Reversible Formation of Alane

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2014 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW and PEER EVALUATION MEETING

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Project ID# ST063

Overview

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Timeline

Start: 10/1/2013

End: 3/31/2016

Percent complete of activities proposed for FY14: 50%*

Barriers

- Low-cost, energy-efficient regeneration
- Full life-cycle analyses is needed
- Reduced cost for alane synthesis
- By-product and/or spent material
- Analysis of alternative production methods

Budget*

- Funding received in FY13
  - $400K
- Funding received in FY14
  - $400K
- Total project value:
  - $1,200K

Collaborators

- Ardica (CRADA Partners)
- SRI

Relevance: Project Objectives

Overall Objectives

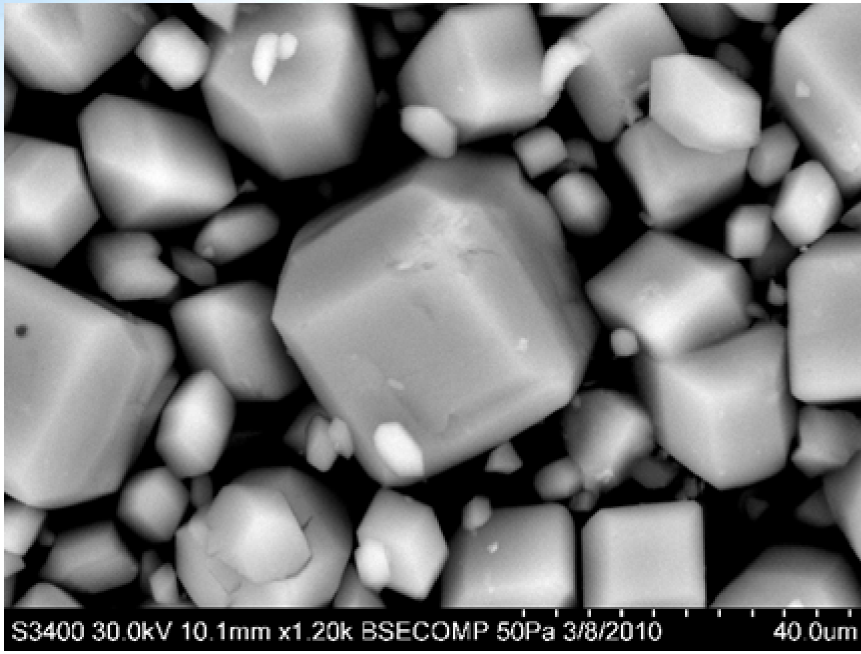
- Develop a low-cost rechargeable hydrogen storage material with cyclic stability, favorable thermodynamics and kinetics fulfilling the DOE onboard hydrogen transportation goals.

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 2017 DOE onboard system desorption targets

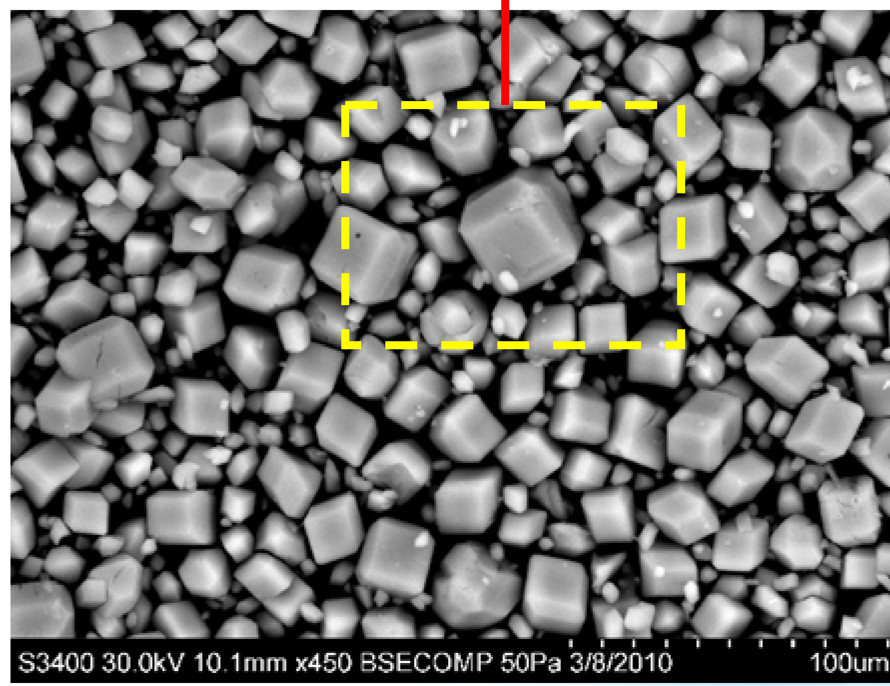
Specific Objectives

- Develop cost effective technique to synthesize alane which avoids the impractically high pressure needed to form AlH_3 directly from Al and H_2.
- Avoid chemical reaction route of AlH_3 that leads to the formation of alkali halide salts such as LiCl or NaCl which require additional steps for removal.
- Utilize electrolytic potential to translate chemical potential into electrochemical potential and drive chemical reactions to form AlH_3.

Relevance: Safety and Alane



Ideal particle size results in enhanced stability



Particle Size: 4 – 32 µm

- 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%.

Relevance: Basic AlH_3 Thermodynamic Cost

$$Al + \frac{3}{2}H_2 \Leftrightarrow AlH_3 \quad \Delta G^0 = 0.431\,\mathrm{kWh/kg}_{\mathrm{AlH_3}}$$

Cost Assumptions

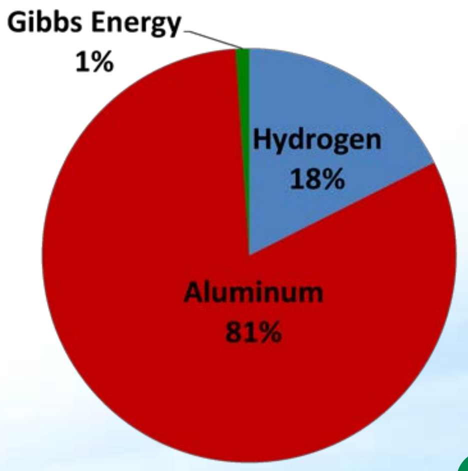
Aluminum Cost	\$2,000	ton
Electricity Cost	\$0.06	kWh
Hydrogen Cost	\$4.25	kg

Cost per kg AlH_3

Hydrogen Cost in AlH_3	\$0.428	\$/kg
Aluminum Cost in AlH_3	\$1.982	\$/kg
Gibbs Energy Input in AlH_3	\$0.026	\$/kg

If it is assumed the Gibbs Energy is provided as electricity with no losses

Thermodynamic AlH_3 Price	\$2.44	\$/kg
Thermodynamic AlH_3 Price Ex-Al	\$0.45	\$/kg



Approach/ Milestones

Qtr	Due Date	Milestones, Deliverables, or Go/No-Go Decision	Status
Q1	12/31/2013	Synthesis and characterization of AlH_3 from $NaAlH_4$ precursors by the dry method to determine optimal compression pressure and reaction conditions to improve yield and optimize alane crystal size.	Completed
Q2	3/31/2014	Demonstration of $NaAlH_4$ electrolyte recycling with a reaction yield above 70% in a system where at least 5 g of $NaAlH_4$ can be produced.	Completed
Q3	6/30/2014	Synthesis of AlH_3 in a divided cell with an electrolyte containing $NaAlH_4$. Synthesis will produce at least 1 g of AlH_3 that can be isolated and products at the sodium electrode will be characterized to demonstrate the potential for electrolyte recycling.	In Progress
Q4	9/30/2014	$NaAlH_4$ and $LiAlH_4$ electrolyte recycling. Identification of low cost catalyst formulations and catalyst loadings necessary to achieve yields above 80%.	In Progress

Approach: Electrochemical AlH_3 Cost by Precursor

$$NaAlH_4 \Leftrightarrow AlH_3 + \frac{1}{2}H_2 + Na^+ + e^- \qquad E^0 = -1.73\ \mathrm{V\ vs.\ SHE}$$

$$Na^+ + \frac{1}{2}H_2 \Leftrightarrow NaH + e^- \qquad E^0 = -2.37\ \mathrm{V\ vs.\ SHE}$$

$$\Delta E^0_{cell} = -0.64\ \mathrm{V} \longrightarrow 1.71\ \mathrm{kWh/kg}_{\mathrm{AlH_3}}$$

$$LiAlH_4 \Leftrightarrow AlH_3 + \frac{1}{2}H_2 + Li^+ + e^- \qquad E^0 = -2.05\ \mathrm{V\ vs.\ SHE}$$

$$Li^+ + \frac{1}{2}H_2 \Leftrightarrow LiH + e^- \qquad E^0 = -2.33\ \mathrm{V\ vs.\ SHE}$$

$$\Delta E^0_{cell} = -0.28\ \mathrm{V} \longrightarrow 0.75\ \mathrm{kWh/kg}_{\mathrm{AlH_3}}$$

Assuming Saline Hydrides Recycled to Aluminum Hydrides →

Thermo. E-chem AlH_3 Price ($NaAlH_4$)	\$2.51	\$/kg
Thermo. E-chem AlH_3 Price ($LiAlH_4$)	\$2.46	\$/kg
Thermo.E-chem AlH_3 Price ($NaAlH_4$) Ex-Al	\$0.53	\$/kg
Thermo.E-chem AlH_3 Price ($LiAlH_4$) Ex-Al	\$0.47	\$/kg

Approach: Cost of Inefficiencies in AlH_3 Production

$$E_{cell} = \left(E^0_{cathode} - \eta_{cathode}\right) - \left(E^0_{anode} - \eta_{anode}\right) + I_{cell} R_{ohmic}$$

$$R_{ohmic} = R_{electric} + R_{contact} + R_{ionic}$$

$$R_{ionic} >> (R_{electric} + R_{contact})$$

$$V_{ohmic} = \frac{i_{cell} \cdot l_{electrodes}}{\kappa_{ionic}}$$

i_{cell}	0.05	A/cm^2
$l_{electrodes}$	0.071	cm
k_{ionic}	0.005	S/cm

$$\eta_{anode} \approx -\eta_{cathode} \approx 0.3\ \text{V}$$

$$V_{ohmic} \approx 0.71\ \text{V}$$

$$E_{cell} \approx E^0_{cell} + 1.31$$

Approx. Total Cell Voltage ($NaAlH_4$)	1.95	V
Approx. Total Cell Voltage ($LiAlH_4$)	1.59	V
Energy needed for E-Chem ($NaAlH_4$)	5.23	kWh/kg
Energy needed for E-Chem ($LiAlH_4$)	4.26	kWh/kg
Electricity Cost ($NaAlH_4$)	\$0.31	\$/kg
Electricity Cost ($LiAlH_4$)	\$0.26	\$/kg

E-chem Input Costs ($NaAlH_4$)	\$2.72	\$/kg
E-chem Input Costs ($LiAlH_4$)	\$2.67	\$/kg

Approach: Electrochemical AlH_3 Production from $NaAlH_4$

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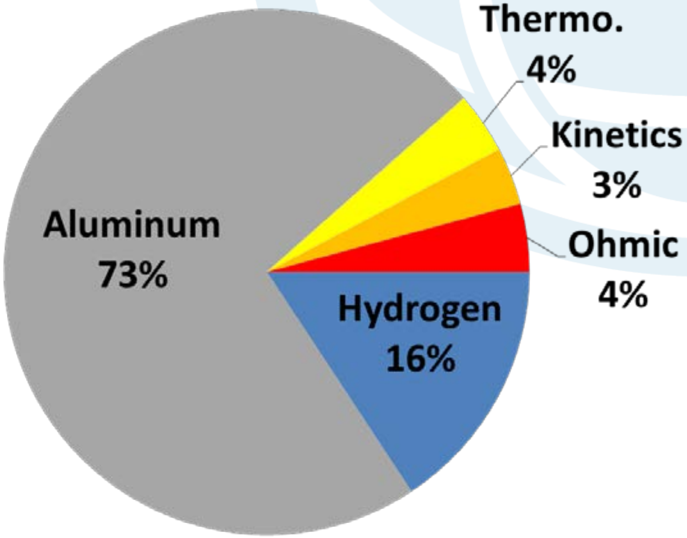
Cost Analysis Including Inefficiencies

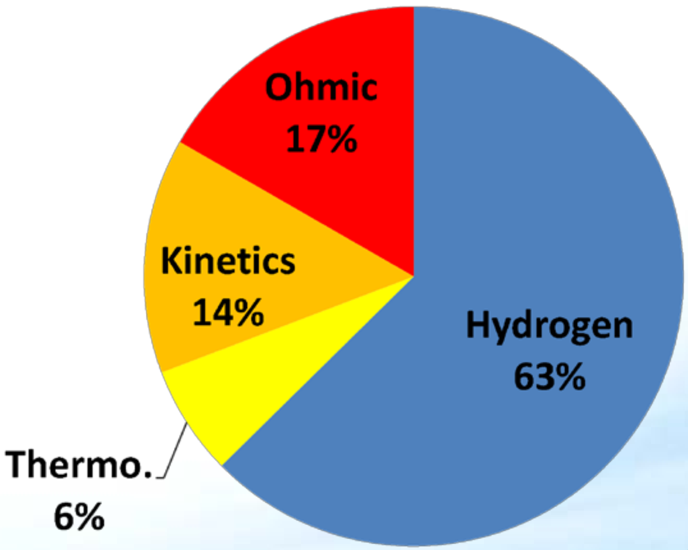
Aluminum not recycled

Hydrogen Cost in AlH_3	$0.428	$/kg
Aluminum Cost in AlH_3	$1.982	$/kg
E-Chem Thermo Cost	$0.103	$/kg
E-Chem Kinetics Cost	$0.096	$/kg
E-Chem Ohmic Cost	$0.114	$/kg
Total E-Chem Cost from $NaAlH_4$	$2.724	$/kg

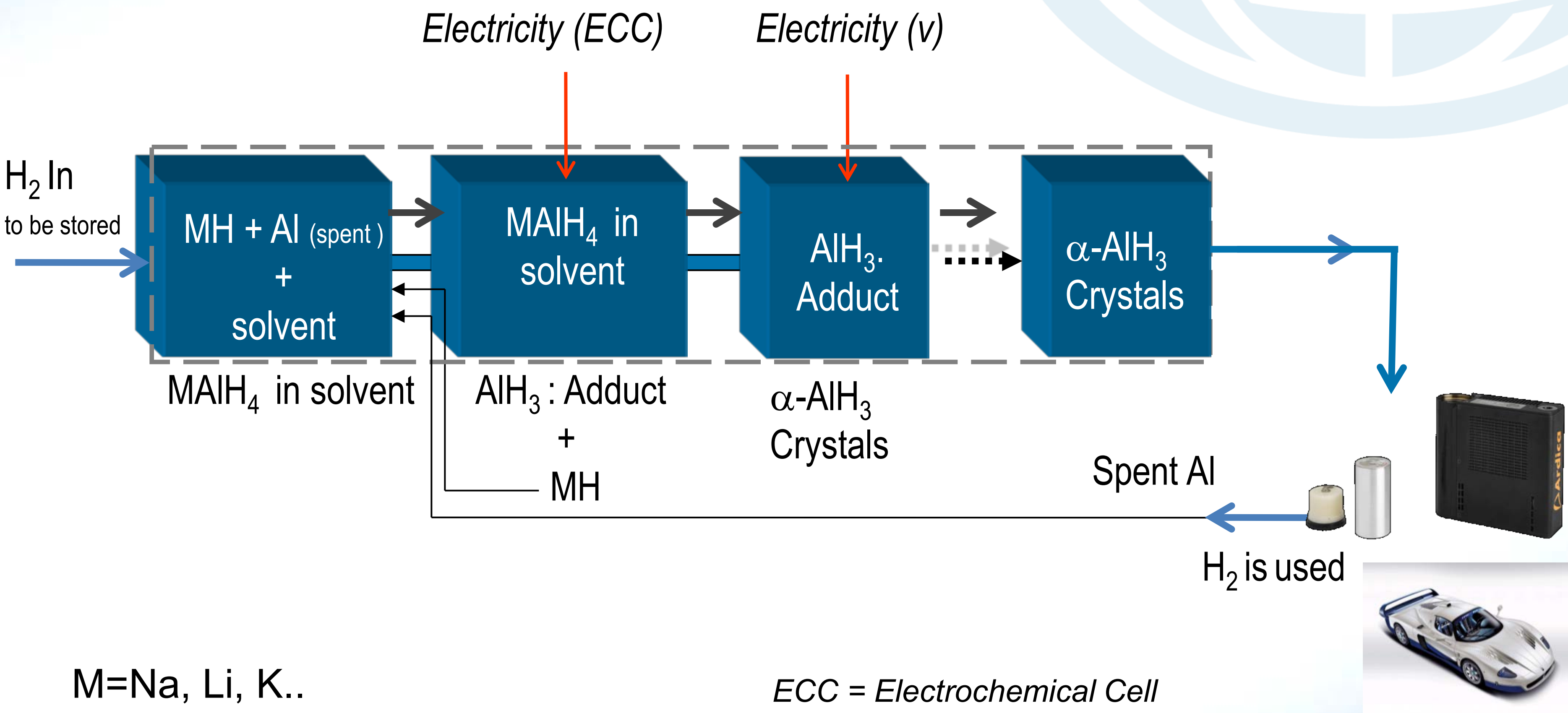


Aluminum recycled

Hydrogen Cost in AlH_3	$0.428	$/kg
E-Chem Thermo Cost	$0.103	$/kg
E-Chem Kinetics Cost	$0.096	$/kg
E-Chem Ohmic Cost	$0.114	$/kg
Total E-Chem Cost from $NaAlH_4$	$0.742	$/kg



Approach: Electrochemical Technique for Alane Generation



M=Na, Li, K..

ECC = Electrochemical Cell
V = Vacuum Pump

Technical Progress: Solid State Alane Production from $NaAlH_4$

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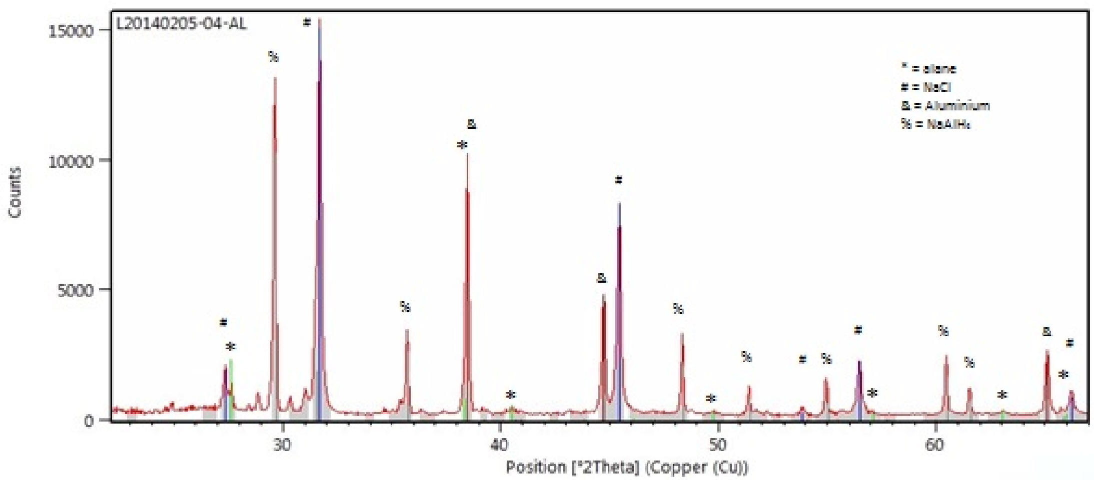
α-Alane present in the crude material shown here before washing to remove impurities.



Milestone #1 – Complete - Demonstrates alane synthesized from $NaAlH_4$ using dry method

Technical Progress: Process and Quantification of Regenerating Electrolyte

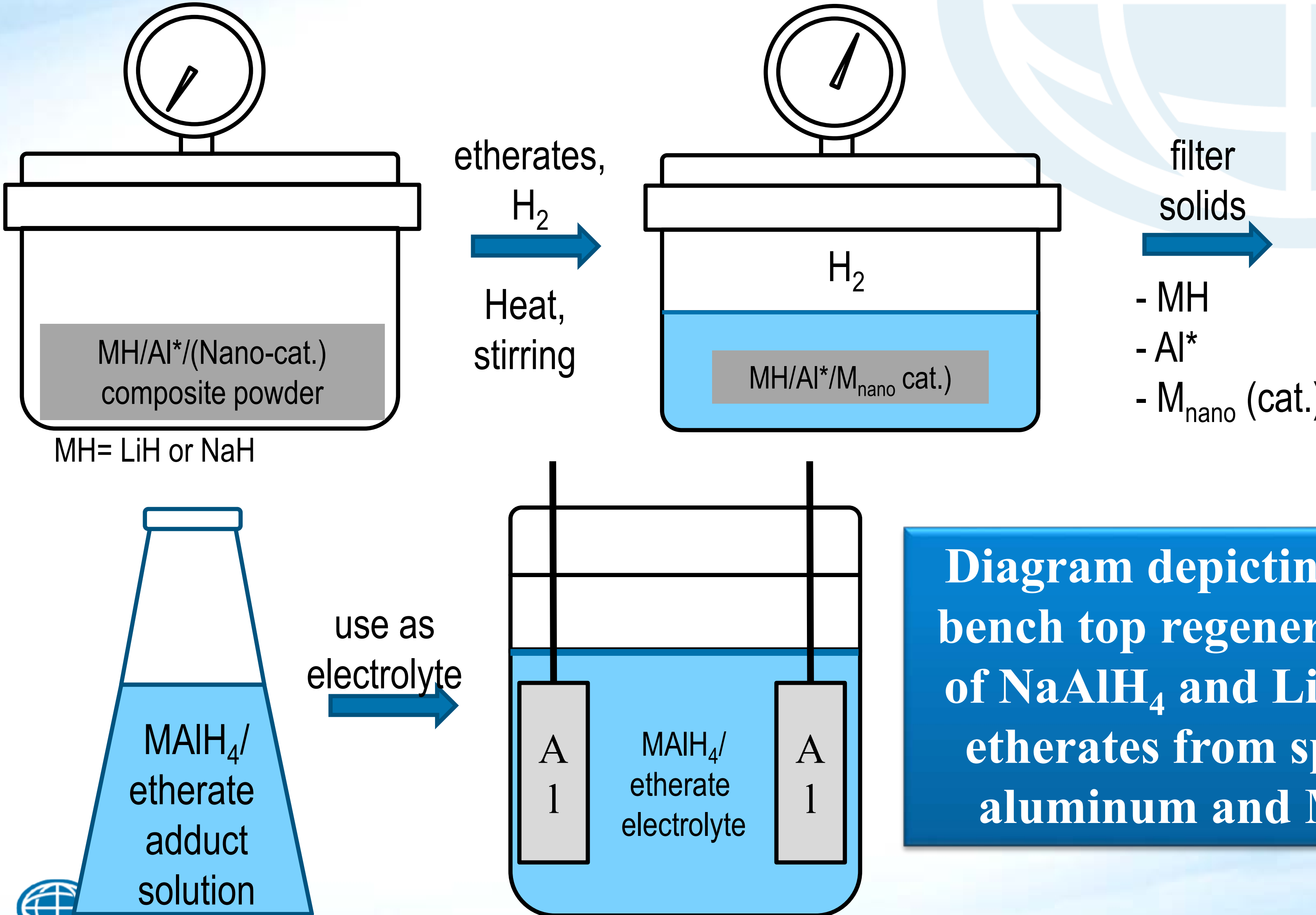


Diagram depicting the bench top regeneration of $NaAlH_4$ and $LiAlH_4$ etherates from spent aluminum and MH

Technical Progress: Regenerating $NaAlH_4$ using Spent Aluminum.

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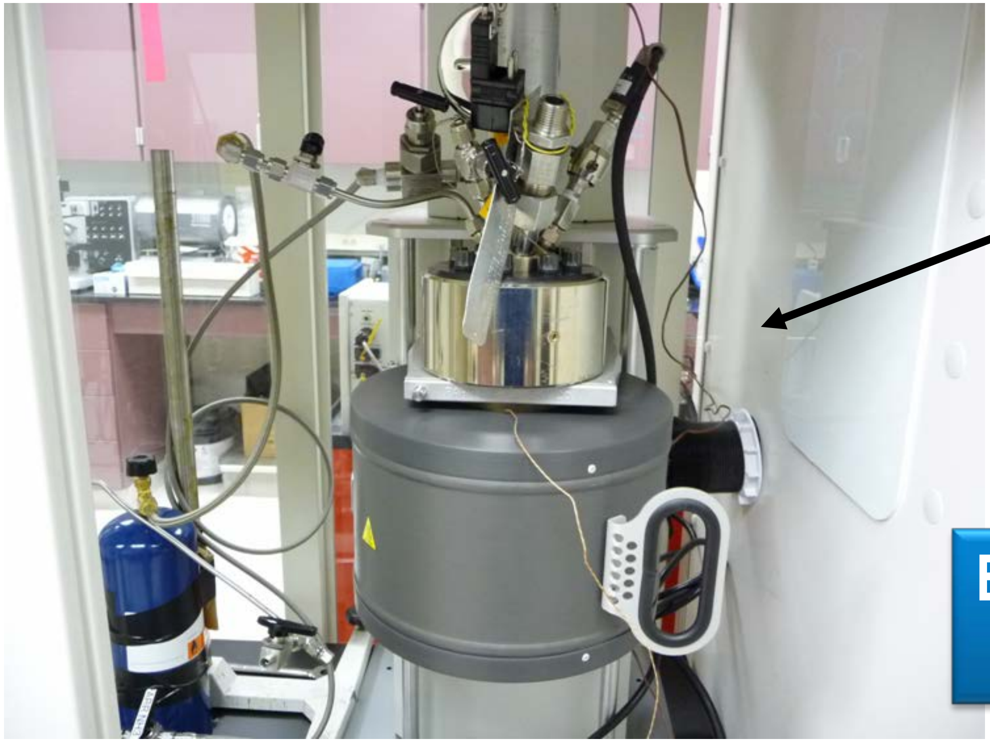
Regenerating $NaAlH_4$ from dehydrogenated AlH_3:

$$2\ NaH + 2\ Al_c^* + 3H_2 \rightarrow 2\ \mathbf{NaAlH_4}$$

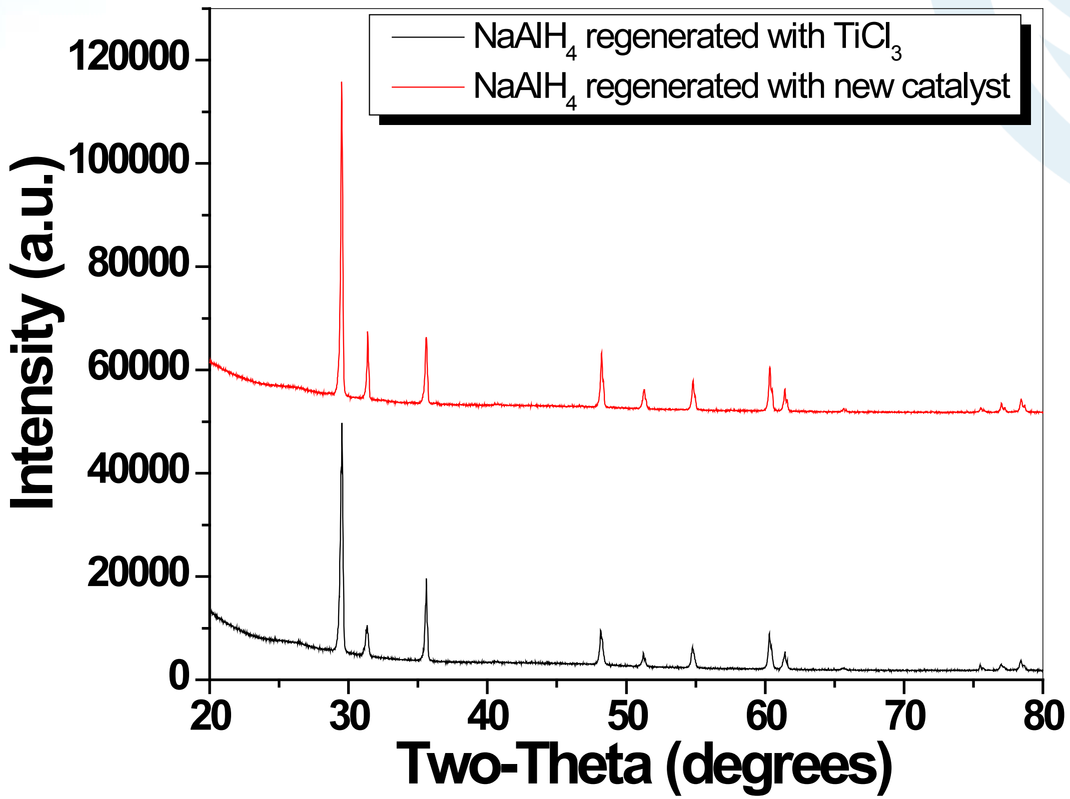
(M= Li, Na, K…) and (Al_c^* = catalyzed and activated Al)



High pressure Parr-reactor

Electrolyte was regenerated from dehydrogenated alane.

Technical Progress: $NaAlH_4$ Regeneration Purity



Pure $NaAlH_4$ was regenerated using both $TiCl_3$ and the new catalyst at 120 °C and 1400 psi H_2.

Technical Progress:
$NaAlH_4$ Regeneration with New, Inexpensive Catalyst

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Temperature and H_2 Pressure	Percent Yield with New Catalyst (5 mol %)	Percent Yield with $TiCl_3$ (5 mol %)
70°C , 1400 psi	17.0 %	31.8 %
120°C , 1400 psi	28.2 %	56.6 %
150°C , 1400 psi	55.5 %	65.5 %
150°C , 1800 psi	57.1 %	73.0 %

$TiCl_3$ is well known to catalyze the reaction of NaH and Al in THF under H_2 pressure to form $NaAlH_4$, but the cost of the new catalyst is significantly less than that of $TiCl_3$.

Milestone #2 – Complete -Demonstrates recycling of $NaAlH_4$ electrolytes at >70% yield

Technical Progress: Electrochemical Alane Production using Diethyl Ether Saturated Solutions

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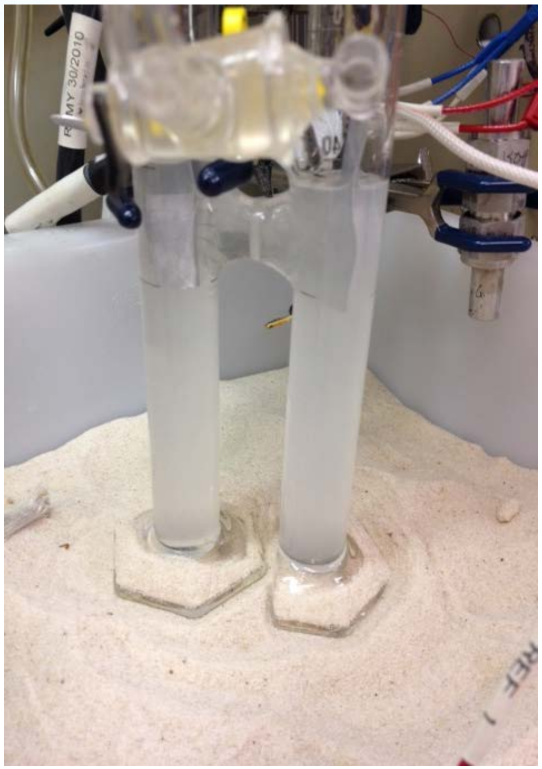
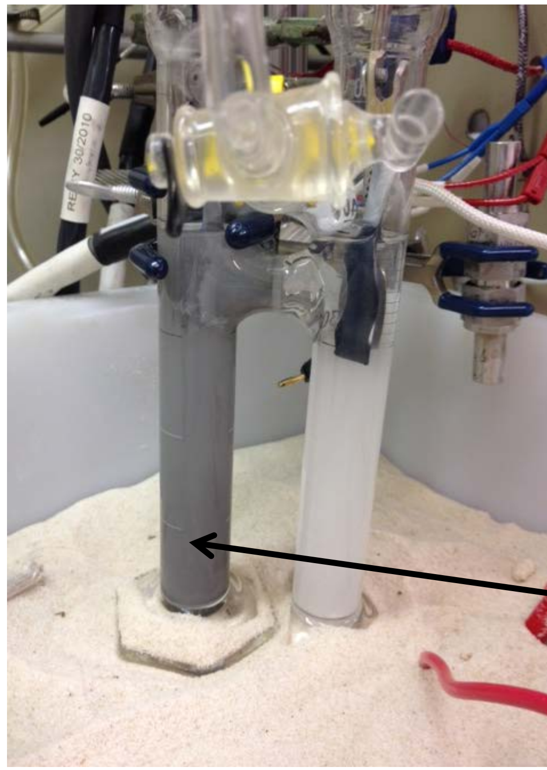
The diethyl ether is saturated with $LiAlH_4$ by simple stirring in solution prior to running the electrochemical process.


Before electrochemical process


After electrochemical process

The AlH_3-diethyl ether precipitates due to it's insolubility in diethyl ether.

The resulting solid is filtered and heated to 65 – 70 °C to break the adduct resulting in alane.

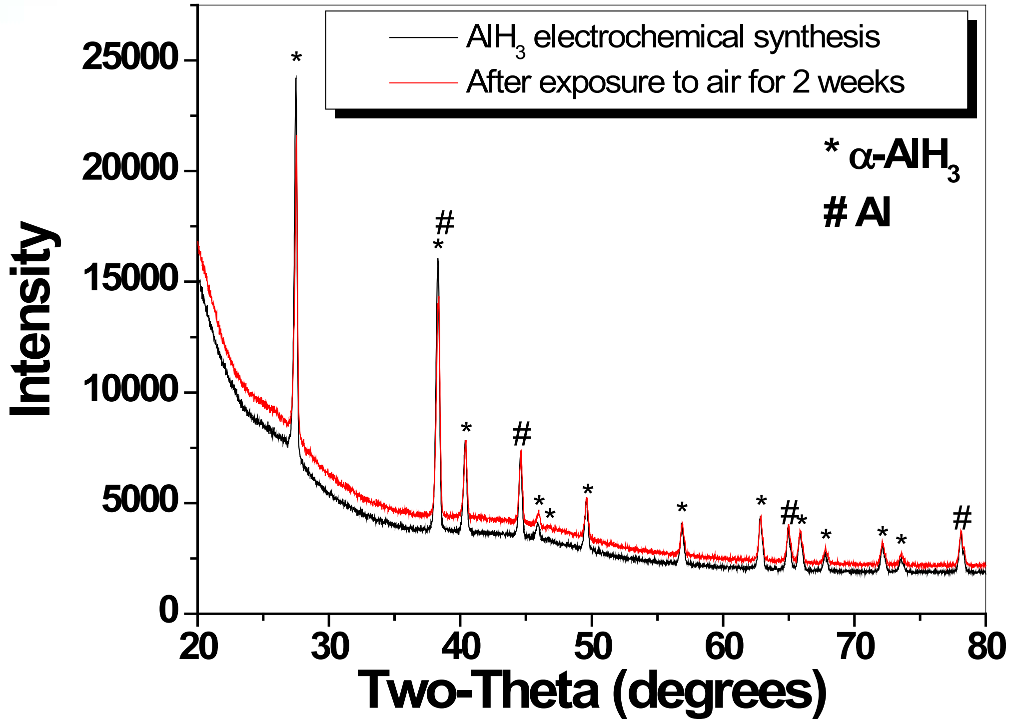
Solid Adduct : AlH_3•Diethyl Ether

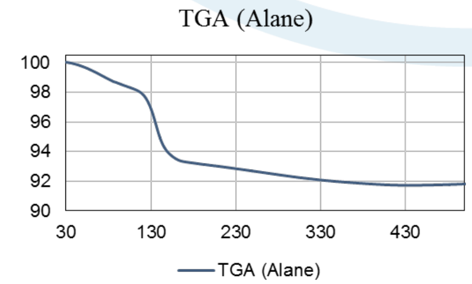
<u>Milestone #3 – In Progress – Improved electrochemical synthesis demonstrated with small batch sizes</u>

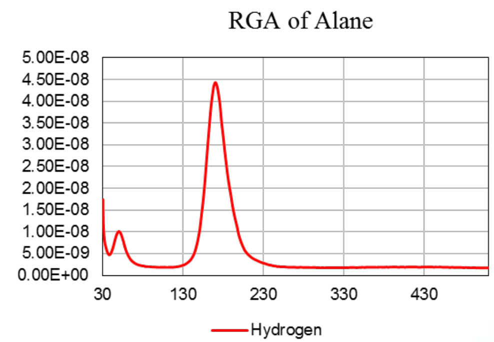
Technical Progress: α-Alane from a Saturated Ether Solution and Air Stability

$$3AlH_4^- + Al\ (\text{Anode}) \rightarrow 4AlH_3 \cdot \textit{Etherate} + 3e^-$$

Electrochemical reaction was preformed in saturated ether solution of $LiAlH_4$







- High purity alane was obtained from the alane:diethyl ether adduct generated electrochemically, using a 2.0 M $LiAlH_4$ solution
- The alane generated was air passivated and was stable in air for 2 weeks

Collaboration

Collaborator	Role
SRNL Ragaiy Zidan (PI), Joe Teprovich, Ted Motyka, Scott Greenway, Patrick Ward, Brent Peters	Prime; Development and characterization of novel alane generation methods that the costs associated with alane synthesis
Ardica Technologies Dick Martin	CRADA Partner; Developer of portable fuel cell systems powered by alane
SRI Robert Wilson	Partner with Ardica; Investigating the scale-up and potential savings with new alane production methods

Replies to Reviewer Comments

- **FY13 Reviewer Comment: It is still not clear the real assistance provided by electrochemically to the reaction $MH+Al+1.5H_2 = MAlH_4$**
  - FY14 Response: Electrochemical is used to drive the reaction $Al+3/2H_2= AlH_3$. This reaction is significantly different than the one referenced in terms of thermodynamics and cannot proceed chemically except at extreme pressures
- **FY13 Reviewer Comment: There is a clear lack of participation by BNL and U of Hawaii**
  - FY14 Response: Participation from BNL and Hawaii was mainly during the Center of Excellence that has now ended, but communication still occurs on relevant issues
- **FY13 Reviewer Comment: The team may want to look at other electrochemical separators**
  - FY14 Response: The project team is investigating a variety of methods to improve the electrochemical efficiency of the cell including electrolyte improvements. However, THF and ethers can dissolve many polymers and polysulfone is not recommended for use with these solvents.

Proposed Future Work

- Improve efficiency of crystallization through use of the use of different solvent/adducting methods
- Demonstrate the generation of AlH_3 particle sizes up to 30 microns from electrochemically produced AlH_3 with stability in air to 100 hours
- Perform electrochemical testing with DME to demonstrate the ability to simplify separation of AlH_3 produced by the electrochemical reactions
- Optimize electrolytes to increase the efficiency of the electrochemical reaction while improving solvent separation

Project Summary

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➢ *Simplify Alane Chemical Synthesis using the Dry Method*

- Provides a potential short term method to simplify the production and separation of alane
- Developing solid-state reaction techniques for synthesizing alane using more inexpensive precursors
- Demonstrated synthesis of alane from $NaAlH_4$ and $AlCl_3$ using the dry method

➢ *Reduce AlH_3 Cost through using Electrochemical Methods*

- Isolated alane crystals from reaction in ether electrolytes to simplify separations
- Improving solvent combinations to provide optimal conductivity of solutions
- Simplifying separation through the use of a divided cell
- Demonstrated precipitation of AlH_3 from concentrated solutions to simplify separations

➢ *Enable Recycling of Al for a Closed Fuel Cycle and Reduced Cost*

- Developed and characterized novel catalysts that enable the regeneration of the electrolyte
- Achieved yield above 70% for regeneration of $NaAlH_4$ electrolyte in THF
- Reaction step enables a full fuel cycle that demonstrates the viability of recycling spent Al

➢ *Optimize Conditions to Acquire Ideal particles Sizes with Solid State Synthesis*

- Optimizing solid-state reaction techniques for synthesizing alane with particle sizes ~30 microns.
- Understanding the impact of the purity of precursors on the reaction kinetics and yield as well as the addition of additives to stimulate the formation of larger particles sizes of alane.

END of Slides

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