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Project ID# ST063

Reversible Formation of Alane

A High Hydrogen Density Material for Energy Storage

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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.*

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

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

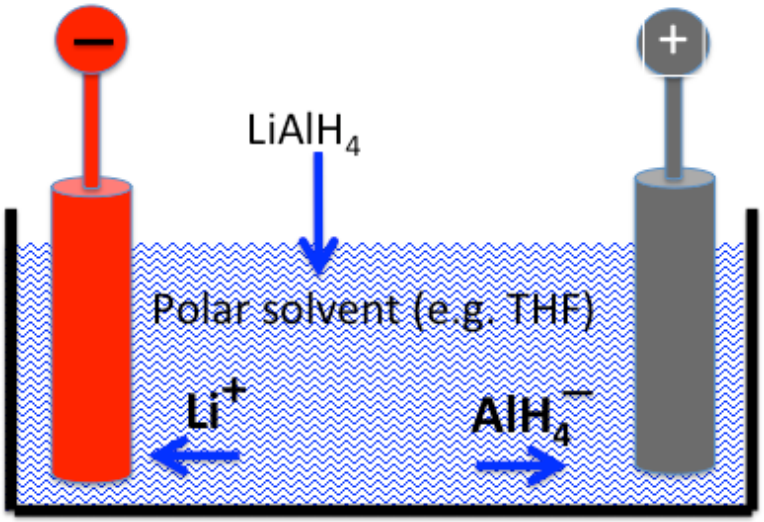
$$AlH_3 : Solvent(Adduct) \rightarrow AlH_3(crystals) + Solvent$$

- *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

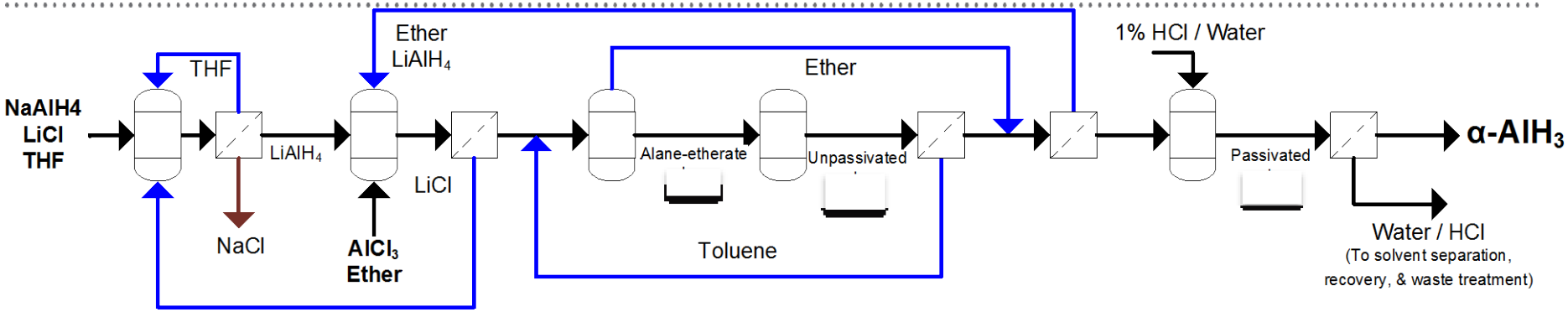
B) Improve conductivity and explore different adducts:

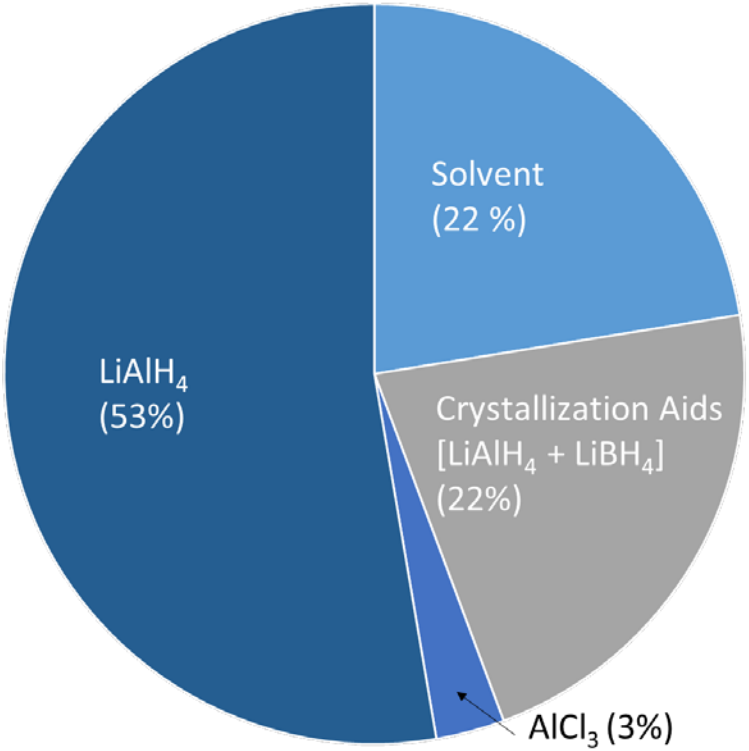
- Use THF in the electrochemical cell
- Use transmutation process to crystal from different adduct

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**

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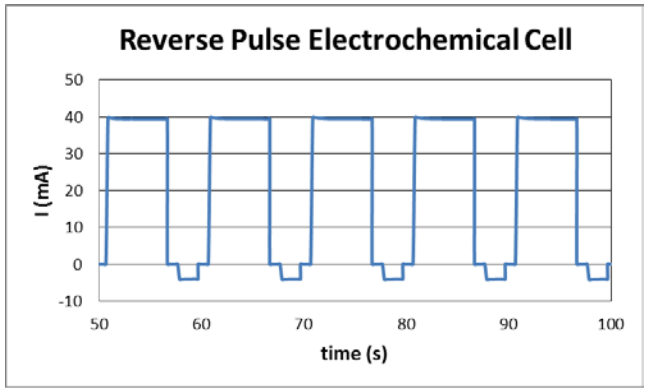
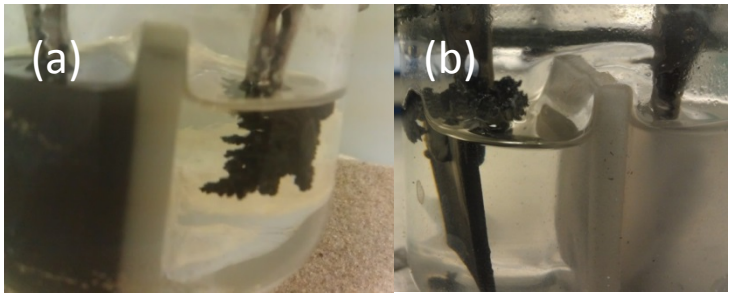
Current Progress: Cathode Optimization/Electrolyte Regeneration

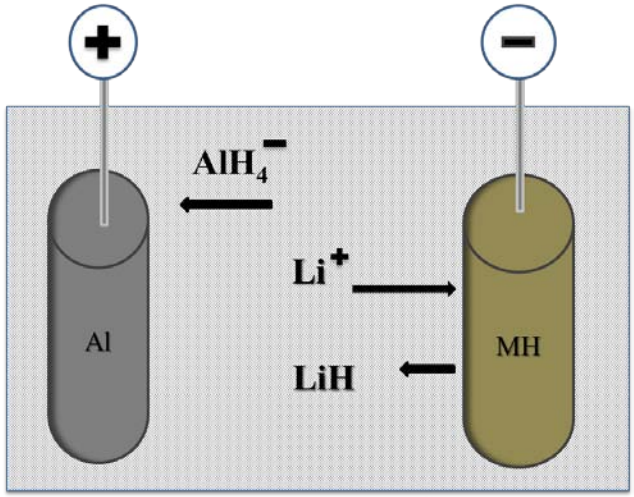
2015 Results: Dendrites were significantly reduced by utilizing a reverse pulse technique during the electrochemical reaction



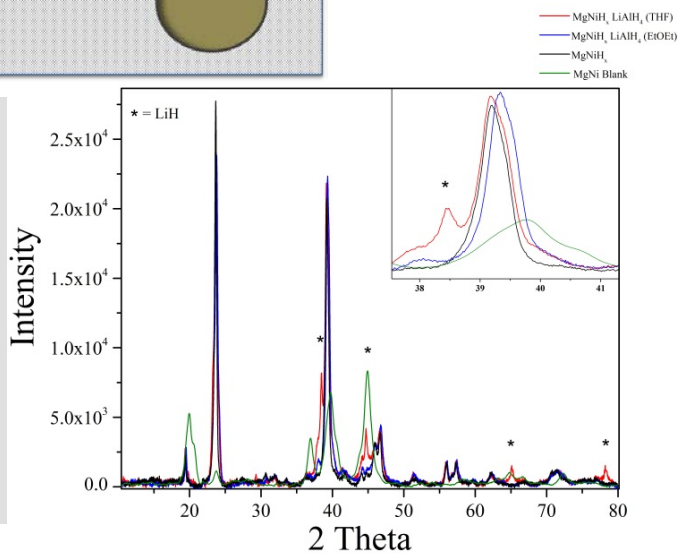


Dendrites from typical 18 hour reaction (a) and (b) reduction after reverse pulsing.

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



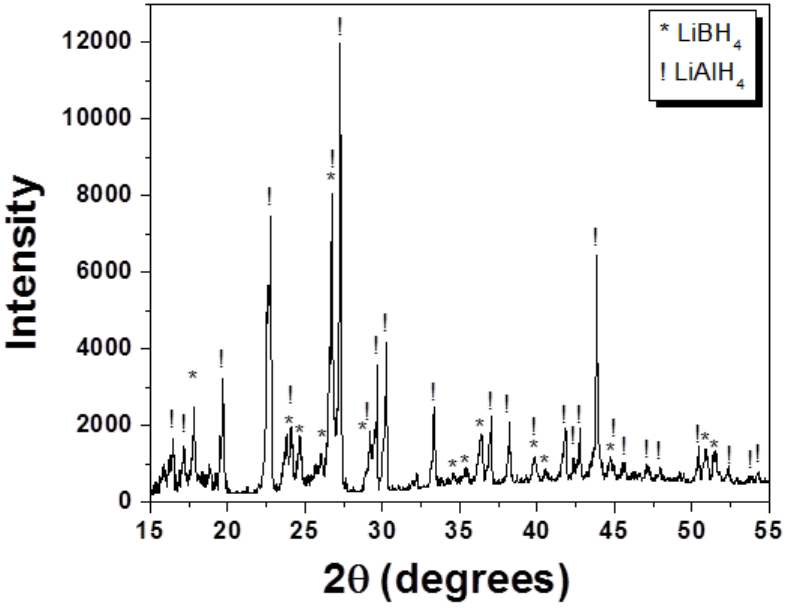
XRD of cycled MgNi electrode in the presence of H_2 reveals the formation of LiH



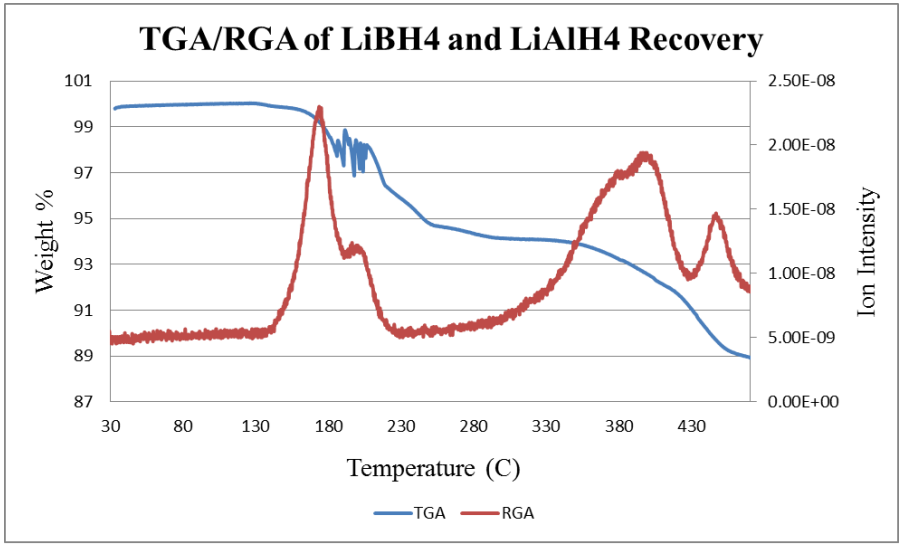
Current Progress: Recovery of $LiBH_4$ and $LiAlH_4$

- $LiBH_4$ 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

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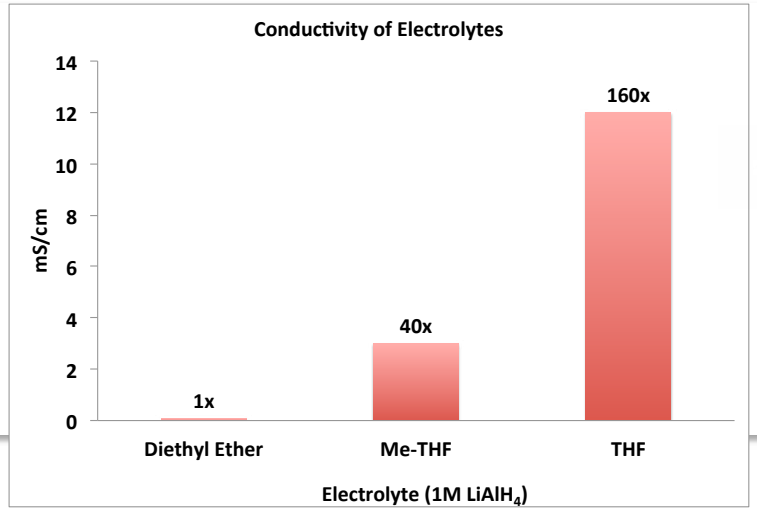

Courtesy of Ardica/SRI presentation

Current Progress: Alane from TEA Adduct

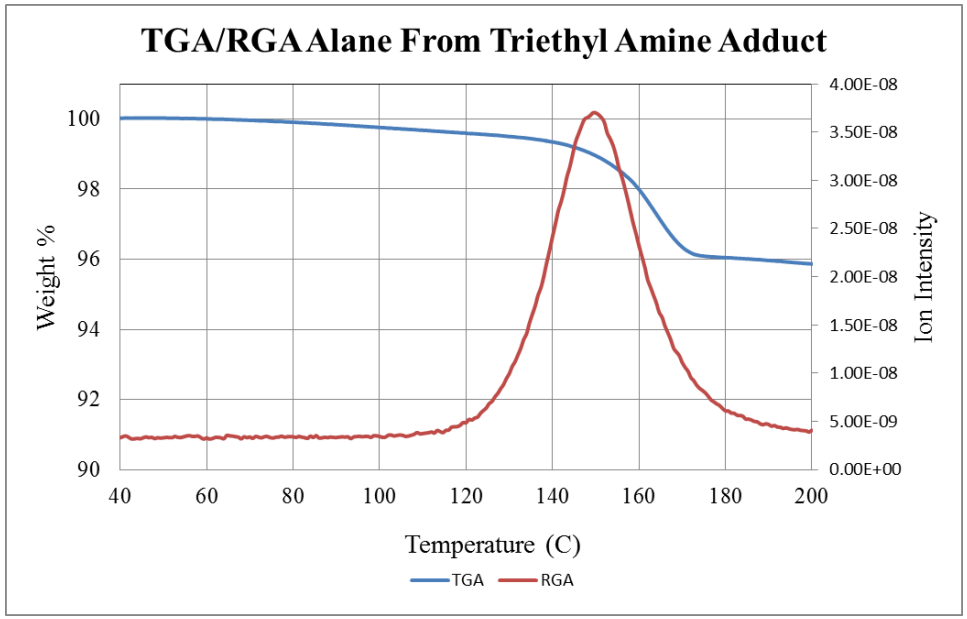

Figure shows the desorption of hydrogen from alane obtained through TEA conversion

- 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: n.THF + TEA → AlH_3:TEA + THF⇧

AlH_3:TEA →AlH_3 (α-Crystals)+ TEA⇧

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

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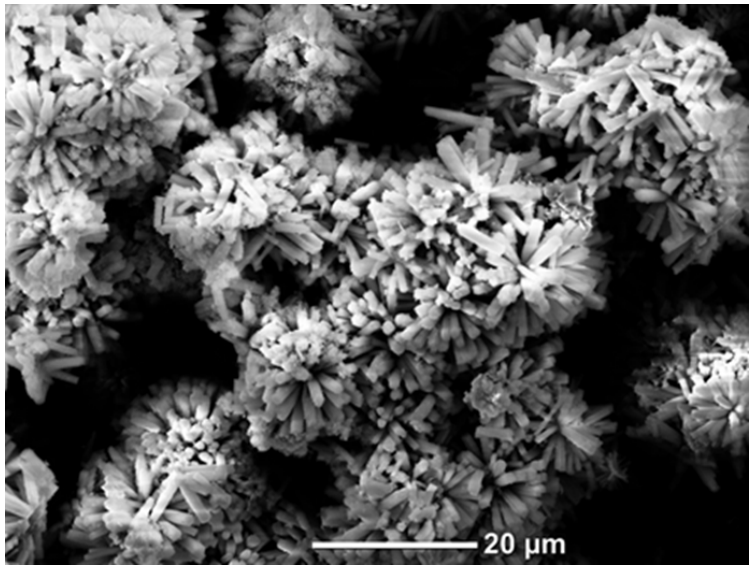
Current Progress: Different Phases of Alane

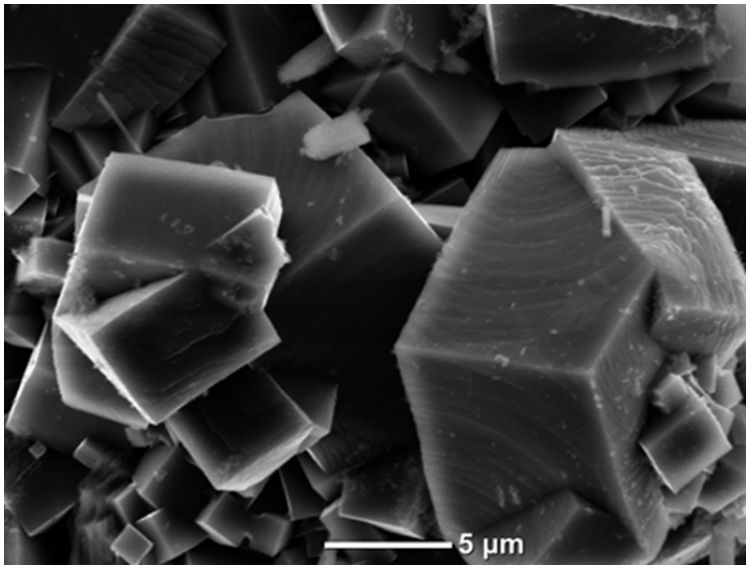
Different Cyclization conditions lead to different phases (e.g. α, α', β and γ)

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 10^{th} of years***
- ***The surface of α-phase crystals can be passivated and proven not to react with air or moisture***

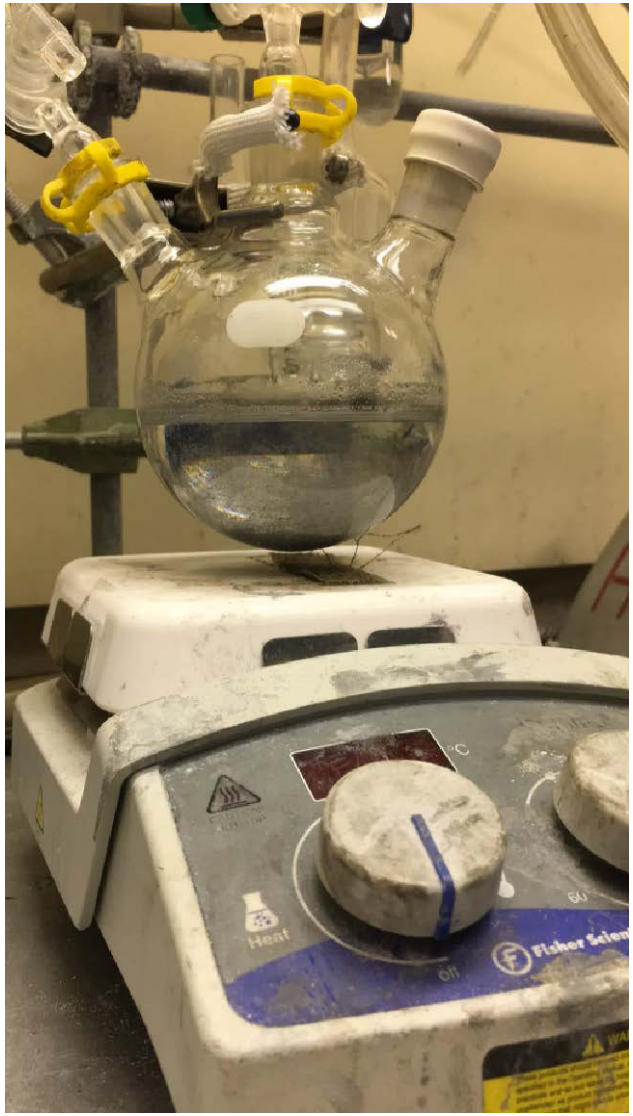


α' crystals are unstable nano rods



α cubical crystals

Current Progress: Stable α-Alane and Passivation Process

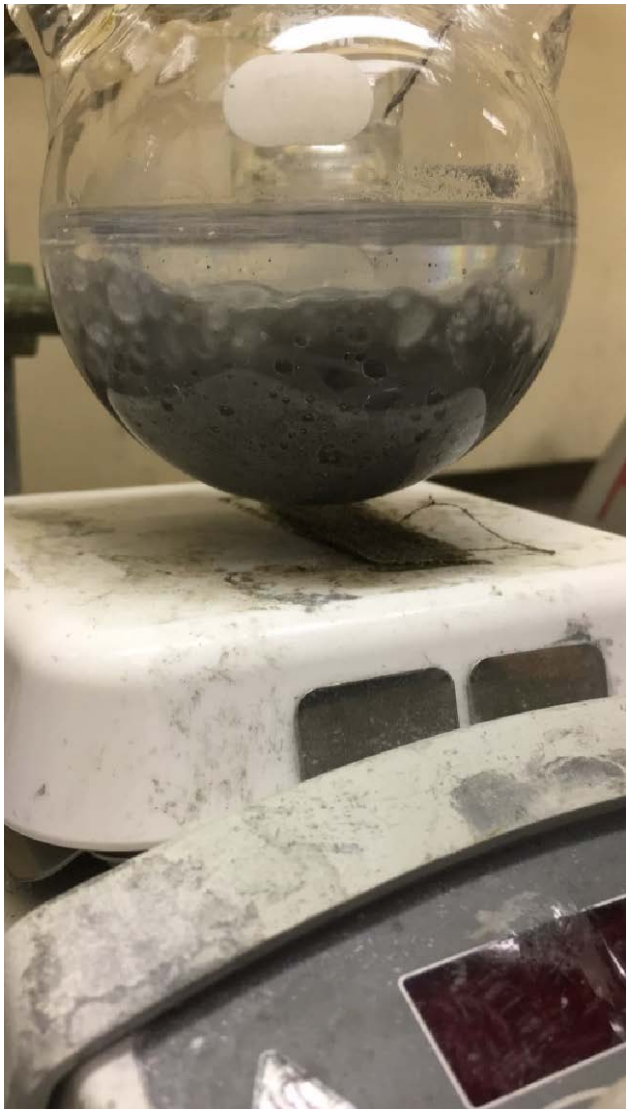


In order to obtain stable alane powder :

- Alane is washed with ether to dissolve any LiAlH4 and LiBH4 residues
- LiAlH4 and LiBH4 can be recovered as shown by our group
- 99.9% of LiAlH4 and LiBH4 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



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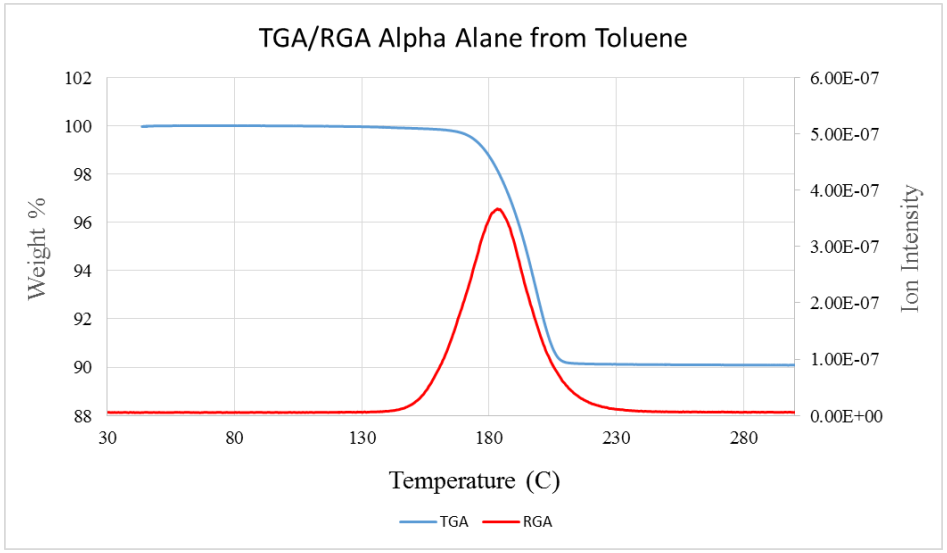
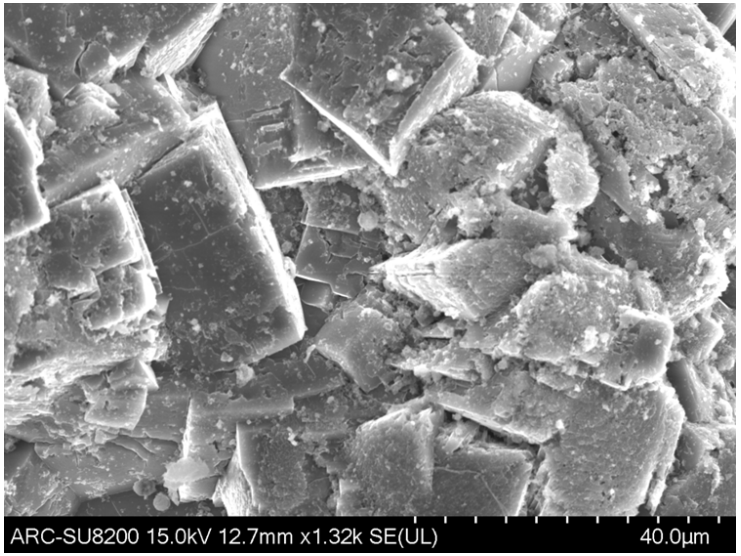
- Alane surface is passivated using acid and water as it's been shown by the DOW's methods
- Unusable and undesired by-products are dissolved and filtered high capacity alane product is obtained

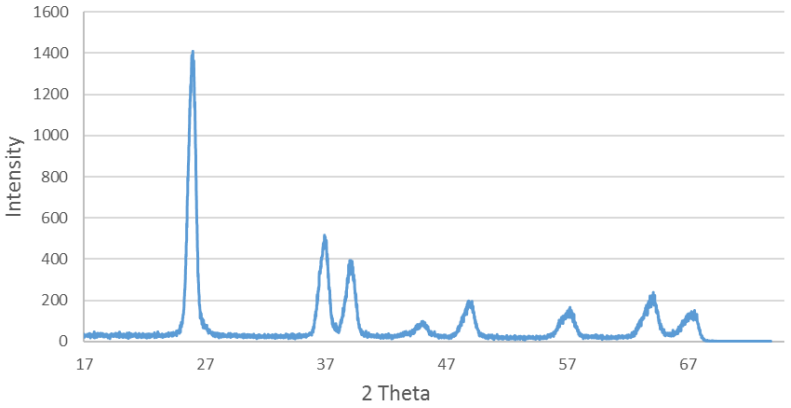
Toward the end of passivation

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