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Project ID# ST063

Reversible Formation of Alane

A High Hydrogen Density Material for Energy Storage

Ragaiy Zidan

Energy Security Directorate

Savannah River National Laboratory

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Overview

Timeline

Start: 10/1/06

End: Continuing

Percent complete of activities proposed for FY15: 50%

Barriers

A. System Weight and Volume

B. System Cost

C. Energy Efficiency

Budget

- Funding received in FY14
  - $400K
- Funding to be received in FY15
  - $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 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 2020 DOE onboard system desorption targets

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: Advantages of Electrochemical Alane Generation

- ***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.***

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

<u>Current price $3,500/kg small scale</u>

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

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

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

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

<u>Cost Analysis Including Inefficiencies</u>

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

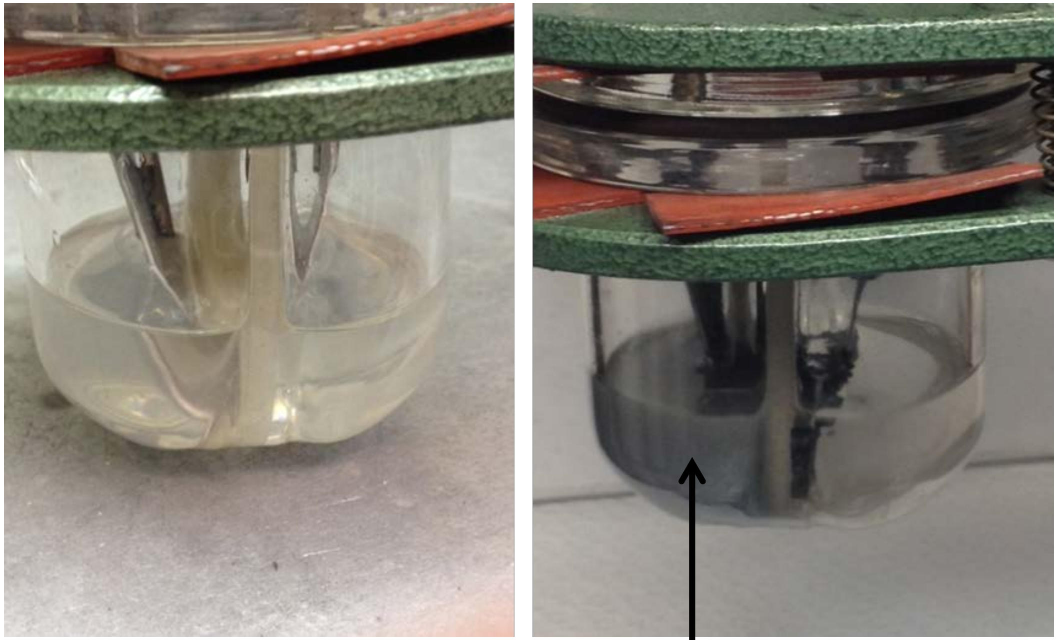
Aluminum recycled

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: Electrochemical Generation of Alane Adduct

Before Electrolysis | After Electrolysis

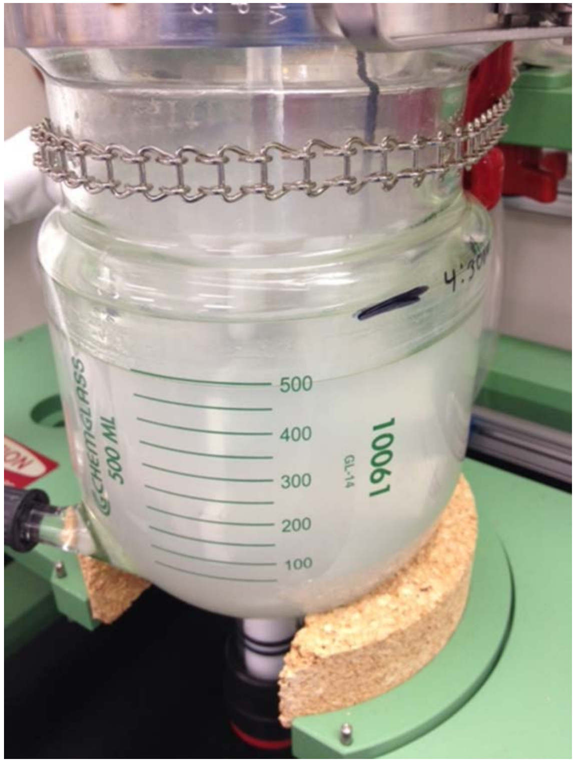


Solid Adduct : AlH_3•Diethyl Ether

- Producing alane directly from the elements requires impractical hydrogen pressure
- Electrochemical alane adduct production significantly reduces the cost of manufacture compared to chemical methods
- The cost of alane production can be significantly reduced due the recyclability of the materials by the electrochemical method
- Electrochemical alane production avoids the production of alkali halides which require large amounts of energy to reverse

Approach: Crystallization of Alane Adduct to α-Alane

- Alane adduct can be crystallized by various methods.
- The conditions used depend highly on the nature of the adduct ligand.
- Dry methods and solution based methods have been explored with the use of additives to assist in the formation of α-alane.



Approach: Regeneration of Spent Alane to Electrolyte

Regenerating $LiAlH_4$ from dehydrogenated AlH_3:

$$2\ LiH + 2\ Al_c^* + 3H_2 \rightarrow 2\ \mathbf{LiAlH_4}$$

(Al_c^* = catalyzed and activated Al)

High pressure Parr-reactor used for the regeneration of electrolyte.

Yields above 80% have been achieved for both $NaAlH_4$ and $LiAlH_4$ regeneration.

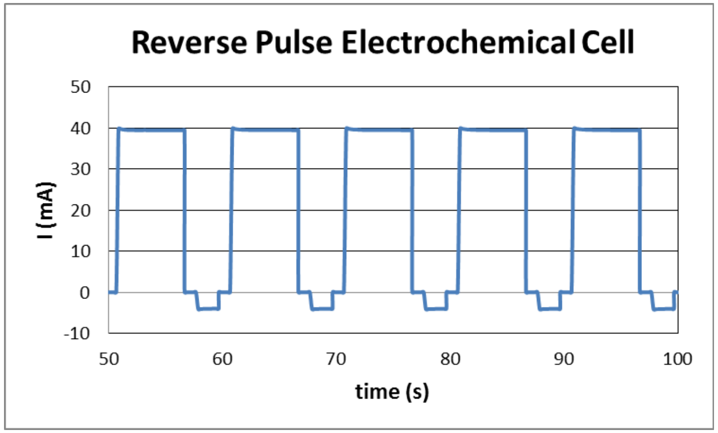
- Regeneration of the electrolyte from spent alane allows for the reversible production of alane.
- This regenerated electrolyte ($LiAlH_4$ or $NaAlH_4$) can then be used in the electrochemical cell to generate the alane adduct.

Current Progress: Electrochemical Alane Production

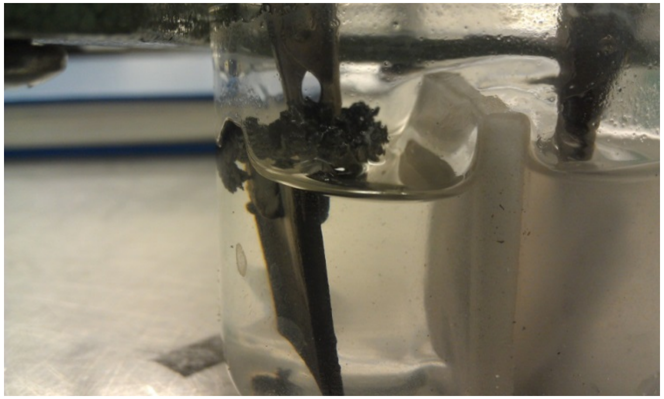
Dendrite Reduction

- Dendrites pose problems for the large scale production of alane since they can grow to an extent where shorting out the cell is possible.
- The dendrites are composed of $(Na/Li)_3AlH_6$ and Al metal.
- The pulsing forms growth in a compact layer

Dendrites were significantly reduced by utilizing a reverse pulse technique during the electrochemical reaction.



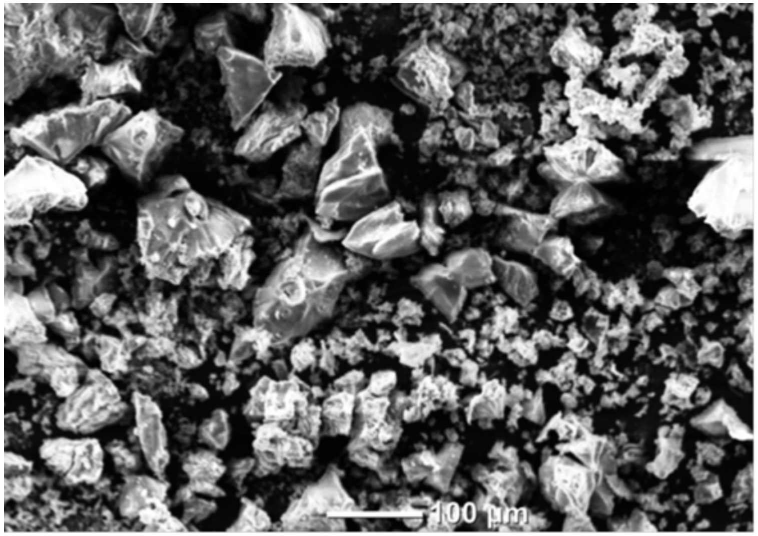

Dendrites from typical 18 hour reaction.

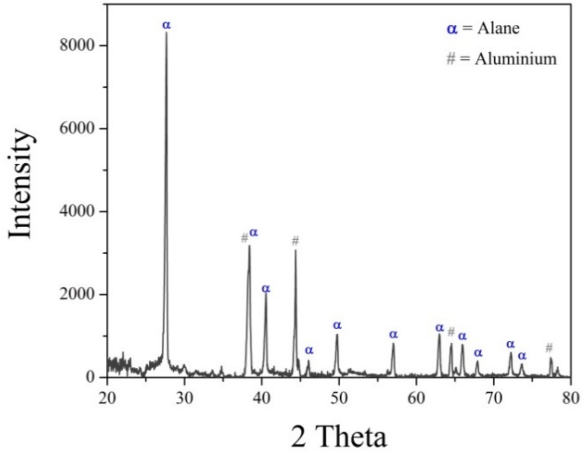

Dendrites from reverse pulsed 24 hour reaction.

Current Progress: Crystallization of Alane Adduct

Methods for Crystallization

- Both chemical and electrochemical production techniques generate the alane adducted to various ligands.
- Crystallization to the right phase and crystal size is essential for stability of the material and hydrogen capacity and release temperatures.
- The conversion of alane adduct to alane occurs in a very small temperature window (75 - 85 °C)
- The alpha phase with symmetrical crystals in the 4-50 µm range is most desired.
- ***The dry method produces large crystals, but with little symmetry and aluminum.***



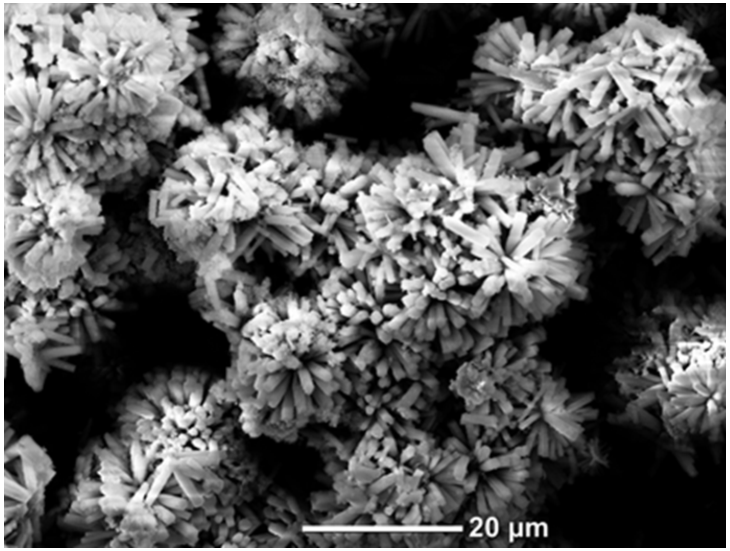


α-alane crystals produced by the dry method.

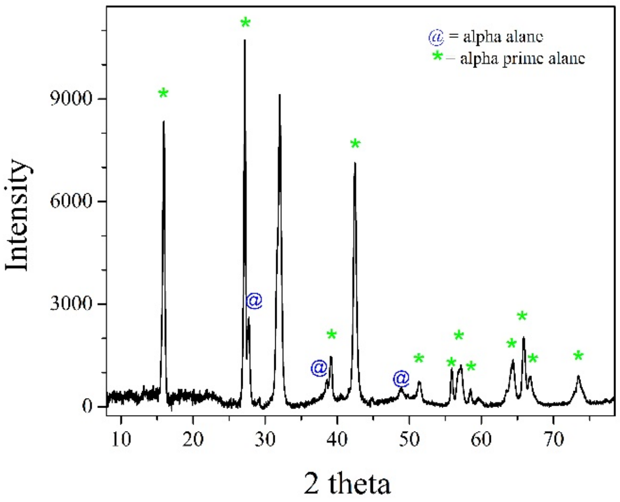
Current Progress: Crystallization of Alane Adduct

Identifying conditions to produce α-alane and avoid other phases using solution methods

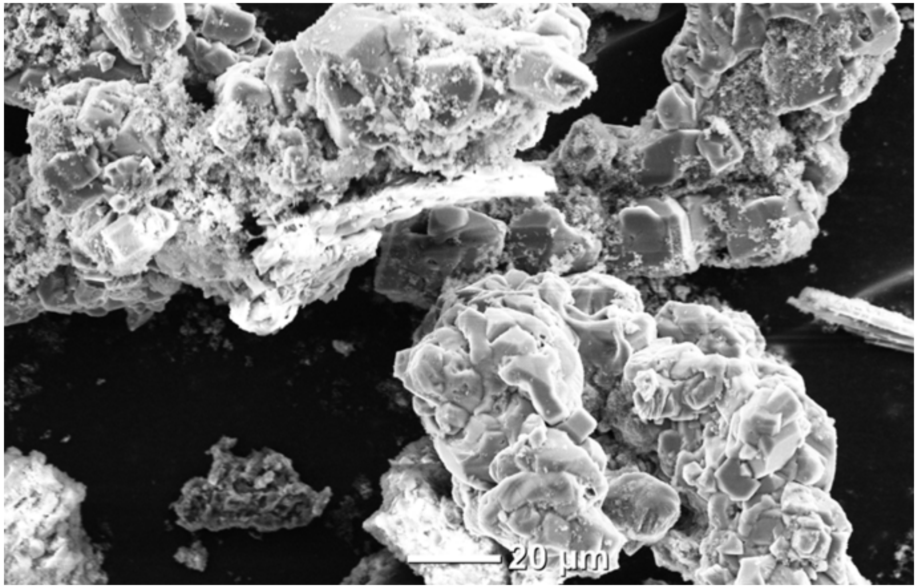
- Solution based methods can produce the alpha prime (α’) phase of alane
- This phase is found to predominate when the crystallization temperature is below 76 °C or the rate of diethyl ether removal is too slow
- While the alpha prime phase has a high hydrogen content, it’s stability is much less than that of α-alane



SEM image of α’ alane

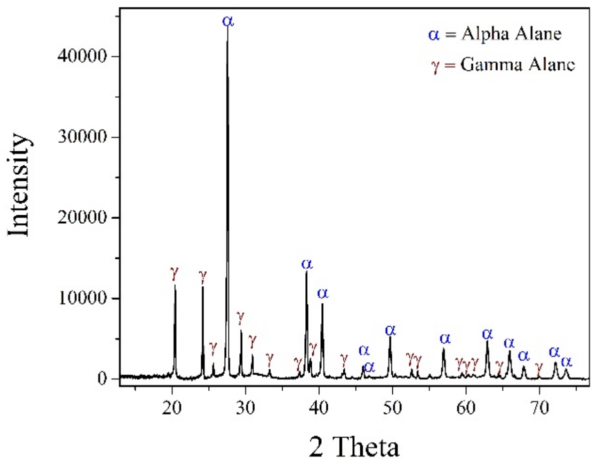


Current Progress: Crystallization of Alane Adduct

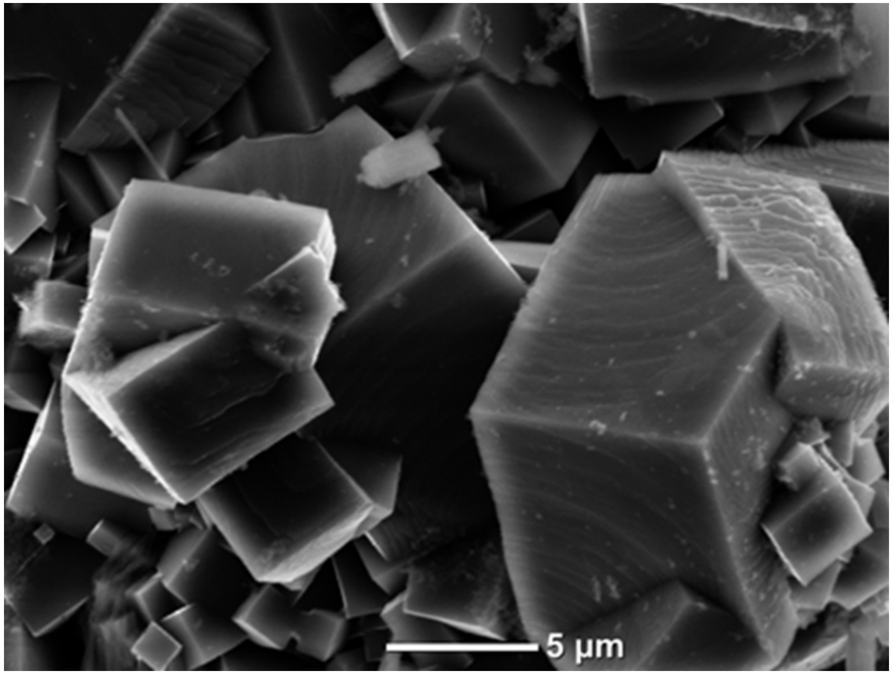


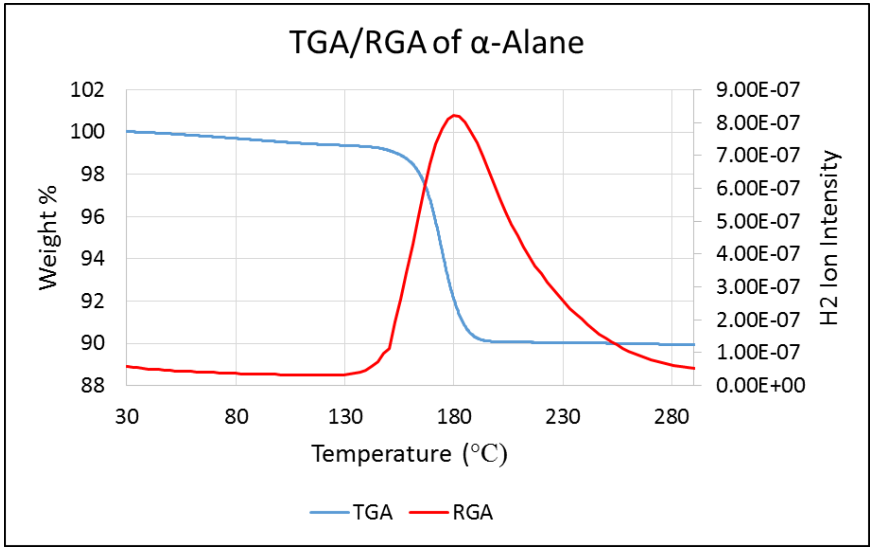
SEM image of Alpha Alane with residual gamma alane.

- The appropriate time, temperature, and ether removal rate must be optimized to produce pure alpha alane.
- Gamma alane will convert to alpha alane with additional heating.

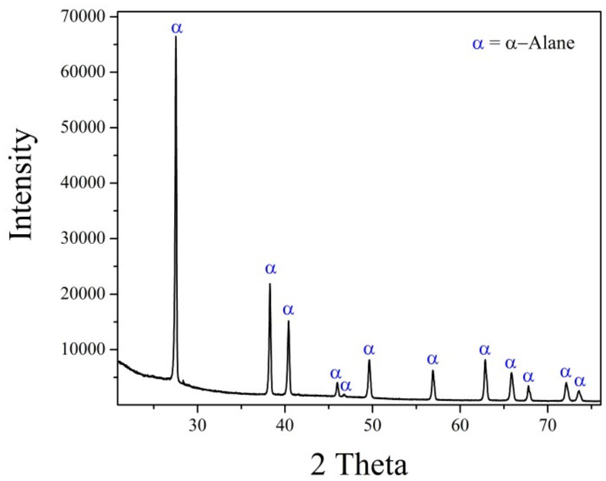


Current Progress: Crystallization of Alane Adduct

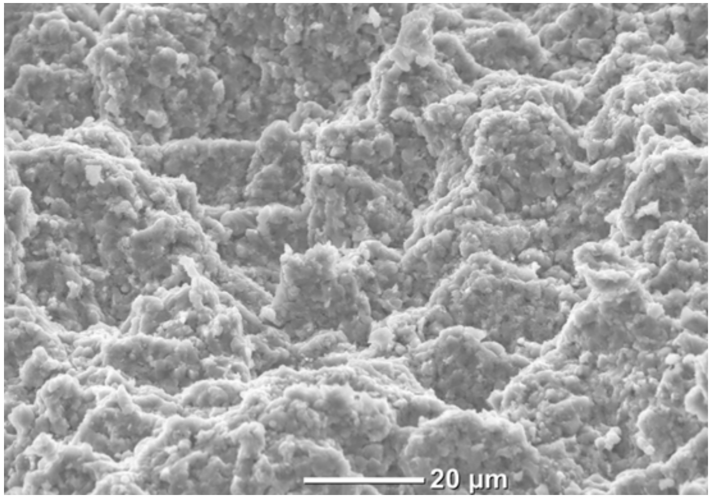




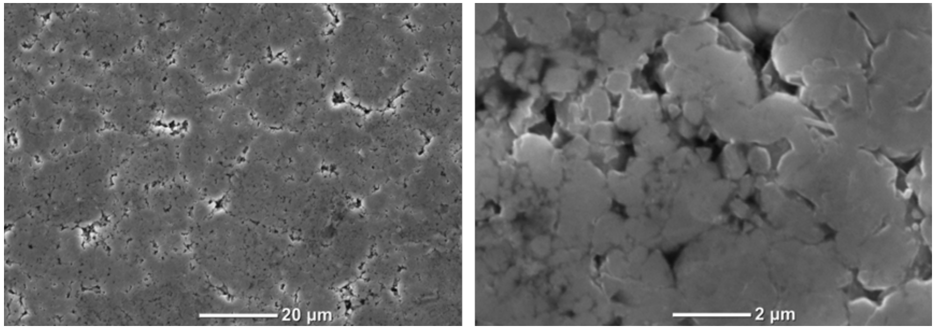
- The alpha alane produced contained 9.2 wt. % H_2 as shown in the TGA/RGA.
- The crystals are of excellent symmetry and size.
- Further work to reduce the agglomeration of these alpha alane crystals is underway.



Current Progress: Recycling Spent Alane for Reuse



SEM image of the inside of a spent alane pellet pressed at 3 tons.



SEM image of the surface of a spent alane pellet pressed at 3 tons. Bright spots show electron build up (charging) which is indicated lower current flow (high resistivity).

- Our collaborators (Ardica) are developing an electrochemical system that regenerates electrolyte in situ.
- Their system is based on an electrochemical flow cell approach.
- Therefore, the use of spent alane for both electrodes would allow for in situ recyclability of spent alane.

- ***SRNL tested spent alane as electrodes in the production of alane***
- ***Spent alane electrodes has a lower current.***
- ***This was due to insufficient electrical contact between the compressed spent alane particles.***
- ***This can easily be avoided by using higher pressure for compaction or electrically conductive binders.***

Collaborations and Team members

SRNL *(TEAM)*
- Ragaiy Zidan
- Patrick Ward
- Scott Greenway
- Scott McWhorter
- Joseph Teprovich
- Ted Motyka

Ardica *(POC)*
- Dick Martin

SRI *(POCs)*
- Robert Wilson
- Mark Petrie

Remaining Challenges and Barriers

- Improve the conductivity of the electrolyte solution to increase the rate of alane production
- Eliminate the dendrite formation on the surface of the electrolyte
- Optimize the crystallization parameters for the large scale production of alpha alane

Future Work: Electrochemical Production of Alane

- Insulate the electrode at the surface of the electrolyte solution to prevent dendrite formation at the location during the reverse pulse method

- Increase conductivity by reducing the distance between the electrodes once dendrites have be eliminated

- Develop efficient method for the crystallization of the alane THF adduct, so THF can be used as the solvent (higher conductivity than Diethyl Ether)

- Explore additives to the electrochemical cell which can increase the conductivity

Future Work: Crystallization

- Develop techniques for the crystallization alane THF adduct with appropriate phase (α) and particle size
- Ensure current technique for the crystallization of alane diethyl ether adduct is reproducible on a larger scale
- Optimize the crystallization technique with toluene instead of benzene to improve commercial production opportunities

Summary

- Dendrites formed during the electrochemical generation of alane have been significantly reduced and a method for removal along the electrolyte surface has been identified.
- Crystallization of alane adduct to alpha alane with appropriate particle sizes has been accomplished.
- Regeneration of spent aluminum to the electrolyte has been achieved in high yields as reported previously.
- Feasibility of using spent alane as electrode in the electrochemical cell has been investigated.