

IV.C.6 Low-Cost α -Alane for Hydrogen Storage

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Overall Objectives

The overall objective of this project is to reduce the 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. This will enable broader applications in consumer electronics (smart phones, tablets, laptops...), back-up power, unmanned aerial vehicles, forklifts, and vehicles.

Fiscal Year (FY) 2015 Objectives

- Complete preliminary process and economic models
- Develop baseline performance of electrochemical process
- Set up fluidized bed reactor and establish test operations

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (J) Thermal Management
- (K) System Life-Cycle Assessments

(Q) Regeneration Processes

Technical Targets

The objective of this project is to reduce the production cost of α -alane by developing, demonstrating, and performing an economic analysis of an electrochemical process to synthesize α -alane. The reduced production cost will enable alane-based hydrogen storage to achieve the DOE portable power cost target of $<\$1/\text{g H}_2$ stored.

FY 2015 Accomplishments

- Preliminary process and economic models were developed for the electrochemical route for the synthesis of α -alane.
- Evaluation of the electrochemical cell reported by Zidan et al. [1], for the electrochemical synthesis of α -alane.
- Candidate materials for the anodic current collector and current collector designs were evaluated. Stainless steel was determined to be the most optimal of the materials tested.
- Particles of aluminum of various sizes were evaluated in the anodic compartment. The consumption of the particles to produce alane was verified. Cell current and resistance were comparable to that observed for a slab aluminum electrode.
- Alane production was verified by the isolation of N-ethylmorpholine and triethylene diamine alane adducts from the electrochemical cell.
- Strategies were developed to mitigate the cathodic production of dendritic material ($\text{Li}_3\text{AlH}_6 + \text{Al}$).
- Preliminary design of a fluidized bed was developed.



INTRODUCTION

This project is developing improvements to the Savannah River National Laboratory (SRNL) lab-scale electrochemical synthesis of alane and Ardica-SRI chemical downstream processes that are necessary to meet DOE cost metrics and transition alane synthesis to large scale production. These modifications are focused on critical cost-saving design improvements to the electrochemical cell.

The use of a fluidized bed reactor will replace the sheet aluminum electrodes of the current SRNL process with a bed of conductive aluminum particles maintained in a state

of agitation by a flowing electrolyte and/or a fluidizing gas. Electrical contact with these particles is maintained through a sheet current collector, and the high surface area of these particles will ensure efficiency of reaction. In our approach, spent alane particles can be provided directly to the reactor. This avoids the costs required to convert spent alane into sheet or rod form for use in other electrochemical reactor designs or the need for costly disposal.

APPROACH

To develop synthesis technology to reduce the cost of α -alane to $< \$4/\text{kg}$, the approach is to transition a bench-scale electrochemical route to alane to an electrochemical process that will be more conducive and economical for large scale alane production (Figure 1). Specifically, we propose a process that uses spent fuel as a starting material in a continuous synthesis/regeneration of alane from less costly elemental aluminum and hydrogen. This technique could greatly reduce fuel costs and accelerate the commercial acceptance of alane-based fuel cell technology. The long-term goal of the project is to reduce the cost of the initial alane charge to $\$4/\text{kg}$ and the recycling cost to $\$2/\text{kg}$. This reduction in fuel costs translates to storage system costs of $< \$1$ per g H_2 , achieving the DOE hydrogen storage system metrics for 2015 and 2020.

RESULTS

- Preliminary process and economic models were completed. The alane production cost is estimated to be $< \$250/\text{kg}$ alane. The economic model shows an estimated storage system cost of $< \$6.7/\text{g H}_2$ for medium power applications (Table 1).
- A baseline was determined for performance of the 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.
- A fluidized bed reactor was set up and is operational (Figure 2). When a sheet aluminum anode is replaced with a fluidized particulate aluminum anode, the increase in cell resistance is to be not more than twice the value of the sheet electrode (Figure 3).
- The identification of process unit operations was included in the Phase 1 process design and economic analysis. The alane product is an amine adduct of alane from the non-fluidized cell.
- The economic model shows an estimated storage system cost of $< \$3.3/\text{g H}_2$ for medium power applications.

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.

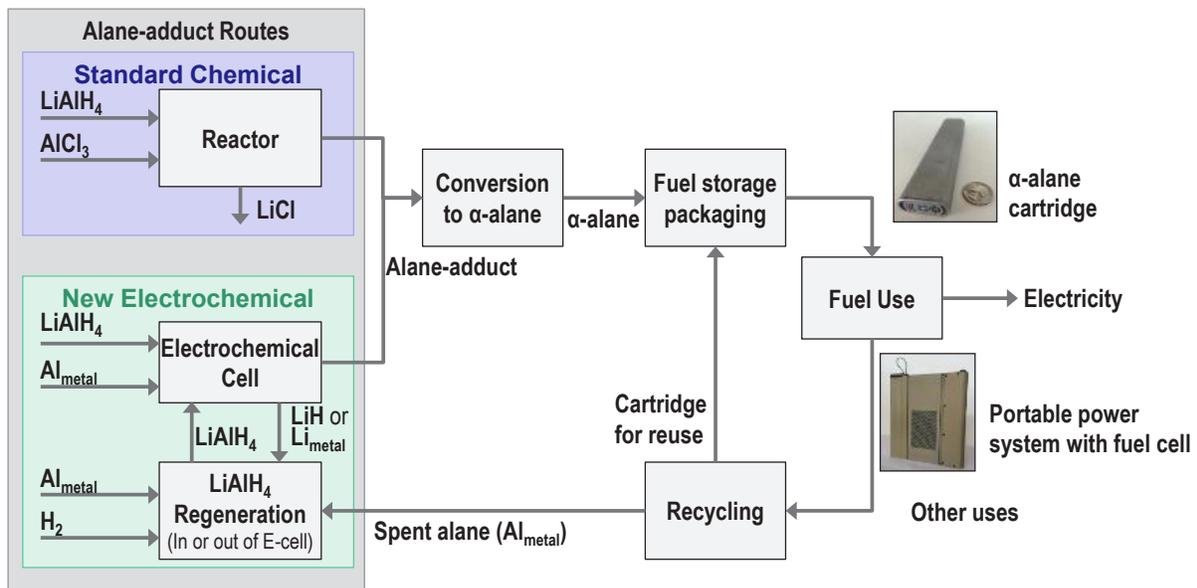


FIGURE 1. Electrolysis process added to alane production

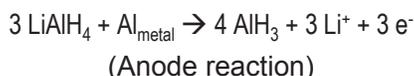
TABLE 1. Progress towards Meeting Technical Targets for Hydrogen Storage

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

Storage System Costs			Current Cost	Chemical Route	Electrochemical Route		
					Improved Anode	Cathode Recycle	Optimized Process
			Pilot Plant	Commercial Scale	(20% AlH ₃ from Al)	(25% AlH ₃ from Al, LiAlH ₄ regenerated)	(25% from Al, LiAlH ₄ recycle/regeneration)
Fuel	\$/kg alane		3,500	112	87	55	34
Cartridge components	\$/kg alane		<u>79</u>	<u>79</u>	<u>79</u>	<u>79</u>	<u>79</u>
Total	\$/kg alane		3,579	191	166	134	113
Storage System Cost	\$/g H ₂		40	2.15	1.87	1.51	1.27
DOE Metrics			\$/g H ₂				
			Target Met?				
Low Power	2015	3	N	Y	Y	Y	Y
	2020	1	N	N	N	N	N
Medium Power	2015	6.7	N	Y	Y	Y	Y
	2020	3.3	N	N	N	Y	Y

Aluminum Particle Fluidized Bed

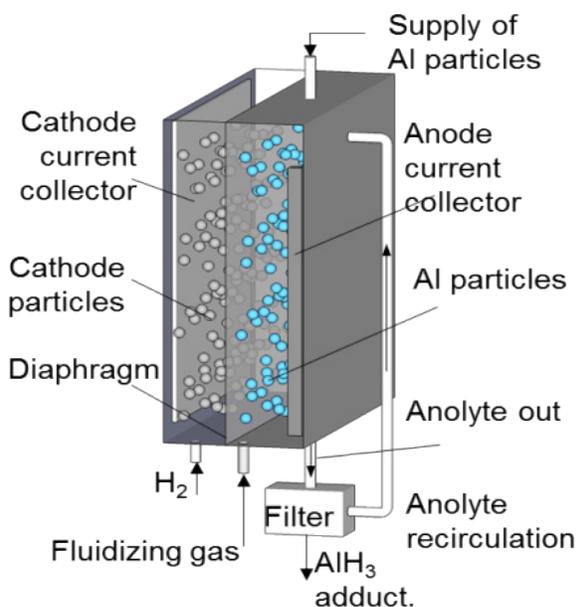
Background



- Electrochemical process developed by Ragaiy Zidan at SRNL
- Uses NaAlH₄ or LiAlH₄ 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

**FIGURE 2.** Aluminum particle fluidized bed

- We demonstrated a gravimetric capacity of >0.7 kWh/kg and a volumetric capacity of >1.0 kWh/L, achieving the 2015 performance metrics.

CONCLUSIONS AND FUTURE DIRECTIONS

- The project will construct a fluidized or moving bed for the anode that optimizes electrode kinetics, enables

high-current, and hence high-throughput, operation. (2015–2017)

- A cathode compartment based on lithium battery technology that prevents dendritic (Li₃AlH₆ + Al) material at the cathode will be constructed, which directly addresses conservation of MAIH₄ (M= Li or Na) and reduces cost. (2016–2017)

Static Bed of Aluminum Particles in Electrochemical Alane Synthesis

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



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

FIGURE 3. Static bed of aluminum particles in electrochemical alane synthesis

- Electrolytes compatible with the deposition of lithium or lithium hydride in the cathodic cell compartment will be optimized. A structural membrane permeable to lithium ion and impermeable to tetrahydroaluminate will be implemented. (2015–2016)
- The project will 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. Cathodic bed particles for deposition of these materials will be fluidized. (2016–2017)
- Conductivity of LiAlH₄/ether electrolyte will be improved to enhance electrical energy efficiency of alane production. Additives and supporting electrolytes will be utilized. (2015–2017)
- The project will optimize the process for complete separation of alane adduct from the concentrated electrolyte and optimize thermal conversion to α -alane. (2015–2017)

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Mark Petrie was recognized by SRI International for his work on alane and other energetics by selection as an SEI Fellow.

REFERENCES

1. Zidan, R., et al., Electrochemical reversible formation of alane, DOE FY 2013 Annual Progress Report (2013).