

Electrochemical Reversible Formation of Alane

Ragaiy Zidan

Energy Security Directorate

Savannah River National Laboratory



2013 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE
TECHNOLOGIES PROGRAM ANNUAL MERIT REVIEW and PEER
EVALUATION MEETING

TEAM



Dr. Scott Greenway

(Electrochemistry)

Dr. Douglas Knight

(Chemical Synthesis and X-ray analysis)

Dr. Joseph Teprovich

(Organic Chemistry and Nano Technology)

Brent Peters

(Synthesis and Instrumental Analysis)

Dr. Robert Lascola

(Raman Spectroscopy)

Overview



Timeline

Start: 10/1/06

End: Continuing

Percent complete of activities
proposed for FY12: 30%*

Budget*

- Funding received in FY11
 - \$450K (\$200K received September 2011)
- Funding for FY12
 - \$400K (\$250K received March 2012*)

Barriers

- Low-cost, energy-efficient regeneration
- Full life-cycle analyses is needed
- Environmental impacts
- By-product and/or spent material
- Infrastructure requirements for off-board regeneration

Collaborators

- Brookhaven National Laboratory
- University of Hawaii

Relevance: Project Objectives

Overall Objectives

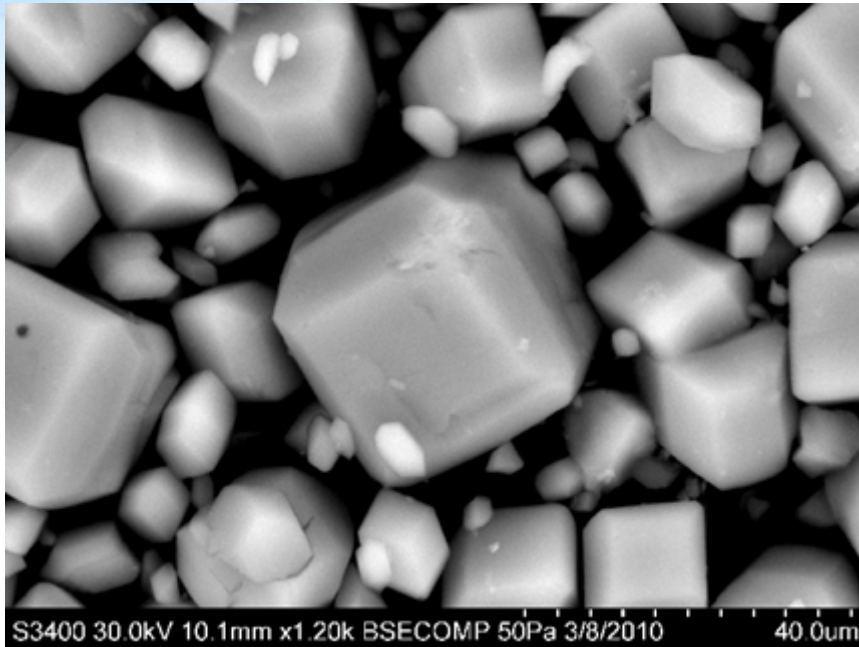
- Develop a low-cost rechargeable hydrogen storage material with cyclic stability, favorable thermodynamics and kinetics fulfilling the DOE onboard hydrogen transportation goals.

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 $\sim 60^\circ\text{C}$ to 175°C (depending on particle size and the addition of catalysts) has potential to meet the 2015 DOE onboard system desorption targets

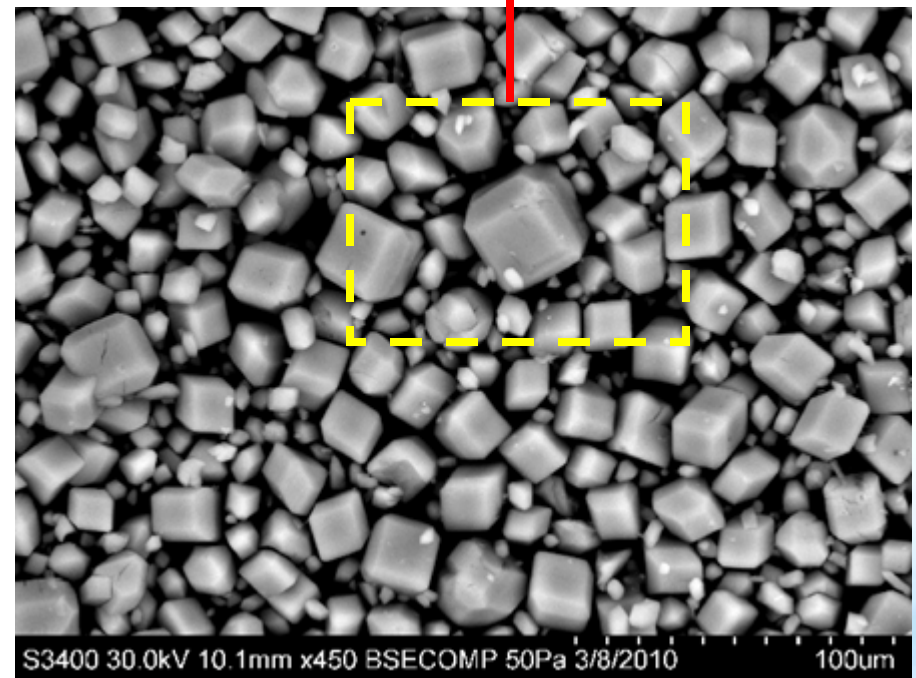
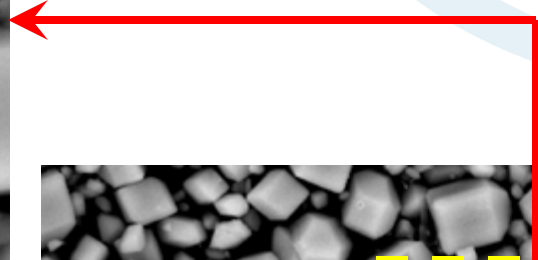
Specific Objectives

- 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

Relevance: Safety and Alane



Safer to handle than complex hydrides



- Simple passivation methods were performed to make alane safe to handle
- After surface passivation, material does not ignite in air or water
- Passivation reduces H₂ capacity by less than 1%.

Particle Size: 4 – 32 μm

Approach: Utilizing Electrochemical Methods

Technique: Utilize electrolytic potential, E , to drive chemical reactions to form AlH_3
Based on Gibbs free energy and Faraday equation:

$$\Delta G = -nF\Delta E \quad \rightarrow \quad \Delta G = RT \ln p$$

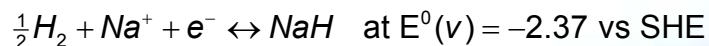
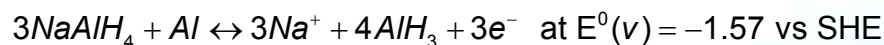
Motivation: Electrochemical generation represents a different, promising, and method to form AlH_3 reversibly

Possible reactions of producing alane from alanes electrolyte

Reactions	E^0 (V) vs SHE	Eq. No.
$4AlH_3 + 3Na^+ + 3e^- \leftrightarrow 3NaAlH_4 + Al$	-1.57	(1)
$AlH_3 + \frac{1}{2}H_2 + Na^+ + e^- \leftrightarrow NaAlH_4$	-1.73	(2)
$Al + 2H_2 + Na^+ + e^- \leftrightarrow NaAlH_4$	-2.28	(3)
$\frac{1}{2}H_2 + Na^+ + e^- \leftrightarrow NaH$	-2.37	(4)
$Na^+ + e^- \leftrightarrow Na$	-2.71	(5)
<hr/>		
$4AlH_3 + 3Li^+ + 3e^- \leftrightarrow 3LiAlH_4 + Al$	-1.89	(6)
$AlH_3 + \frac{1}{2}H_2 + Li^+ + e^- \leftrightarrow LiAlH_4$	-2.05	(7)
$Al + 2H_2 + Li^+ + e^- \leftrightarrow LiAlH_4$	-2.56	(8)
$\frac{1}{2}H_2 + Li^+ + e^- \leftrightarrow LiH$	-2.33	(9)
$Li^+ + e^- \leftrightarrow Li$	-3.04	(10)

- Requires polar, aprotic, anhydrous solvent
- Must have good solubility for reactants
- THF and Et_2O are proven, stable solvents

Actual reaction using $NaAlH_4$



* Values were obtained using HSC Chemistry 5.11

Approach:

Electrochemical Synthesis of Alane

Possible Reactions When AlH_3 is Generated in a Closed Material Cycle, starting with MAIH_4 dissolved in polar solvents (M= Li, Na, K...)

Anode:

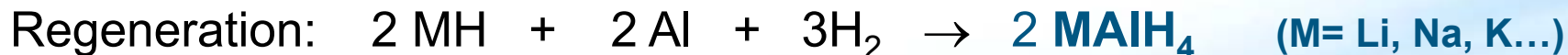
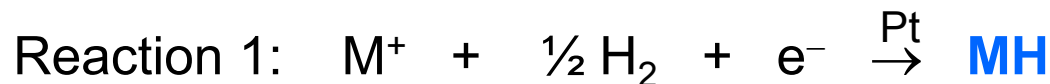


Hydrogen bubbles at the anode

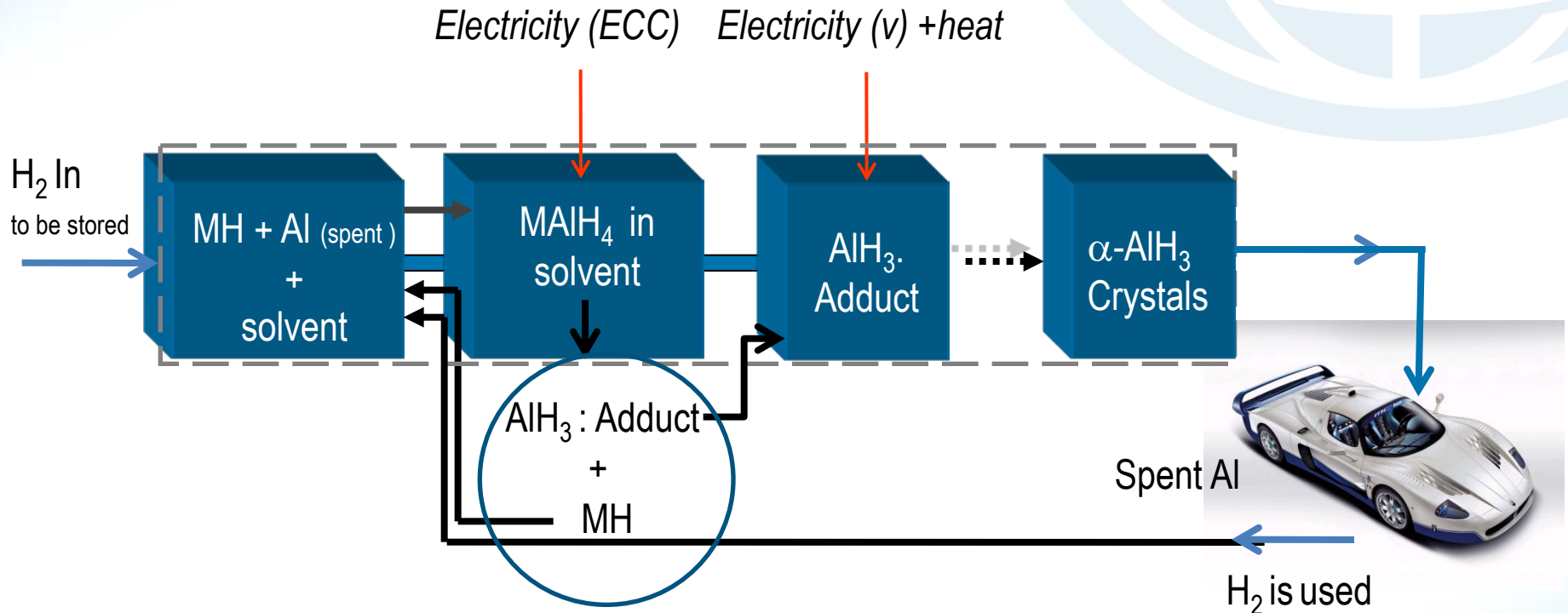


Electrode is expected to dissolve

Cathode:



Approach: Electrochemical Technique for Off Board Regeneration of Alane



M=Na, Li, K..

ECC = Electrochemical Cell
V = Vacuum Pump

Regeneration chart is also used for identifying means to lower cost

Approach : Efficiency and Feasibility of Processes (electrochemical efficiency)

Identifying losses

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

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

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

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

Energy Consumption Relative to Energy Stored

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

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

Efficiency

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

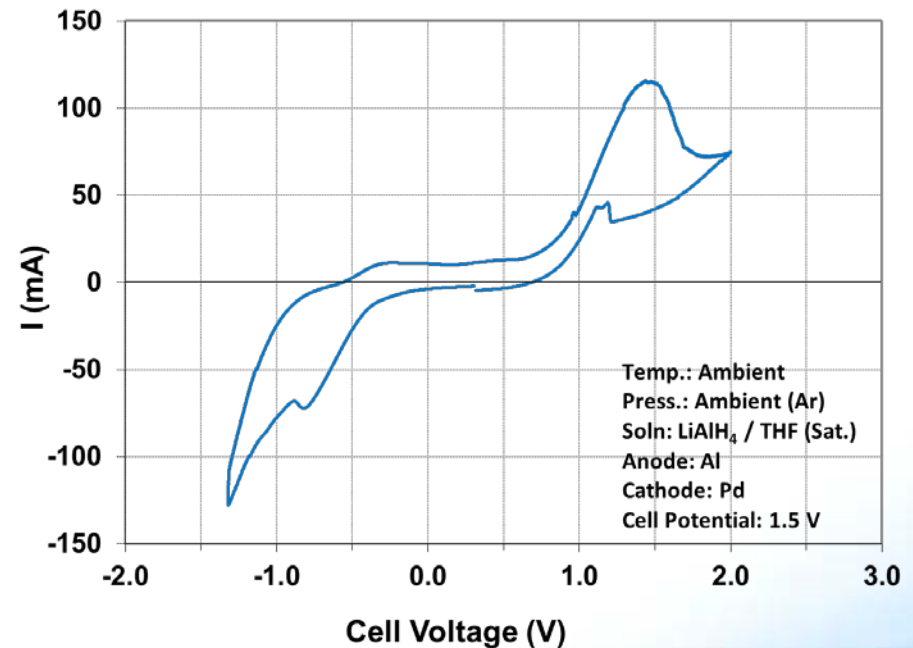
$$\text{Actual} = 68-75\%$$

This efficiency is only the electrochemical efficiency

Technical Progress: Electrochemical Electrolyte Regeneration

More practical route for alane separation from solution

Obtaining solid $\text{AlH}_3 \cdot 2\text{THF}$ *in-Situ*

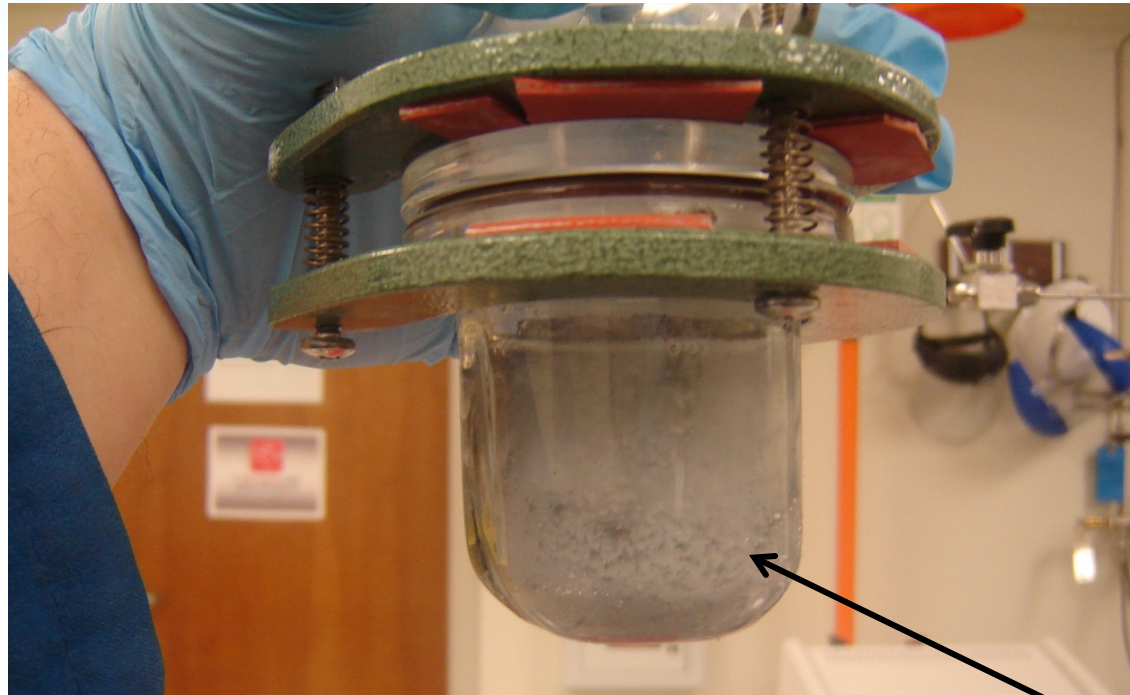


- Glass frit divided cell for alane formation
- Saturated LiAlH_4 / THF solution is viscous

- Saturation gives high currents
- Alane formation starts at low potentials (0.6 V)

Technical Progress: Electrochemical Alane Production using Highly Saturated Electrolyte Solutions

The THF is saturated with LiAlH_4 using a Parr reactor prior to running the electrochemical process.



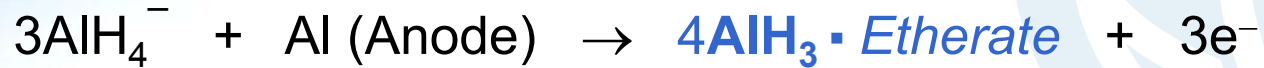
The $\text{AlH}_3 \cdot 2\text{THF}$ precipitates as the entire solution becomes saturated with the electrochemically formed alane.

The resulting solid is easily removed from the solvent by simple filtration.

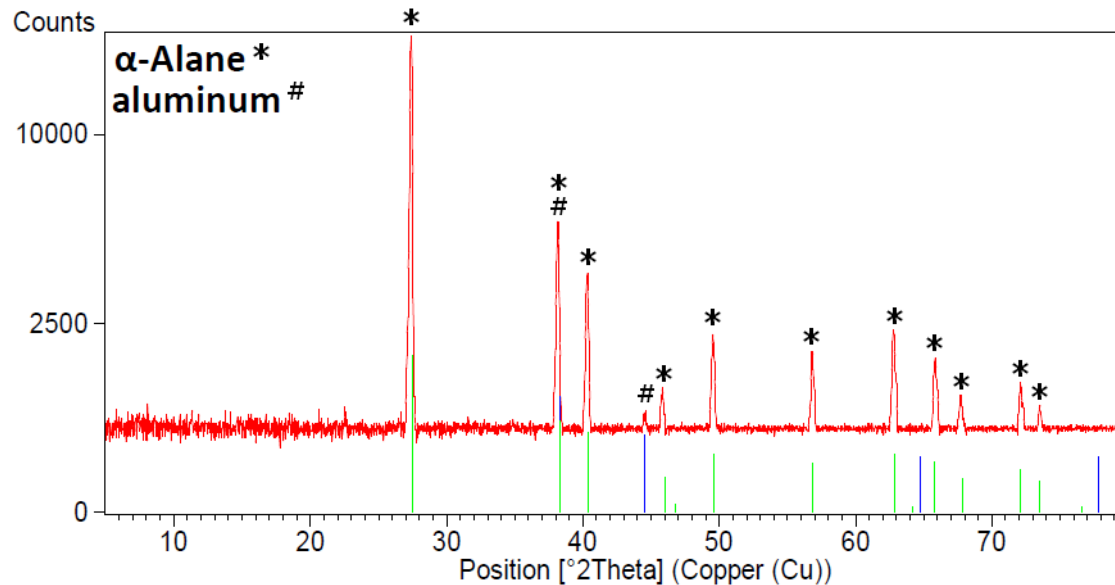
Solid Adduct : $\text{AlH}_3 \cdot 2\text{THF}$

The goal here is to demonstrate the ability to precipitate solid alane adduct from the electrolyte to save cost emanating from the removal of excess solvent

Technical Progress: α -Alane from a Saturated Ether Solution



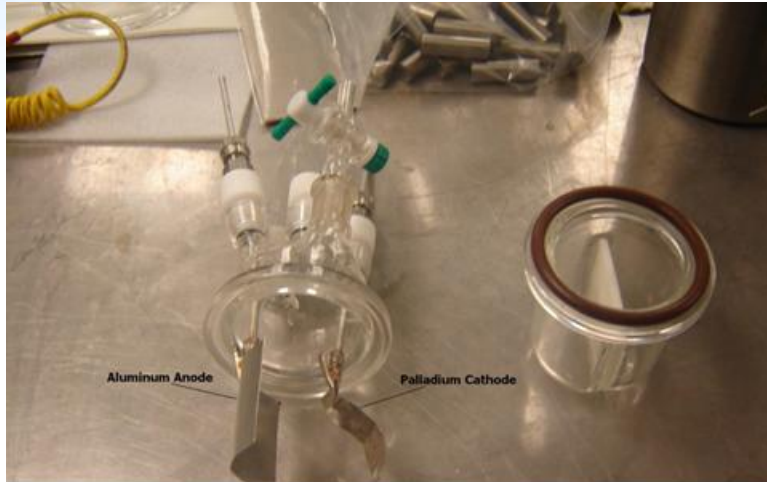
Electrochemical reaction was preformed in saturated ether solution of LiAlH_4



Peak List
Al
Al H3

High purity alane was obtained from alane ether adduct, using saturated solution

Technical Progress: Electrochemical Cell is Redesigned



The traditional electrochemical cell tends to be problematic as dendrites (composed mostly of Li_3AlH_6) grow across the electrodes and short out the cell.

The H-cell did not entirely solve the problem of dendrites



This H-cell prototype still resulted in dendrites reaching across the cell.

Technical Progress: Electrochemical Cell is Redesigned Again



The current cell design is the most promising, using a divider fitted with a Nafion film that effectively separates the cathode side from the anode side of the cell.

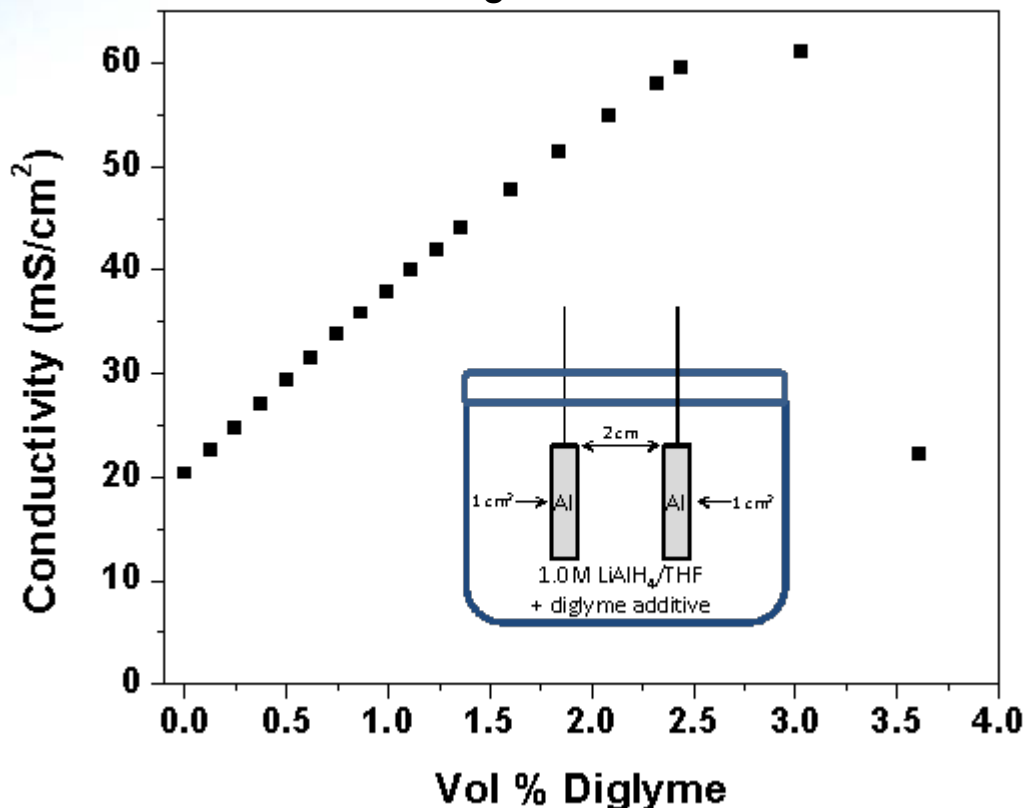
The Nafion® film barrier allows for the use of a variety of solvents on either side of the cell with alane forming on the anode and the remaining lithium ion transported through the Nafion and reduced to metal on the cathode.

Preliminary studies have identified both the presence of alane forming on the anode as well as the formation of lithium metal on the cathode.

The presence of lithium on the cathode confirms that the membrane in the cell is selective, as intended

Technical Progress: Increasing Conductivity of Electrolyte

Previously the conductivity of the electrolyte was doubled, using LiCl resulting in doubling the rate of forming alane.



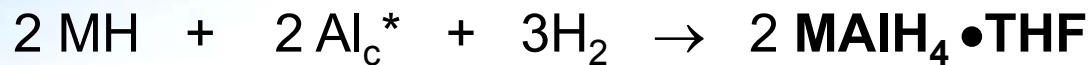
Electrochemical Impedance Spectroscopy was utilized to measure the enhanced conductivity of a 1.0M LiAlH₄ in ether solution with incremental addition of diglyme. The conductivity of the solution increases linearly with the addition of diglyme until ~2.5 vol% diglyme. After this saturation point, the conductivity of the solution begins to plateau and eventually decrease with increasing amount of added diglyme.

Conductivity of electrolyte is now tripled, to result in tripling the rate of producing alane Using inexpensive additive (small amount of diglyme)

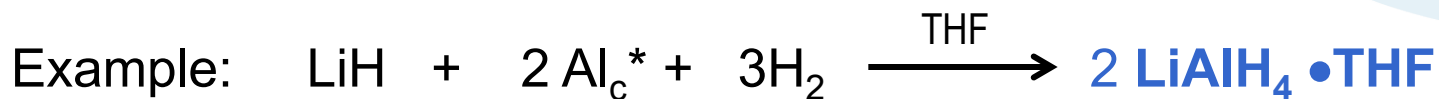
Technical Progress:

Regenerating Electrolyte using Spent Aluminum

Concept of regenerating electrolyte from spent aluminum:



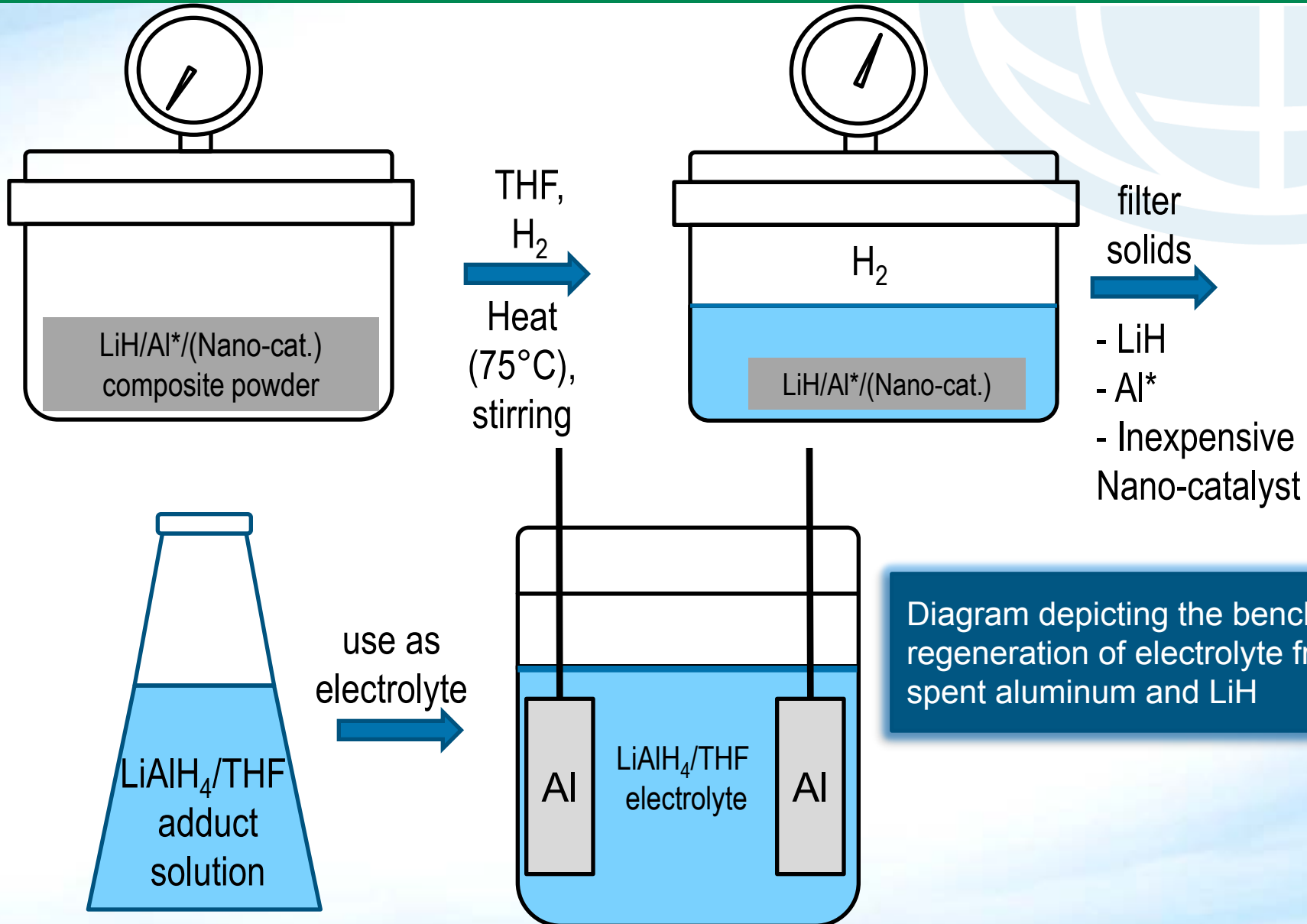
(M= Li, Na, K...) and (Al_c^* = catalyzed and activated Al)



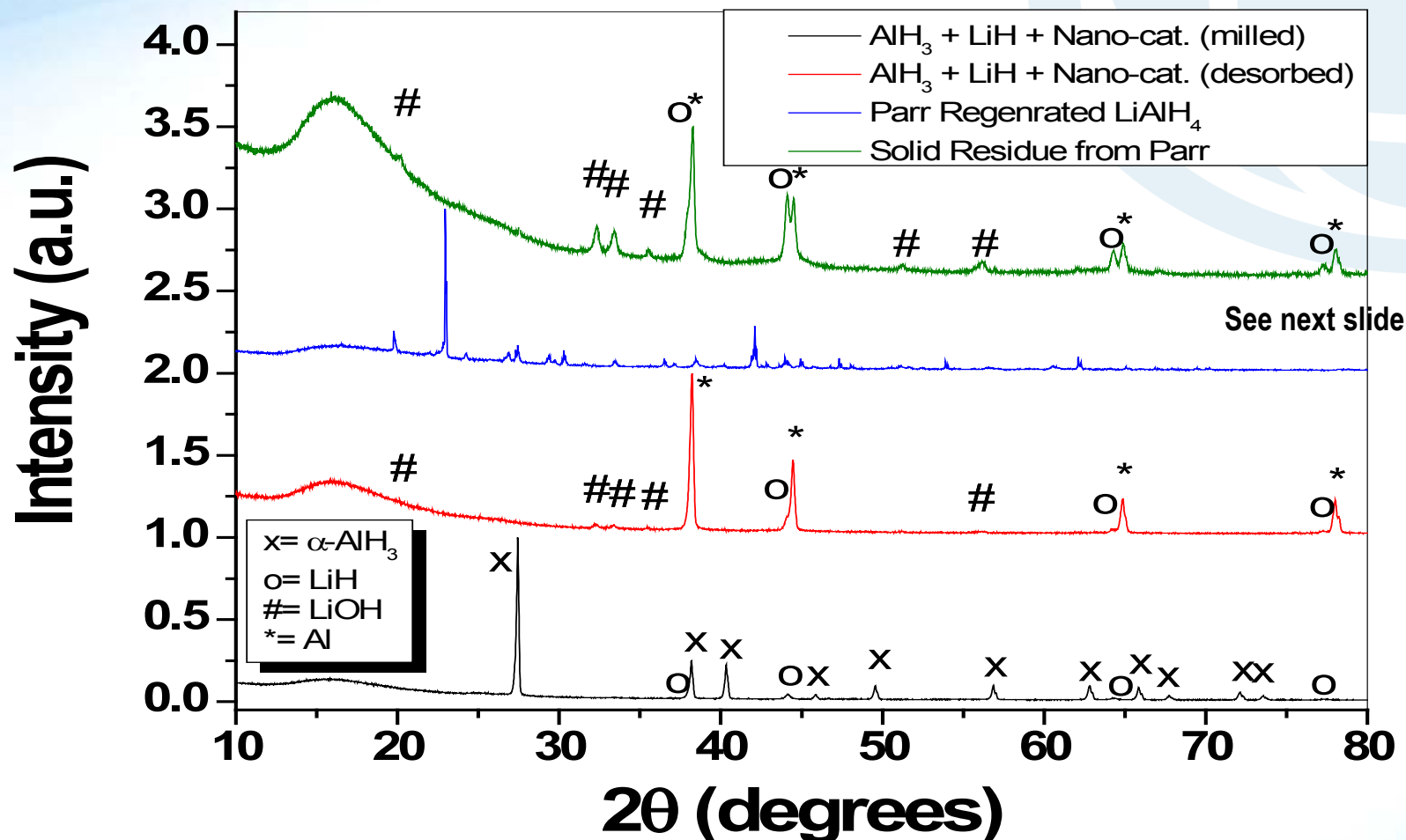
High pressure
Parr-reactor

Electrolyte was regenerated from
spent aluminum

Technical Progress: Process and Quantification of Regenerating Electrolyte



Technical Progress: XRD Analysis of Regenerated LiAlH_4



- In this reaction, LiH was used in excess relative to the amount of Al^*
- The intensity of the Al^* peaks (*) decreases relative to the LiH peaks (o) during the regeneration of LiAlH_4 (see red vs. green pattern) indicating the consumption of Al^* occurred during the reaction

Technical Progress: Yield and Purity of LiAlH_4 Produced

Stoichiometric (Al:LiH)

Nano-Cat.=1.4 wt%

Al*=76 wt%

LiH=22.6 wt%

Yield=20 % LiAlH_4

LiH rich (x3 stoichiometry)

Nano cat. =1.2 wt%

Al*=46 wt%

LiH=52.8 wt%

Yield=35.7 % LiAlH_4

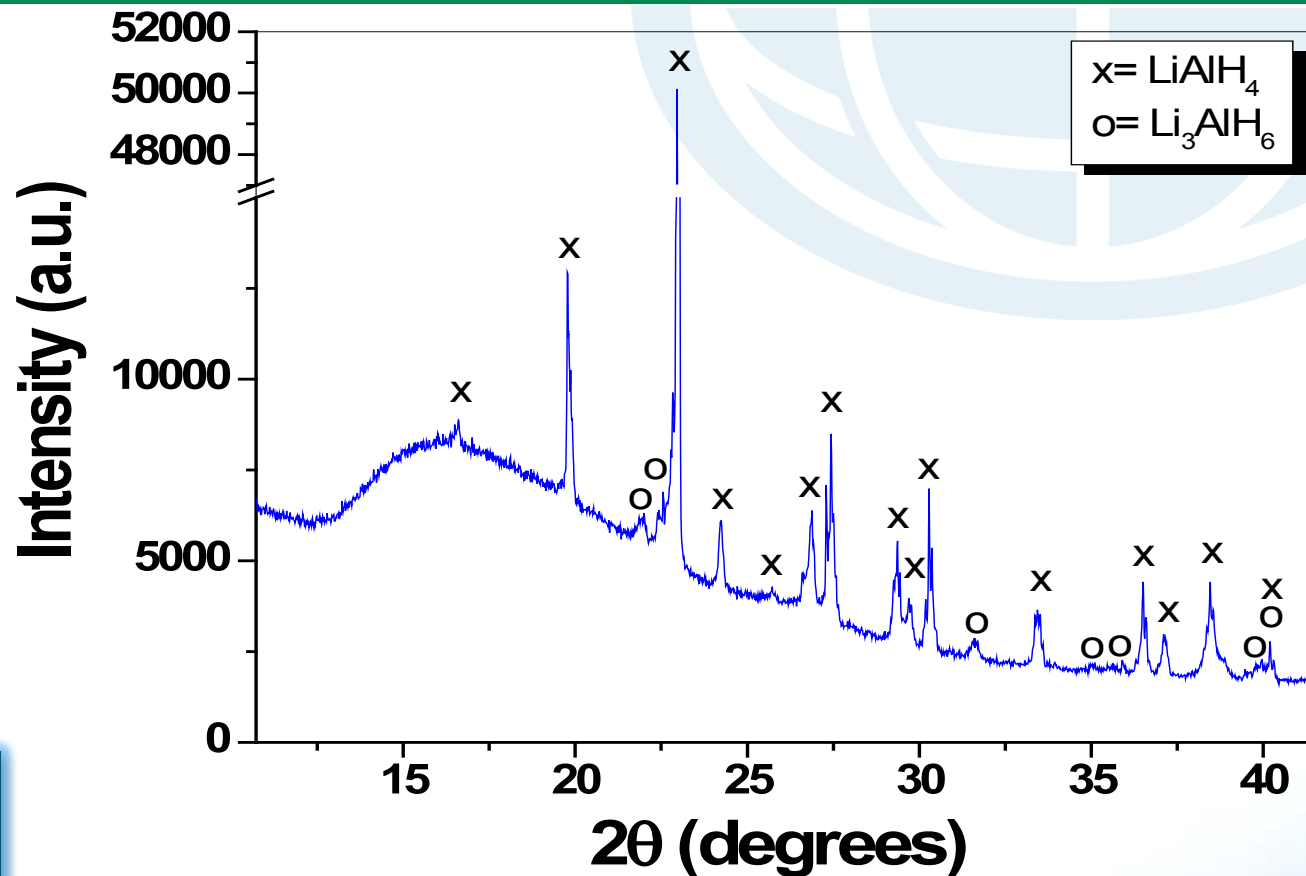
Increased Nano-Cat.

Nano-Cat.=6.3 wt%

Al*=52.3 wt%

LiH=41.4 wt%

Yield=78.5 % LiAlH_4



- The filtered solution contained nearly pure LiAlH_4 based on XRD analysis
- The minor phase in this spectrum is Li_3AlH_6 and is likely formed as a result of the heat and vacuum utilized to remove the THF from the LiAlH_4 -THF adduct

Technical Progress: Percent Yield of Regenerated LiAlH_4

Starting Materials (desorption):

LiH= 1.242g (41.4 wt %)
 $\alpha\text{-AlH}_3$ = 1.56g (52.2%)
 Nano cat.= 0.192 (6.4 wt%)



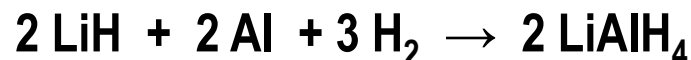
Starting Materials (LiAlH_4 Synthesis):

LiH= 1.242g (x3 stoichiometric ratio)
 Al^* = 1.404g (limiting reagent)
 Nano cat.= 0.192
 THF= 100 mL

Parr Reactor Vessel volume (empty)= 0.257L
 After addition of LiH, Al, Nano cat., and THF = 0.154L

Applied H_2 pressure to vessel w/o stirring at 22°C = 1309 psi
 Applied H_2 pressure to vessel after stirring at 22°C = **1287 psi**

Heat sample to 75°C and soak for 12 hours, then allow Parr vessel to cool to 22°C
 Final pressure =**1146 psi (141 psi/9.72 bar H_2 consumed)**



$$PV=nRT$$

$$9.72 \text{ bar H}_2(0.154\text{L}) = n (0.08314 \text{ bar L mol}^{-1}\text{K}^{-1})(295\text{K})$$

$$1.497=n(24.526)$$

$$n=0.061 \text{ mol H}_2$$

$$0.061 \text{ mol H}_2 \times \frac{2 \text{ mol LiAlH}_4}{3 \text{ mol H}_2} = 0.0407 \text{ mol LiAlH}_4 \times \frac{37.95\text{g LiAlH}_4}{1 \text{ mol H}_2} = 1.54\text{g LiAlH}_4 \text{ produced}$$

(recovered 1.4g solid from THF)

Al^ is the limiting reagent in the reaction (calculate % yield based on Al^*):*

$$1.4\text{g Al}^* \times \frac{1 \text{ mol Al}}{27\text{g}} = 0.0518\text{mol Al} \longrightarrow 0.0518\text{mol LiAlH}_4 \text{ (theoretical)}$$

$$\frac{0.0407 \text{ mol LiAlH}_4 \text{ (actual)}}{0.0518\text{mol LiAlH}_4 \text{ (theoretical)}} = 78.5\% \text{ yield of LiAlH}_4 \text{ based on Al}^* \text{ as limiting reagent}$$

Proposed Future Work

Start working with industry through CRADA, which has been signed

➤ *Develop In-situ Recycling Methods*

- Characterize electrodes for making LiH (use different materials electrode)
- Develop cell designs that allow for increased LiH production efficiency (use membranes)
- Understand the role of the solvents and the used precursors to promote selectivity and yield
- Optimize condition to increase the yield

➤ *Improve Electrochemical Cell Design*

- Investigate the selectivity offered by the use of the Nafion® divided H-cell
- Identify solvent combinations to provide optimal conductivity of solutions
- Characterize the resulting material developed at both anode and cathode reactions

➤ *Advanced Alane Separation and Analytical Procedures*

- Develop advance adduct systems to facilitate the crystallization of AlH_3 in DME
- Use saturated solution methods with DME
- Utilize electrochemistry to produce AlH_3 in DME and detail the electrochemical potentials
- Demonstrate DME separation process and analyze the crystallized alane product

Project Summary

Relevance

- 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 $\sim 60^\circ\text{C}$ to 175°C has potential to meet the 2015 DOE onboard system desorption targets.
- Starting material (aluminum) is relatively inexpensive
- Safer to handle in air and moisture than complex hydrides and many other high capacity hydrides
- Safety technology is well developed and understood

Approach

- Utilize electrolytic potential, E , to drive chemical reactions to form AlH_3 , based on Gibbs free energy relation to applied potential
- Non-Aqueous electrolytes need to be identified to use in the Electrochemical Cell
- The electrolysis is carried out in an electrochemically stable, aprotic, and polar solvent such as THF or ether. MAlH_4 ($M = \text{Li}, \text{Na}$) is dissolved in this solvent,
- Adducts such as $\text{AlH}_3 \cdot n\text{THF}$ or $\text{AlH}_3 \cdot \text{ETO}_2$ are expected to form and alane is separated from the adducts
- Efficiency is an important issue and lowering cost is the number one priority

Project Summary (cont.)

Technical Accomplishments and Progress (as of 3/16)

- Continued to produce gram quantities of alane with high purity
- LiAlH_4 was also used to produce alane in a saturated solution
- A new inexpensive additive was tried and found to greatly enhance the process
- Continuing to Improving efficiencies in every step of the regeneration method and achieved success
 - Yield was increased and higher conductivity was achieved leading to higher electrochemical cell (ECC) efficiency
 - Demonstrated the formation and precipitation of alane.THF *in-situ* during electrochemical process
 - Continue using pressurized ECC to achieve in-situ regeneration cycle and achieve a more efficient separation of products

➤ **CRADA has been signed with industry to work on commercializing the process**

Proposed Future Work

- Start working with industry through CRADA
- Continue work to increase yield and efficiency
- Electrochemical Process Optimization
- Advanced Alane Separation and Analytical Procedures
- Scale Up a closed cycle

END of Slides

Ragaiy Zidan

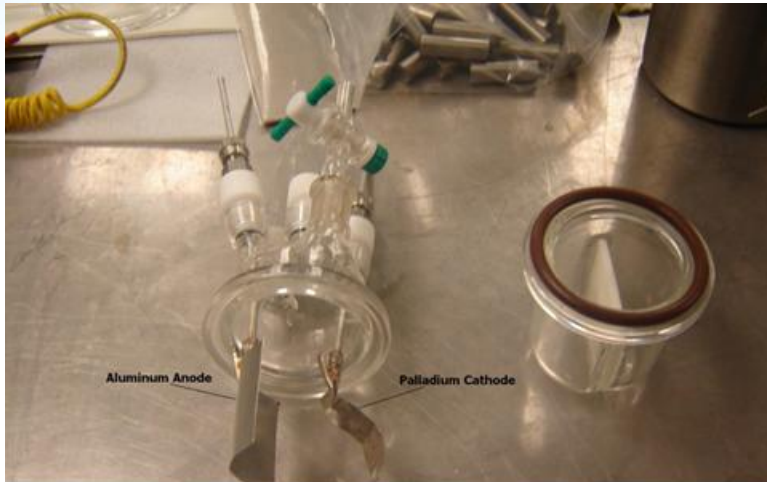
999-2W

Clean Energy Directorate

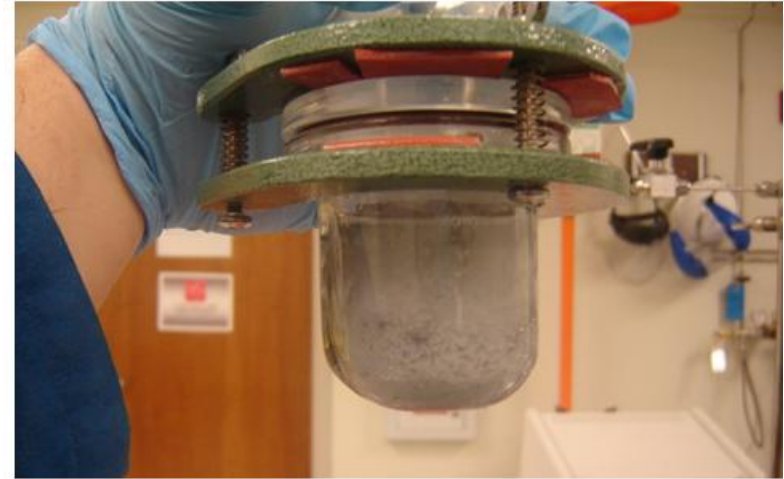
Savannah River National Laboratory

Extra Slides

Electrochemical alane production is optimized through the use of highly saturated electrolyte solutions



THF is saturated LiAlH_4 using a Parr reactor under moderate heat and hydrogen pressure.



The AlH_3 -2THF precipitates as the entire solution becomes saturated with the electrochemically formed alane.