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Project ID# ST063

Formation and Regeneration of Alane

A High Hydrogen Density Material for Energy Storage

Advances Toward Lower Cost

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Energy Security Directorate
Savannah River National Laboratory
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2017 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 FY17: 60%

Barriers

- Recycle or reduce dendrite formation for lower cost of electrochemical production
- Reduced overall cost for alane synthesis
- Increase conductivity or exchange and crystallize alternative adduct from AlH_3•THF to increase efficiency of alane production/regeneration

Budget

- **FY15** - $400K
- **FY16** - $400K
- **FY17** - $400K

Collaborators

- Ardica (CRADA Partners)
- SRI

Relevance: Alane as a Hydrogen Storage Material

AlH_3

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.

Overall Objectives

Develop a low-cost hydrogen storage material having favorable thermodynamics, kinetics, and high volumetric and gravimetric hydrogen densities

Specific Objectives

Develop less expensive techniques to synthesize alane (AlH_3) to support scale-up, production, quality control, and implementation

Relevance: Traditional Methods to Synthesize Alane

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

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

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

- AlH_3 Adduct consists of AlH_3 and a coordinating ligand (e.g., Et_2O)
- Depending on crystallization conditions different phases can form (e.g. α, α', and γ)
- Only the alpha phase is stable over long periods of time
- LiCl is unrecoverable making this chemical route a costly process when losing expensive Li

Approach: Alane as a H2 Storage Material at Lower Cost

Specific Objectives

Develop less expensive techniques to synthesize alane AlH_3 to support scale-up, production, quality control and implementation

- Utilize methods developed and improved by SRNL to form and regenerate AlH_3 electrochemically from spent aluminum
- Achieve lower cost and higher conductivity by using **$NaAlH_4$** in THF instead of $LiAlH_4$ in diethyl ether for electrolyte
- Achieve low cost using **$NaAlH_4$** instead of **$LiAlH_4$** in a new SRNL chemical method to produce easily crystallized AlH_3•EtOEt
- Develop crystallization methods to produce alpha phase alane that is stable over time

Methodology & Path Toward Lower Cost

Lower cost sodium (Na) is used instead of Li since Na is Earth's sixth most abundant element and it is the most abundant alkali metal. Sodium can be obtained commercially by electrolysis of molten sodium chloride.

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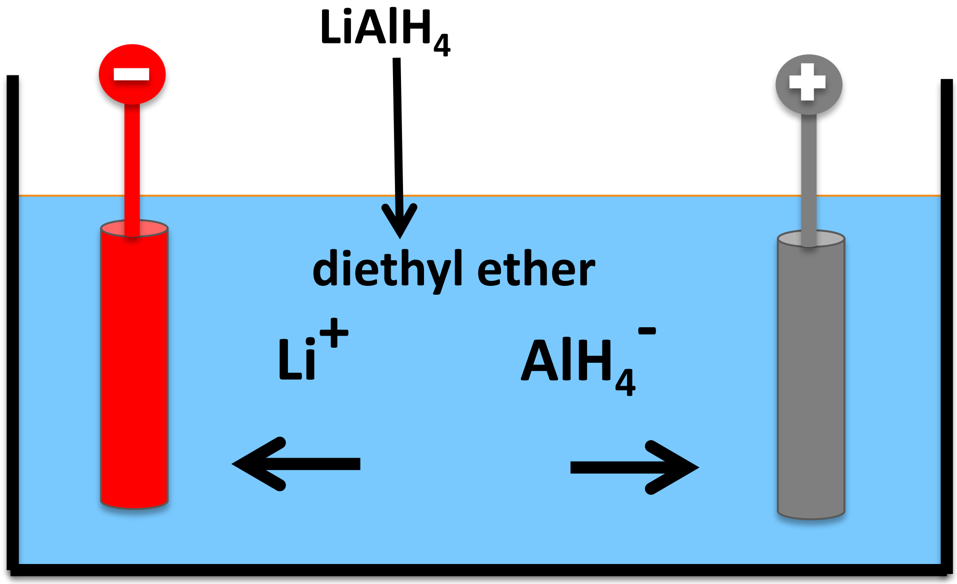
Methodology & Path Toward Lower Cost

Relevance: Advantages of Electrochemical Alane Generation

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



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

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

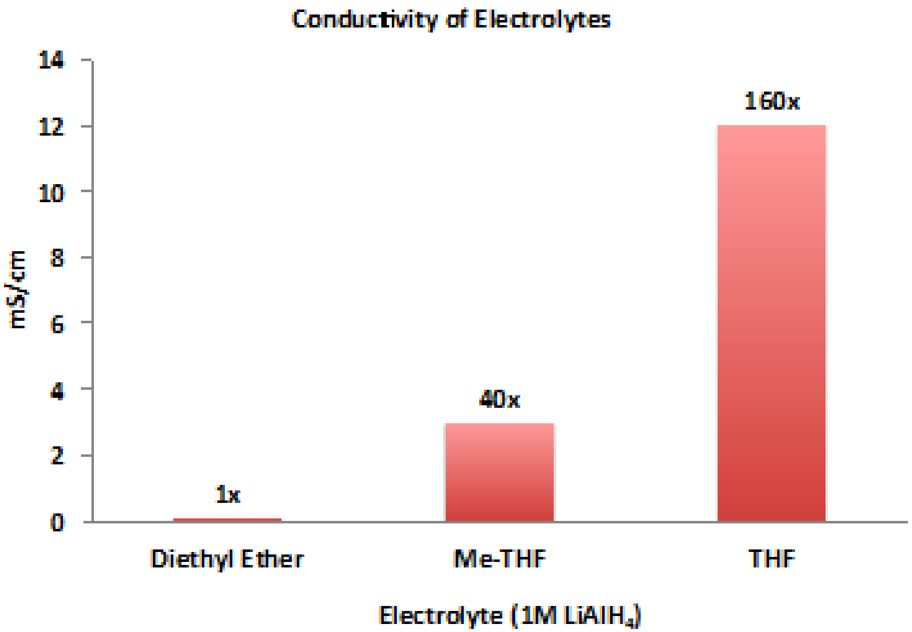
$$LiH + Al + {}^3/_2\, H_2 \Leftrightarrow LiAlH_4$$

Approach: Resolving Issues to Further Lower Cost of Alane

Increasing Efficiency and Yield

Improve conductivity and explore different adducts

- Use THF in the electrochemical cell
- Use DFT calculations to determine suitable ligands for exchange
- Exchange and crystallize alternative adducts of AlH_3



Courtesy of Ardica/SRI presentation

Approach: Alane as a H2 Storage Material at Lower Cost

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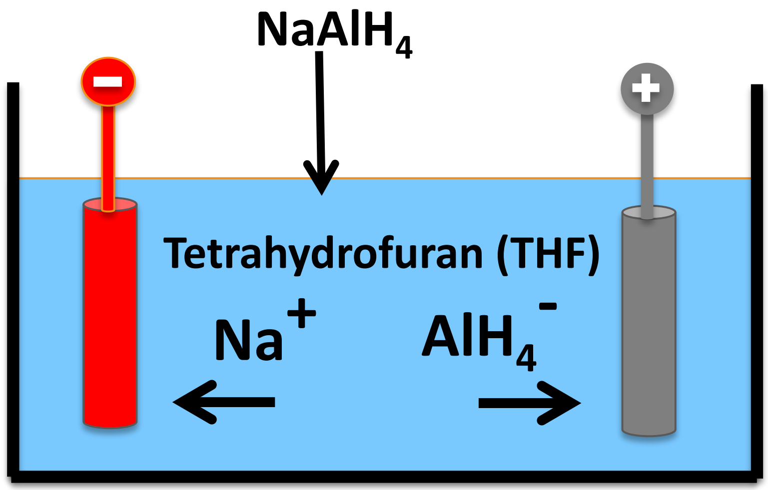
Methodology & Path Toward Lower Cost

Relevance: Electrochemical Alane Generation using $NaAlH_4$



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

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

$$NaH + Al + {}^3/_2 H_2 \Leftrightarrow NaAlH_4$$

Cost Analysis Including Inefficiencies of the formation Alane: adduct

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

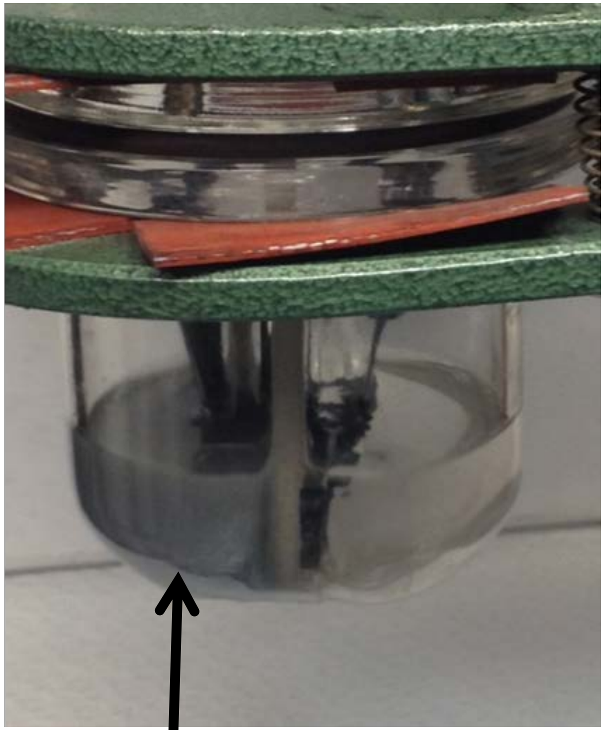
Hydrogen Cost in AlH_3	\$0.428	\$/kg
E-Chem Thermo Cost	\$0.103	\$/kg
E-Chem Kinetics Cost	\$0.096	\$/kg
E-Chem Ohmic Cost	\$0.114	\$/kg
Total E-Chem Cost from NAH	\$0.742	\$/kg

AlH_3 produced from electrochemically using $NaAlH_4$ is an alane adduct that still needs crystallization and passivation, adding to cost. Large scale production will be useful to further reduce cost

Current Progress: Electrochemical Formation of AlH_3 from $NaAlH_4$ in THF

Before Electrolysis

After Electrolysis



Solid Adduct: AlH_3•THF

Collaboration with Ardica/SRI

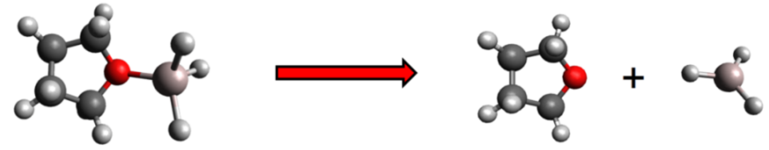
- The AlH_3-THF precipitates due to being in saturated solution of $NaAlH_4$ THF electrolyte
- The resulting solid can be filtered and exchanged with another solvent such as TEA to form TEA:AlH3
- Alpha alane can be obtained by heating the isolated TEA alane adduct under vacuum at 65-70 °C

Current Progress: Exchanging Alane from THF Adduct

Adduct	Bond Dissociation Enthalpy (kJ/mol)	Bond Dissociation Enthaply (kcal/mol)
AlH_3•Me_2EtN	110.27	26.36
AlH_3•Me_2O	85.40	20.41
AlH_3•Et_2O	74.90	17.90
AlH_3•Et_2MeN	73.13	17.48
AlH_3•2-MeTHF	93.24	22.28
AlH_3•N-MeMorp_N	97.03	23.19
AlH_3•IsoproMe2N	92.35	22.07
AlH_3•THF	94.94	22.69
AlH_3•Et3N	98.23	23.48
AlH_3•DiisoproMeN	87.51	20.92
AlH3•EtButylO	76.01	18.17
AlH3•ProButylO	76.26	18.23
AlH3•MeButylO	77.70	18.57
AlH3•MTBE	73.16	17.49
AlH3•Pro2O	77.41	18.50
AlH3•Butyl2O	77.45	18.51
AlH3•MeProO	81.18	19.40
AlH3•MeEtO	81.00	19.36

The above results were calculated at the B3LYP/6-311g** level of theory

Collaboration with Ardica/SRI



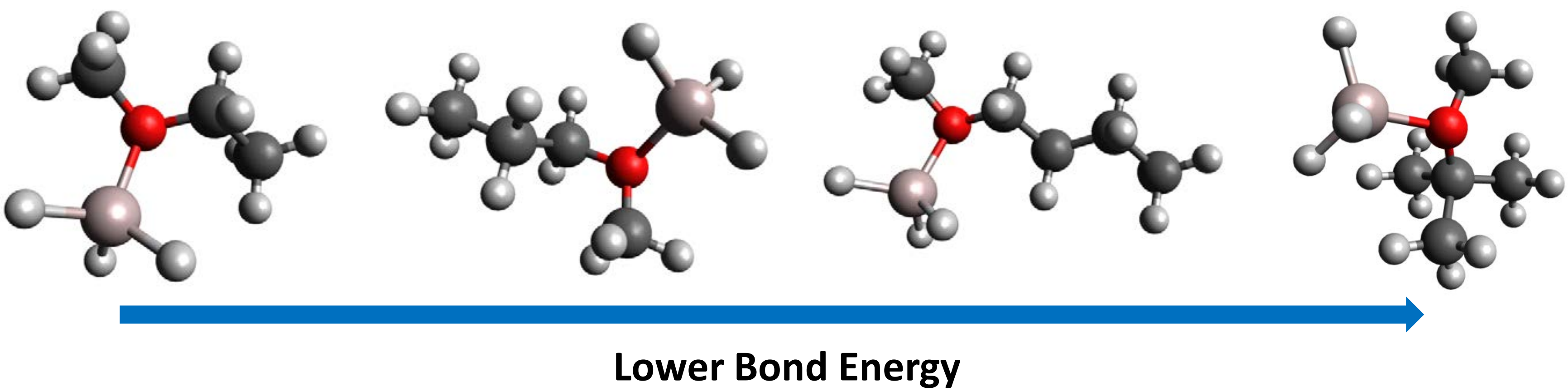
- B3LYP and CCSD(T) bond dissociation energies for various adducts
- Exchange with THF in the AlH_3•nTHF adduct will be most efficiently carried out with ligands which have similar or greater bond strengths
- This bond strength does **NOT** convey the **FULL** picture for **crystallization** since the crystallization of these adducts rarely occur by a one step process, but rather by first crystallizing to an adduct which has AlH_3•nL (n<1)

Current Progress: Crystallizing Alternative Adducts

Collaboration with Ardica/SRI

- Bond dissociation energies calculated show a trend in both symmetry and steric hindrance
- Asymmetric and bulky ligands tend to reduce the bond energy
- Boiling point also plays a crucial role in the crystallization process since removal of the ligand solvent in a timely fashion is essential for the formation of the α phase

Adduct	Bond Dissociation Enthalpy (kJ/mol)	Bond Dissociation Enthaply (kcal/mol)
AlH_3•MeEtO	81.00	19.36
AlH_3•MeProO	81.18	19.40
AlH_3•MeButylO	77.70	18.57
AlH_3•MTBE	73.16	17.49



Current Progress: Alane from TEA Adduct

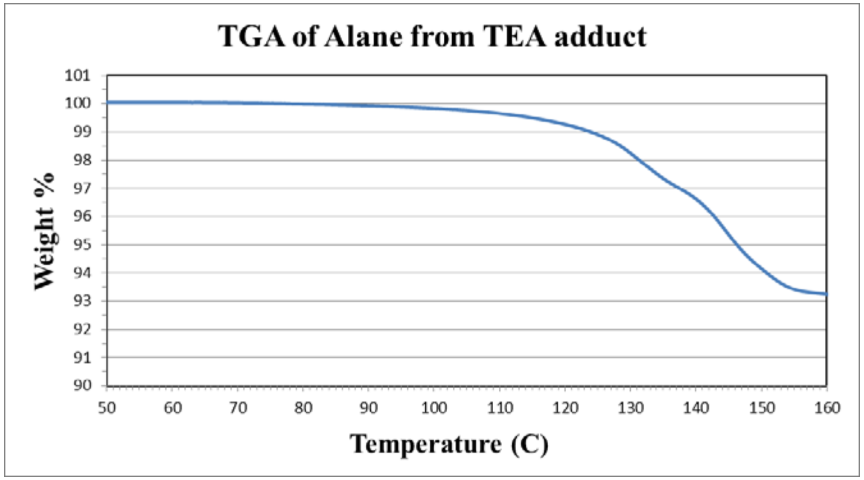
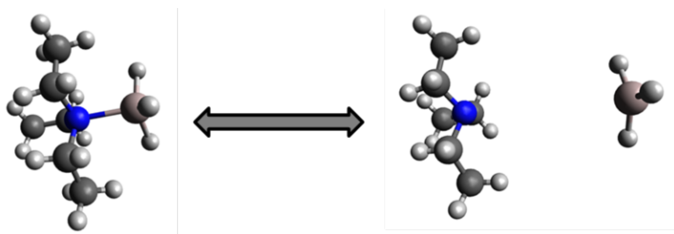


Figure shows the desorption of hydrogen from alane obtained through TEA conversion

AlH_3: n THF + TEA → AlH_3:TEA + THF$\Uparrow$

AlH_3:TEA → AlH_3 (α-Crystals)+ TEA$\Uparrow$



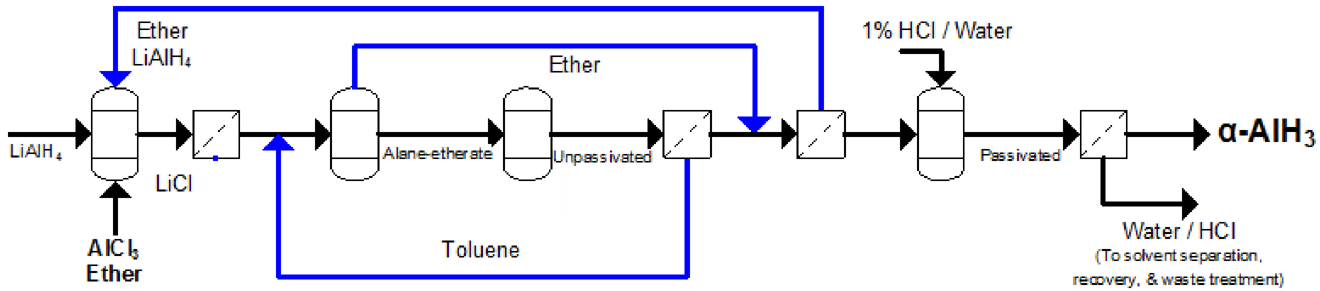
Using different electrolyte as a route to improve conductivity

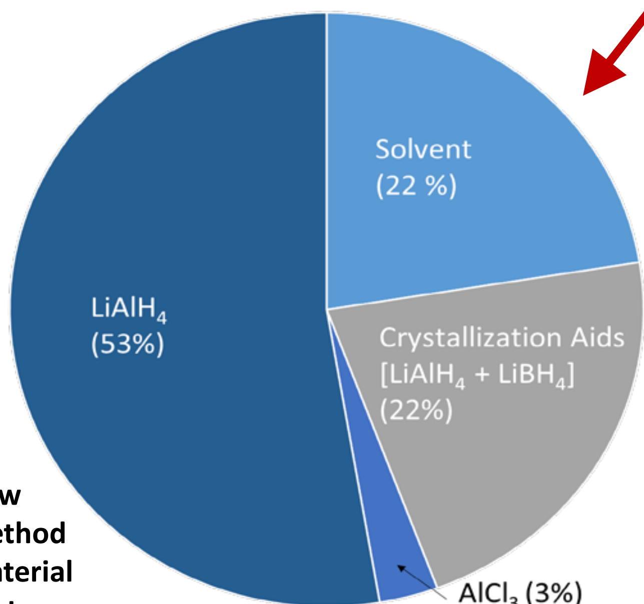
- Using THF/$LiAlH_4$ or THF/$NaAlH_4$ electrolytes are **1.5X** more conductive than ether/LiAlH4 electrolyte
- However, Alane forms too stable of an adduct which makes it difficult to break into AlH_3 crystals and THF
- Previous results show that it is possible to convert alane THF adduct to alane Triethylamine (TEA) adduct and obtain alane*
- Although not to assist in increasing ionic conductivity similar conversion processes was shown by Graetz el.**, using TMA

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

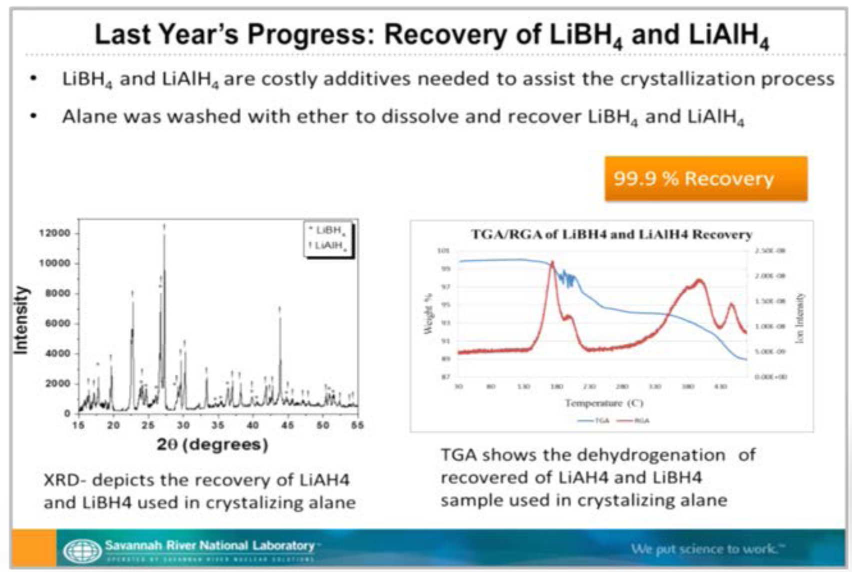
Jason Graetz, et al. *J. Phys. Chem. C*, **2011, *115* (9), 3789–3793

Relevance: Cost Chart of Forming AlH_3 Chemically using $LiAlH_4$





Dow Method Material Costs



Last Year's 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

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Even when solvent is recovered more than 50% of the material cost is due the use of $LiAlH_4$ as a precursor.

Approach: Lowering Cost using $NaAlH_4$ instead of $LiAlH_4$

Specific Objectives

Develop less expensive techniques to synthesize alane AlH_3 to support scale-up, production, quality control and implementation

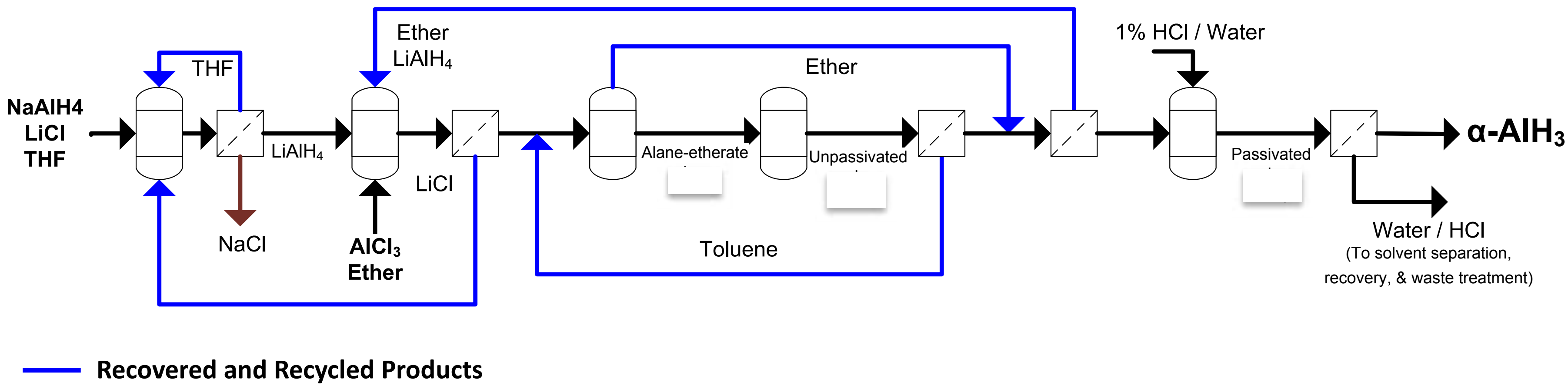
- Utilize methods developed and improved by SRNL to form and regenerate AlH_3 electrochemically from spent aluminum
- Achieve lower cost and higher conductivity by using $NaAlH_4$ in THF instead of $LiAlH_4$ in diethyl ether for electrolyte
- **Achieve low cost using $NaAlH_4$ instead of $LiAlH_4$ in a new SRNL chemical method to produces easily crystallized AlH_3•EtOEt**
- Develop crystallization methods to produce alane of alpha phase that is stable over time

Methodology & Path Toward Lower Cost

Using sodium which is Earth's sixth most abundant element and the most abundant alkali metal leading to lower cost with scaling up

Relevance: Dow used $NaAlH_4$ as a Precursor to Lower Cost

Dow Method using $NaAlH_4$



- Dow method used $NaAlH_4$ as precursor by reacting it with LiCl in THF to produce $LiAlH_4$
- Separating $LiAlH_4$ from THF needs extensive chemical processing of heating and vacuuming
- The resultant $LiAlH_4$ was found to contain traces of THF:$LiAlH_4$
- THF:$LiAlH_4$ results in the formation THF alane adduct
- THF alane adduct leads to the formation of undesired nano aluminum particles

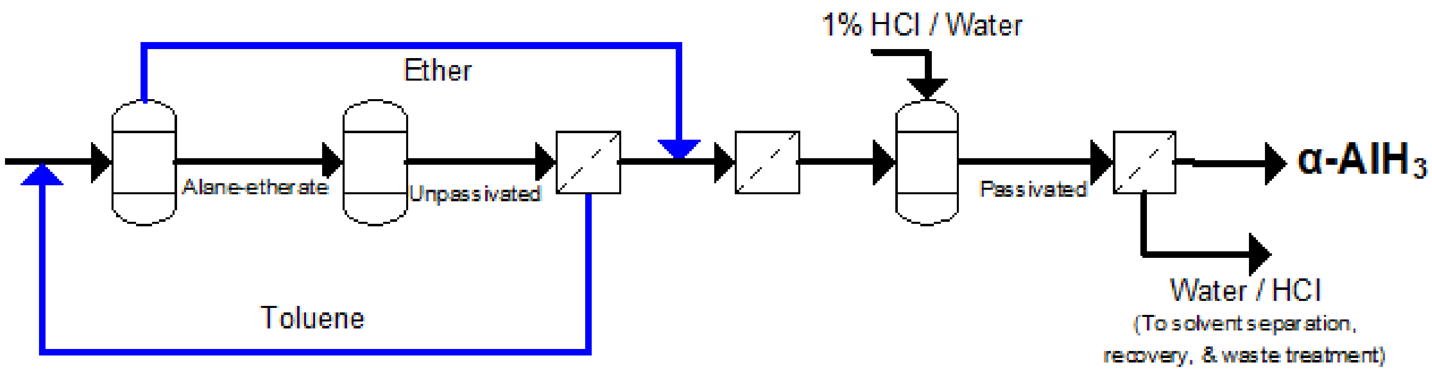
$NaAlH_4$ does not dissolve in diethyl ether

Accomplishment: SRNL Method using $NaAlH_4$ as a Precursor

- Crystallizing alane from diethyl ether alane adduct is the most well-known method to obtain alpha alane with appropriate crystal sizes compared to crystallization of other adducts (e.g. THF, TMA, etc.).
- The diethyl ether bond with AlH_3 can be broken at temperatures lower than temperature at which AlH_3 decomposes, in contrast to THF•AlH_3 bond
- $LiAlH_4$ is soluble in diethyl ether and therefore can chemically produce diethyl ether alane adduct after reaction with $AlCl_3$
- $NaAlH_4$ is not soluble in diethyl ether, but is soluble in THF. Inability to produce alpha alane (without aluminum) from the THF•AlH_3 adduct makes typical chemical production of alpha alane from $NaAlH_4$ impractical.
- Four years ago, SRNL developed a patented method* (Dry Method) to form alane mechano-chemically from $LiAlH_4$ and $AlCl_3$ or from $NaAlH_4$ and $AlCl_3$
- The alane resulted from the dry method was nano crystalline in size and not stable over time

*Ragaiy Zidan, Douglas A. Knight, Long V. Dinh; Novel Methods for Synthesizing Alane without the Formation of Adducts and Free of Halides US20120141363 Feb 2013

Accomplishment: New SRNL Method using $NaAlH_4$

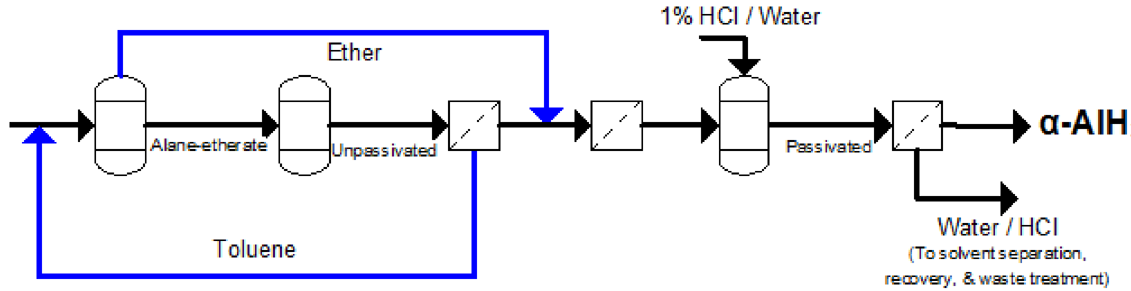


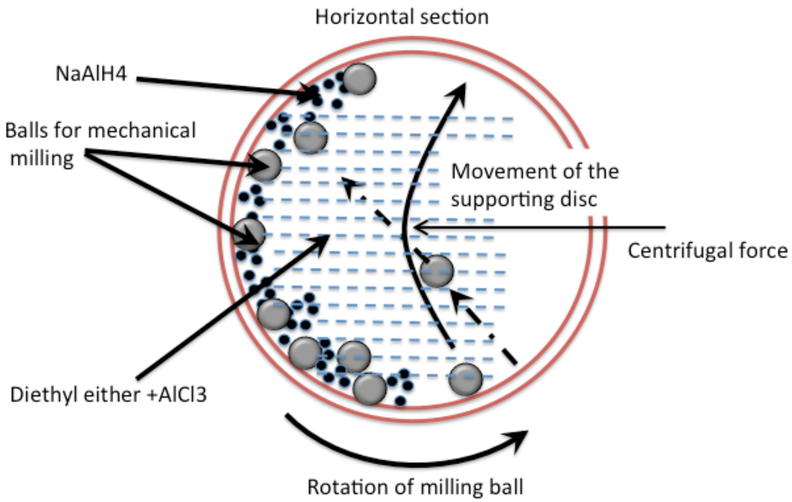
Alane-etherate Formed Using Mechanochemical Method

- SRNL modified the mechano-chemical method to form alane etherate from $NaAlH_4$ and $AlCl_3$, to be able to produce larger crystals of alpha alane
- The reaction between $NaAlH_4$ and $AlCl_3$ was carried out mechano-chemically in diethyl ether
- The diethyl ether stabilizes AlH_3 as it forms mechano-chemically to produce the AlH_3:Et_2O adduct
- The adduct can be used in the DOW crystallization process shown previously

Accomplishment: New SRNL Method using $NaAlH_4$

Alane-etherate Formed Using Mechanochemical Method





Schematic of planetary ball milling method for AlH_3 production from $NaAlH_4$

__Essential Variables:__

- Temperature = X
- Pressure = X
- Concentration = X
- Residence Time = X

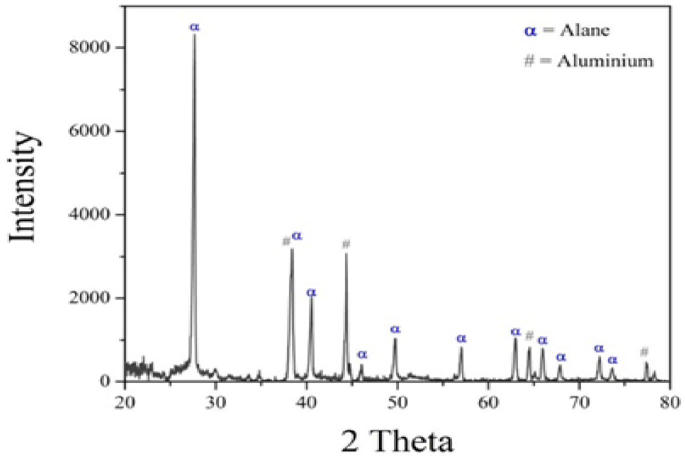
EXPORT CONTROL

Patent: U.S. Application No.: 15/482,913

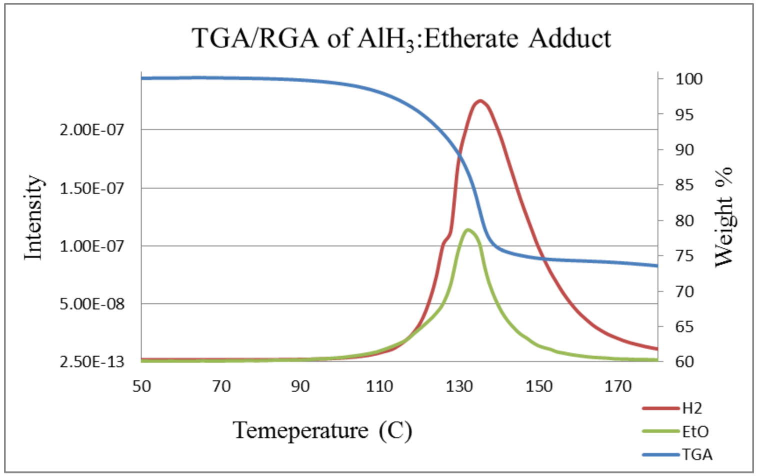
Planetary ball milling used for AlH_3 production from $NaAlH_4$

Accomplishment: New SRNL Chemical Method using $NaAlH_4$

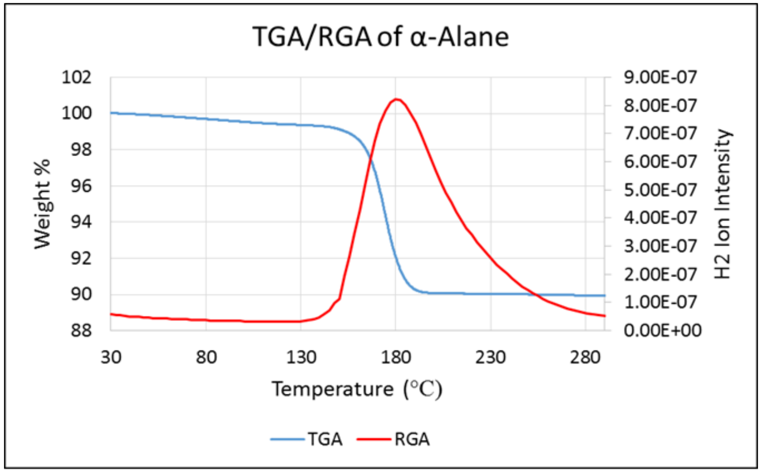
- Mechanochemical method results in the formation of soluble AlH_3•EtOEt which can be removed from unreacted reagents by filtration.
- This alane etherate was crystallized via the "dry method" as a proof of concept
- Full scale crystallization of etherate produced by this method is currently limited by the size of the planetary mill.



XRD of alane produced from etherate generated by mechanochemical process



TGA/RGA of crude alane etherate produced by mechanochemical process



TGA/RGA of alane produced from etherate generated by mechanochemical process

Approach: Alane as a H_2 Storage Material at Lower Cost

Specific Objectives

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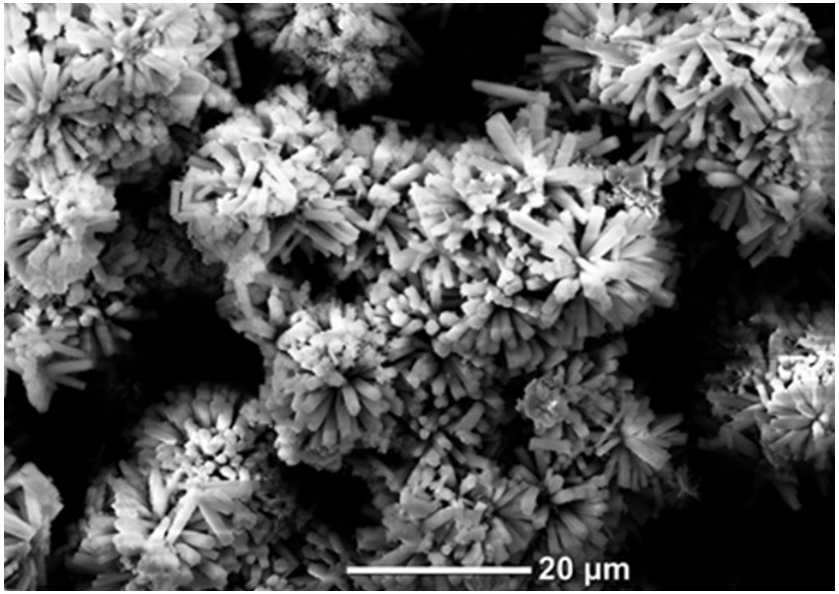
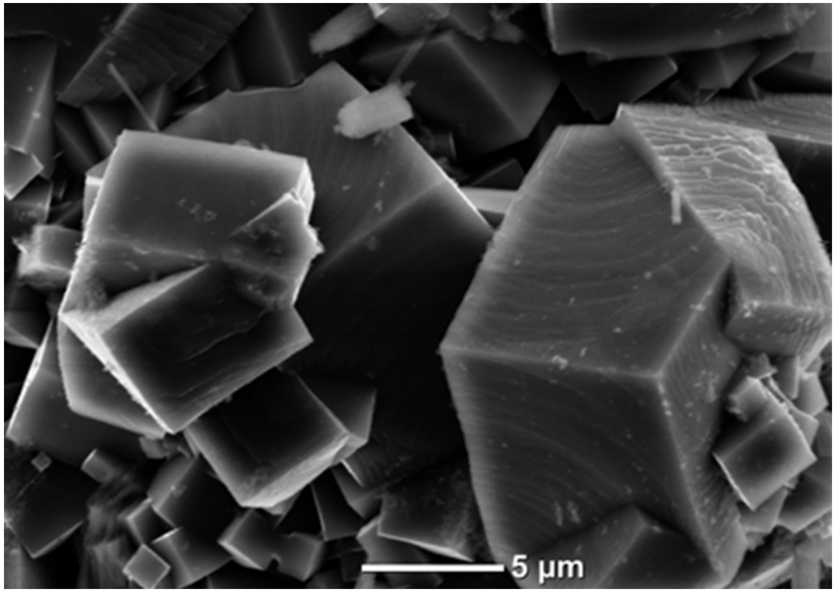
- **Develop crystallization methods to produce alpha phase alane that is stable over time**

Toward High Quality Alane

Relevance: Crystallization and Different Phases of Alane



α' crystals are unstable nano rods

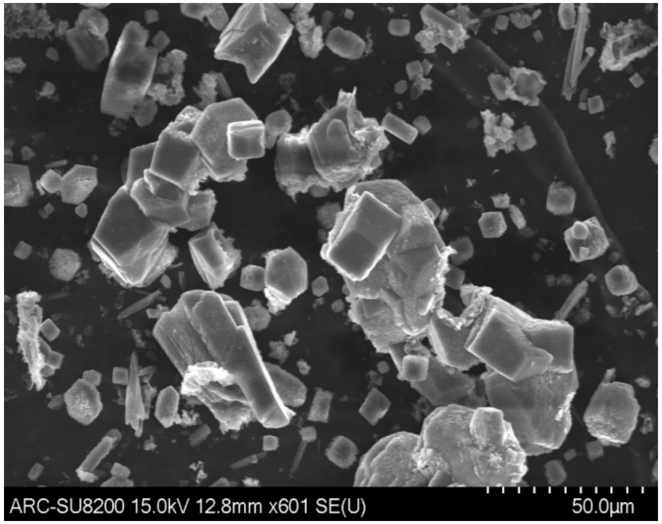


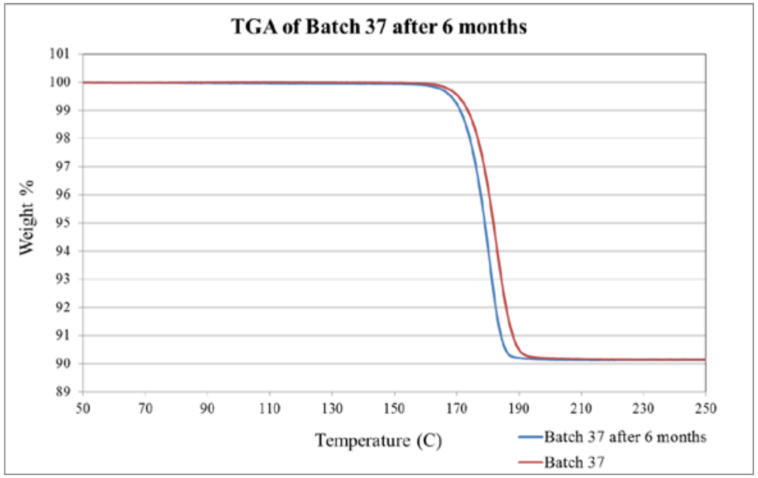
α cubical crystals

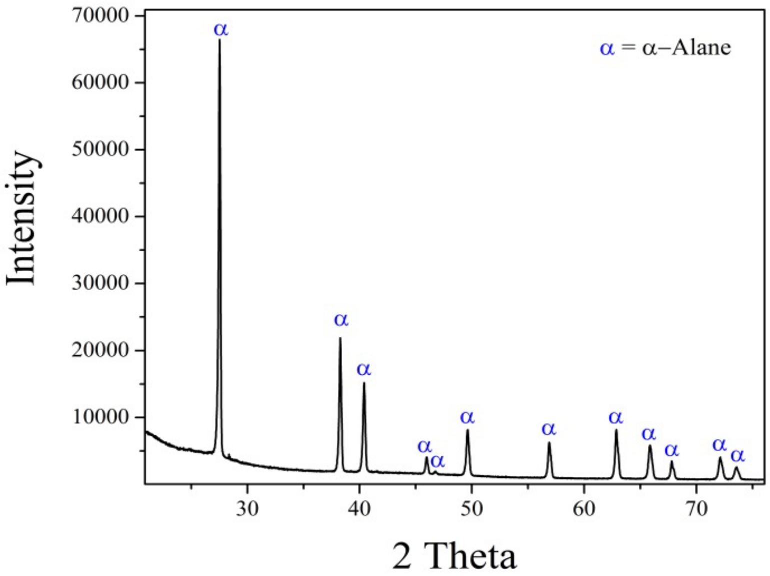
Different Crystallization conditions lead to different phases (e.g., *α, α', β* and y); Not all phases are suitable storage materials due to their instability and high reactivity.

- 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

Accomplishment: Crystallization Method for High Quality Alane



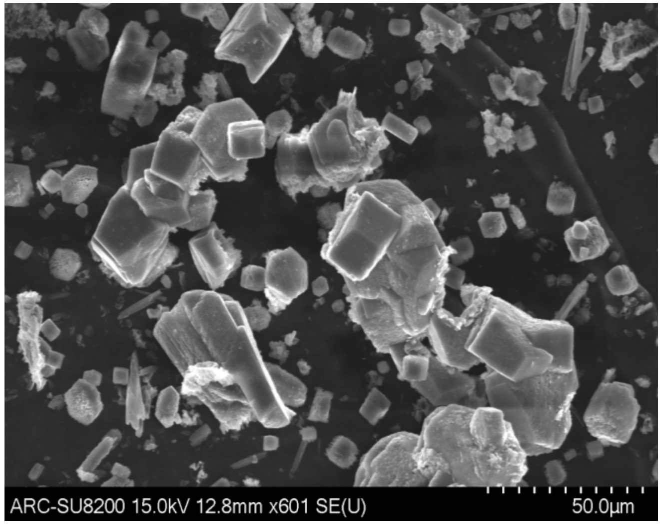


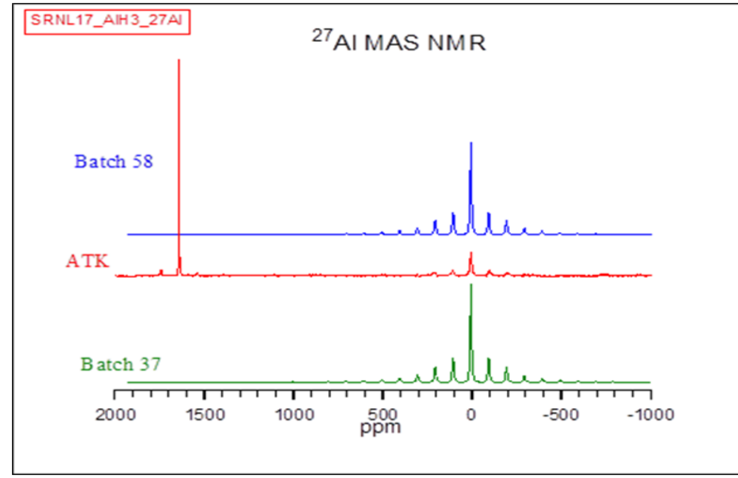


SRNL working with ARDICA achieved crystallization methods, from etherate adduct, producing pure alpha alane of > 9.9 H_2 wt. % at the 200 g scale.

Accomplishment: Stability of Large Scale Alpha Alane

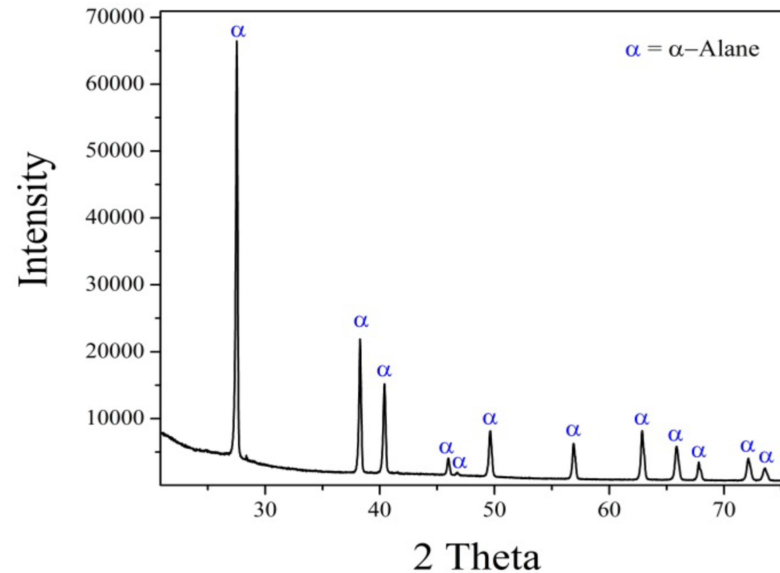
Dr. Sonjong Hwang Caltech





SRNL working with Ardica achieved crystallization methods, from etherate adduct, producing pure alpha alane of > 9.9 H_2 wt. % at the 200 g scale

The alpha alane produced has shown shelf stability with no degradation over more than 6 months



Collaborations and Team Members

Organization	Team Members
Savannah River National Lab (SRNL)	Ragaiy Zidan Patrick Ward Joseph Teprovich Jr. Scott McWhorter
Ardica	Tibor Fabian
SRI	Robert Wilson Mark Petrie Henry Fong Steven Crouch-Baker
SRC	Scott Greenway Aaron Wilber
Caltech	Sonjong Hwang

Remaining Challenges and Barriers

- Optimize crystallization parameters for the crystallization of adducts other than AlH_3•EtOEt
- Cost of labor significantly affects the price of alane and therefore, large scale production processes must be automated – **Small Business Voucher project currently ongoing**
- Develop guidelines for global production of alane to guarantee safety and quality
- Although we demonstrated producing highly stable product, methods for the certification of alane quality and guidelines for shipping and storage need to be developed

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 a route to produce alpha alane from AlH_3•THF produced electrochemically from $NaAlH_4$ that enables the use of high ionic conductivity electrolyte
- Demonstrated a route to produce alane chemically using $NaAlH_4$ as a precursor instead of the more expensive $LiAlH_4$
- Demonstrated production of high hydrogen content alane (9.9 wt%) with high stability at ≥ 200 g scale