Low-Cost α-Alane for Hydrogen Storage

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Project ID #
ST116

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Overview

Timeline

Project Start Date: 15 July 2014
Project End Date: 14 July 2017

Percent complete of activities proposed for FY17: 50%*

* As of 4/10/17

Barriers

- 3.3.5 A: System weight and volume
- 3.3.5 B: System cost

Budget

Total Project Budget: $1,500,514
- Total Recipient Share: $301,266
- Total Federal Share: $1,199,248
- Total DOE Funds Spent*: $1,040,816

Collaborators

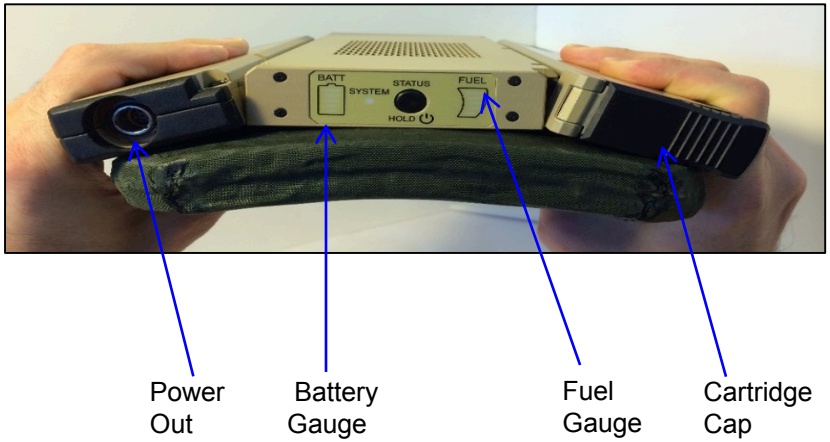
- SRI International
- SRNL (CRADA Partner)

Relevance: Project Objectives

Overall: Reduce production cost of α-alane (AlH_3) to meet the DOE 2015 and 2020 hydrogen storage system cost targets for portable low- and medium-power applications. Enables broader applications in consumer electronics (smart phones, tablets, laptops…), back-up power, UAVs, forklifts, and vehicles.

- Engineering cost analyses of electrochemical and chemical processes to meet the cost targets for synthesis and regeneration of α-alane throughout the program
- Establish design criteria for practical *electrochemical process* to synthesize alane adduct
- Demonstrate conversion of electrochemical anode product to α-alane
- Demonstrate recovery of $MAlH_4$ (M = Li, Na) electrolyte from cathode product

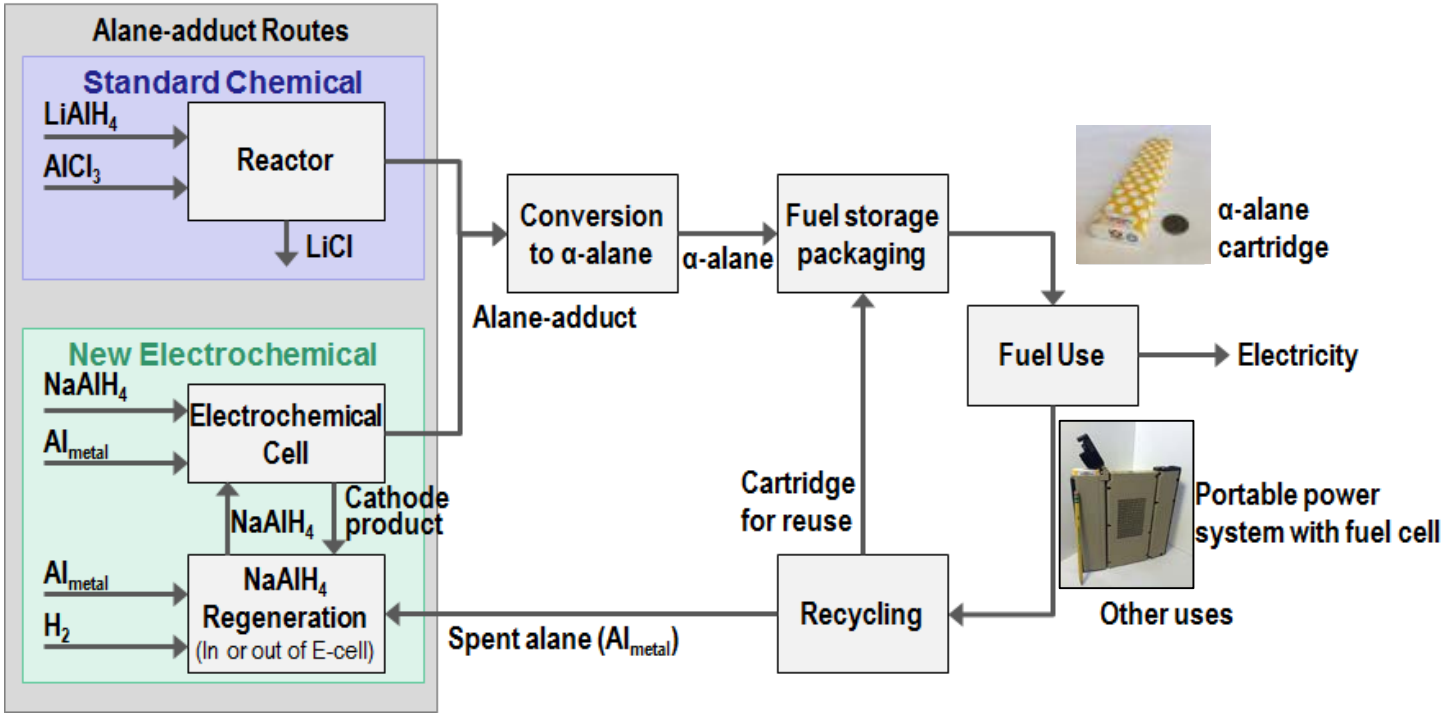
Relevance: Wearable Power System for a Dismounted Soldier (WPS20)



Features	
Fuel	α-alane (85 grams per cartridge)
Dimensions	7” x 8” x 0.89” with flexibility to conform to a small arms protective insert (SAPI) plate
Power Output	20 W continuous, 35 W peak
Storage System Energy Density	0.98 KWh/kg, 1.26 KWh/L
System Compatibility	Standards for soldier power distribution manager

Approach: Electrochemical Process added to Alane Production

Electrochemical process provides cost and energy efficient reaction product recovery.



Anode Reactions

(**R1**) $3\ NaAlH_4 + Al_{metal} \rightarrow 4\ AlH_3 + 3\ Na^+ + 3\ e^-$

(**R2**) $NaAlH_4 \rightarrow AlH_3 + 1/2H_2 + Na^+ + e^-$

Cathode Reactions

$3\ NaAlH_4 + 3\ Na^+ + 3\ e^- \rightarrow 2\ Na_3AlH_6 + Al_{metal}$

$2\ NaAlH_4 + 3\ Na^+ + 3\ e^- \rightarrow Na_3AlH_6 + 2\ NaH + Al_{metal}$

Approach: Year 3 Outline

There are three major components of the "electrochemical process" that drive the final alane cost; specifically, the yields of:

A. Electrochemical alane adduct manufacture
B. Chemical conversion of adduct to alane
C. Cathode product conversion to electrolyte

<u>All three components affect reactor design; cannot consider electrochemical step in isolation</u>

Our effort was building on pioneering work from SRNL and in close collaboration with SRNL.

Component	Ardica role	SRNL role
Electrochemical adduct manufacture	Cell design, experimental characterization	Support
Adduct conversion to alane		DFT calculations
	Ligand selection, synthesis, exchange, and alane crystallization	
Cathode product conversion to electrolyte	Reactor design, experimental characterization	Support

Primary goal for year 3: Refine cost analysis of the overall process by establishing improved quantitative understanding of B. and C. in addition to further characterization of A. under high current density conditions.

Progress: Predicted Cost Reduction Compared to the Chemical Synthesis Route to Alane

Reduce $NaAlH_4$ cost component of electrochemical alane production cost by use of consumable Al anode and regeneration of electrolyzed $NaAlH_4$.
Milestone M1.04: estimated storage system cost of <$1/g H_2 stored.

Storage System Costs			Chemical Route [1,2]	Electrochemical Route [3]	
				Baseline [1,4a]	Cathode Recycle [1,4b]
			Commercial Scale	No NaAlH4 regeneration	80% NaAlH4 regenerated
Alane Fuel Costs		$/kg alane	112	82	50
Cartridge Cost [4]		$/kg alane	53	53	53
Total		$/kg alane	165	135	103
Storage System Cost		$/g H2	1.79	1.47	1.12
DOE Metrics		$/g H2	Target Met?		
Low Power	2015	3	Y	Y	Y
	2020	1	N	N	N
Medium Power	2015	6.7	Y	Y	Y
	2020	3.3	Y	Y	Y

1. Chemical and electrochemical route productions costs are for a 320 MT/y process.
2. Commercial scale estimate provided by industrial partner.
3. Assumes 90% electrochemical utilization of $NaAlH_4$ and 90% adduct conversion.
4. Cost of alane entirely from reaction (R2) is (a) $101; (b) $54.
5. New cartridge costs based on manufacturer estimates: $53/kg AlH_3 at 4 M cartridges/year.

Anode Reactions

(**R1**) $3\ NaAlH_4 + Al_{metal} \rightarrow 4\ AlH_3 + 3\ Na^+ + 3\ e^-$

(**R2**) $NaAlH_4 \rightarrow AlH_3 + 1/2H_2 + Na^+ + e^-$

Model assumes > 80% of alane adduct produced by reaction R1

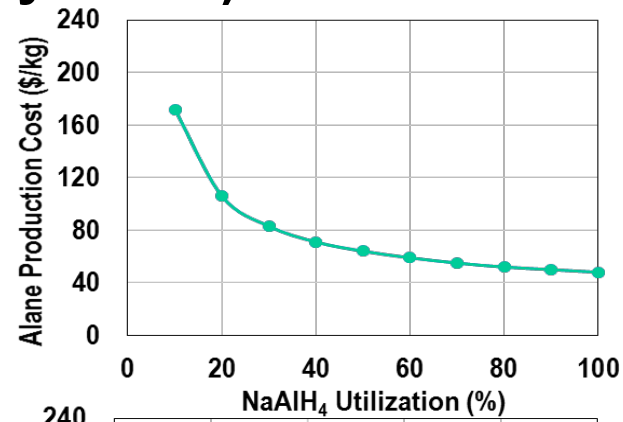
Progress: Sensitivity Analysis for Yields in the "Electrochemical Process" (at 320 MT/y scale)

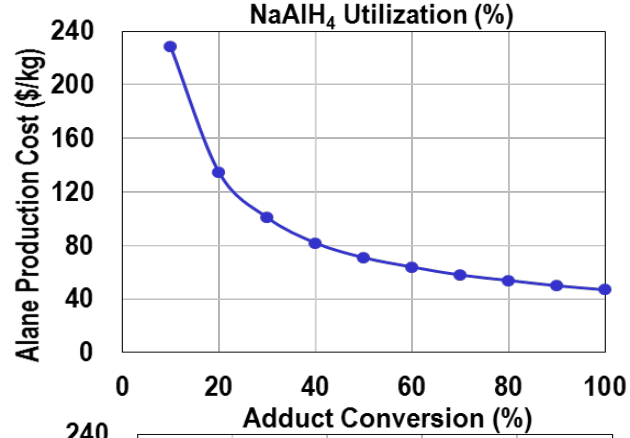
Consider cost impact of yield variation for:

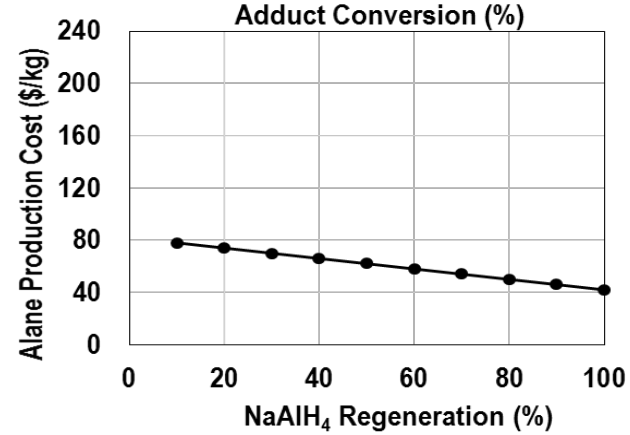
- **$NaAlH_4$ utilization:** % of $NaAlH_4$ consumed in the cell that leads to recoverable alane adduct formation; nominal value: 90%.
- **Adduct conversion:** % of alane-THF adduct recovered from cell converted to α-alane; nominal value: 90%.
- **$NaAlH_4$ regeneration:** % of recovered cathode product converted to electrolyte salt; nominal value: 80%.

Impact:

- For increasing yield values >60%, all three processes have similar alane cost benefits
- For decreasing yield values <40%, the $NaAlH_4$ utilization and adduct conversion yields have an increasingly negative impact.







Determined that three key processes contribute to overall alane cost.

Scaling the Electrochemical Vision

Assumptions:

- For a 320,000 kg/yr (292 days/yr) plant:
  → 46 kg/h (1.6 kmol/h) AlH_3
- Assume 80% of alane is produced from R1:
  → ~33 kA of current required
- Cell contains 1 m^2 of (consumable) anode area

Key design considerations

- Balance needs for minimal (solvent) volume and thermal management;
  → Recirculating electrolyte
- Minimal electrode spacing for high current density
- Optimized current pulse protocol
  → Avoid cathode dendrite formation
  → Maintain practical net anodic current density
  → Facilitate cathode product collection

Current Density (mA/cm^2)	Number of Cells	Alane Production Rate* (kg/h) / cell	Adduct Production Rate** (kg/h) / cell	$NaAlH_4$ Consumption Rate (kg/h) / cell	Power Dissipation @ 5V applied*** kW / cell
50	66	0.7	2.4	1.4	2.2
100	33	1.4	4.8	2.7	4.3
200	17	2.8	9.6	5.4	8.6

* Alane content of adduct; ** $AlH_3 \cdot THF$ adduct; *** OCV: 0.7 V

Progress: Electrochemical Alane Adduct and Cathode Product Manufacture at 100 mA cm^{-2} with $NaAlH_4$

Alane adduct and cathode product formation demonstrated at high current density with at least 70% $NaAlH_4$ utilization.

Separator Type	% Alane-Adduct Isolation[2]	% Alane-Adduct Formation[3]	% Cathode Formation[4]
Non-porous polymeric membrane[1]	71	87	99
Porous silica[5]	58	84	85
Porous silica[6]	61	93	95
No separator	0	97	16

Anolyte-catholyte separator is important aspect of electrochemical cell design. Reason for adduct isolation yield < adduct formation yield remains to be determined.

1. Modified for Na-ion transport.

2. Determined by mass adduct *isolated* relative to expected mass based on charge passed.

3. Determined by mass loss of aluminum anode and charge passed according to anode reaction: $NaAlH_4 + 1/3Al = 4/3AlH_3 + Na^+ + e$

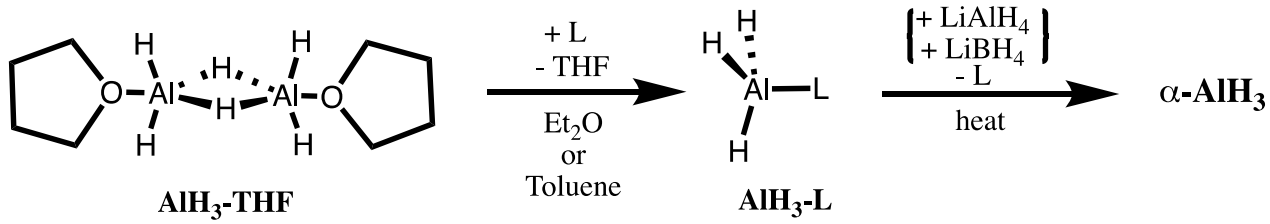
4. Determined by mass gain of cathode and charge passed according to the cathode reaction $Na^+ + e + NaAlH_4 = 2/3Na_3AlH_6 + 1/3Al$ as confirmed by powder X-ray characterization of the solid cathode product.

5. 4-5.5 μm dia. pores.

6. 1-1.6 μm dia. pores.

Approach: Alane-Amine Adduct (Al-L) Synthesis & Crystallization of α-Alane

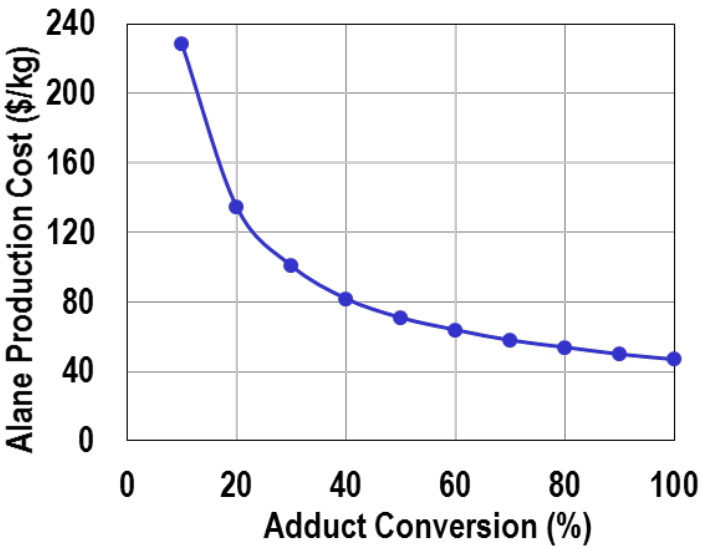
Efficiency of conversion of AlH_3 adduct isolated from the cell to α-AlH_3 is critical driver of alane production cost.



<u>Adduct Conversion</u>

Interrelated factors affecting efficiency:

- AlH_3-L bond dissociation energy (BDE; SRNL DFT calcs.)
- Sterics: *t*-Bu > *i*-Pr > Et > Me
- Amine volatility (b.p.)
- Basicity (pK_b of amine)
- Amine inversion barrier



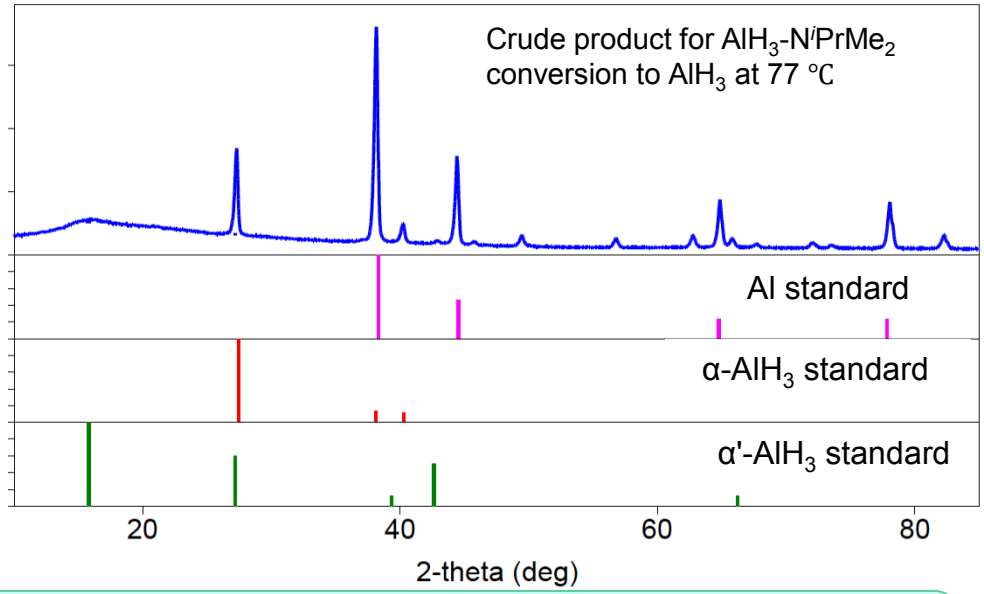
Technical Accomplishments: Alane-Amine Adduct Synthesis & Crystallization to α-Alane

Candidate amine adducts were chosen based on the following criteria:

- Literature reports showing conversion to α-alane
- Amines with large alkyl groups increasing steric requirements and reducing BDE's
- Amines having high volatility (low b.p.) to reduce the potential for reverse reaction.

Thermal conversion experiments were performed under vacuum or inert gas purge.

Ligand	Amine adduct yield[a] (%)	Alane yield[b] (%)
NEt_2Me	60	0
NEt_3	83	TBD[c]
N^iPrMe_2	75	20 - 40
N^iPr_2Et	0	N/A
N-Et-Morpholine	97	20 - 40



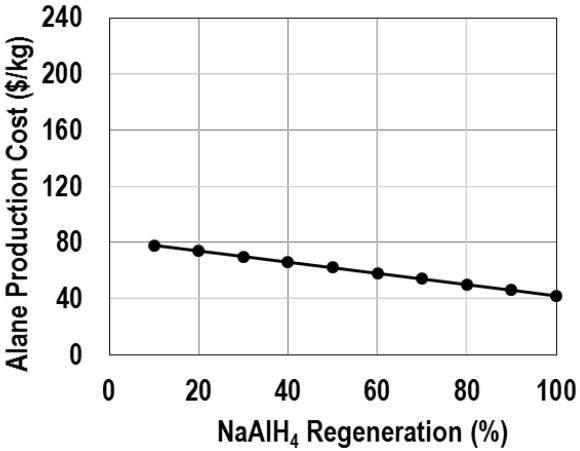
Amine adducts with high AlH_3.THF substitution yields were identified. Alane crystallization needs further optimization.

[a]Un-optimized yield of AlH_3-amine from AlH_3-THF;
[b]Un-optimized yield of α-alane from AlH3-amine;
[c]Under investigation at SRNL

Approach: Cathode Product Conversion to Electrolyte Salt

Electrolyte recovery lowers alane production cost linearly with increasing yield.

- Recovered cathode product heated under pressure with additional Al and H_2 in a 100 mL Parr reactor
- Method effective for Na_3AlH_6/Al/NaH mixture produced from $NaAlH_4$/THF electrolysis
- Initial experiments conducted with "spent alane" as Al source and no conventional activator
  - Derived from dehydriding FSU alane
  - Conventional activator (e.g. TM-based) may lead to product contamination
- Control experiments with added commercial Al powder and no Al added



$$\text{"Cathode Product"}\ (Na_3AlH_6 + NaH + Al) + \text{Decomposed FSU-Alane}\ (Al^0) \xrightarrow[\text{THF/Toluene (3:1)},\ 18\ h]{H_2\ (1100\ psi),\ 150\ ^oC} NaAlH_4$$

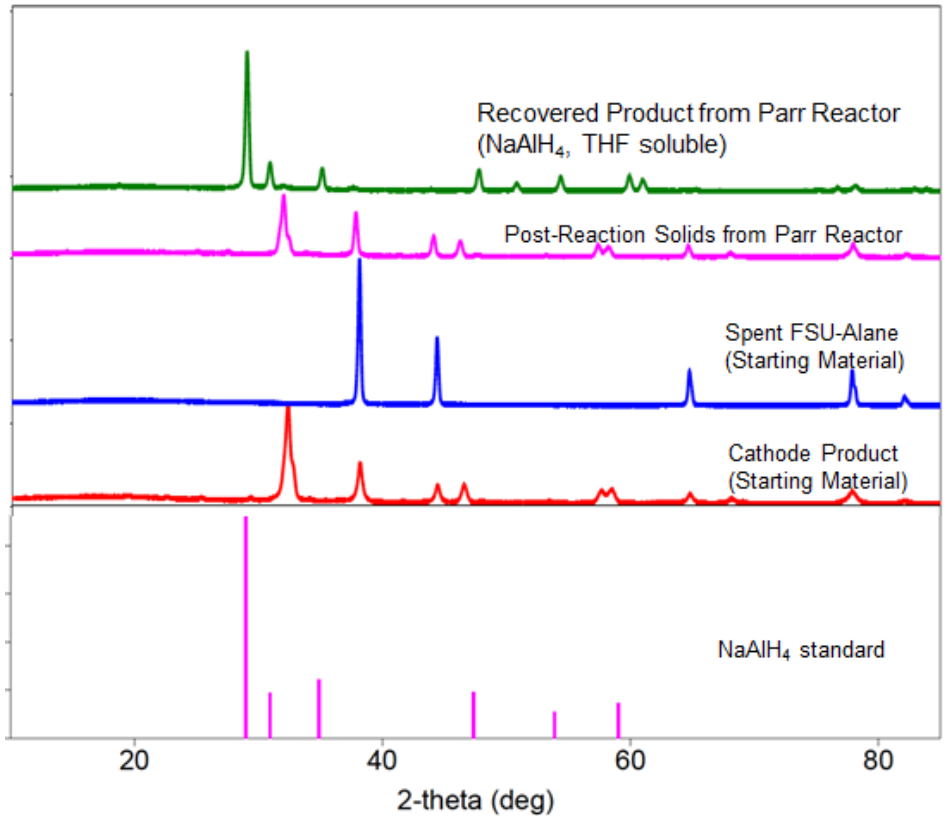
Conditions adapted from: Murib, J. H. U.S. Patent 3,649,223, March 4, 1972; Beaird Jr., F. M.; Kobetz, P. U.S. Patent 3,355,262, November 28, 1967.

Technical Accomplishments: Recycling of Cathode Product

Demonstrated 58% $NaAlH_4$ recovery yield from spent alane and cathode products generated at 100 mA cm^{-2}.

Run	Time / h	Al source	Activator	% Yield
1	18	FSU[1]	No	19
2	69	FSU	No	58
3	18	No Al added	No	0
4	18	Commercial[2]	No	0
5	18	FSU	10 mol%	29

[1] Decomposed ("spent") FSU-alane
[2] 44-75 μm particle size Al powder



Cathode product conversion to $NaAlH_4$ proceeds slowly with potentially high yield (runs 1-2).
Na_3AlH_6 itself is stable under reaction conditions used (run 3).
Commercial Al ineffective in absence of activator under conditions employed (run 4)
Activator imparts modest benefit (run 5).

Needs, Challenges and Solutions Addressed in this Program

1. Electrochemical reactor design

Need: Establish electrochemical reactor design that is compatible with high rate electrolysis under the following constraints:

- Use of a relatively resistive electrolyte solution derived from high purity electrolyte salt
- Use of current pulse protocol to avoid formation of a voluminous, dendritic cathode product
- Need to capture with high efficiency cathode material and remove periodically for chemical conversion to electrolyte salt
- Need to capture with high efficiency dissolved adduct before decomposition

Challenge: Demonstrate acceptable recovery of THF adduct from electrochemical cell

Solutions: Use of recirculating anolyte liquid to capture THF adduct

In situ chemical conversion of cathode product to electrolyte salt

2. Alane-THF adduct conversion to α-alane

Need: Demonstrate conversion of alane-THF to alane via intermediate formation of amine (or other) adduct at high yield and purity

Challenge: Alane-THF adduct is relatively strongly bonded; this hinders direct conversion

Solution: Further synthesis and conversion of promising amine adduct candidates guided by additional DFT calculations

3. Cathode product conversion to electrolyte salt

Need: Demonstrate that this process can be performed in a commercially viable manner

Challenge: Although a catalyst-free, high yield process has been identified, it's rate is relatively low

Solution: Identify and qualify suitable TM-free catalyst

Proposed Near-Term Future Development

1. Design, fabricate, and test a scalable electrochemical cell that builds on our experience with the H-cell that optimizes electrode kinetics, enables high-current, and hence high-throughput operation.

2. Further develop technologies to minimize potentially deleterious anolyte/cathode interactions.

3. Optimize solvent swap methods for complete separation of alane adduct from the concentrated $NaAlH_4$ based electrolyte. Optimize thermal conversion to α-alane from amine adducts using crystallization aides and heating profiles.

Project Summary

Evaluate electrochemical/chemical routes to reduce alane synthesis cost

- Full engineering cost analysis of electrochemical and chemical processes to meet DOE metrics
- Initial analysis shows the electrochemical synthesis affords a max. ~50% reduction in alane cost
- Na-based process affords lower cost than Li-based analogue

Establish design criteria for electrochemical reactor

- Demonstrated particle bed electrochemical reactor (moving or static)
- Determined key reactor design considerations for large-scale implementation

Demonstrated electrolyte ($NaAlH_4$) recovery from cathode product

- Demonstration performed with actual cathode product
- Spent alane used as Al source; no conventional catalyst required

Demonstrated conversion of electrochemically-generated AlH3.THF adduct to α-alane

- Na-based electrochemical process facilitates isolation of THF adduct
- Wide range of amine adducts synthesized from THF adduct
- Several amine adduct show promise in conversion to α-alane

Collaborations

Collaborators	Role
Ardica Technologies: Tibor Fabian (PI)	Development of alane-based hydrogen storage system for portable power
SRI International: Mark Petrie (PI), Steve Crouch-Baker, Henry Fong, Georgina Hum, David Stout, Fran Tanzella	Development of low-cost electrochemical and chemical synthesis production methods for alane production scale-up
SRNL: Ragaiy Zidan, Patrick Ward, Joseph Teprovich, Scott McWhorter	DFT calculations of amine-alane adducts and their thermal conversion to alpha-alane.
UC Berkeley: James Evans	Expert advisor on fluidized bed design

Technical Back-Up Slides

Approach: Process and Economic Modeling Methodology

Process Modeling:

- Process flow diagram and mass/energy balance for all unit operations.
- End-to-end process including feedstock preparation, down-stream chemical workup, and materials recycling and regeneration.

Economic Modeling:

- Using methodology laid out by Peters, Timmerhaus, and West[1]
- Higher multipliers and ratio factors account for increased costs associated with the safety and air sensitive materials handling requirements of this process compared to a typical chemical process.

Work Flow

Process Flow Diagram
- Identify all process steps and unit operations for the end-to-end synthesis→ process flow diagram

Mass & Energy Balance
- Perform a mass and energy balance across all unit operations → estimate materials and utilities

Equip. Sizing
- Identify equipment, materials of construction, and estimate hold-up/residence times

Capital Equip. Costs
- Utilize tables & formulas, with multipliers for materials/features → estimate capital equipment costs

Total Capital
- Estimate total capital costs from the capital equipment costs using ratio factors

Labor
- Estimate labor requirement via number of staff per shift and wages

Other Costs
- Estimate other production costs, fixed expenses, and general expenses using ratio factors

Alane Product Cost

1) Peters, M. S., Timmerhaus, K. D., West, R. E., Plant Design and Economics for Chemical Engineers, Fifth Edition, McGraw Hill (2003).