Project ID# ST063

Electrochemical Reversible Formation of Alane

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2012 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES PROGRAM ANNUAL MERIT REVIEW and PEER EVALUATION MEETING

TEAM

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Dr. Scott Greenway	*(Electrochemistry)*
Dr. Douglas Knight	*(Chemical Synthesis and X-ray analysis)*
Dr. Joseph Teprovich	*(Organic Chemistry and Nano Technology)*
Dr. Robert Lascola	*(Raman Spectroscopy)*

Overview

Timeline

Start: 10/1/06

End: Continuing

Percent complete of activities proposed for FY12: 30%*

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

Collaborators

- 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 and Project Objectives

Overall Objectives :

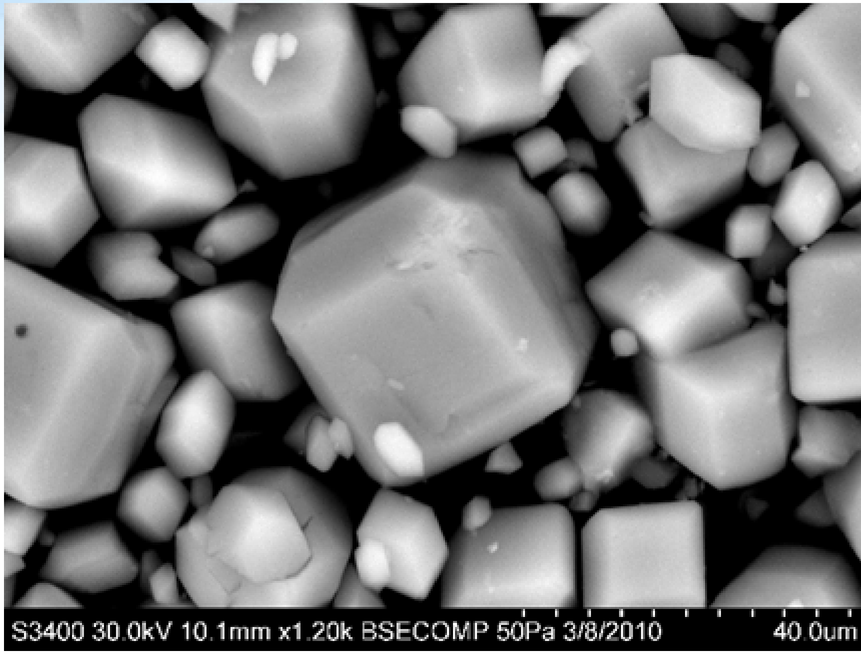
Develop Economical Methods to form Aluminum Hydride (AlH_3) from Aluminum (Al) and dehydrogenated AlH_3

Specific Project Objectives:

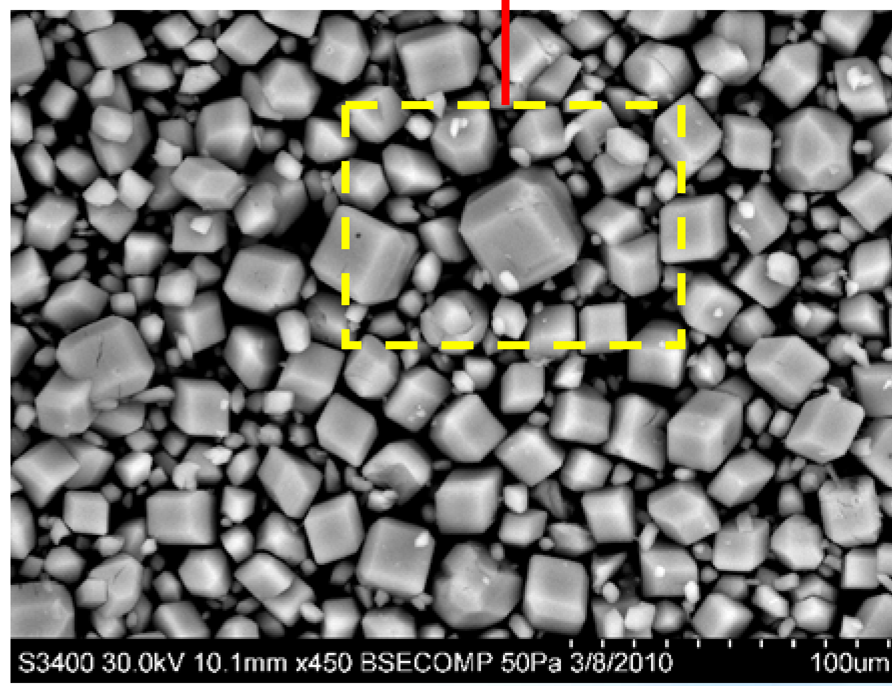
- Avoid the impractical high pressure needed to form AlH_3
- Avoid chemical reaction route of AlH_3 that leads to the formation of alkali halide salts such as LiCl or NaCl
- Utilize electrolytic potential to translate electrochemical potential into chemical potential and drive chemical reactions to form 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 H_2 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 recharging represents a different, promising, and AlH_3 recharging

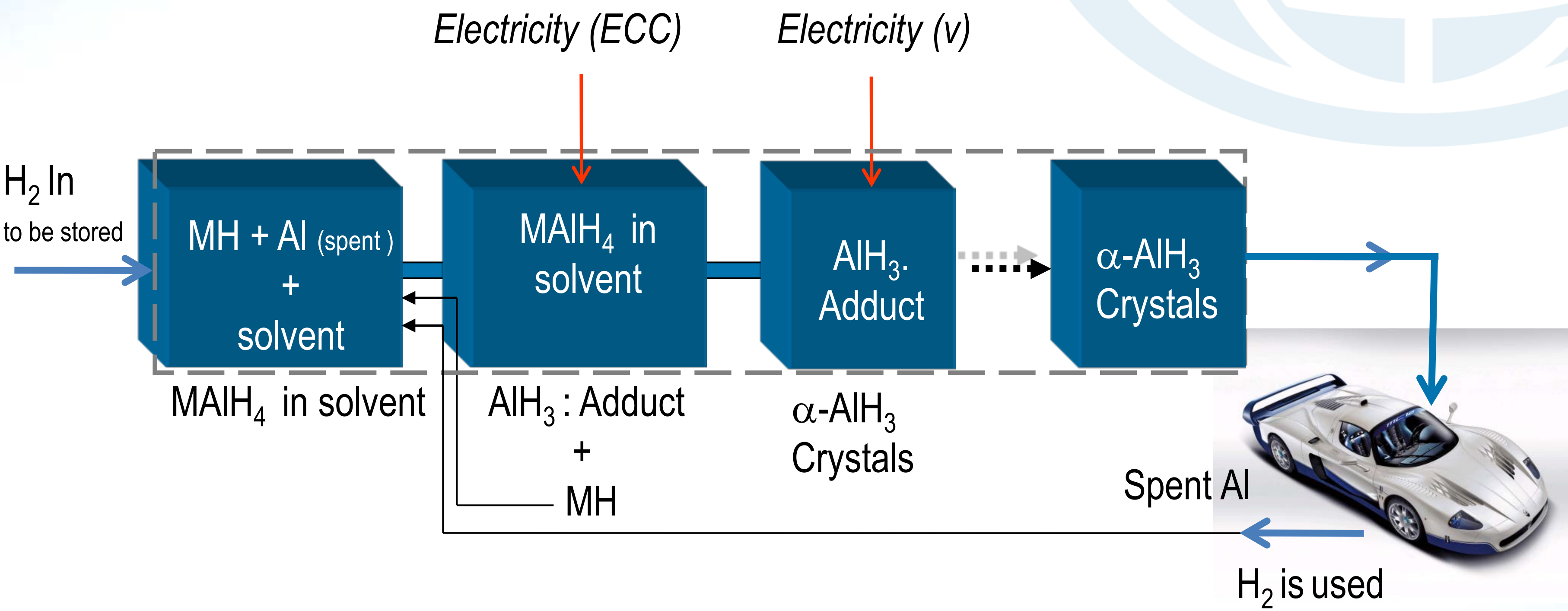
Reactions	E^0 (V) vs SHE	Eq. No.
$4AlH_3 + 3Na^+ + 3e^- \leftrightarrow 3NaAlH_4 + Al$	−1.57	(1)
$AlH_3 + \frac{1}{2}H_2 + Na^+ + e^- \leftrightarrow NaAlH_4$	−1.73	(2)
$Al + 2H_2 + Na^+ + e^- \leftrightarrow NaAlH_4$	−2.28	(3)
$\frac{1}{2}H_2 + Na^+ + e^- \leftrightarrow NaH$	−2.37	(4)
$Na^+ + e^- \leftrightarrow Na$	−2.71	(5)
$4AlH_3 + 3Li^+ + 3e^- \leftrightarrow 3LiAlH_4 + Al$	−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)

* Values were obtained using HSC Chemistry 5.11

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

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

Approach: Electrochemical Technique for Off Board Regeneration of Alane



M=Na, Li, K..

ECC = Electrochemical Cell
V = Vacuum Pump

Approach: Electrochemical Synthesis of Alane

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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: $2\ MH + 2\ Al + 3H_2 \rightarrow 2\ \mathbf{MAlH_4}$ **(M= Li, Na, K…)**

Approach : Efficiency and Feasibility of Processes (electrochemical efficiency)

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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%

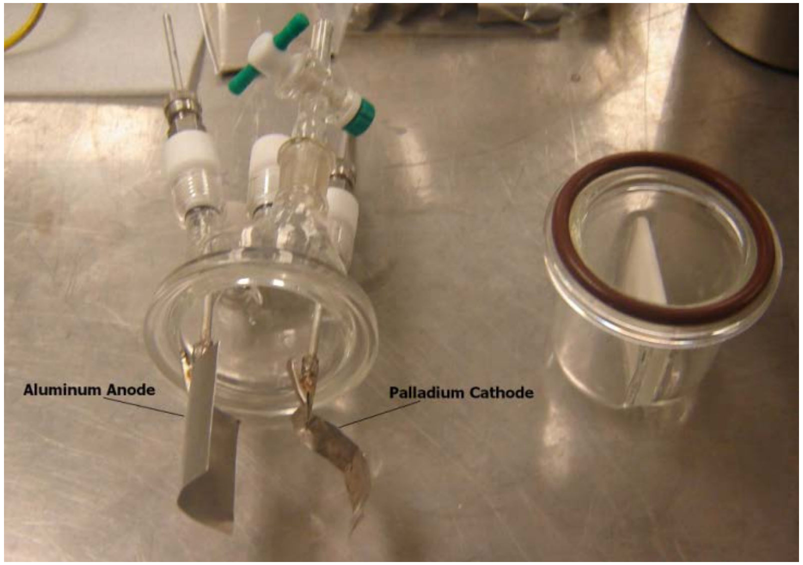
Actual = 68- 75%

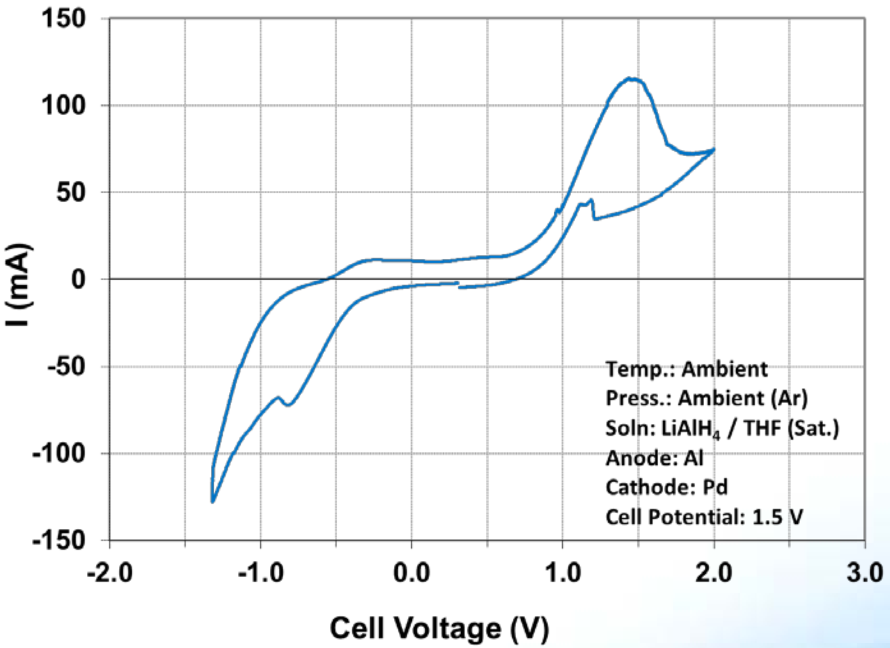
This efficiency is only the electrochemical efficiency

Technical Progress: Electrochemical Electrolyte Regeneration

More effective route for alane separation

Obtaining solid $AlH_3 \cdot 2THF$ *in-Situ*





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

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

Technical Progress: Electrochemical Alane in Saturated Electrolyte Solutions

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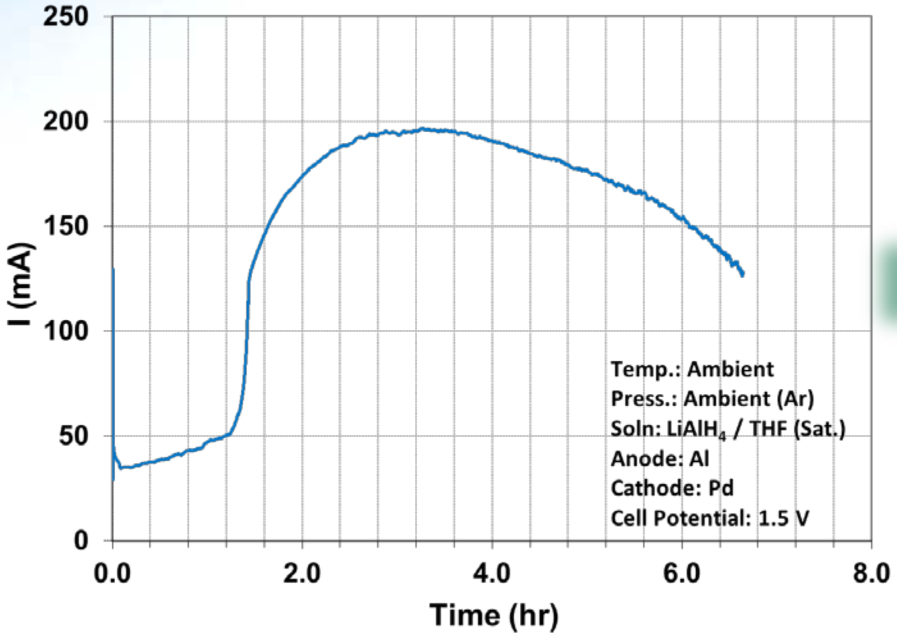
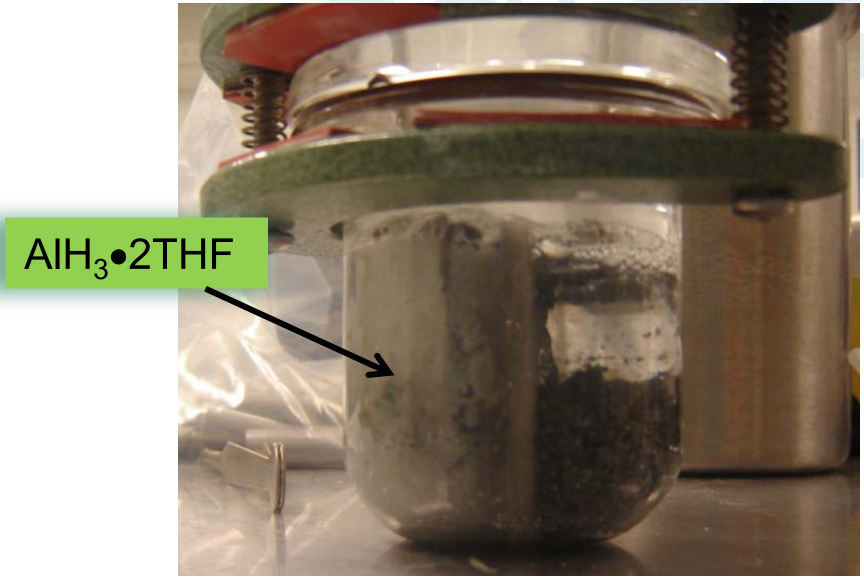


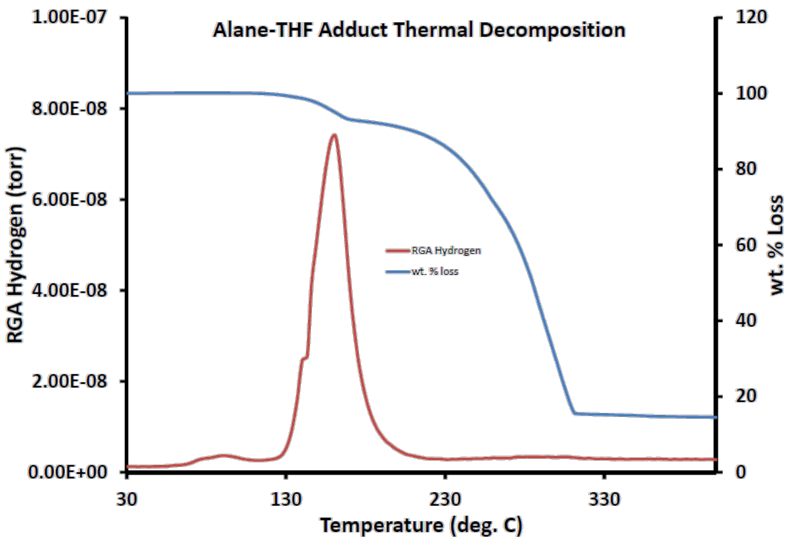


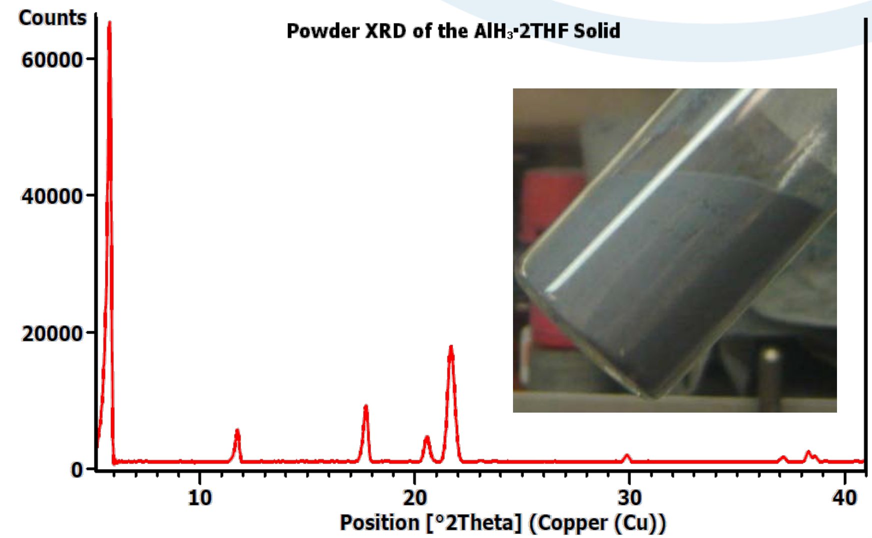
- Pd forms activated Al layer in one hour
- Highest alane form currents observed in this cell
- Alane adduct only precipitates on one side
- Gray-white AlH_3•2THF adduct precipitates at cathode
- Pd electrode contains low density activated aluminum product
- $LiAlH_4$ not present in precipitate

Technical Progress: Precipitation of Alane•THF

$$3AlH_4^{-} \;+\; Al\ (Anode) \;\rightarrow\; 4AlH_3 \cdot 2THF \;+\; 3e^{-}$$

Electrochemical reaction was preformed in saturated solution of $LiAlH_4$





- Alane-THF forms minutes during heating
- Solid insoluble in most solvents

- Gray solid typical of Alane-THF
- Improving economical route for alane synthesis

Solid AlH_3•2THF successfully precipitated, same precipitation is expected with other solvents

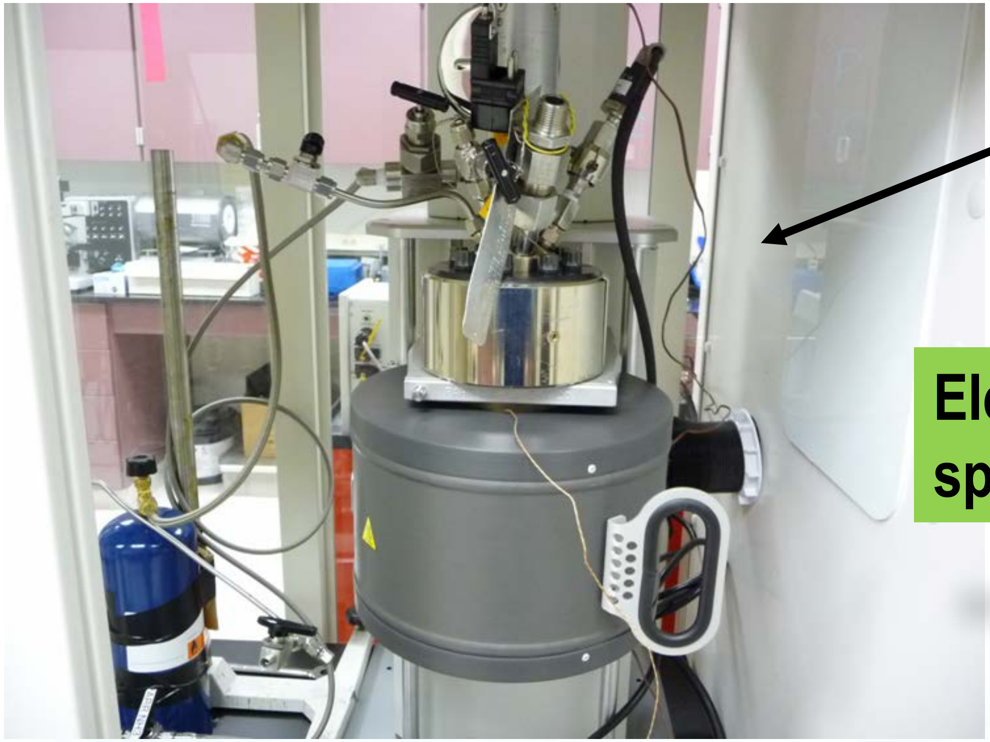
Technical Progress:
Regenerating Electrolyte, using Spent Aluminum

Concept of regenerating electrolyte from spent aluminum:

$$2\ MH\quad +\quad 2\ Al_c^*\quad +\quad 3H_2\ \rightarrow\ 2\ \mathbf{MAlH_4 \bullet THF}$$

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

$$LiH\quad +\quad 2\ Al_c^* +\quad 3H_2\ \xrightarrow{THF}\ 2\ \mathbf{LiAlH_4 \bullet THF}$$



High pressure
Parr-reactor

Electrolyte was regenerated from spent aluminum

Technical Progress: Recycle Spent Aluminum

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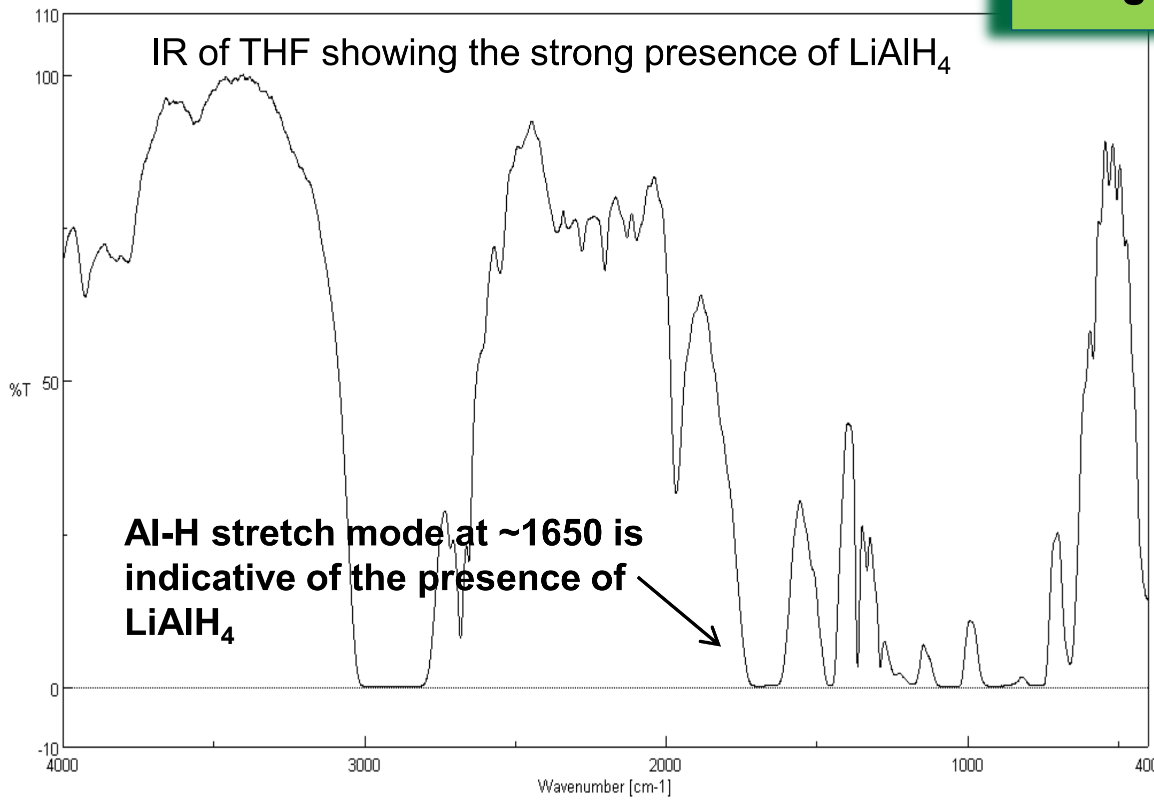
$$Al^{*} \text{ (spent Al)} + LiH \text{ (in THF)} \xrightarrow[800\text{psi } H_2]{70°C} LiAlH_4$$

Verifying electrolyte being regenerated



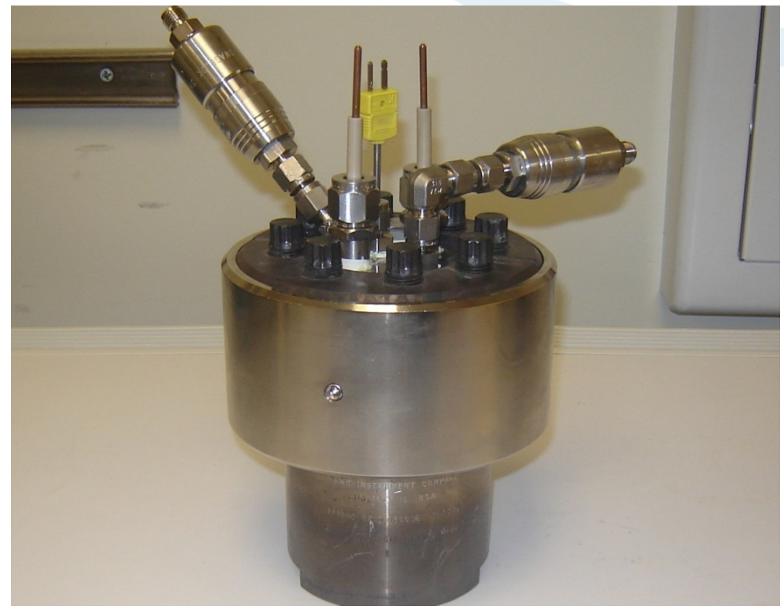
- Electrolyte recycled chemically
- Inexpensive catalyst is identified for reaction
- Investigating best electrodes for electrochemical recycling

Technical Progress: High Pressure Cell for Alane Regeneration

The aluminum anode in a H_2 pressurized electrochemical cell is rapidly consumed

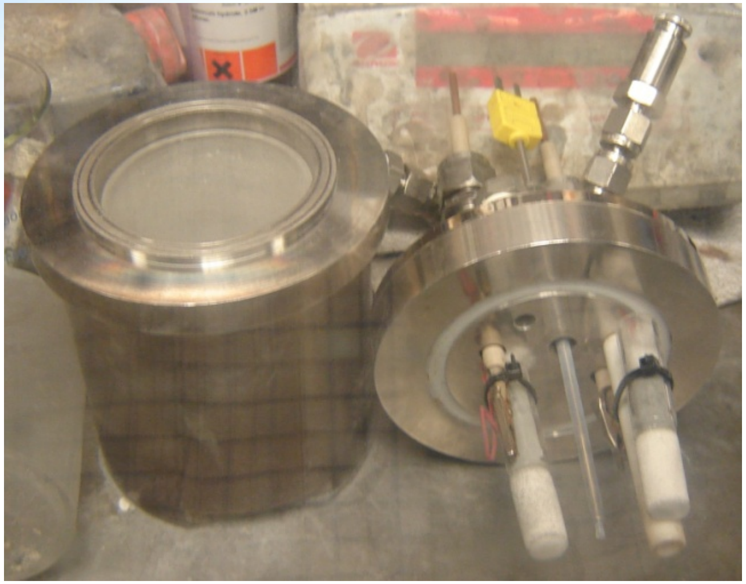
- Pressure: 500 psig
- Potential: 1.5 V

The Pressurized Electrochemical cell in

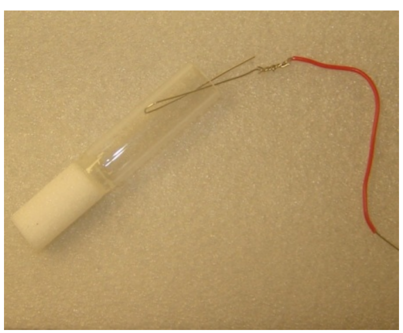


Cell is capable of operating at elevated pressures and temperatures

Technical Progress:
High pressure cell for alane regeneration



Anode: Activated Al (from AlH_3)



The spent alane can be either pressed into solid electrodes or inserted as a powder into porous electrodes as shown below.

The Pressurized Electrochemical cell in operation

Electrochemical regeneration, using spent aluminum was performed in high pressure cell

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)

Proposed Future Work

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➢ *Develop In-situ Recycling Methods*

- Characterize electrodes for LiH production
- Develop cell designs that allow for increased LiH production efficiency
- Understand the role of the solvents and alane precursors to promote selectivity and yield

➢ *High-Pressure Electrochemistry to Improve Selectivity and Yield*

- Investigate the selectivity improvement for electrochemical reactions at high pressure
- Characterize changes in product composition when changing reaction conditions
- Characterize the effect of hydrogen gas bubbling on improving mass transfer in the system

➢ *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 ~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 3/16)

- **Continued to produce gram quantities of alane with high purity**
- **$LiAlH_4$ was also used to produce alane in a saturated solution**
- **An electro-catalytic additive was discovered was added 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
  - Absence of dendrites
  - Demonstrated the formation and precipitation alane.THF *in-situ* during electrochemical process
  - A pressurized ECC is constructed and used for close 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

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

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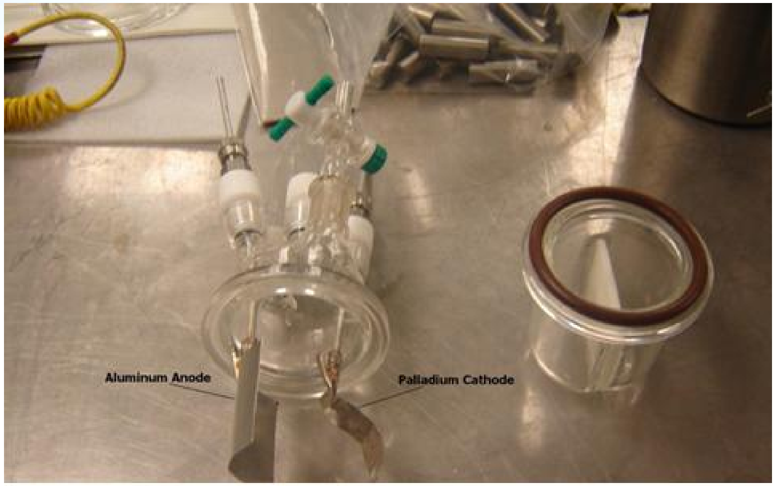
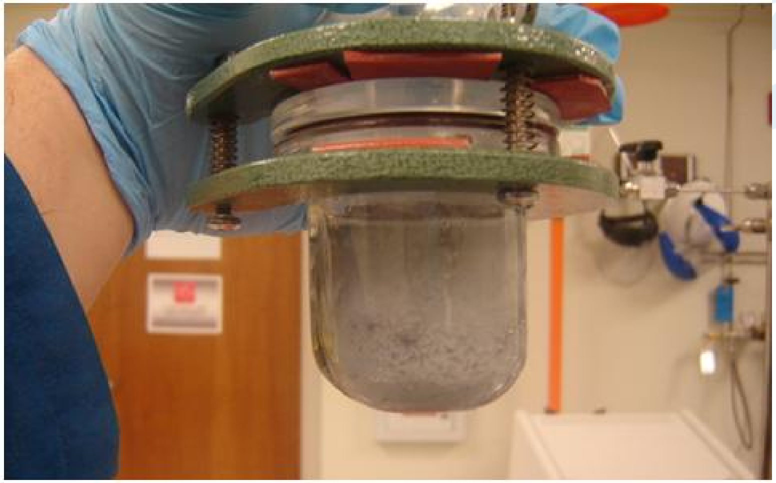
Extra Slides

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.