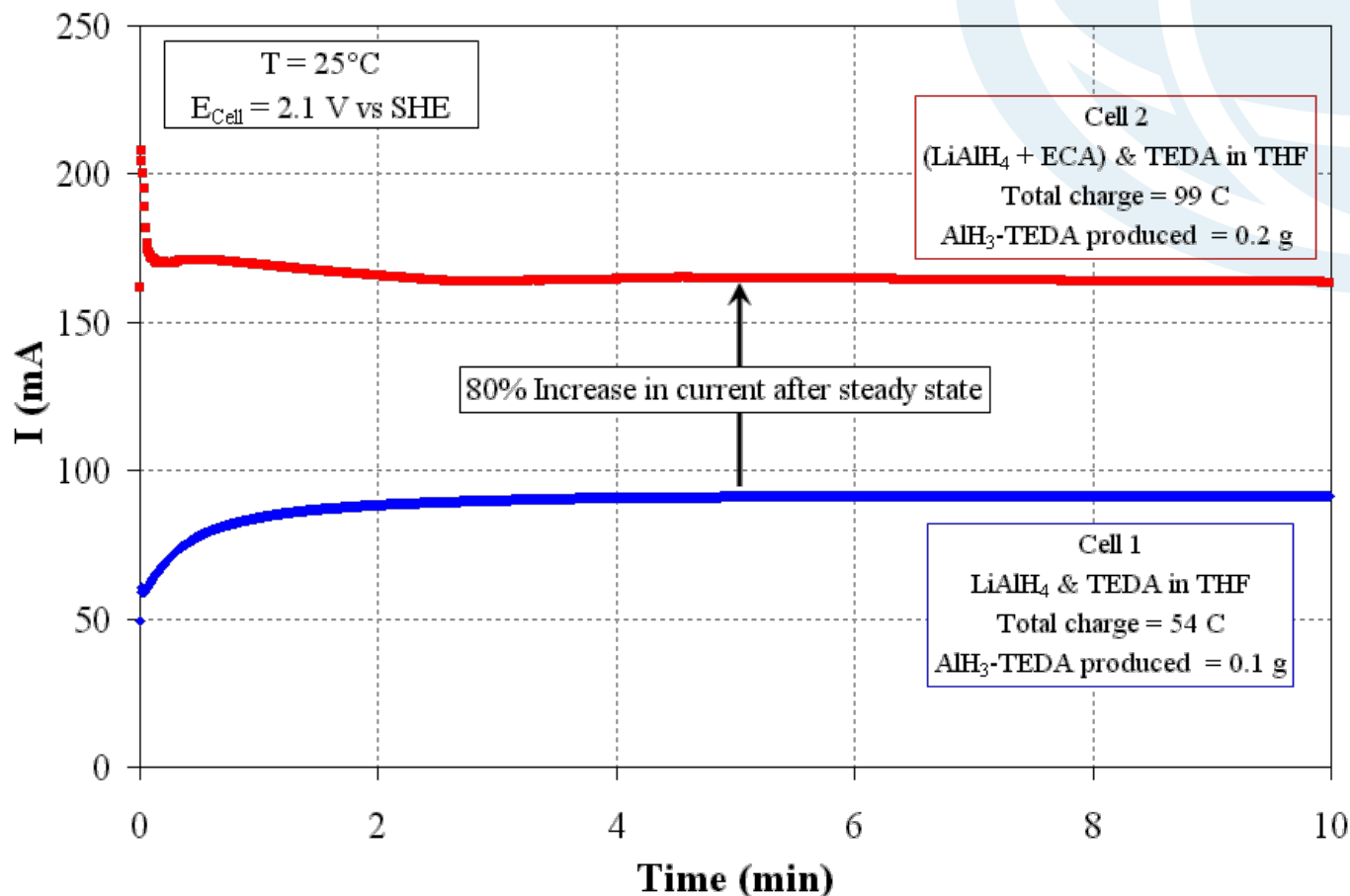


After

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.

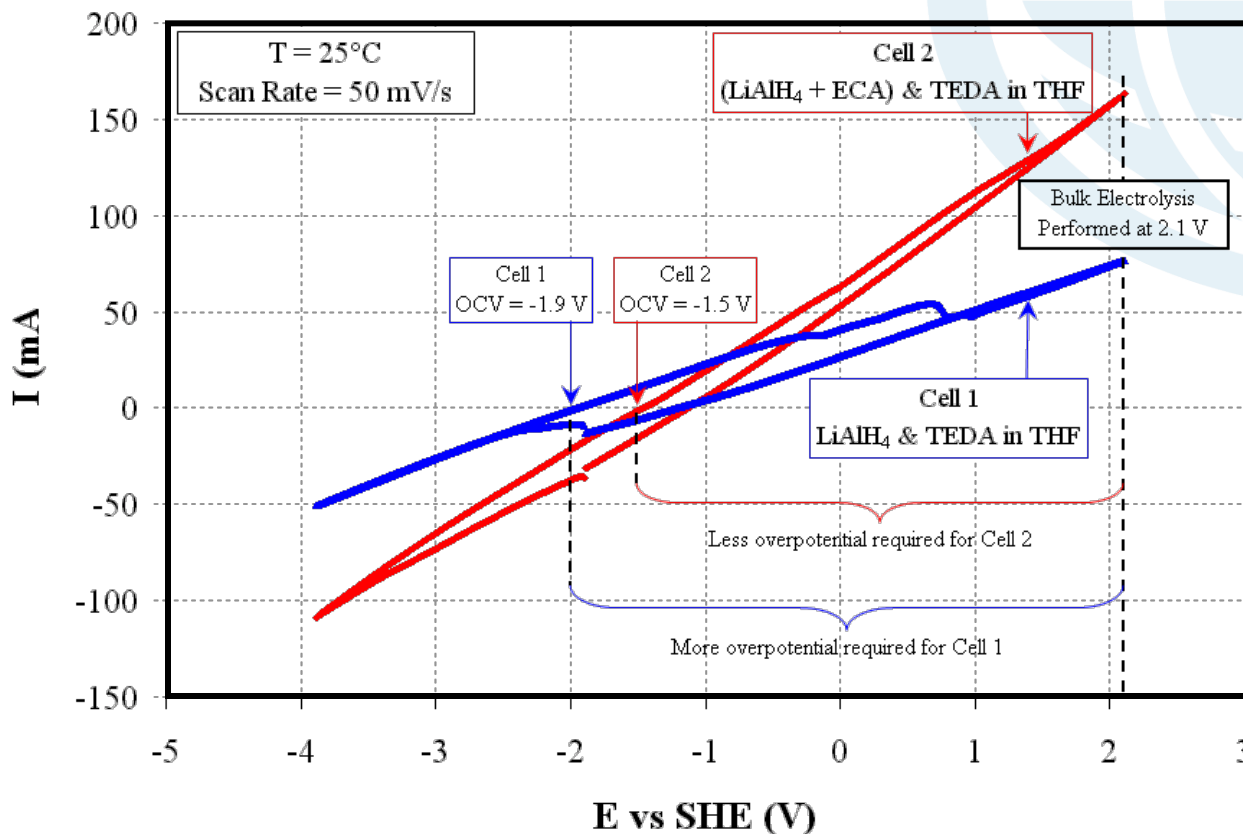




The bulk electrolysis to produce alane show that cell 2 has almost two times of the total charge and the amount of AlH<sub>3</sub>-TEDA as compared to cell 1. An 80% increase in current was observed after the current is steady.

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<sub>3</sub>, which implies that cell 2 is more efficient because it has more current with less voltage input.

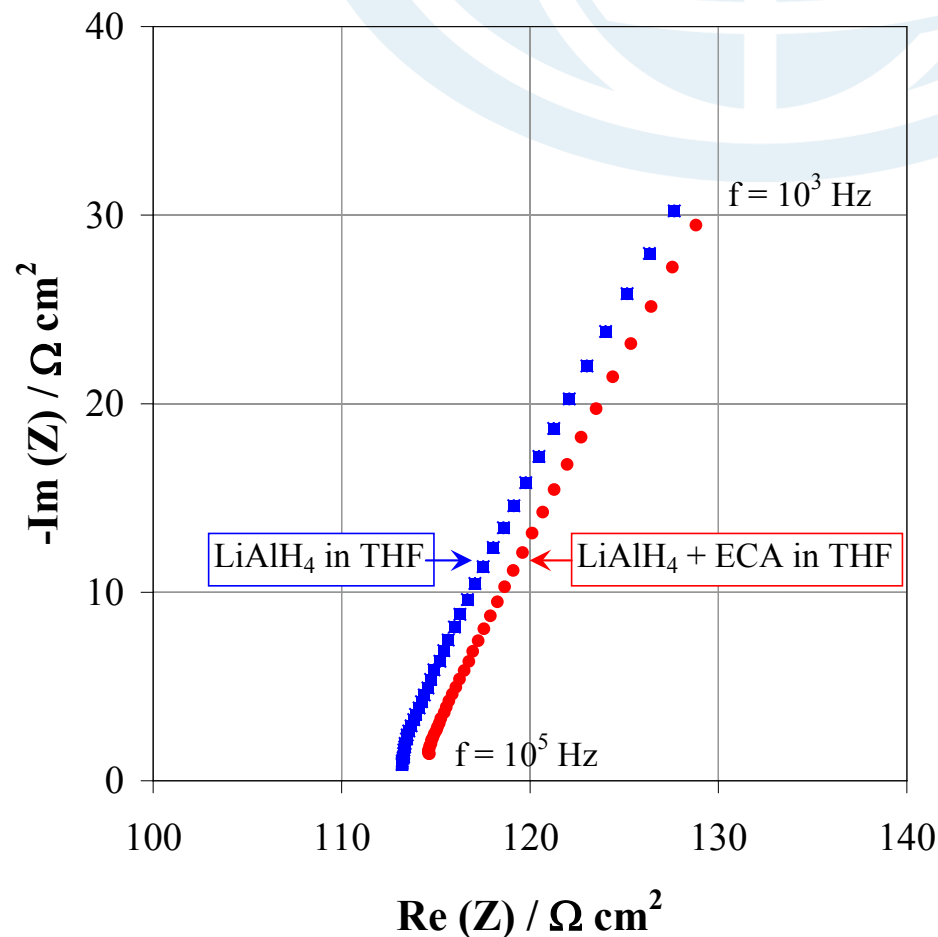
ECA improves cell efficiency.	Without ECA	75%
	With ECA	78%



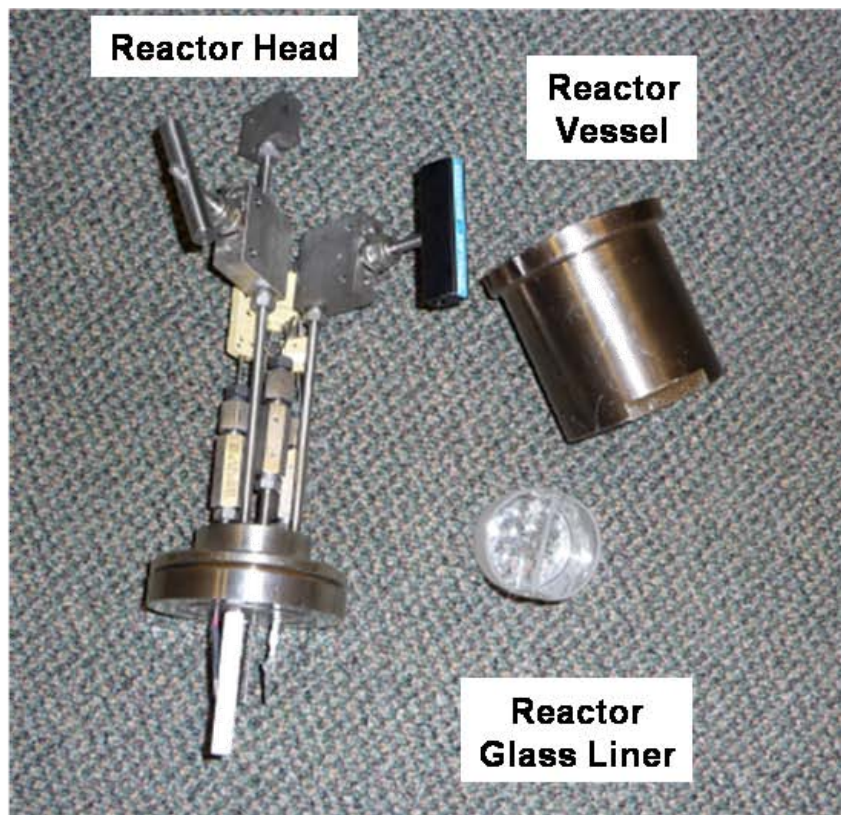
## ECA Function:

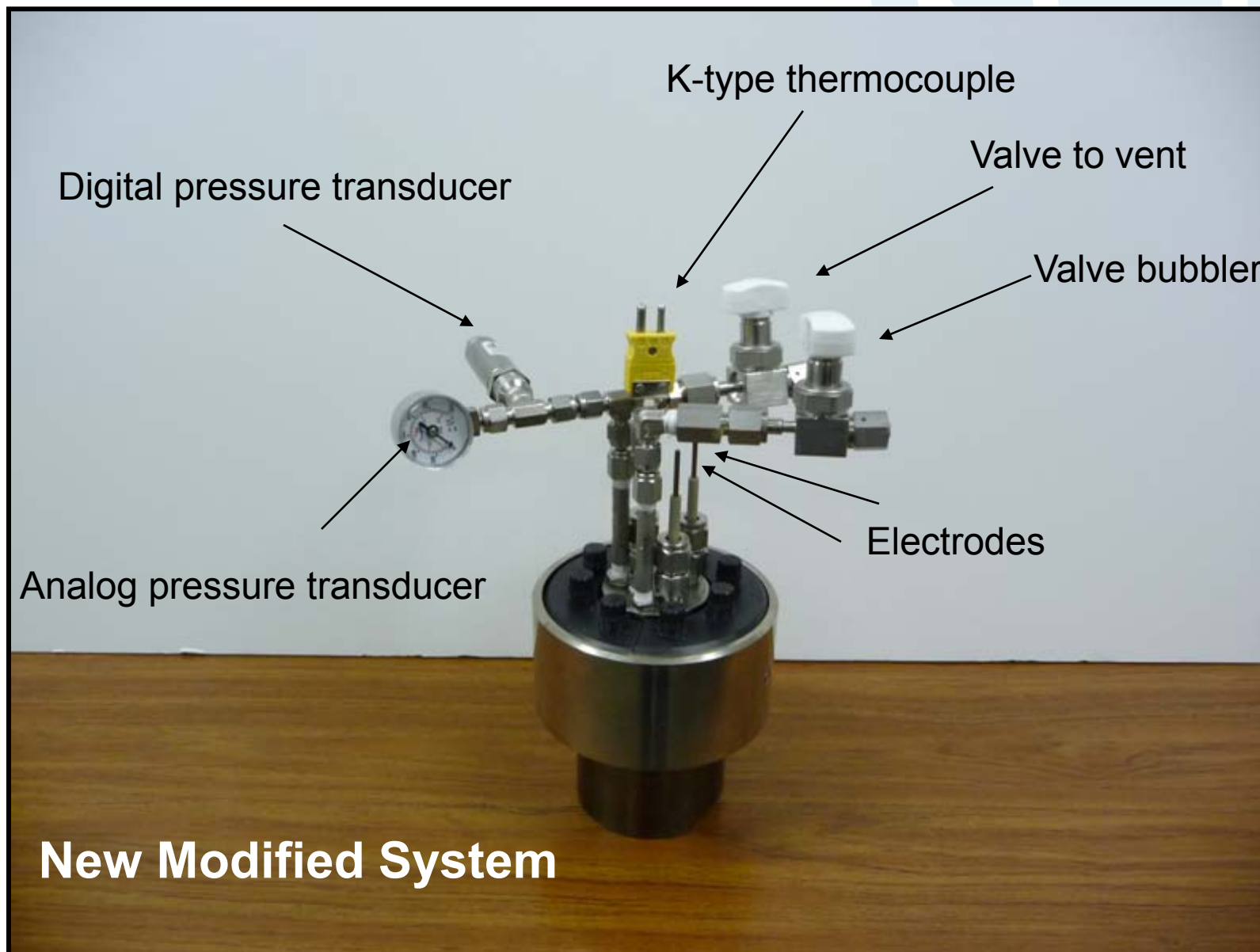
Electrochemical impedance spectroscopy (EIS) was performed on the cells with and without the ECA. The resistance for both cells is  $\sim 112 \Omega\text{cm}^2$ . This shows that the ECA does not have a significant effect in the resistance (or conductivity) of the solution. That is, the ECA is not acting 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



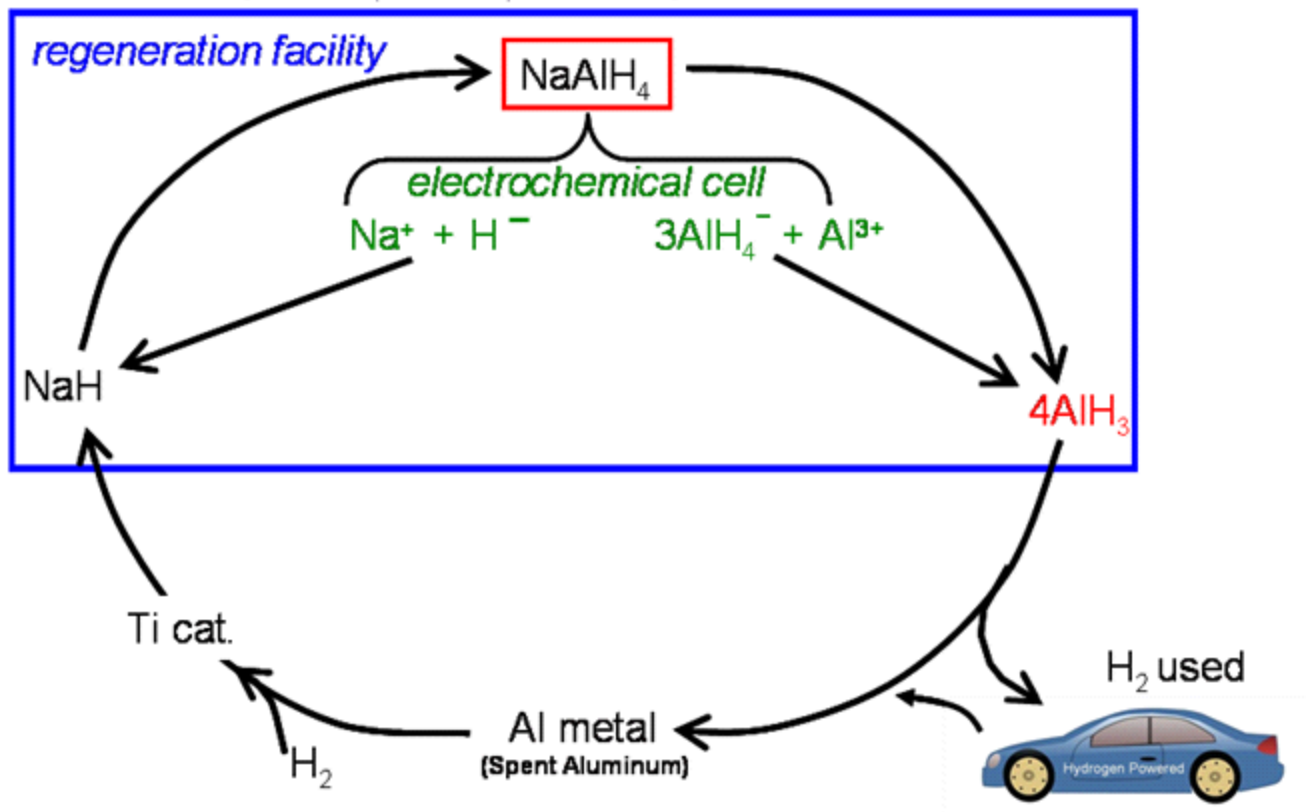
## $\text{H}_2$ Pressurized Electrochemical Cell





## Non-Aqueous Solution Electrochemical System

( $\text{NaAlH}_4$ ,  $\text{KAlH}_4$  or  $\text{LiAlH}_4$ )/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.

- Continued to produce gram quantities of alane with high purity.
- $\text{LiAlH}_4$  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.



- 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  $\text{AlH}_3$ -  
**On going**
- Optimization and Scale-Up Electrolytic Cell
  - Develop closed and efficient  $\text{AlH}_3$  extracting system based on new solvents-**Started**
  - Optimize all parameters needed for producing several grams of  $\text{AlH}_3$  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 larger electrochemical cell capable of producing larger quantities of  $\text{AlH}_3$

## SRNL:

- Doug Knight
- Long Dinh
- Christopher Fewox
- Jennifer Pittman
- Ashley C. Stowe
- Andrew G. Harter
- Joshua Gray
- Rob Lascola
- Don Anton
- Ted Motyka
- Joe Wheeler

## Collaboration:

- Jason Graetz, James Wegrzyn and Jim Reilly (**BNL**)
- Craig Jensen (**University of Hawaii**)
- Sean McGrady (**University of New Brunswick**)
- Rana Mohtadi and Sivasubramanian PremKumar (**Toyota**)
- Rosario Cantelli (**Università di Roma**)
- Ned Stetson (**US-DOE**)