Low-Cost α-Alane for Hydrogen Storage

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Presenter: Bob Wilson

10 June, 2015

Project ID # ST116

Overview

Timeline

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

Percent complete of activities proposed for FY14: 75%*

* As of 3/31/15

Budget

Total Project Budget: $1,500,514

- Total Recipient Share: $301,266
- Total Federal Share: $1,199,248
- Total DOE Funds Spent*: $250,911

Barriers

- Low-cost production of α-alane by electrochemical / chemical pathways
- Engineering cost analysis of entire alane synthesis and regeneration process
- Conservation of lithium aluminum hydride electrolyte
- Development of a fluidized/moving bed reactor

Collaborators

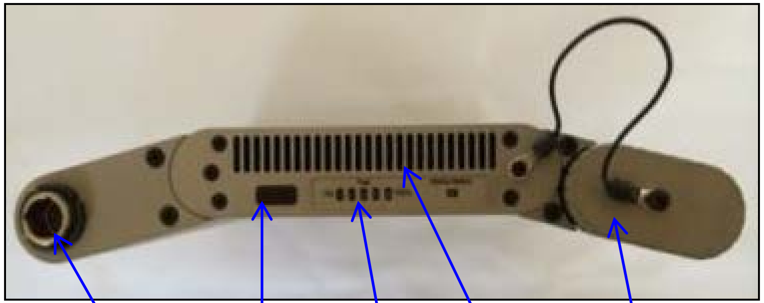
- SRI International
- SRNL (CRADA Partner)

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
- Demonstrate practical *electrochemical process* to synthesize alane adduct building on Ragaiy Zidan's (SRNL) pioneering work that can be transitioned to a large-scale facility
- Develop an electrochemical fluidized particle bed design that enables increased rate of reaction and a continuous process
- Demonstrate regeneration of spent alane fuel by the fluidized bed process
- Develop an efficient process for recrystallization, passivation and formulation of the alane product

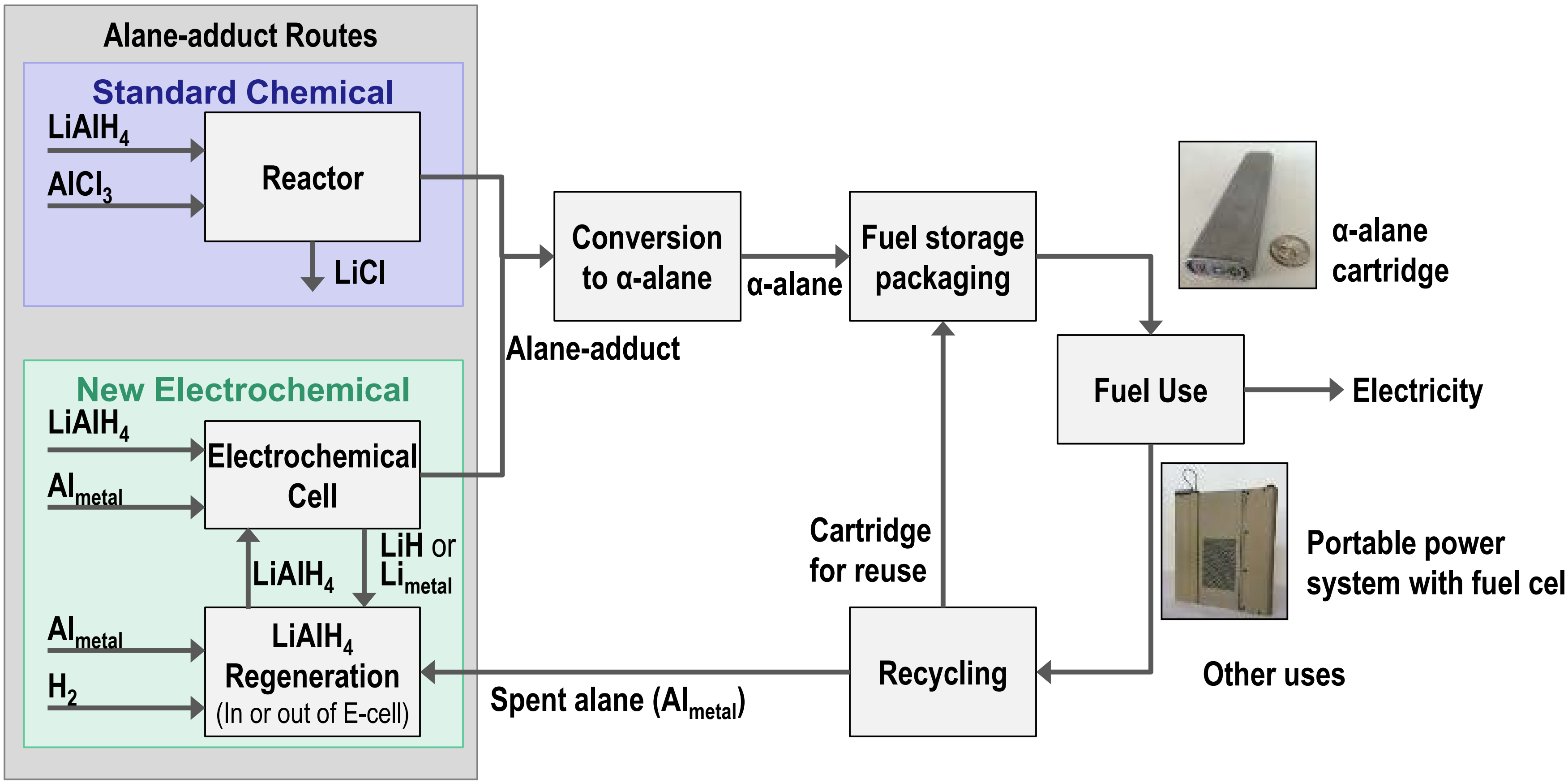
Relevance: Wearable Power System for a Dismounted Soldier (WPS20)



Features	
Fuel	α-alane (80 grams per cartridge)
Dimensions	7" x 8" x 0.83" with flexibility to conform to a small arms protective insert (SAPI) plate
Power Output	20 W continuous, 35 W peak
System Energy Density	466 Wh/kg, 577 Wh/L (72h at 20W continuous)
System Compatibility	Standards for soldier power distribution manager

Approach: Electrolysis Process added to Alane Production

Reducing costs in the chemical process is difficult due to feedstock costs. Changing the front end to the electrolysis process for alane-etherate production can reduce these costs.



Approach: Cost Reduction Compared to the Chemical Synthesis Route to Alane

Electrochemical process reduces alane cost from an improved, consumable aluminum anode to regenerate $LiAlH_4$ and optimize recycling of unreacted $LiAlH_4$.

Storage System Costs		Current Cost	Chemical Route	Electrochemical Route: Improved Anode	Electrochemical Route: Cathode Recycle	Electrochemical Route: Optimized Process
		Pilot Plant	Commercial Scale	(20% AlH3 from Al)	(25% AlH3 from Al, LiAlH4 regenerated)	(25% from Al, LiAlH4 recycle / regeneration)
Fuel	$/kg alane	3500	112	87	55	34
Cartridge components	$/kg alane	79	79	79	79	79
Total	$/kg alane	3579	191	166	134	113
Storage System Cost	$/g H2	40.21	2.15	1.87	1.51	1.27
DOE Metrics	$/g H2		Target Met?			
Low Power 2015	3	N	Y	Y	Y	Y
Low Power 2020	1	N	N	N	N	N
Medium Power 2015	6.7	N	Y	Y	Y	Y
Medium Power 2020	3.3	N	N	N	Y	Y

Production cost broken down on the next slide

Note: Chemical and electrochemical route productions costs are for a 320 Mton/yr process

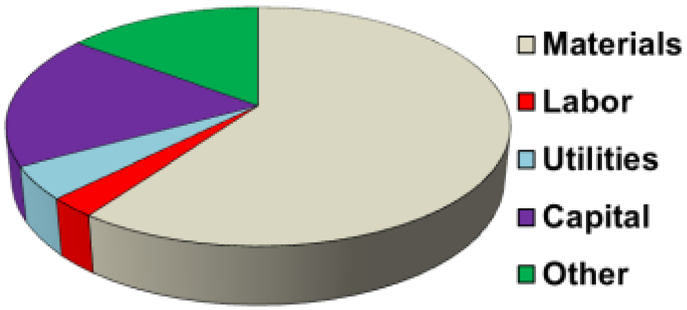
M1.01 **100% Complete**: Alane cost is estimated to be < $250/kg. Estimated storage system cost of < $6.7/g H_2 for medium power applications.

Approach: Process and Economic Modeling

- **Process Modeling:** Process flow diagram and mass/energy balance for all unit operations
- **Economic Modeling:** Using standard chemical engineering methodology
    - Materials, electricity, and utilities cost estimates based on mass and energy balance
    - Capital equipment costs are estimated from mass balance using standard formulas
    - Other costs are separately calculated from the capital equipment costs using standard ratio factors related to one of the above values

Detailed economic model example shows alane production cost of $87 per kg from the electrochemical process in which 20% of the alane is produced from an aluminum anode with no further optimization for $LiAlH_4$ regeneration or materials recycling.

Productions Costs	Basis	$/kg	
Raw materials*	Mass balance	$	52
Labor	Labor estimate	$	2
Electricity and utilities	Energy balance	$	4
Capital costs (depreciation and financing)	Capital Estimate	$	16
Other (Maintenance, supplies, plant and admin overhead, etc.)	Various ratio factors	$	13
Total Alane Production Cost		**$**	**87**



M1.01 **100% Complete:** Alane cost is estimated to be < $250/kg. Estimated storage system cost of < $6.7/g H_2 for medium power applications.

Approach: Aluminum Particle Fluidized Bed

Background

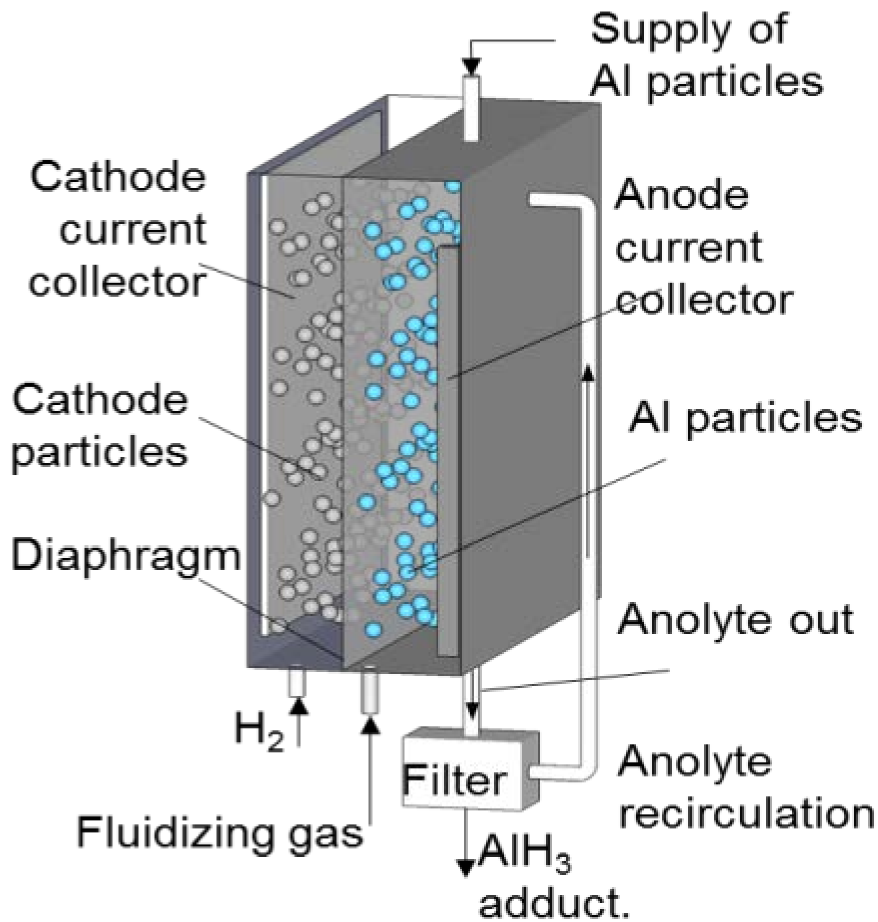
$$3\ LiAlH_4 + Al_{metal} \rightarrow 4\ AlH_3 + 3\ Li^+ + 3\ e^-$$

(Anode reaction)

- Electrochemical process developed by Ragaiy Zidan at SRNL
- Uses $NaAlH_4$ or $LiAlH_4$ electrolyte, Pt cathode, and Al anode

Proposed Fluidized Bed Reactor

- Fluidized bed of conductive particles act as electrodes, ideally both anode and cathode
- High surface to volume enhance kinetics enabling high current and throughput. Potential for continuous process.
- Direct regeneration of spent alane fuel now feasible



Approach: Milestones

Task	Task Title or Subtask Title	MS #	Milestone Description (Go/No-Go Decision Criteria)	Qtr.	End Date	Progress Made (%)
1.1	Create and update preliminary process and economic models	M1.01	Complete preliminary process & economic models. The alane production cost is estimated to be <$250/kg alane. The economic model shows an estimated storage system cost of <$6.7/g H2 for medium power applications.	2	02/15/15	100%
2.1	Establish cell design and preliminary characterization	M2.01	Baseline performance of electrochemical process. The performance of the electrochemical cell is such that sufficient alane is produced from aluminum rather than $NaAlH_4$ to meet the cost target in Task 1.1. Target was >25% $NaAlH_4$ recovery, >20% was achieved which still met the cost targets.	1	11/15/14	100%
2.2	Bench-scale evaluation of fluidized-bed reactor	M2.04	Fluidized bed reactor set up and operational. Metric is not more than a 2 times increase in the cell resistance when a sheet aluminum anode is replaced with a fluidized particulate aluminum anode.	3	5/15/15	100%
3.1	Develop crystallation and passivation procedures	M3.01	The identification of process unit operations included in the Phase 1 process design and economic analysis. The alane product is an amine adduct of alane from the non-fluidized cell.	2	2/15/15	100%
	Go/No-Go Decision		The economic model shows an estimated storage system cost of <$3.3/g H2 for medium power applications. The hydrogen storage device achieves a gravimetric capacity of >0.7 kWh/kg and a volumetric capacity of >1.0 kWh/L, achieving the 2015 performance metrics.	4	8/15/15	100%

Technical Progress: Conservation of Electrolyte ($MAlH_4$)

Reduction of electrolyte ($MAlH_4$) (M = Li or Na) consumption reduces cost

- Anode: Consumption of aluminum pebbles (~0.25 cm) contributed to 20% of total alane production. Results in cost savings.
- Assumption: All electrical charge utilized for Reactions 1 and 2
- Cathodic dendrites formed: $Li_3AlH_6 + Al_{(metal)}$ by XRD. Represents $LiAlH_4$ loss

Al Pebbles/1.0M $LiAlH_4$ in THF/ Pt Cathode

(Steel Current Collector minimizes Rxn. 2)

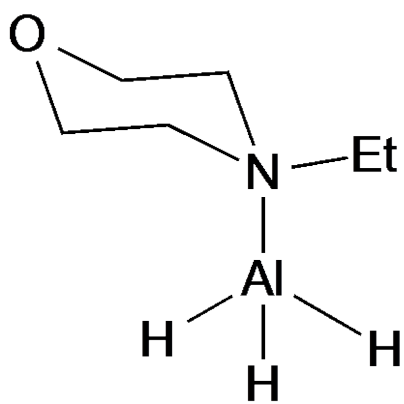
<u>Relevant Anodic Reactions</u>

1. **$3\ LiAlH_4 + Al_{metal} \rightarrow 4\ AlH_3 + 3\ Li^+ + 3\ e^-$**
2. $LiAlH_4 \rightarrow AlH_3 + ½\ H_2 + Li^+ + e^-$

M 2.01 **100% Complete**: Target was >25% NaAlH4 recovery, >20% was achieved which still met the cost targets.

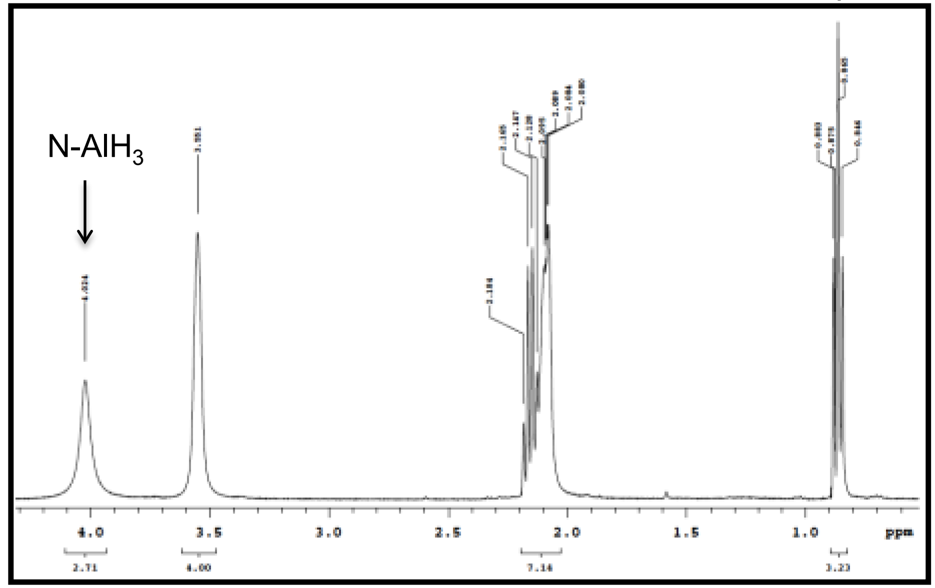
Technical Progress: Effective Separation of Produced Alane from Electrolyte

"Alane Adduct"



Verified by ^{1}H NMR

(Graetz, J., *J. Phys. Chem*. C 2013, 117, 14983−14991)



Al plate Anode//2.0.M $LiAlH_4$ Ethyl Ether Electrolyte//Pt Cathode.

4-Ethylmorpholine added after electrochemistry. Isolated 372 mg 4-Ethylmorpholine-Alane adduct from the electrolyte by toluene extraction. Al anode mass loss (35 mg) or 189 mg of the adduct.

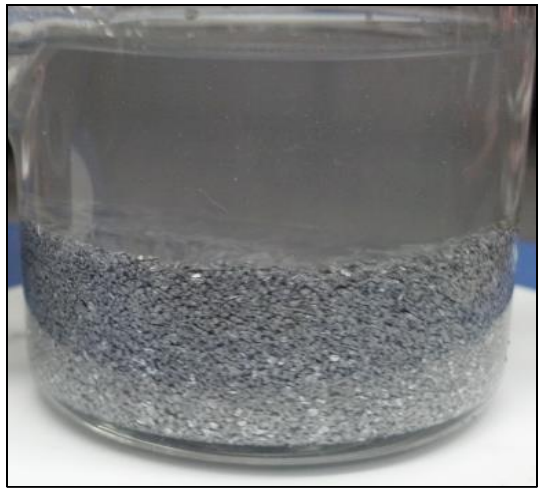
Effective separation of AlH_3 from a concentrated 2.0 M $LiAlH_4$ ether electrolyte

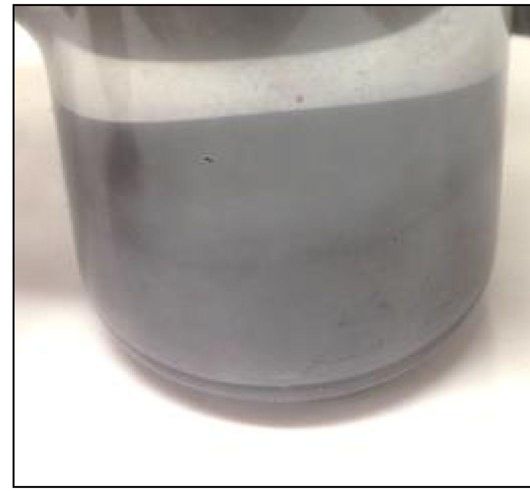
M 3.01 **100% Complete**: Isolation of an amine-alane product from the non-fluidized cell.

Technical Progress: Static Bed of Aluminum Particles in Electrochemical Alane Synthesis

Next Step

Pebbles (0.25cm) → Particles (< 1mm) → Spent Alane (10-30μm)

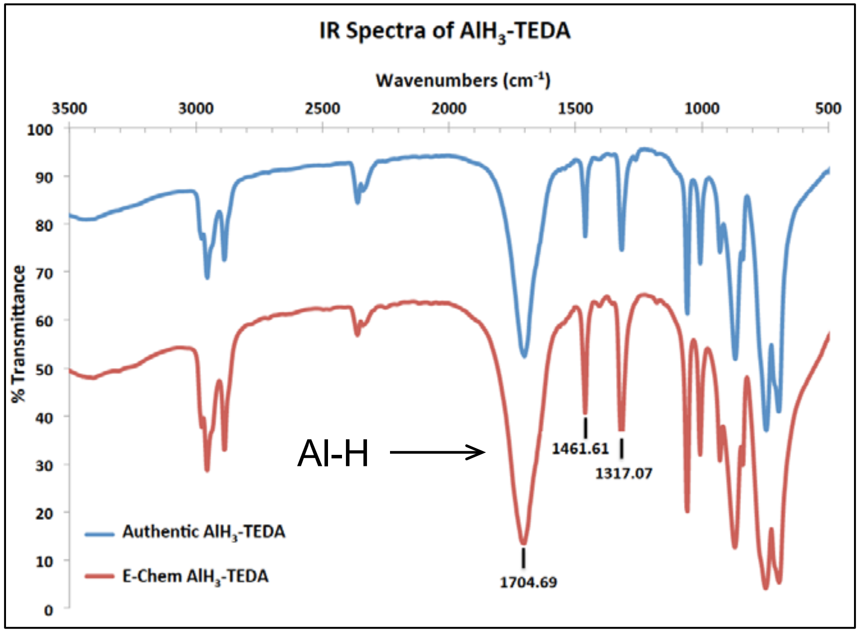




- Initial aluminum particle size reduced over a series of electrochemical runs
- Cell conductance and resistance does not appreciably change with reduction in particle size

Technical Progress: Moving Bed of Aluminum Particles for Electrochemical Alane Synthesis

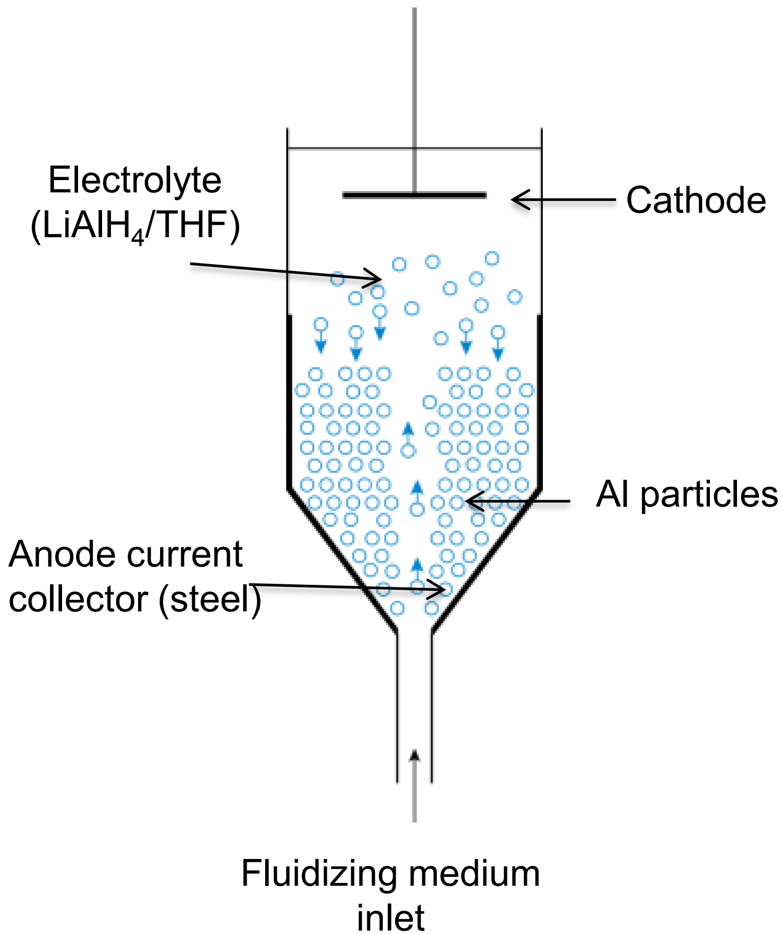
Anode: Al particles over steel current collector

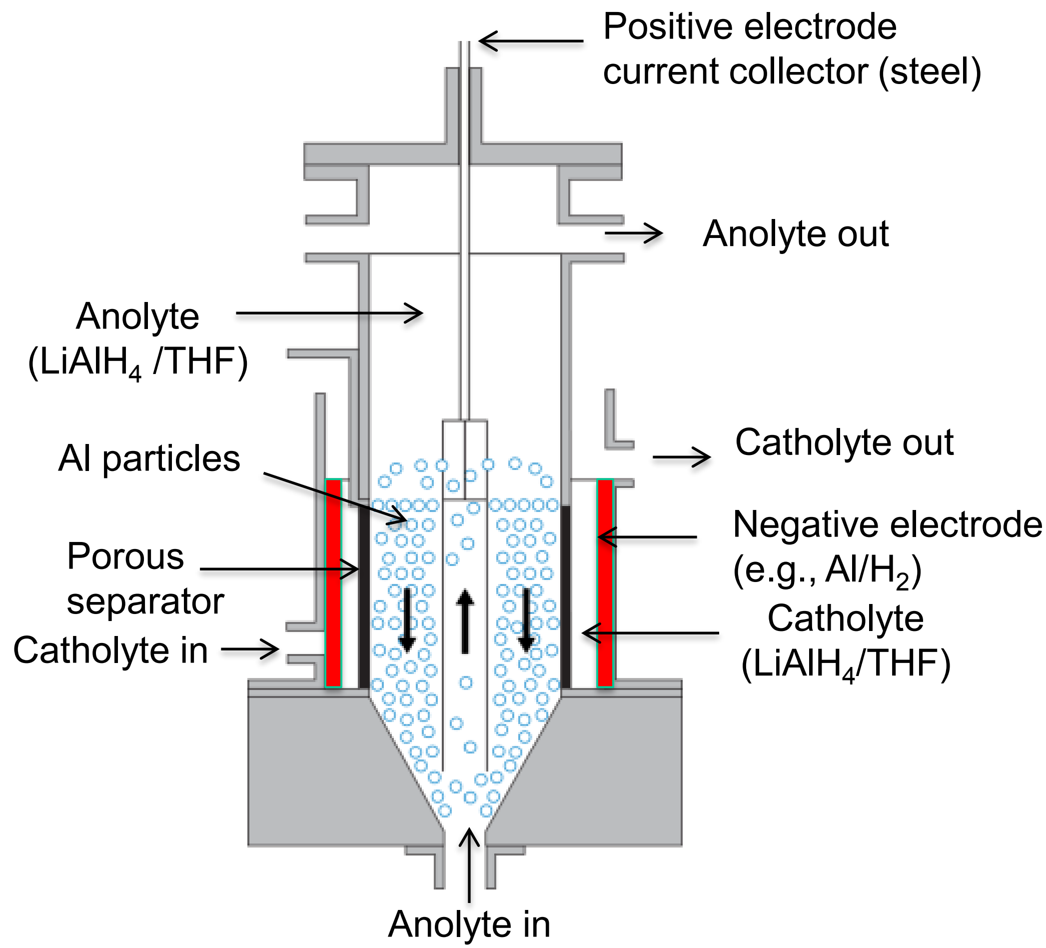


- Aluminum particles (< 1 mm) used in a 1.0 M $LiAlH_4$ in THF electrolyte
- Conductivity and resistance of cell similar to static beds
- Aluminum particles partially consumed to make alane
- Verified alane product as the triethylene diamine adduct (TEDA-AlH_3)

Generation of alane from a moving bed of aluminum particles

Technical Progress: Fluidized Bed Design Options





Simple design-cathodic $LiAlH_4$ degradation may cause issues

Complex design-separate cathode/anode compartments

Technical Progress: Alternative Cathode Approach

$LiAlH_4$ may be consumed in various, deleterious cathode-related reactions:

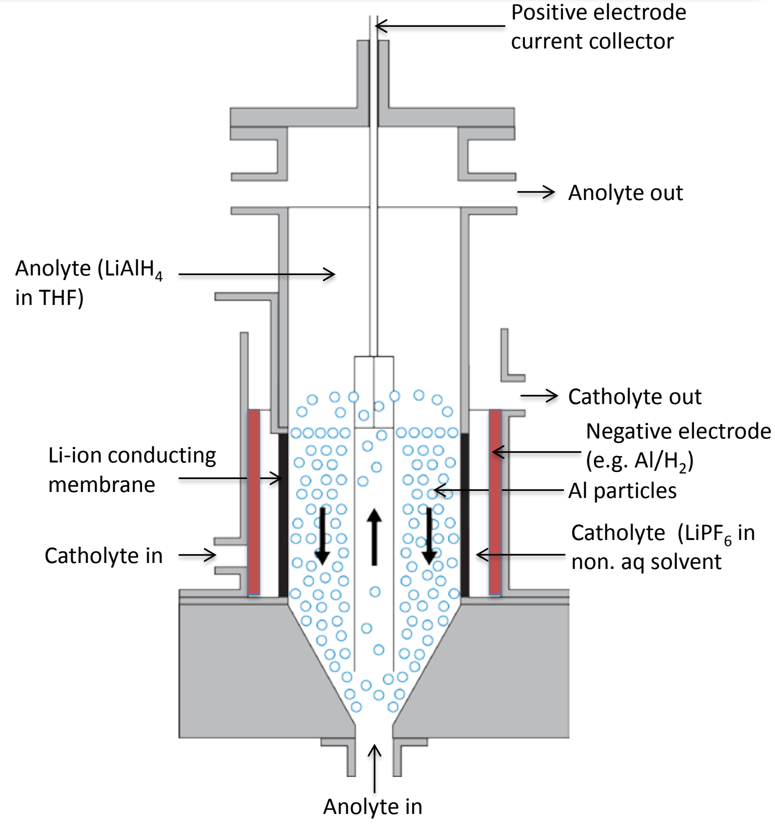
Primarily, $3LiAlH_4 + 3Li^+ + 3e^- \rightarrow Al + 2Li_3AlH_6$ $E^o = 1.1$ V vs. Li

Also, $LiAlH_4 + 2LiH \rightarrow Li_3AlH_6$ $\Delta G^o = -44$ kJmol^{-1}

Data taken from: J-W. Jang *et al*, J. Alloy. Compounds, **420**, 286 (2006).

Employ divided cell and exploit "lithium battery" chemistry on cathode side allows for increased $LiAlH_4$ recovery.

- Mitigates Al/Li_3AlH_6 material formation with no consumption of tetrahydroaluminate at the cathode
- Generation of lithium at high activity on/in the cathode in the presence of hydrogen may lead to formation of LiH with acceptable yield. Which cathode materials provide optimum hydrogen activation?
- Li ion-conducting polymer membrane required to be stable in presence of both anode- and cathode-compartment solvents



Collaborations

Collaborators	Role
Ardica Technologies: Dick Martin (PI) (Receiving DoE project funds)	Development of alane-based hydrogen storage system for portable power
SRI International: Mark Petrie (PI), Steve Crouch-Baker, David Stout, Fran Tanzella (Receiving DoE project funds)	Development of low-cost electrochemical and chemical synthesis production methods for alane production scale-up
SRNL: Ragaiy Zidan (Receiving DoE funds)	Development of novel methods for the synthesis of low-cost alane
Albemarle: Rich Holub (Receiving Ardica funds)	Industrial partner for the scale up of alane production. Currently optimizing the chemical route.
UC Berkeley: Prof. James Evans (Receiving Ardica funds)	Expert advisor on fluidized bed design

Remaining Challenges and Barriers

- Increase rate of alane production in the electrochemical cell. Improve conductivity of LAH/ether electrolyte to enhance electrical energy efficiency of alane production
- Design fluidized, moving or slurry bed of spent alane fuel that maximizes the consumption of the particles in the synthesis of alane
- Eliminate the formation of material (Li_3AlH_6 + $Al_{(m)}$) on the cathode side of the cell
- Regeneration of $LiAlH_4$ or generation of lithium metal or lithium hydride precursors on the cathode side of the cell
- Facile isolation of an isolable and stable alane adduct from the electrochemical reaction that is readily converted to alpha alane

Proposed Future Work

1. Construct a fluidized or moving bed for the anode that optimizes electrode kinetics, enables high-current, and hence high-throughput operation. Collaboration with Prof. Evans (UCB) is critical for this activity. (2015-2017)
2. Construct a cathode compartment based on “lithium battery technology” that prevents dendritic (Li_3AlH_6 + Al) material at the cathode. Directly addresses conservation of $MAlH_4$ (M= Li or Na) and reduction in cost. (2016-2017)
3. Optimize electrolytes compatible with the deposition of lithium or lithium hydride in the cathodic cell compartment. Implement structural membrane permeable to lithium ion and impermeable to tetrahydroaluminate. (2015-2016)
4. Optimize deposition of lithium or sodium or metal hydrides at high activity and yield for further reaction and regeneration of lithium or sodium aluminum hydride. Fluidize cathodic bed particles for deposition of these materials. (2016-2017)
5. Improving the conductivity of $LiAlH_4$/ether electrolyte to enhance electrical energy efficiency of alane production. Utilize additives and supporting electrolyte (2015-2017)
6. Optimize process for complete separation of alane adduct from the concentrated electrolyte. Optimize thermal conversion to α-alane. (2015-2017)

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. ~70% reduction in alane cost

Minimize electrolyte ($LiAlH_4$) consumption in electrochemical alane synthesis

- Verified ~20% alane originates from the Al anode (plate/particles); therefore, ~20% $LiAlH_4$ recovered
- Observed dendritic (Li_3AlH_6 + $Al_{(metal)}$) on the cathode side of the cell representing $LiAlH_4$ loss
- SRI and SRNL working on strategies to inhibit cathode $LiAlH_4$ degradation processes
- Strategies include Li+ battery cell, pulse methods

Optimize particle bed EC reactor (fluidized, moving or static)

- Maximize particle/collector contact, electrolyte circulation and facilitation of a continuous process
- Study different materials that serve as current collectors to minimize side reactions
- Collaboration with Prof. James Evans for particle bed design

Optimize separation of Alane from the concentrated electrolyte

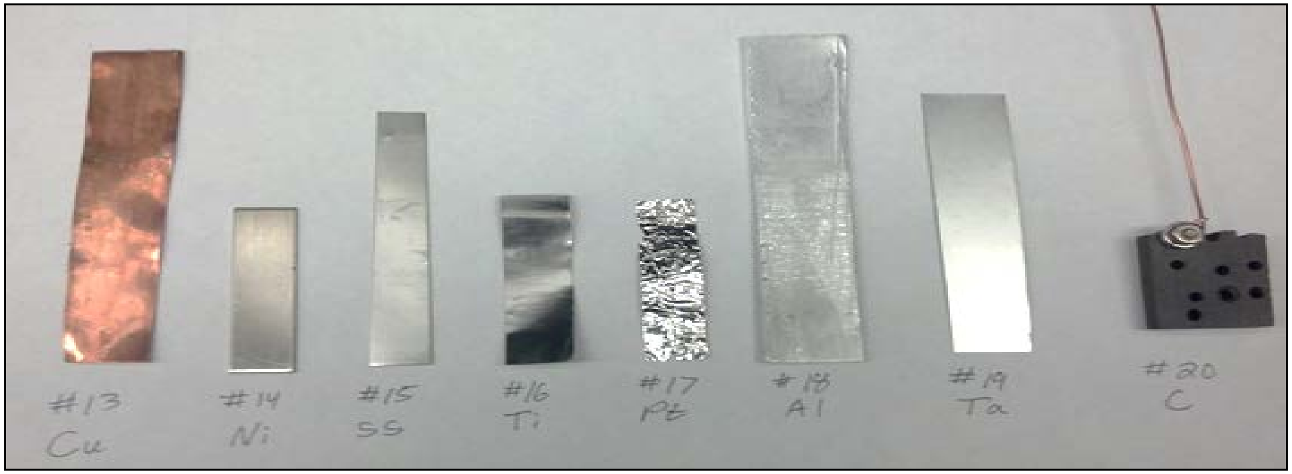
- Efficient recovery of alane produced in an electrochemical cell in the form of an alane adduct
- Capture all alane produced during electrochemical experiment
- Optimize transformation of the alane adduct to the alpha alane product

Technical Back-Up Slides

Approach: Milestones (Full List)

Task	Task Title or Subtask Title	MS #	Milestone Description (Go/No-Go Decision Criteria)	Qtr.	End Date	Progress Made (%)
1.1	Create and update preliminary process and economic models	M1.01	Complete preliminary process & economic models. The alane production cost is estimated to be <$250/kg alane. The economic model shows an estimated storage system cost of <$6.7/g H2 for medium power applications.	2	02/15/15	100%
		M1.02	End of Phase 1 process design and economic analysis. The alane production cost is estimated to be <$180/kg alane. The economic model shows an estimated storage system cost of <$3.3/g H2 for medium power applications.	4	8/15/15	100%
2.1	Establish cell design and preliminary characterization	M2.01	Baseline performance of electrochemical process. The performance of the electrochemical cell is such that sufficient alane is produced from aluminum rather than NaAlH4 to meet the cost target in Task 1.1. Target was >25% $NaAlH_4$ recovery, >20% was achieved which still met the cost targets.	1	11/15/14	100%
		M2.03	Performance data included in the Phase 1 process design and economic analysis. The performance of the cell is such that sufficient alane is produced from aluminum rather than NaAlH4 to meet the cost target in Task 1.1. Target is >50% $NaAlH_4$ recovery, or 1 mol $NaAlH_4$ recovered per 4 mol alane produced.	4	8/15/15	50%
2.2	Bench-scale evaluation of fluidized-bed reactor	M2.04	Fluidized bed reactor set up and operational. Metric is not more than a 2 times increase in the cell resistance when a sheet aluminum anode is replaced with a fluidized particulate aluminum anode.	3	5/15/15	100%
		M2.05	Performance data provided to Task 1.1 to be included in the Phase 1 process design and economic analysis. The FBR achieves a current density of 10 mA/cm2.	4	8/15/15	50%
3.1	Develop crystallation and passivation procedures	M3.01	The identification of process unit operations included in the Phase 1 process design and economic analysis. The alane product is an amine adduct of alane from the non-fluidized cell.	2	2/15/15	100%
		M3.02	Performance data and the identification of process unit operations included in the Phase 2 process design and economic analysis. The alane product is an amine adduct of alane from the fluidized bed.	4	8/15/15	100%
4.1	Package, test, and evaluate alane fuel during Phase 1.	M4.01	Performance data and results included in the Phase 1 final report. The hydrogen storage device achieves a gravimetric capacity of >0.7 kWh/kg and a volumetric capacity of >1.0 kWh/L, achieving the 2015 performance metrics.	4	8/15/15	100%
5.1	Phase 1 Final Report to support Go/No-Go Decision	M5.01	Report provided to the client that summarizes all results from Phase 1 and provides a comparison to the cost and performance metrics. Includes the results for milestones M1.02 and M4.01.	4	8/15/15	100%

Technical Progress: Evaluation of Anode Charge Collector for Fluidized Bed Cell



Material	Area	Current After 1 hr.	Current/ area
	cm^2	mA	mA/cm2
Copper	5.4	48	8.9
Nickel	3.6	41	11.4
Stainless Steel	3.0	12	4.0
Titanium	4.5	29	6.4
Platinum	1.0	18.5	18.5
Aluminum	6.6	34	5.2
Tantalum	4.8	24	5.0
Carbon	4.8	39	8.1

Best Choice: “Steel”

Requirements

- Minimal H_2 gas evolution from rxn # 2
- Low current per area
- High chemical stability
- No discoloring of electrolyte or anode