We put science to work.™

Project ID# ST063

Reversible Formation of Alane

A High Hydrogen Density Material for Energy Storage

Ragaiy Zidan

Energy Security Directorate

Savannah River National Laboratory

June 2016

2016 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW and PEER EVALUATION MEETING

Overview

Timeline

Start: 10/1/06

End: Continuing

Percent complete of activities proposed for FY16: 50%

Barriers

- Low-cost, energy-efficient regeneration
- Dendrite Formation
- Reduced cost for alane synthesis
- Increase conductivity
- Perfect crystallization methods

Budget

- FY14 - $400K
- FY15 - $400K
- FY16 - $400K

Collaborators

- Ardica (CRADA Partners)
- SRI

Relevance: Alane as a Hydrogen Storage Material

Overall Objectives

- Develop a low-cost rechargeable hydrogen storage material with cyclic stability, favorable thermodynamics and kinetics with high volumetric gravimetric hydrogen density

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 excellent potential for application in high energy density devices

Specific Objectives

- Develop cheaper techniques to synthesize alane which avoids the chemical reaction route of AlH_3 that leads to the formation of alkali halide salts such as LiCl or NaCl.
- Utilize efficient electrolytic methods to form AlH_3.
- Develop crystallization methods to produce alane of the appropriate phase, crystal size and stability.

Relevance: Traditional Methods to Form Alane

- *Current alane production techniques use $AlCl_3$ and $LiAlH_4$ in a solution based chemical reaction which is costly due LiCl formation which is not easily reversible.*

$$3LiAlH_4 + AlCl_3 \Leftrightarrow 4AlH_3 + 3LiCl$$

$$3LiAlH_4 + AlCl_3 \Leftrightarrow 4AlH_3 : Adduct + 3LiCl \downarrow$$

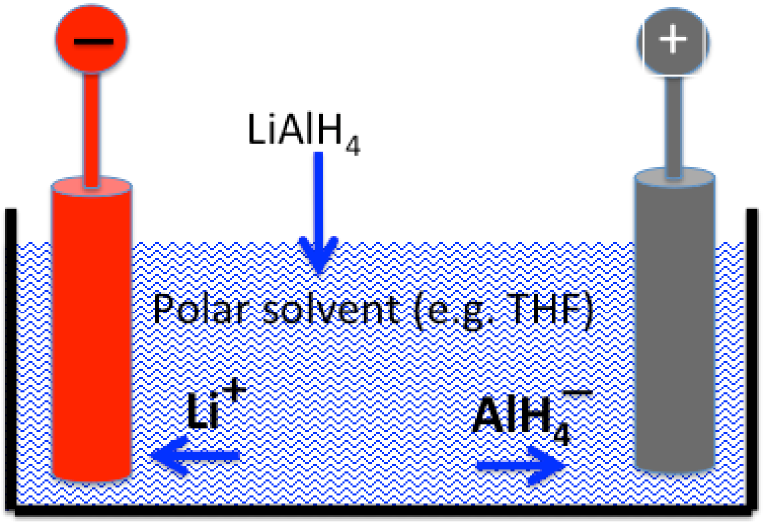
$$AlH_3 : Solvent(Adduct) \rightarrow AlH_3(crystals) + Solvent$$

- *AlH_3 Adduct consists of AlH_3 and etherates (e.g. THF, or* Et2O)
- *AlH_3 Adduct can also consists of AlH_3 and amines (e.g. TEA, TMA)*
- *Depending on conditions different phases can form (e.g. α, α', and γ)*
- *Only the alpha phase is the most stable*
- *LiCl is unrecoverable making the chemical rout a costly process*

Current price $3,500/kg small scale

Relevance: Advantages of Electrochemical Alane Generation

Generating alane electrochemically allows for the exclusion of halide salts and simple aluminum recycling methods.



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

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

$$LiH + Al + {}^3/_2\, H_2 \Leftrightarrow LiAlH_4$$

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 NAH	\$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 NAH	\$0.742	\$/kg

Large scale production using electrochemical method expected to reduce cost below \$100/kg

Approach: Resolving Issues to Further Lower Cost of Alane

Increasing efficiency and yield by:

A) Recycling materials and additives used in making alane during:

- Electrochemical process
- And crystallizations

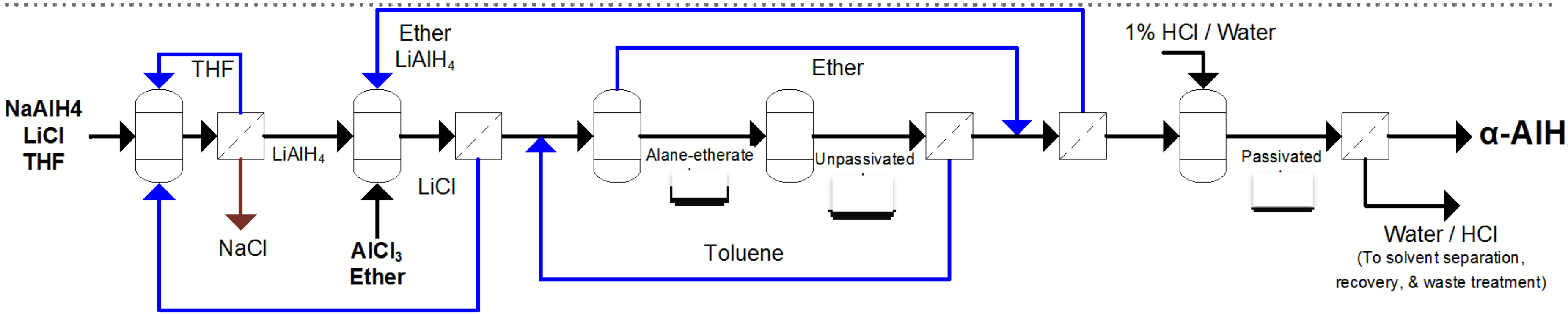
B) Improve conductivity and explore different adducts:

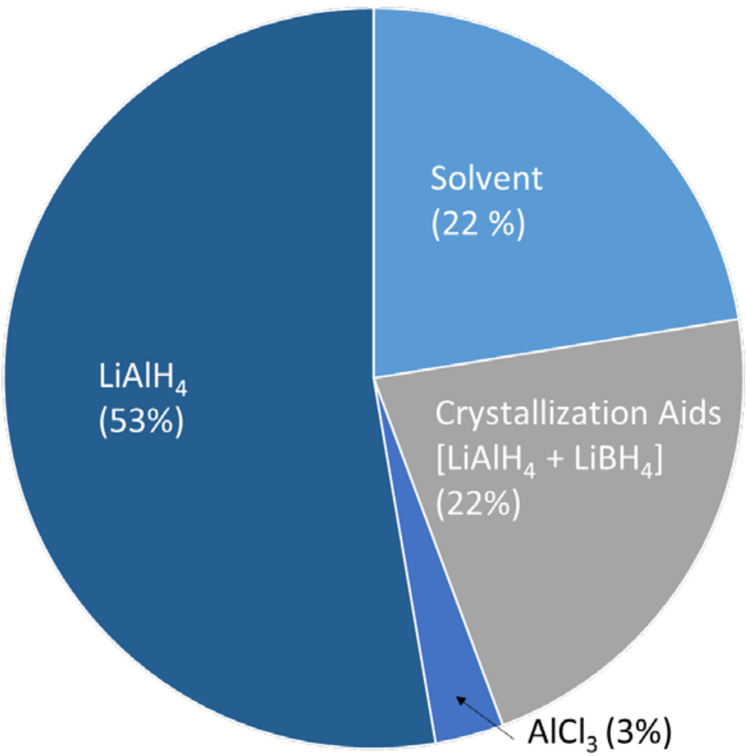
- Use THF in the electrochemical cell
- Use transmutation process to crystal from different adduct

C) Producing alane of high value by producing:

- Stable alpha alane with Crystal size larger than 5 microns
- High capacity product that is safe to handled in air and the presence of moisture

Approach: Crystallization and Reagent Recycling for Alane





Dow Method Material Costs

- Focusing on methods to reduce materials and processing costs of **front end synthesis** and **back end crystallization**
- Efforts address both the **recycling of solvent and crystallization aids** as well as the use of **alternative adducts** to ether to use feedstock alternatives to $LiAlH_4$
- Improvements to the electrochemical generation of alane are underway to **generate LiH at the cathode for electrolyte regeneration**

Approach: Resolving Issues to Further Lower Cost of Alane

Increasing efficiency and yield by:

A) Recycling materials and additives used in making alane during:

- Electrochemical process
- And crystallizations

B) Improve conductivity and explore different adducts:

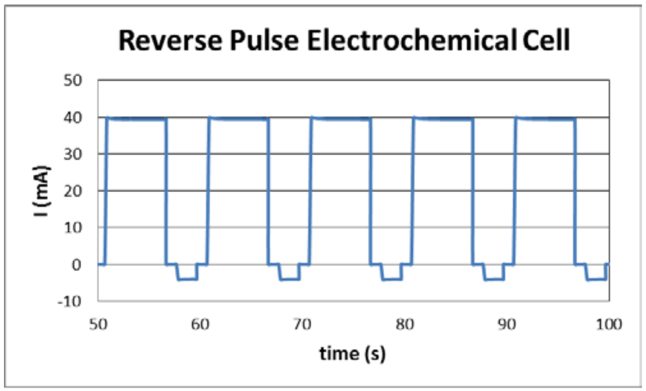
- Use THF in the electrochemical cell
- Use transmutation process to crystal from different adduct

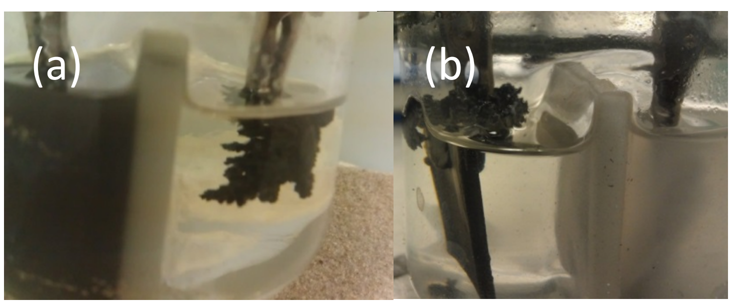
C) Producing alane of high value by producing:

- Stable alpha alane with Crystal size larger than 5 microns
- High capacity product that is safe to handled in air and the presence of moisture

Current Progress: Cathode Optimization/Electrolyte Regeneration

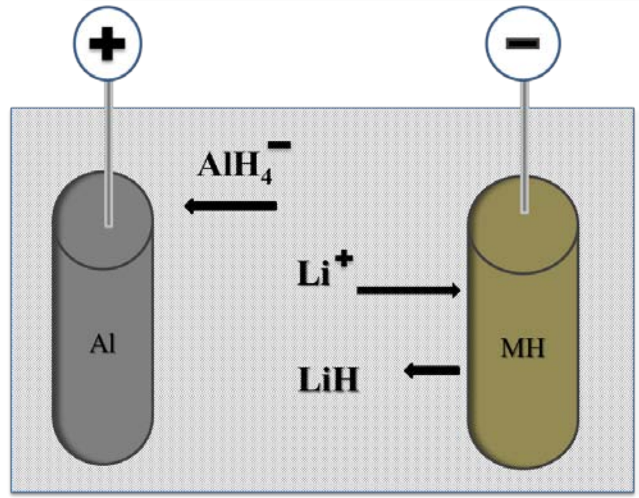
2015 Results: Dendrites were significantly reduced by utilizing a reverse pulse technique during the electrochemical reaction



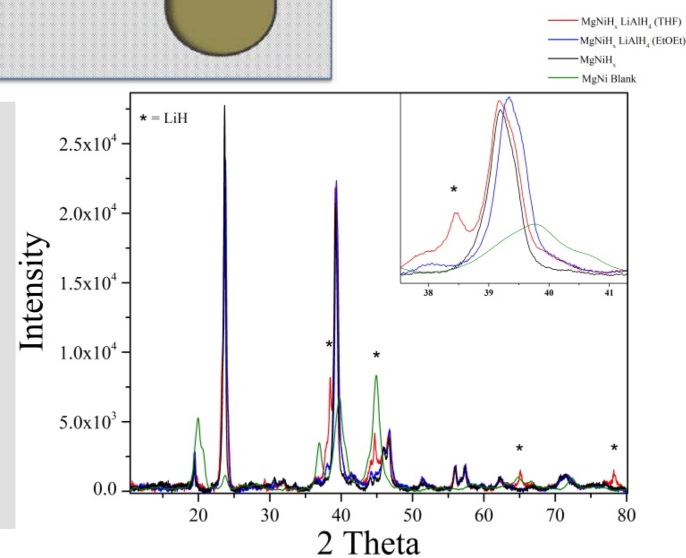


Dendrites from typical 18 hour reaction (a) and (b) reduction after reverse pulsing.

2016 Results: MgNiHx-based cathode reduces/eliminates dendrite formation while capturing Li^+ for regeneration of LiH



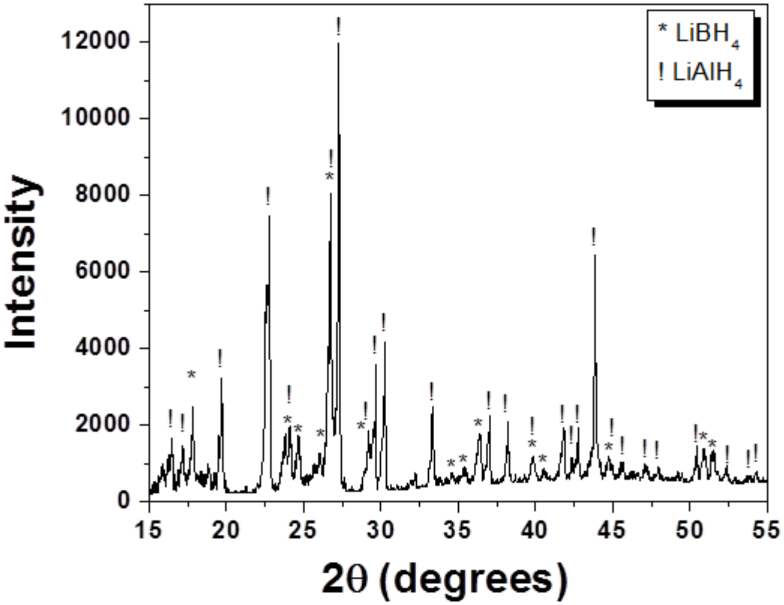
XRD of cycled MgNi electrode in the presence of H_2 reveals the formation of LiH



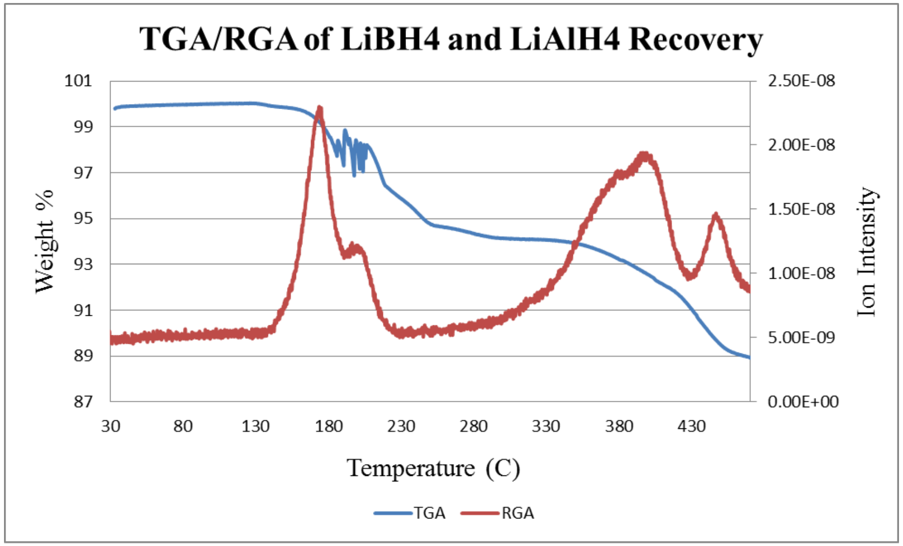
Current Progress: Recovery of $LiBH_4$ and $LiAlH_4$

- $LiBH_4$ and $LiAlH_4$ are costly additives needed to assist the crystallization process
- Alane was washed with ether to dissolve and recover $LiBH_4$ and $LiAlH_4$

99.9 % Recovery



XRD- depicts the recovery of LiAH4 and LiBH4 used in crystalizing alane



TGA shows the dehydrogenation of recovered of LiAH4 and LiBH4 sample used in crystalizing alane

Approach: Resolving Issues to Further Lower Cost of Alane

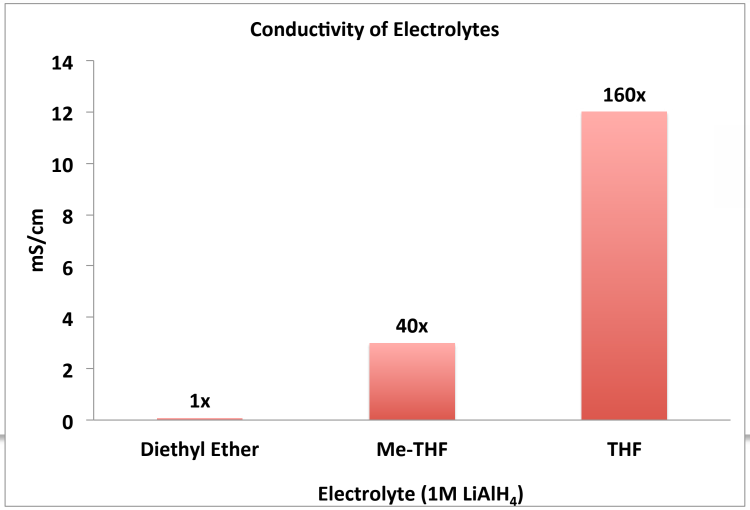
Increasing efficiency and yield by:

A) Recycling materials and additives used in making alane during:

- Electrochemical process
- And crystallizations

B) Improve conductivity and explore different adducts:

- Use THF in the electrochemical cell
- Use transmutation process to crystal from different adduct



Courtesy of Ardica/SRI presentation

Current Progress: Alane from TEA Adduct

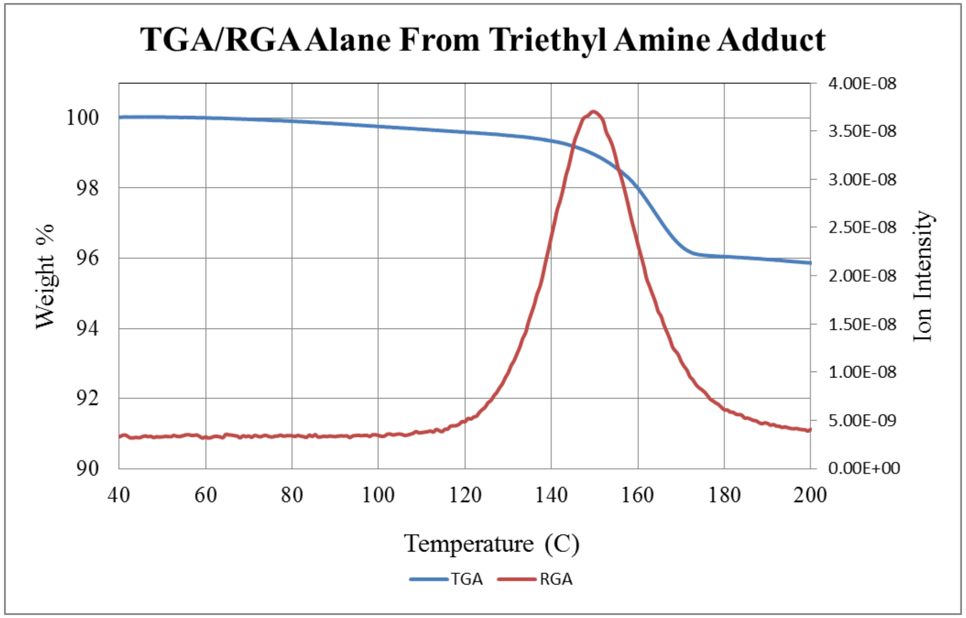


Figure shows the desorption of hydrogen from alane obtained through TEA conversion

- Using THF/LiAlH4 or THF/NaAlH4 electrolytes are an order and half of magnitude more conductive than ether/LiAlH4 electrolyte
- However, Alane forms too stable of an adduct which makes it difficult to break into AlH_3 crystals and THF
- We have shown in the past that it is possible to convert alane THF adduct to alane Triethylamine (TEA) adduct and obtain alane*
- Although not to assist in increasing ionic conductivity similar conversion processes was shown by Graetz el.**, using TMA

$$AlH_3\text{: n.THF} + \text{TEA} \rightarrow AlH_3\text{:TEA} + \text{THF}\Uparrow$$

$$AlH_3\text{:TEA} \rightarrow AlH_3\ (\alpha\text{-Crystals}) + \text{TEA}\Uparrow$$

Using different electrolyte as a route to improve conductivity

*Zidan, R.; et. al . *Chem. Comm* **2009.** (25): 3717–3719

Jason Graetz, et al. *J. Phys. Chem. C*, **2011, *115* (9), 3789–3793

Approach: Resolving Issues to Further Lower Cost of Alane

Increasing efficiency and yield by:

A) Recycling materials and additives used in making alane during:

- Electrochemical process
- And crystallizations

B) Improve conductivity and explore different adducts:

- Use THF in the electrochemical cell
- Use transmutation process to crystal from different adduct

C) Producing alane of high value by producing:

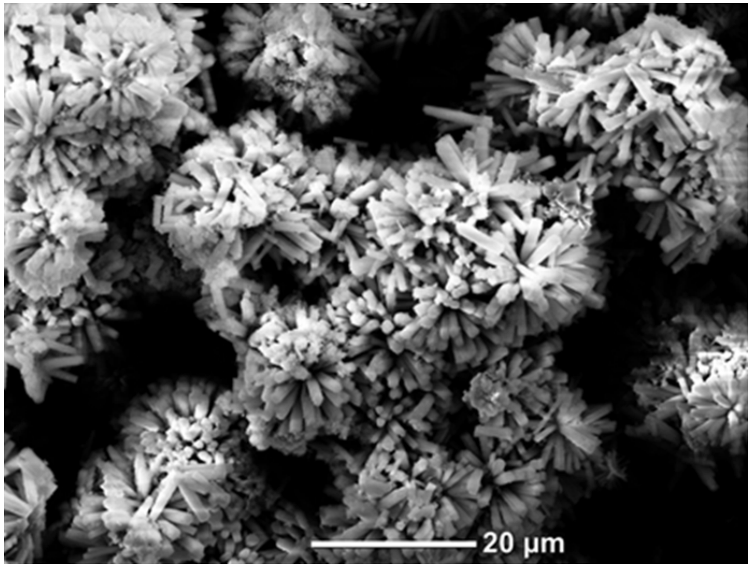
- Stable alpha alane with Crystal size larger than 5 microns
- High capacity product that is safe to handled in air and the presence of moisture

Current Progress: Different Phases of Alane

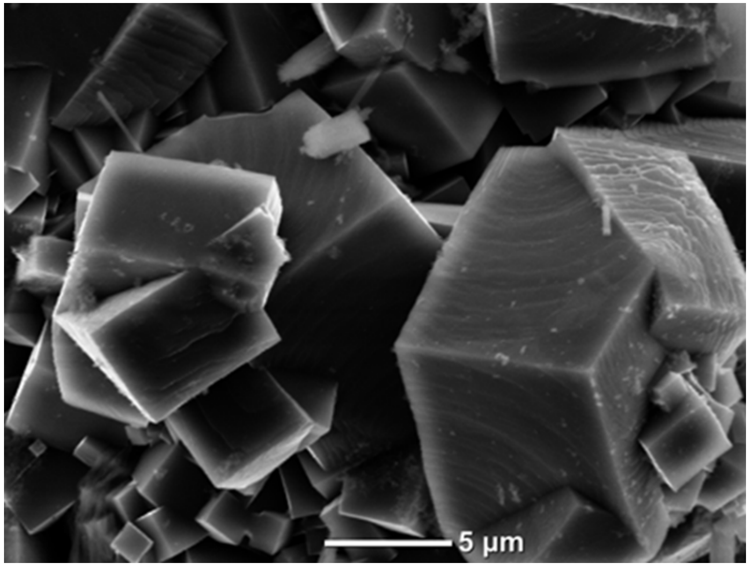
Different Cyclization conditions lead to different phases (e.g. α, α', β and γ)

Not all phases are suitable storage materials due to their instability and high reactivity

- ***Only α-phase > 5 micron crystal size is proven to keep its capacity for 10th of years***
- ***The surface of α-phase crystals can be passivated and proven not to react with air or moisture***



α' crystals are unstable nano rods



α cubical crystals

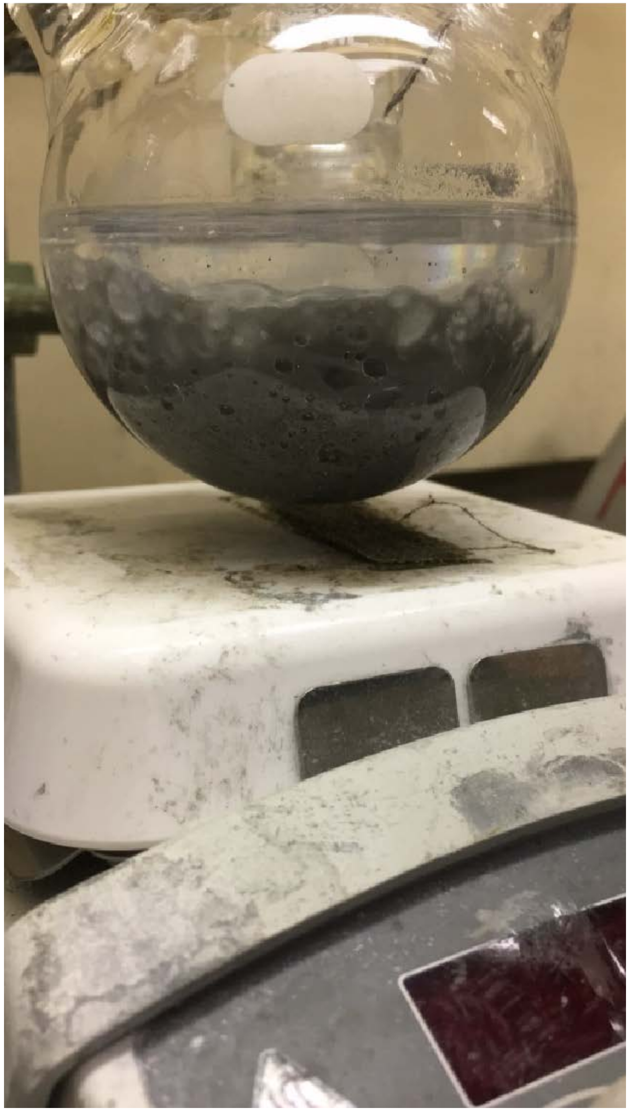
Current Progress: Stable α-Alane and Passivation Process

In order to obtain stable alane powder :

- Alane is washed with ether to dissolve any $LiAlH_4$ and $LiBH_4$ residues
- $LiAlH_4$ and $LiBH_4$ can be recovered as shown by our group
- 99.9% of $LiAlH_4$ and $LiBH_4$ was recovered from the wash
- Alane surface is passivated using acid and water as it's been shown by the DOW's methods
- Unusable and undesired by-products are dissolved and filtered high capacity alane product is obtained

← **At the beginning of passivation**

Current Progress: Stable α-Alane and Passivation Process

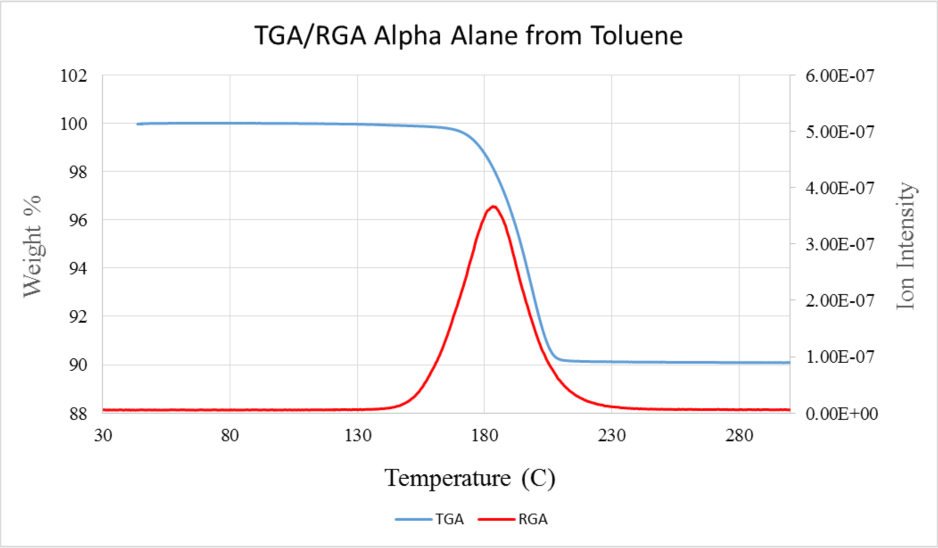


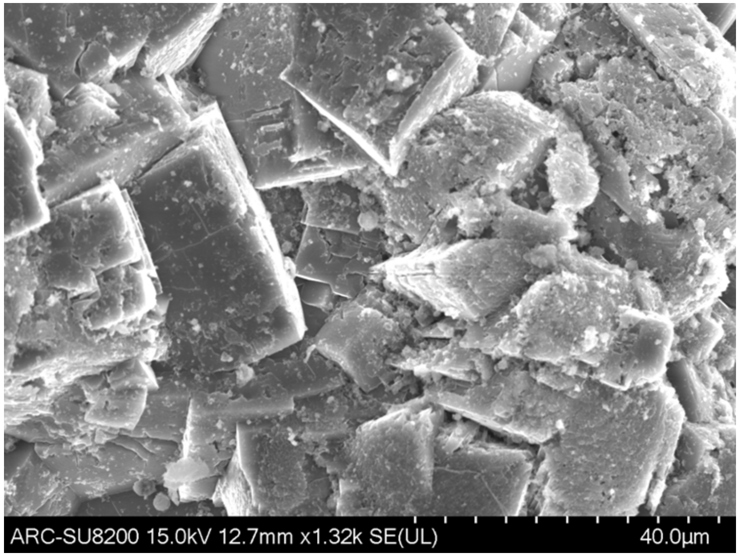
In order to obtain stable alane powder :

- Alane is washed with ether to dissolve $LiAlH_4$ and $LiBH_4$ residues
- $LiAlH_4$ and $LiBH_4$ can be recovered as shown by our group
- 99.9% of $LiAlH_4$ and $LiBH_4$ was recovered from the wash
- Alane surface is passivated using acid and water as it's been shown by the DOW's methods
- Unusable and undesired by-products are dissolved and filtered high capacity alane product is obtained

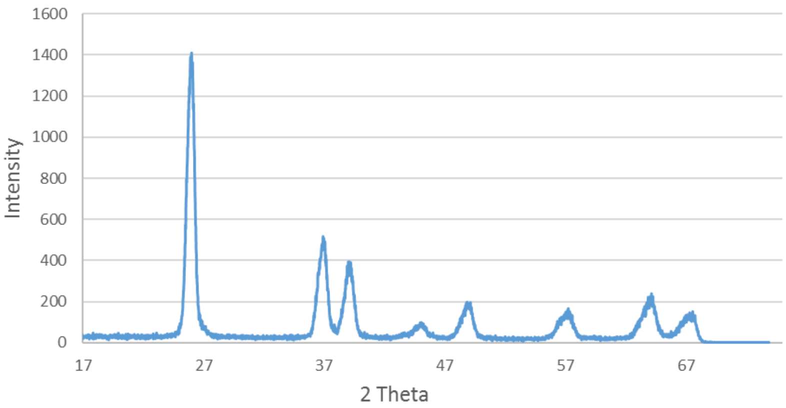
← **Toward the end of passivation**

Current Progress: Improvement of H_2 Content & Crystal Quality





- SRNL has achieved the crystallization of alane etherate adducts that have a 9.8 H_2 wt% at the 15 g scale
- SRNL is working with partners including Ardica, SRI, Albemarle, and other to better understand the crystallization process and enable scale-up of production to meet demand for portable power systems
- Work is ongoing to optimize the yield
- Utilizing process analytical to understand and control formation kinetics and thermodynamics



XRD confirming α-alane formation

Collaborations and Team members

SRNL

- Ragaiy Zidan
- Scott McWhorter
- Rob Lascola
- Joseph Teprovich
- Patrick Ward
- Scott Greenway
- Ted Motyka

Ardica and SRI

- Dick Martin
- Robert Wilson
- Mark Petrie
- Steve Crouch-Baker

Remaining Challenges and Barriers

- Identify additives to further improve the conductivity of the electrolyte solution to increase the rate of alane production
- Develop improved understanding of crystallization processes for improved thermal control and processing kinetics
- Optimize the crystallization parameters for the large scale production of alpha alane
- Obtain high yield from alternative adduct

On-Going and Future work

- Using THF as solvent in electrolyte to increase conductivity
- Establishing efficient methods for crystallization of alane from different adducts such as TEA or TMA to enable the use of THF in the electrolyte
- Exploring using additives to the electrochemical cell which can increase the conductivity further
- Using *in-situ* spectroscopy (e.g. Raman) to identify the crystallization mechanisms
- Establishing advanced process analytical techniques that enable a continuous large-scale alane production operation

Summary

- Identified and addressed the most significant costs for the production of α-alane
- Demonstrated recovery techniques for the expensive crystallization additives to reduce cost of alane production
- Demonstrated the formation of LiH during the electrochemical production of alane that further reduces dendrite formation
- Demonstrated a route to crystallize the alternative adduct produced by a transamination reaction from the THF adduct that enables the use of high ionic conductivity electrolyte
- Demonstrated production of high hydrogen content alane (9.8 wt%) at 15 g scale with high improved crystal quality