

IV.C.12 Low-Cost α -Alane for Hydrogen Storage

Richard Martin

Ardica Technologies, Inc.
2325 3rd Street, Suite 424
San Francisco, CA 94107
Phone: (415) 445-8612
Email: dmartin@ardica.com

DOE Manager: Katie Randolph
Phone: (240) 562-1759
Email: Katie.Randolph@ee.doe.gov

Technical Advisor: Mark Petrie
Phone: (650) 859-4574
Email: mark.petrie@sri.com

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(i.e., smart phones, tablets, laptops), back-up power, unmanned aerial vehicles, forklifts, and vehicles.

Fiscal Year (FY) 2016 Objectives

- Update 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

Table 1 shows the progress made towards the DOE technical targets.

Overall Objectives

- 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. This will enable broader applications in consumer electronics

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 <small>(1,2)</small>	Electrochemical Route		
					Baseline <small>(1,3)</small>	Cathode Recycle <small>(1)</small>	Increased Scale to 3,200 MT/yr
			Pilot Plant	Commercial Scale	(80% AlH3 from R1)	(80% AlH3 from R1, 80% LiAlH4 regenerated)	(80% AlH3 from R1, 80% LiAlH4 regenerated)
Alane Fuel Costs	\$/kg alane	3500	112	81	56	29	
Cartridge Cost ⁽⁴⁾	\$/kg alane	79	53	53	53	44	
Total	\$/kg alane	3579	165	134	109	73	
Storage System Cost	\$/g H2	38.91	1.79	1.46	1.18	0.79	
DOE Metrics		\$/g H2	Target Met?				
Low Power	2015	3	N	Y	Y	Y	
	2020	1	N	N	N	Y	
Medium Power	2015	6.7	N	Y	Y	Y	
	2020	3.3	N	Y	Y	Y	

1. Chemical and electrochemical route productions costs are for a 320 MT/yr process.

2. Commercial scale estimate provided by Albemarle.

3. Cost of alane entirely from reaction (R2) is \$101, compared to \$81 for 80% from reaction (R1).

4. New cartridge costs based on manufacturer estimates. \$79/kg AlH_3 at small scale production, \$53/kg AlH_3 at 4 M cartridges/year and \$44/kg AlH_3 at 20 M cartridges/year. Further cost savings of 25-33% per cartridge can be realized through recycling, not shown.

Baseline (Anode Reactions)

(R1-80%) $3 \text{LiAlH}_4 + \text{Al}_{\text{metal}} \rightarrow 4 \text{AlH}_3 + 3 \text{Li}^+ + 3 \text{e}^-$

(R2-20%) $\text{LiAlH}_4 \rightarrow \text{AlH}_3 + 1/2 \text{H}_2 + \text{Li}^+ + \text{e}^-$

FY 2016 Accomplishments

Accomplishments include:

- Updated the cost model.
- Designed a fluidized bed in collaboration with Prof. Jim Evans (University of California, Berkeley).
- Calculated minimal flow rates for fluidization of various particle sizes. Determined the optimal dimensions of the anode cell and size of the pump.
- Constructed the cell (Adams & Chittenden scientific glass) and the system that pumps the electrolyte through the bed of aluminum particles.
- Investigated the dependence of current versus distance between electrodes in the fluidized bed reactor system. Performed experiments that determined the amount of alane produced from the anode in the current fluidized bed cell configuration.
- Investigated the cathode products under various electrochemical reactor conditions.
- Performed initial experiments to isolate the N-ethylmorpholine alane adduct from $\text{LiAlH}_4/\text{NaAlH}_4$ tetrahydrofuran (THF)-based electrolytes and its conversion into α -alane.



INTRODUCTION

This project is developing improvements to the Savannah River National Laboratory 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 Savannah River National Laboratory process with a bed of conductive aluminum particles maintained in a stage 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 $<\$5/\text{kg}$, 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. 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 cost of alane produced by the electrochemical route (Table 1) translates to a storage system cost of $<\$1/\text{g H}_2$, achieving the DOE hydrogen storage system metrics for 2015 and 2020 for both low and medium portable power. The longer-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 will result in hydrogen costs that are competitive with the cost of gasoline.

RESULTS

During Phase 2, updates were made to the process and economic models for the electrochemical route for the synthesis of α -alane. The costing included detailed estimates for material and utilities requirements and capitol and manufacturing costs. The updated cost table shows alane fuel costs associated with the chemical route (pilot plant and 320 MT/yr scale) and different developmental stages of the electrochemical process. The alane production cost is estimated to be $<\$81/\text{kg alane}$ at 320 MT/yr and an estimated storage system cost of $<\$1.46/\text{g H}_2$ for worst-case scenario.

Cathode products were evaluated and analyzed under various electrochemical conditions and electrolytes. Gravimetric and X-ray diffraction analysis of the solid cathode products in lithium-based systems were also carried out. Figure 1 shows the dependencies of cathode mass on charge that was passed in pulsed and non-pulsed experiments

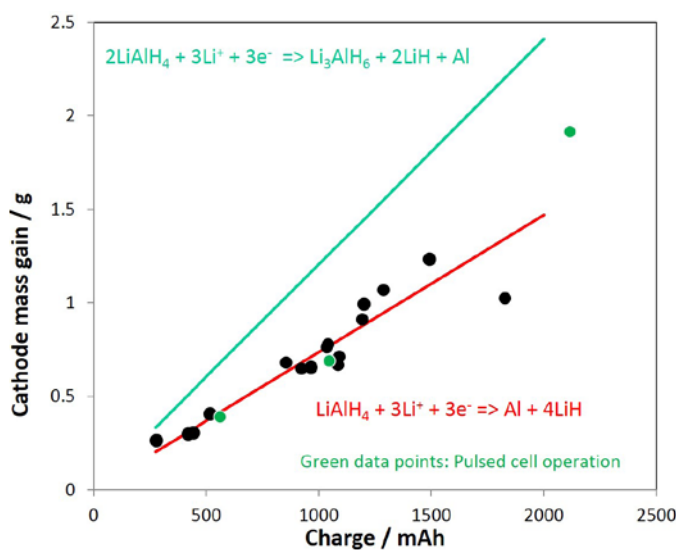


FIGURE 1. Cathode reaction products

(points) as compared with the expected dependencies for two putative cathode reactions (lines) using 1 M LiAlH_4 in THF as the electrolyte. In agreement with X-ray diffraction and elemental analysis data, the dominant cathode products include lithium hydride and aluminum which may be used to regenerate LiAlH_4 in a separate operation.

During Phase 2, a fluidized bed reactor shown in Figure 2 was designed and set up with recirculating electrolyte. Fluidization experiments were performed on <1 mm particles and a mixture consisting of particles that ranged from 106–150 μm . The critical point of fluidization

was achieved at ~ 2.0 L/hr using the 106–150 μm -sized particles. Current densities of $10 \text{ mA}/\text{cm}^2$ to $>100 \text{ mA}/\text{cm}^2$ were observed that meet and/or exceed the milestone current densities of M2.06 ($10 \text{ mA}/\text{cm}^2$) and M2.08 ($100 \text{ mA}/\text{cm}^2$).

As expected, reduction of the electrode spacing increases current dramatically. THF-based electrolytes provide strikingly higher conductivities compared to diethyl ether. (Figure 3)

The alane fuel storage system energy densities based on the hydrogen produced were:

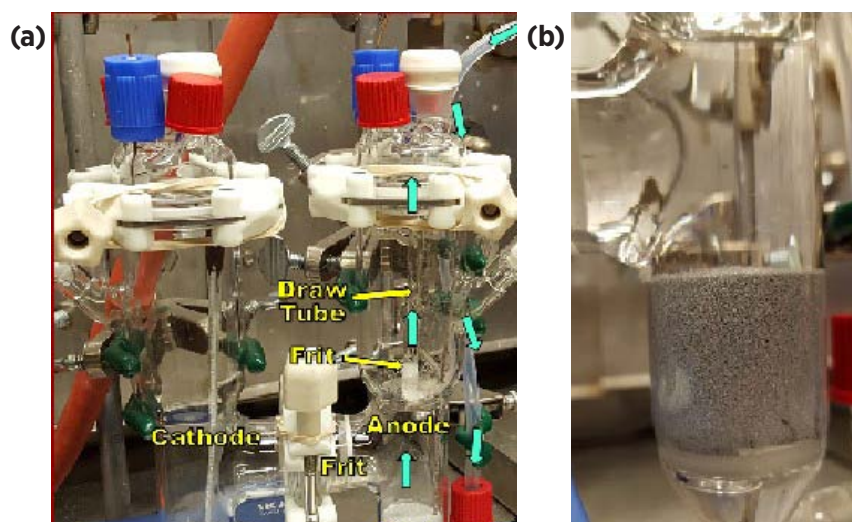


FIGURE 2. (a) Picture of the fluidized electrochemical cell system. (b) The fluidized anode compartment using aluminum particles with sizes that ranged from 106–150 μm .

Design critical for optimized cell conductance

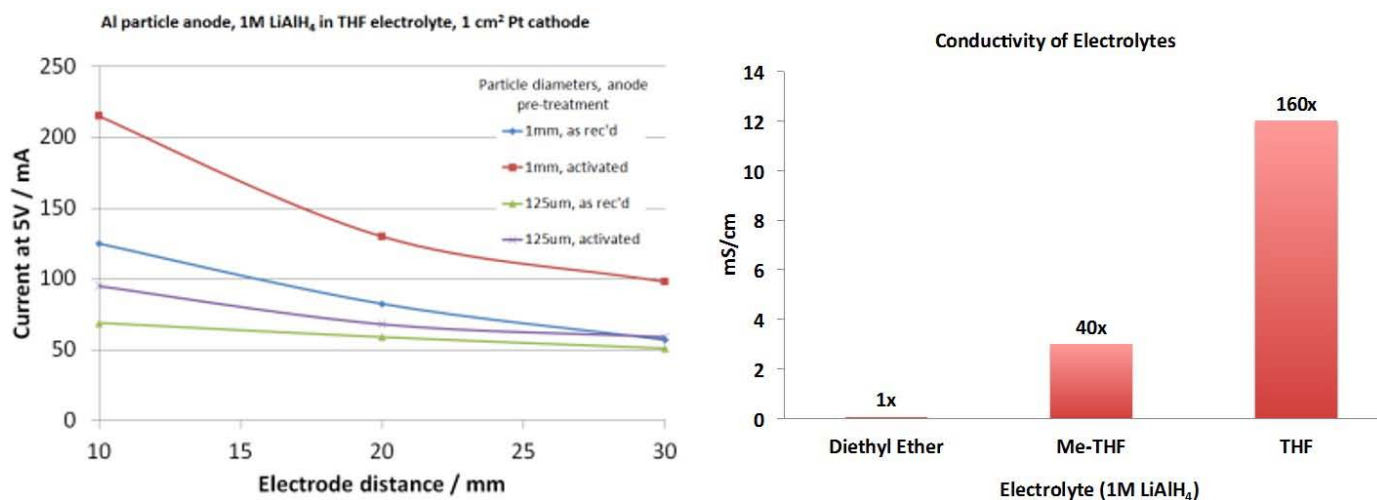


FIGURE 3. Current at constant voltage (5 V) vs. electrode separation

- 0.98 kWh/kg (target was 1.0 kWh/kg)
- 1.26 kWh/L (target was 1.3 kWh/kg)

CONCLUSIONS AND FUTURE DIRECTIONS

- 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. Collaboration with Prof. Evans (University of California, Berkeley) is critical for this activity. (2016–2017)
- Deposition of cathode products at high activity and yield for further reaction and regeneration of lithium or sodium aluminum hydride ($\text{MAI}H_4$). Modify pulse methods and fluidization of cathodic bed aluminum particles for deposition/capture of these materials. Improve morphology and optimize conversion to $\text{MAI}H_4$. (2016–2017)
- 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. (2016–2017)

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

The Ardica alane-fueled soldier Wearable Power System (WPS) participated in the Army Expeditionary Warrior Exercise at Ft. Benning, Georgia, in January–February 2016. The exercise uses realistic 72-hr missions to test new technology solutions in combat scenarios with aggressor forces. The WPS performed to specification and was highlighted in the senior leader wrap up briefing as reducing the battery weight carried by soldiers by 55%. DOE paid for developing the electrochemical processes to lower the cost of alane while the Army paid for the WPS development. The Army has concluded the following: the WPS has a significant weight advantage over the conformal wearable battery option for a centralized power source in the small unit power suite of equipment. The current cost of alane fuel makes the cost of the fuel cartridge prohibitively expensive. Implementation of large scale alane production and development of electrochemical routes to manufacture of alane are likely means of making the cartridges affordable for the army.