Electrochemical Reversible Formation of Alane

Ragaiy Zidan

Energy Security Directorate

Savannah River National Laboratory

2011 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES PROGRAM ANNUAL MERIT REVIEW and PEER EVALUATION MEETING

TEAM

Dr. Michael Martínez-Rodríguez	*(Electrochemistry)*
Dr. Brenda García-Díaz	*(Electrochemistry)*
Dr. Long Dinh	*(Chemical Synthesis and Catalysis)*
Dr. Robert Lascola	*(Raman Spectroscopy)*
Dr. Douglas Knight	*(Chemical Synthesis and X-ray analysis)*
Dr. Joseph Teprovich	*(Organic Chemistry and Nano Technology)*

Overview

Timeline

Start: 10/1/06

End: Continuing

Percent complete of activities proposed for FY11: 50 %

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

Budget

- Funding received in FY10
  - $375K
- Funding for FY11
  - $150K

Partners

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

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.

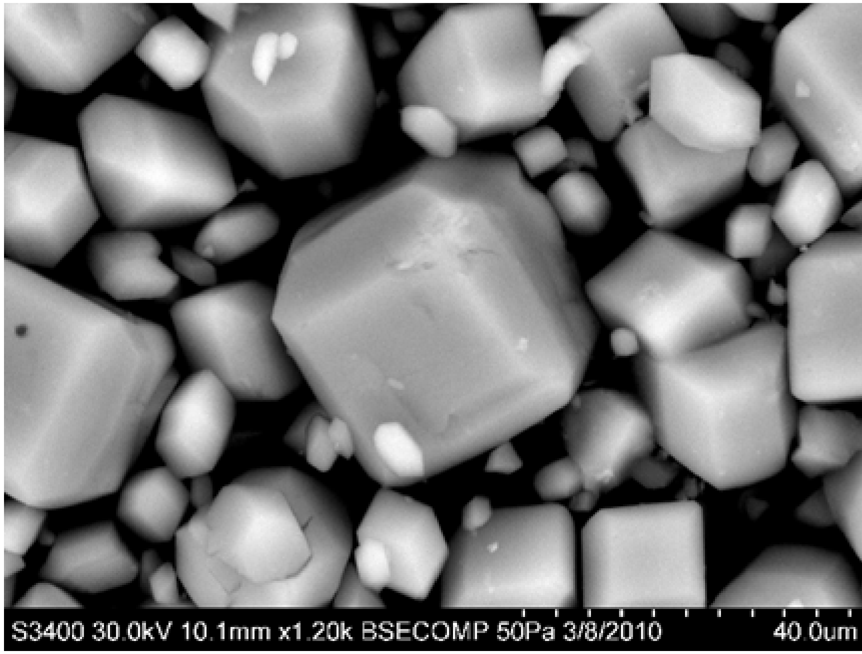
Aluminum hydride (Alane - AlH_3), having a gravimetric capacity of 10 wt% and volumetric capacity of 149 g/L H_2 and a desorption temperature of ~60°C to 175°C (depending on particle size and the addition of catalysts) has potential to meet the 2015 DOE onboard system desorption targets

Specific Objectives

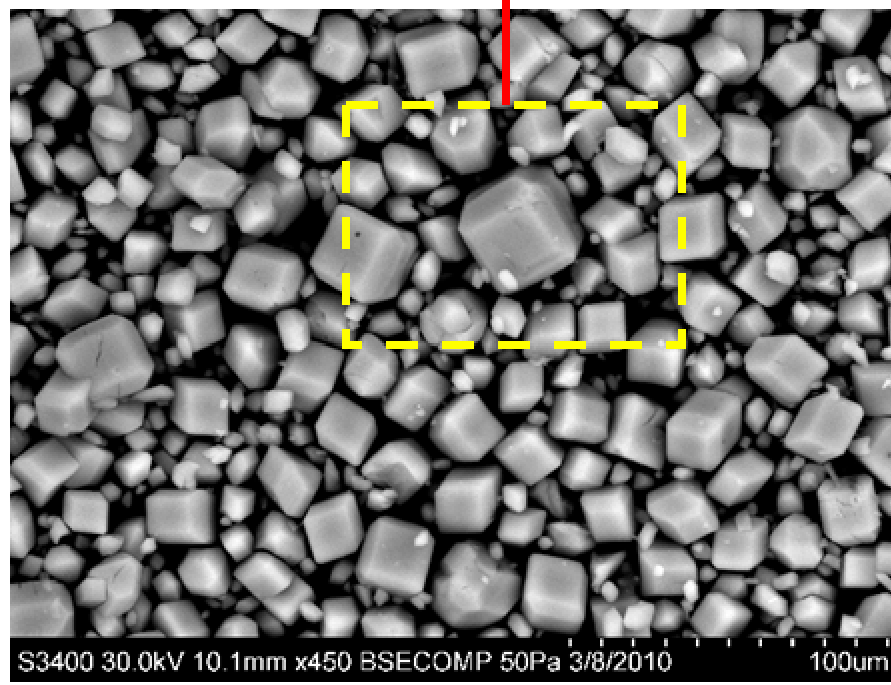
- Avoid the impractical high pressure needed to form AlH_3
- Avoid chemical reaction route of AlH_3 that leads to the formation of alkali halide salts such as LiCl or NaCl
- Utilize electrolytic potential to translate chemical potential into electrochemical potential and drive chemical reactions to form 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 mm

Approach: Known Methods to Produce Alane

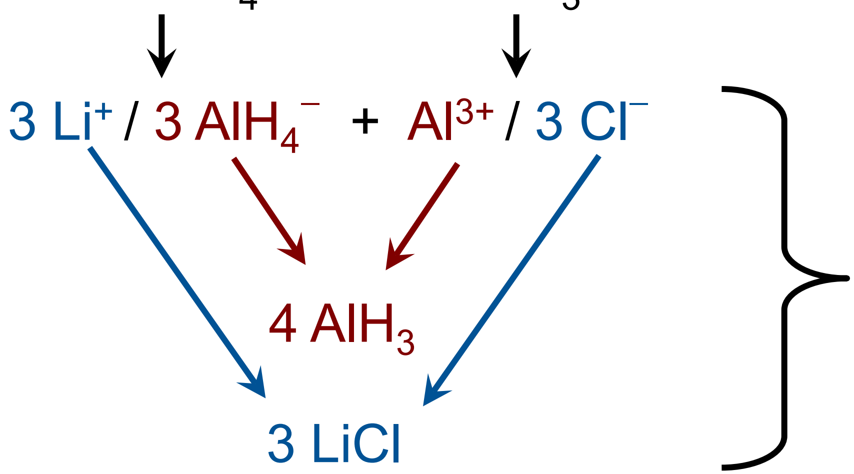
A) Formation of alane from the elements:

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

B) Traditional chemical method to produce alane:

Thermodynamic sink

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



Develop a method to avoid the formation of halides.

~~LiCl~~

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

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

Concern: Al and AlH_3 will be oxidized in aqueous environment. This requires using non-aqueous approaches.
We use Non-Aqueous electrolytes in Electrochemical Cell.

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.[1,2]

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

Approach: Previous Attempts and Acknowledgement

We acknowledge attempts made in the past to make alane electrochemically[3,4]. However, none of these attempts have reported 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.

It should be noted that we synthesize alane adducts electrochemically and crystallize α-alane from the adducts.

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

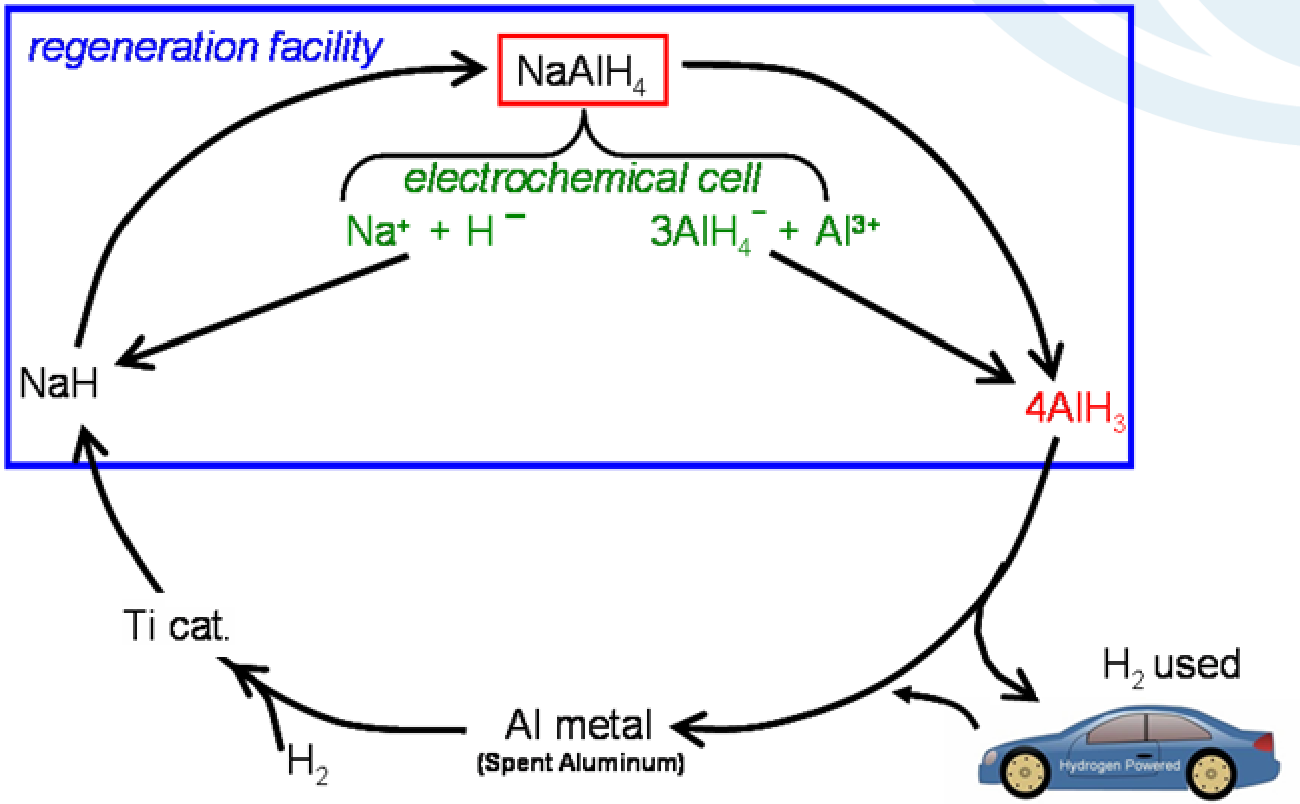
3- H. Clasen, Ger. Pat., 1141 623, 1962.

4- N. M. Alpatova, T. N. Dymova, Y. M. Kessler and O. R. Osipov, *Russ. Chem. Rev.*, 1968, 37, 99–114.

Approach: Alane Generation Reversible Cycle

Non-Aqueous Solution Electrochemical System

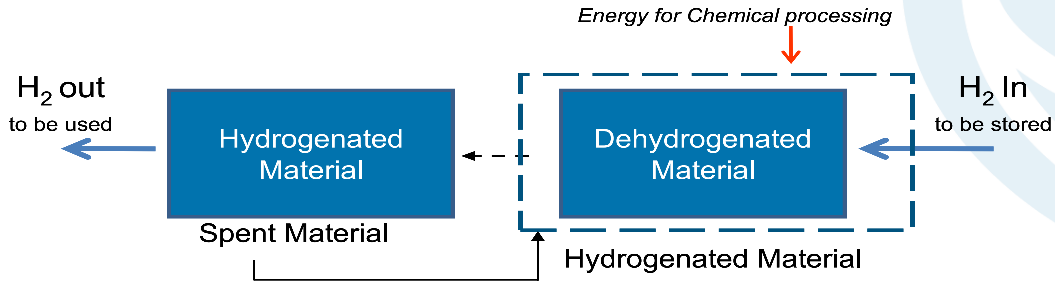
($NaAlH_4$, $KAlH_4$ or $LiAlH_4$)/THF or Ether

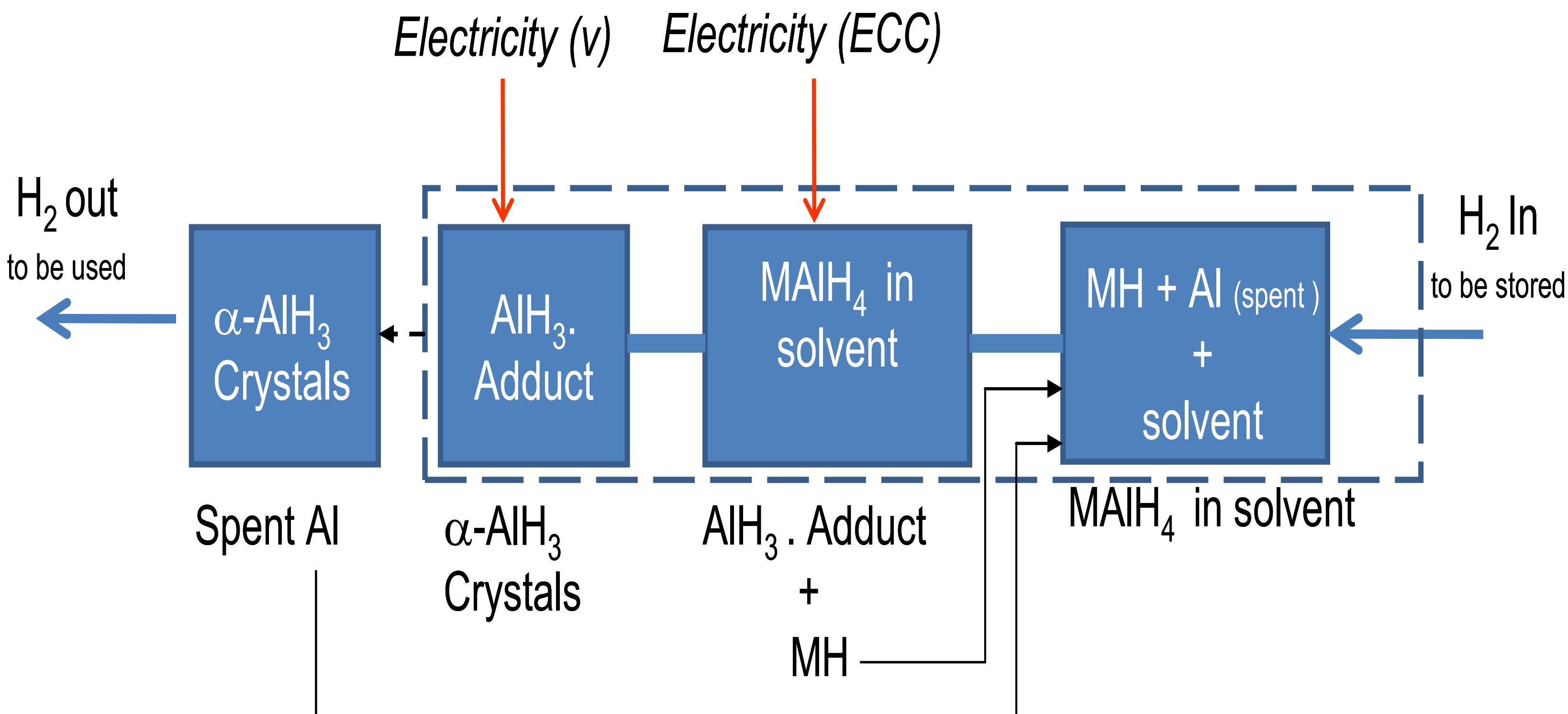


Reversible cycle for alane. All components of the electrochemical process can be recycled to continually afford a viable solid-state storage material.

Approach: Electrochemical Technique for Off Board Regeneration of Alane

Off Board Regeneration





ECC = Electrochemical Cell
V = Vacuum Pump

M=Na, Li,..

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

Electrode is expected to dissolve

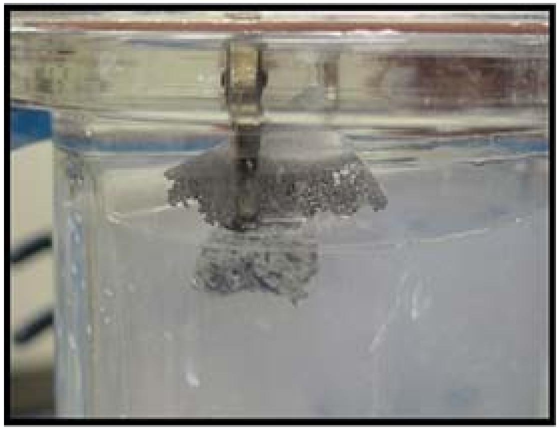
Cathode:

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

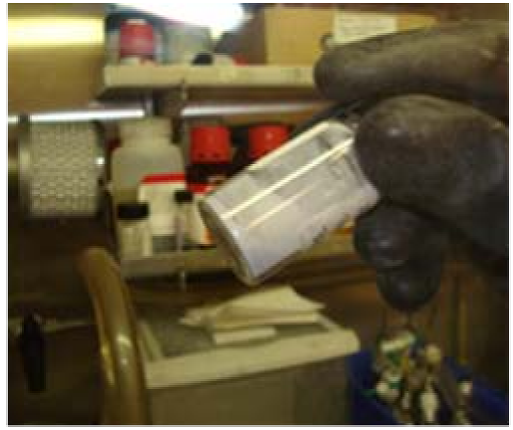
Reaction 2: $M^+ + PdH\ (\text{Cathode}) + e^- \rightarrow \mathbf{MH} + Pd$

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

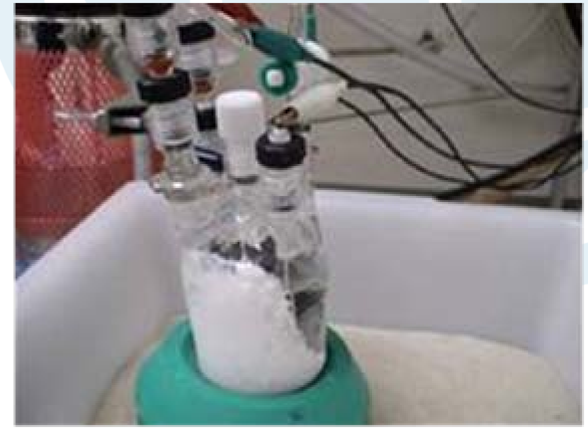
Accomplishments: Electrochemically Generated AlH_3



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



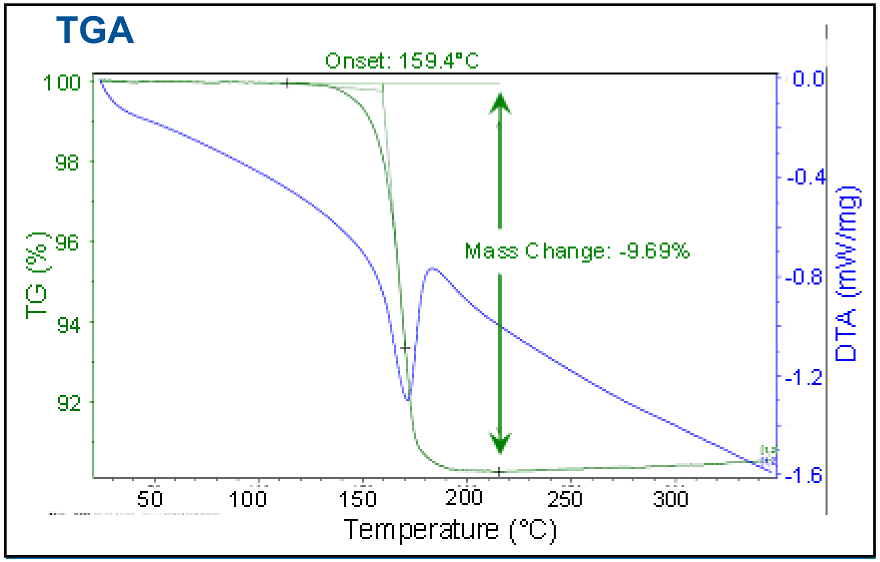
Two grams of AlH_3 electrochemically generated.

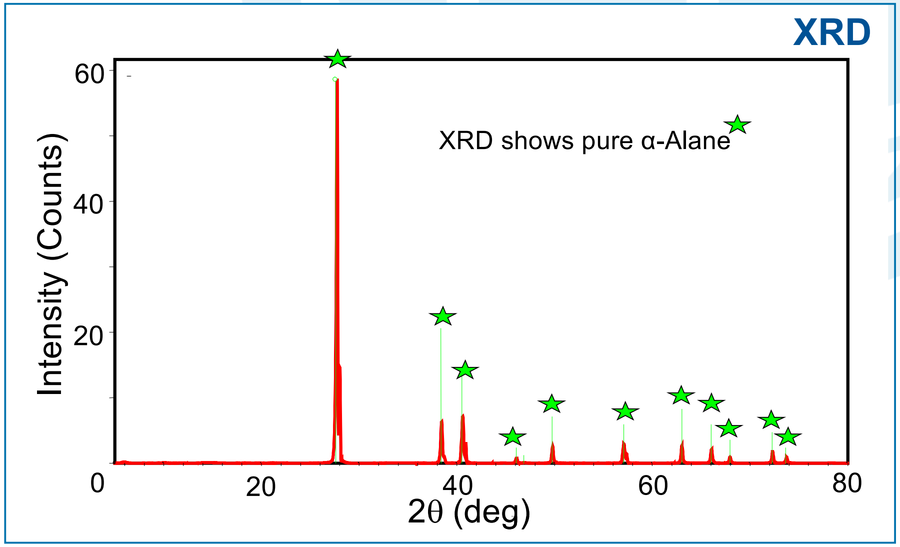


Electrochemically generated AlH_3-TEDA

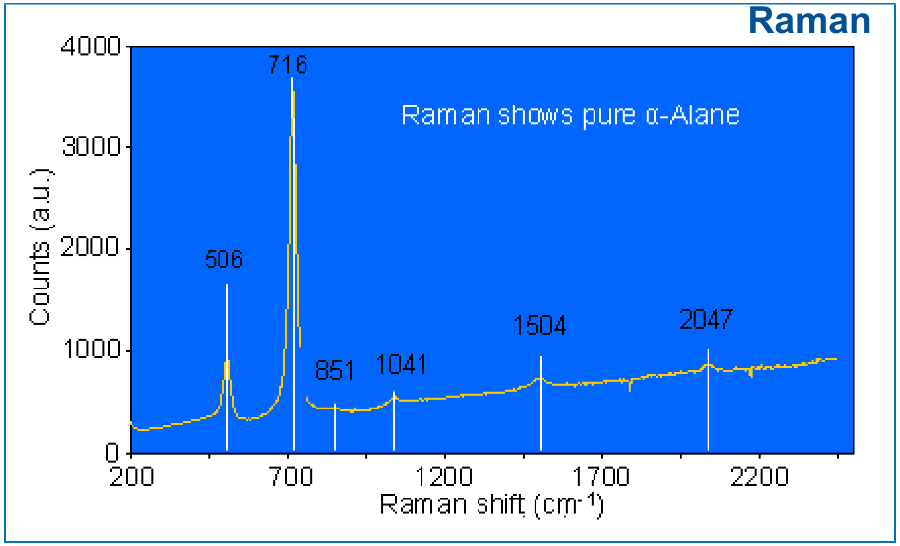
Results show that our approach has been successful in producing alane. Additionally, the formation of high purity alane adducts was made possible using our electrochemical methods.

Accomplishments: Past Results on Electrochemically Generated AlH_3





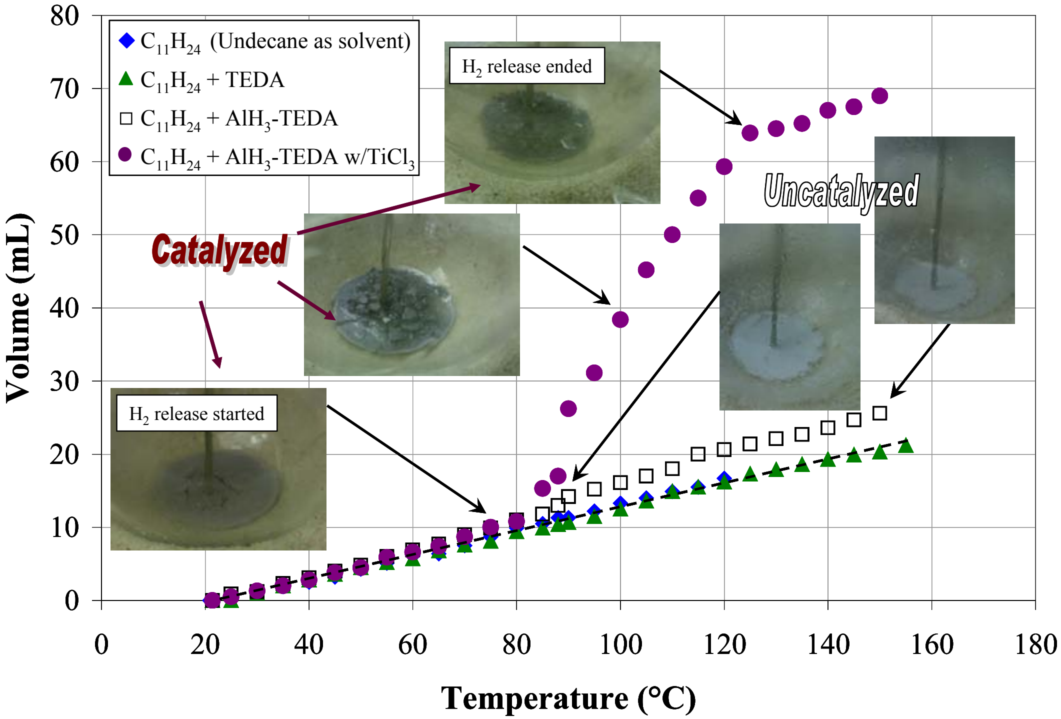
TGA decomposition of electrochemically generated alane releases almost full H_2 capacity expected in AlH_3.



TGA, XRD, Raman confirm the product is high purity AlH_3, alane.

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

Accomplishments: Electrochemically Formed AlH_3-TEDA



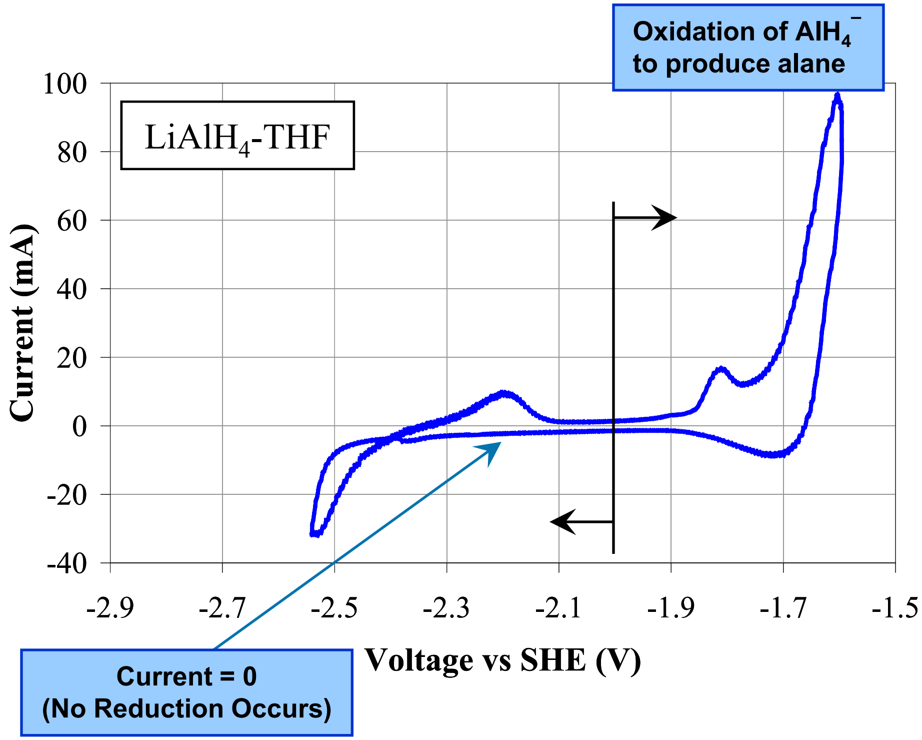
AlH_3-TEDA release H_2 easily when catalyzed

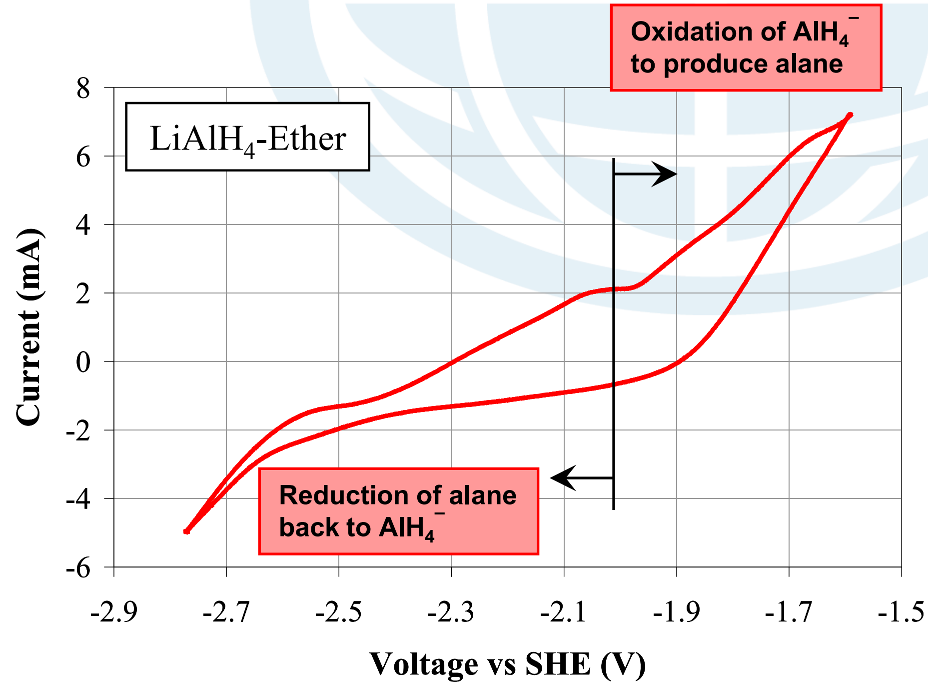
TEDA (triethylenediamine) is known to complex with AlH_3, appearance of precipitate signals alane formation.

Electrochemical Cell Generating AlH_3 - TEDA

This material is reversible and can be used for Near Term Applications, (e. g. stationary H_2 storage systems). Less costly. Other Adducts need to be investagted

Accomplishment: AlH_3▪nTHF Adduct versus AlH_3▪$n$$Et_2O$ Adduct





Formation of a strong bonded AlH_3▪nTHF adduct

Weaker AlH_3▪nEt2O adduct releases the alane to form AlH_4^-

$AlH_4^- \rightarrow$ **AlH_3▪nTHF** + ½ H_2↑ + e^-

$E^o \approx -2$ V

$AlH_4^- \leftrightarrow$ **AlH_3▪$n$$Et_2O$** + ½ H_2↑ + e^-

$3AlH_4^-$ + Al (Anode) $\rightarrow$ **4AlH_3▪nTHF** + $3e^-$

$E^o \approx -1.9$ V

$3AlH_4^-$ + Al (Anode) $\leftrightarrow$ **4AlH_3▪$n$$Et_2O$** + $3e^-$

Accomplishments: Efficiency and Feasibility of Processes

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Identifying losses

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

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

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

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

68% is based on overpotential value

Energy Consumption Relative to Energy Stored

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

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

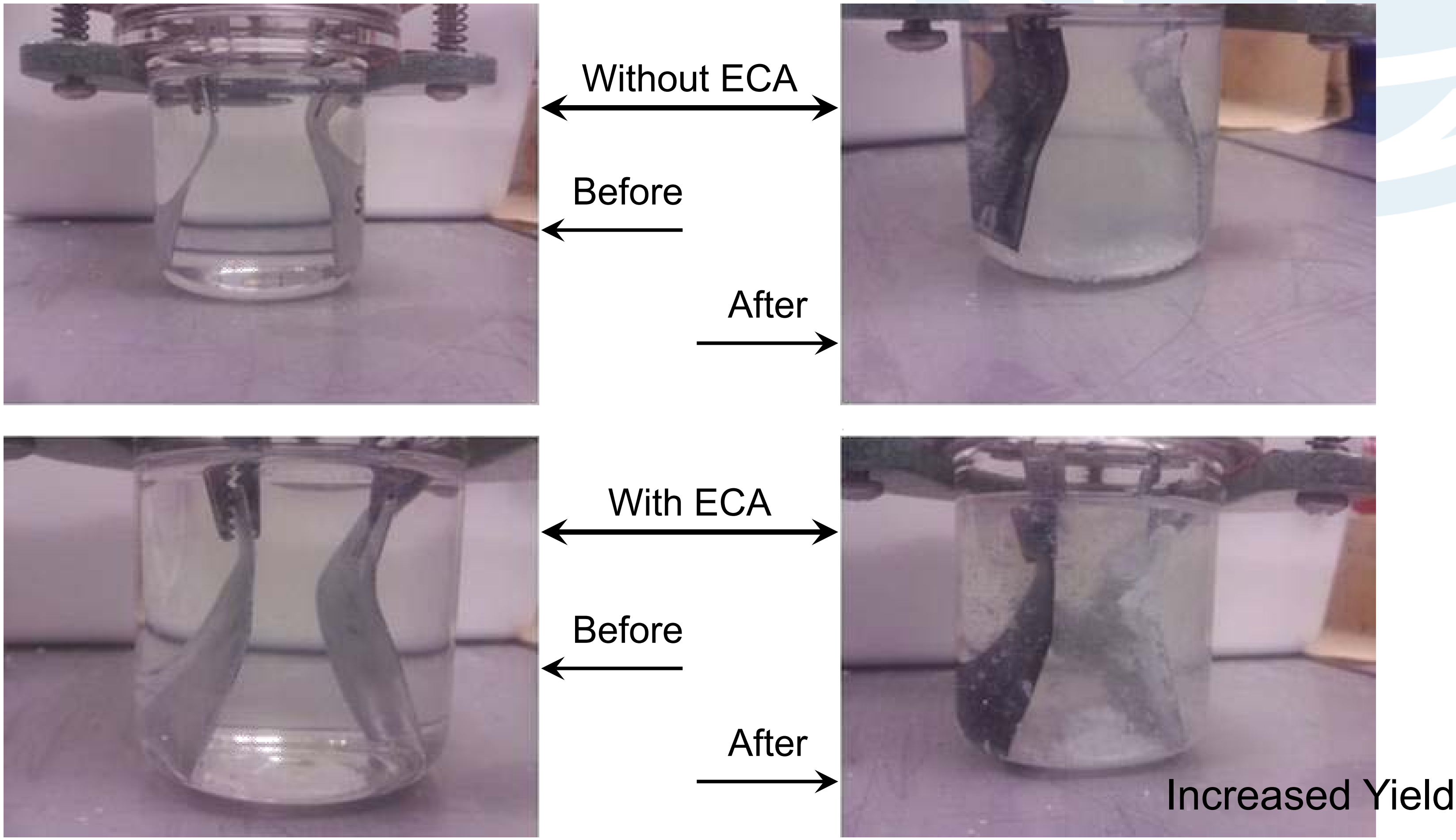
Efficiency

Ideal = 83%

Actual = 68- 75%

Accomplishments: Electro-Catalytic Additive (ECA) to Increase Yield

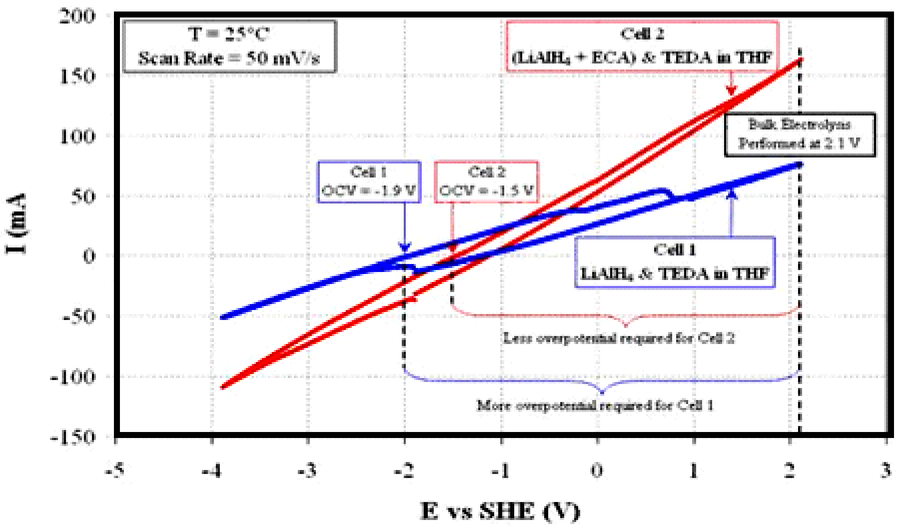
Visual Observation of Higher Yield



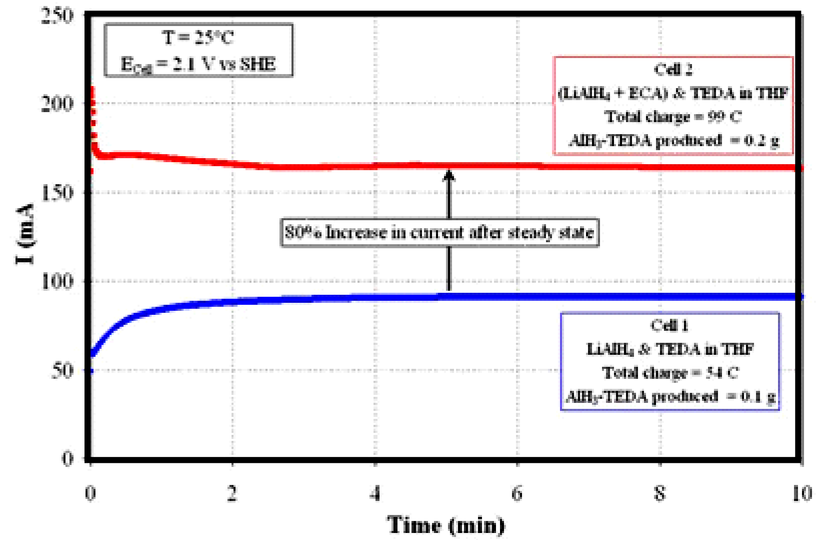
Electrochemical cells producing AlH_3 with and without ECA. Also very small amount of dendrites.

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

Accomplishments: 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 <u>more efficient</u> because it has more current with less voltage input.



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% <u>increase in current</u> was observed after the current is steady.

Based on Tafel equation $\frac{\Delta V_{ECA}}{\Delta V_w} = \ln 2$, ΔV : overpotential

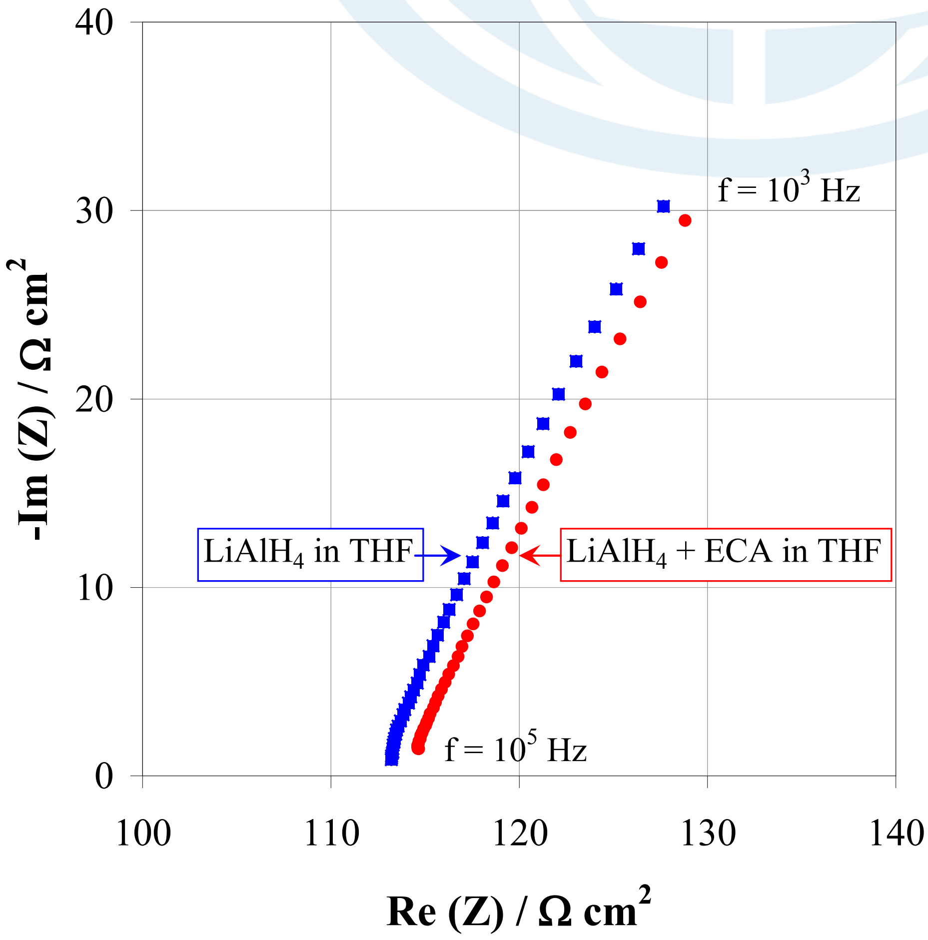
Consistent with measurements

Without ECA 75% With ECA 78%

ECA improves cell efficiency ECA and increased current and alane yield

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

Accomplishments: Reactions at the Anode with ECA- LiCl

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Realizing that Lithium Chloride dissolves in THF:

$LiCl / THF \leftrightarrow Li^{+} / Cl^{-} / THF$

<u>Suggested mechanism, however further investigation is planed:</u>

$$3LiAlH_4 + Al \rightarrow 4AlH_3 + 3Li^{+} + 3e^{-} \qquad E^0 = -1.89\ V$$

$$3LiCl + Al/(AlH_4) \rightarrow AlCl_3 + 3Li^{+} + 3e^{-} \qquad E^0 = 1.23\ V$$

$$+$$

$$3LiAlH_4 \rightarrow 4AlH_3 + 3LiCl$$

Patent Pending

Accomplishments: Electrochemical Synthesis, using DME for Higher Efficiency

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$LiAlH_4$ /DME (ECC)

Minimizing the use vacuum pump

Anode:

Reaction 1: $AlH_4^- \rightarrow$ **$AlH_3 \cdot$ *DME*** $+ \frac{1}{2} H_2\uparrow + e^-$

Reaction 2: $3AlH_4^- + Al\ (Anode) \rightarrow$ **$4AlH_3 \cdot$ *DME*** $+ 3e^-$

$$AlH_3 \cdot DME \xrightarrow{\text{Lower Pressure}} \alpha\text{-}AlH_3 + DME\uparrow$$

Cathode:

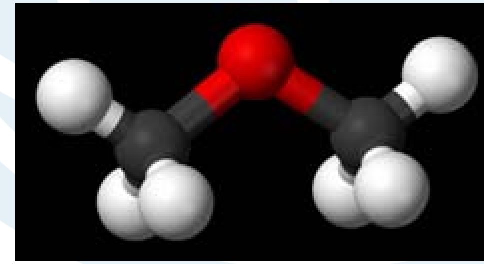
Reaction 1: $Li^+ + \frac{1}{2} H_2 + e^- \xrightarrow{Pt} LiH$

Reaction 2: $Li^+ + PdH\ (Cathode) + e^- \rightarrow LiH + Pd$

Regeneration: $2\,LiH + 2\,Al + 3H_2 \rightarrow$ **$2\,LiAlH_4$**

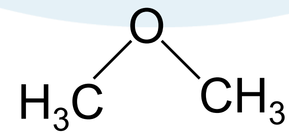
Accomplishments: Synthesis of Alane in DME

Dimethyl ether (DME) is the simplest ether and is a low-temperature solvent with boiling point of −23 °C. The same property facilitates its removal from reaction mixtures.



Simulating Separation:

Forming Alane-Dimethyl ether (DME) Adduct



Chemical method to produce Alane-Dimethyl ether:

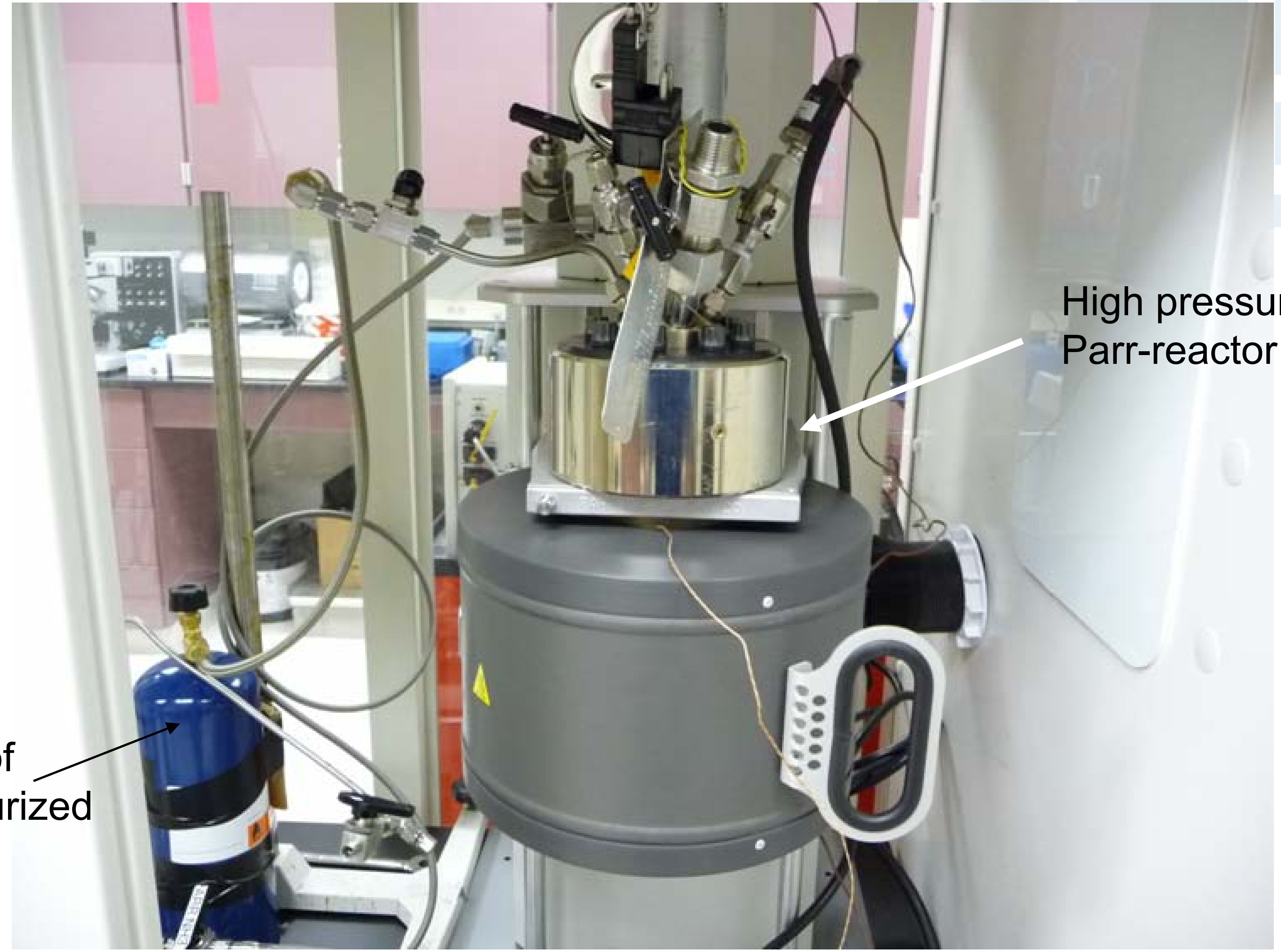
$$3\ LiAlH_4 + AlCl_3 \xrightarrow{\text{Liquid-DME}} 4\ AlH_3.nDME + 3\ LiCl$$

$AlH_3.nDME$ } α-Alane was obtained

Heating for few minutes

Innovative method to avoid costly alane crystallization

Accomplishments: Higher Efficiency AlH_3 Separation processes, using DME

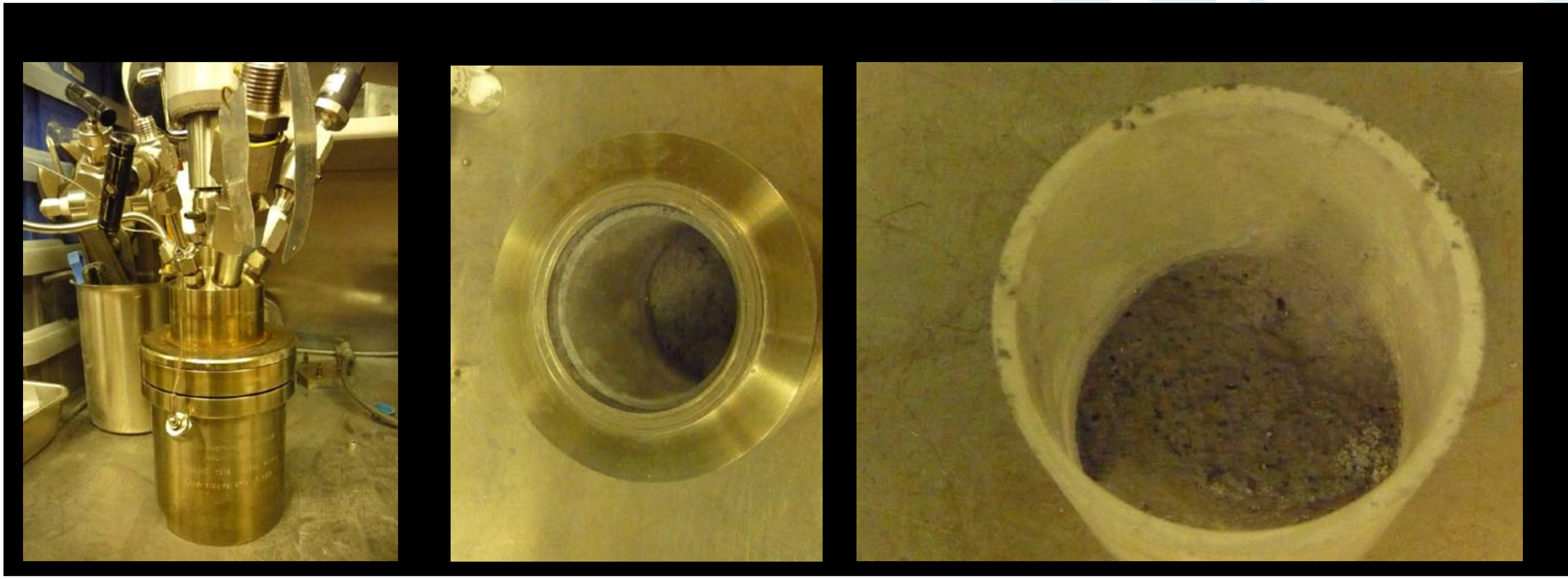


Tank of pressurized DME

High pressure Parr-reactor

Accomplishments: AlH_3 Separation using DME

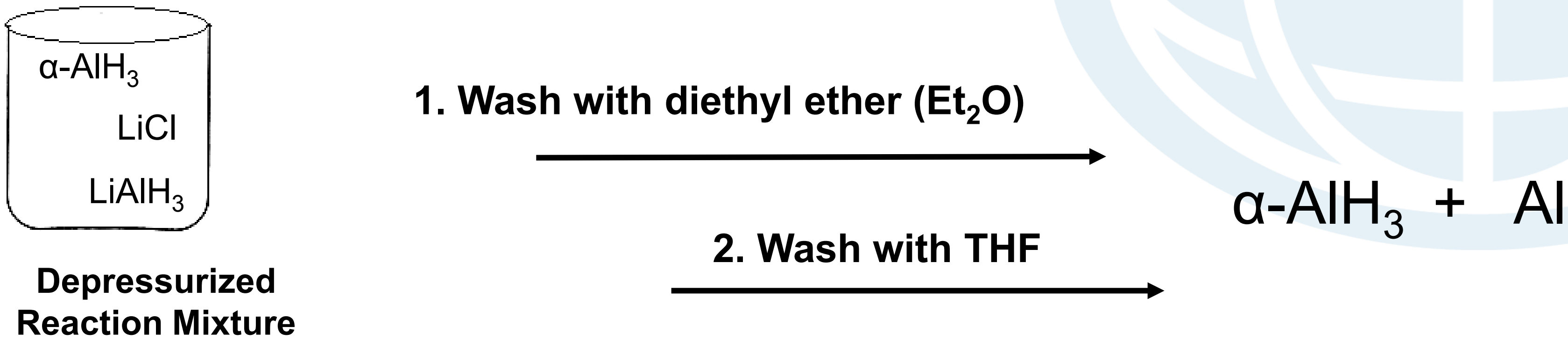
Reaction Processes and Recovered Material

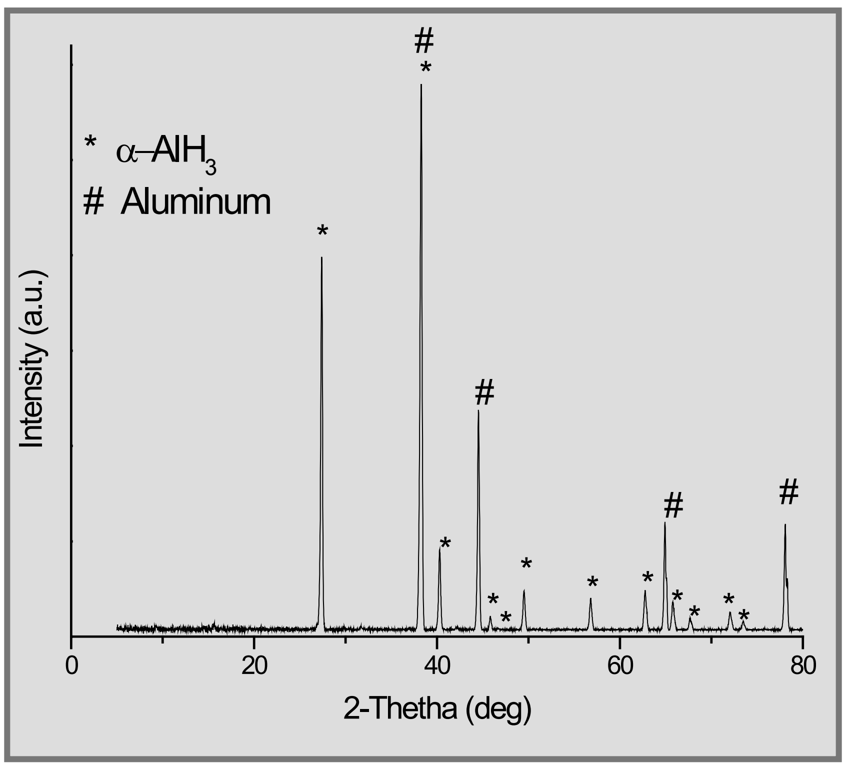


Reaction in High Pressure Parr Reactor

Depressurized After the Reaction

Accomplishments: Separation of Alpha Alane



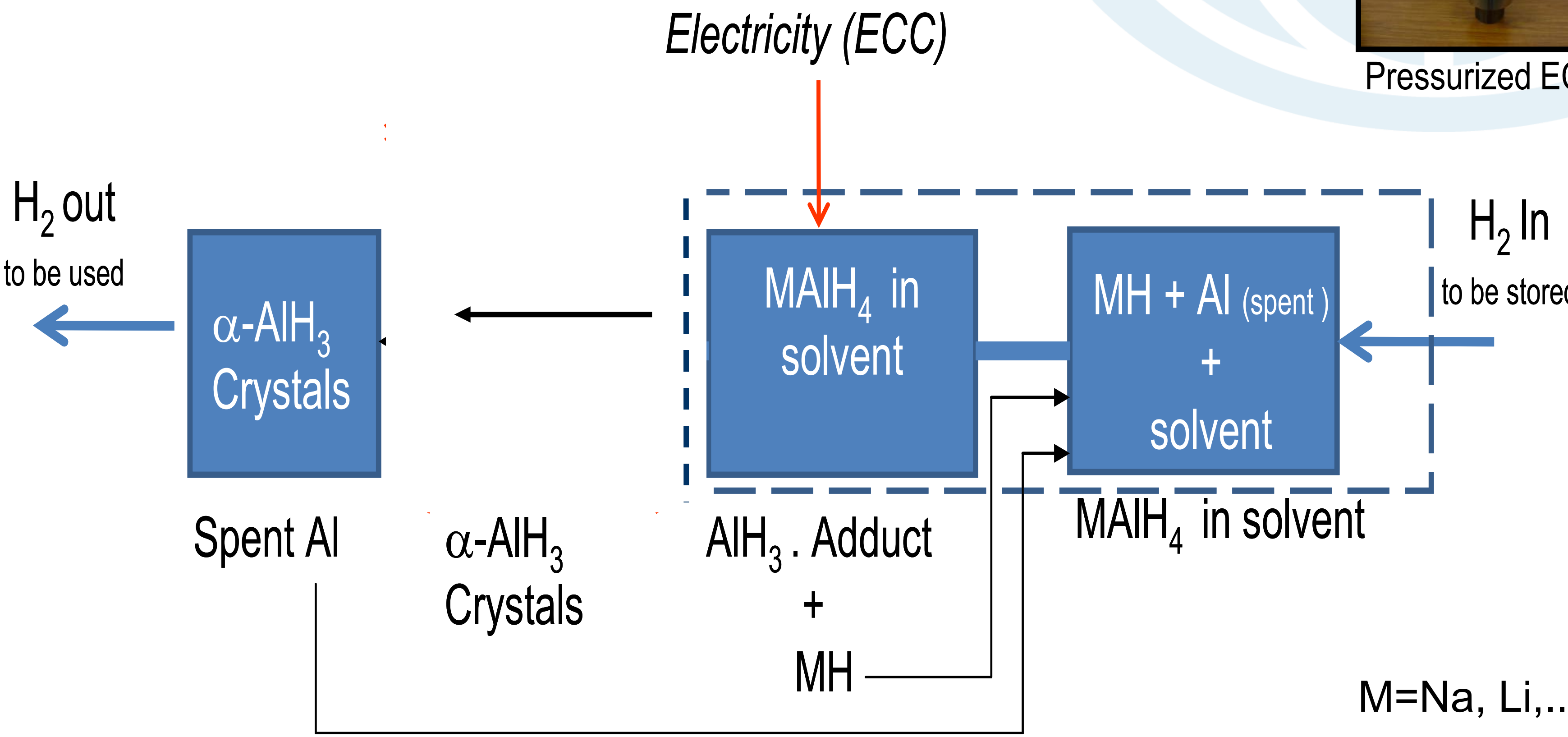


- LiCl and excess $LiAlH_4$ was easily washed
- Only minimal evacuation is required during the washing process (few minutes)
- $[AlH_3{*}nL]$ adducts were not observed ($L = CH_3OCH_3$, $CH_3CH_2OCH_2CH_3$, THF)

Using DME to make α- alane was successful

Electrochemical Methods for Off Board Regeneration of Alane

Pressurized ECC



ECC = Electrochemical Cell
V = Vacuum Pump

Increased Efficiency for Electrochemical Regeneration of Alane

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)

Proposed Future Work

➢ *Continue work to increase yield and efficiency*

- Explore using other hydrides such as $Ca(AlH_4)_2$ to form alane
- Explore the use of other halides such as LiI, LiB (similar to LiCl?)
- Utilize the use of the pressurized electrochemical cell reactor
- Investigate other alane adducts for near term applications

➢ *Electrochemical Process Optimization*

- Vary combination of halides and alanates similar to LiCl and $LiAlH_4$
- Explore the use of solvents and amine mixtures for easier alane separation
- Control condition of separation to affect particle size
- Use spent aluminum to obtain clean surface
- Start using metal hydrides such as PdH for counter electrode

➢ *Advanced Alane Separation and Analytical Procedures*

- Optimize system that uses dimethyl ether (Me_2O)
- Use other techniques (e.g. NMR, Prompt Gamma Activation Analysis (PGAA) and Raman, neutron scattering) to quantify and characterize AlH_3 formation *in situ*

➢ *Scale Up of a Closed Cycle*

- Pursue collaboration with industry to determine scale up requirements
- Off-Board hydrogen storage can be a useful mean for hydrogen transportation and delivery

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 ~60°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. MAlH4 (M = Li, Na) is dissolved in this solvent,
- Adducts such as $4AlH_3$ ▪ nTHF is expected to form and alane is separated from the solvent
- Efficiency is an important issue and lowering cost must be taken into account

Technical Accomplishments and Progress (as of 3/11)

- **Continued to produce gram quantities of alane with high purity**
- **$LiAlH_4$ was also used to produce alane**
- **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
  - Very small amount of dendrites
  - Demonstrated the formation and separation of alane from DME
  - A pressurized ECC is constructed for close material regeneration cycle and the use of more efficient separation
- **Brought to the forefront interest in the field of organic based electrolyte electrochemistry**

Collaborations

BNL, University of Hawaii, University of New Brunswick, Toyota research center, Università di Roma

Proposed Future Work

- 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
Energy Security Directorate
Savannah River National Laboratory