

## IV.C.17 Low-Cost $\alpha$ -Alane for Hydrogen Storage

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

### Technical Targets

The following was the progress made towards the DOE technical targets (Table 1).

### FY 2017 Accomplishments

- Cost modeling. Using lab results, updated the cost model showing the cost of alane produced by the electrochemical route (Table 1) translates to a storage system costs of  $< \$1/\text{g H}_2$ , achieving the DOE hydrogen storage system metrics for 2015 and 2020.
- Electrochemical alane adduct generation. Implemented a sodium-ion conducting, non-porous membrane as the electric cell separator raising alane-THF adduct formation to 71% with a cathode product formation yield of 99%.
- Alane adduct conversion. Determined that for trans-ligation of THF for another Lewis base (in which the resulting  $\text{AlH}_3\text{-L}$  adduct can be converted to  $\alpha\text{-AlH}_3$ ) the N-ethylmorpholine (NEM) and N,N-dimethylisopropylamine ( $\text{N}^i\text{PrMe}_2$ ) had the highest overall conversion yield, 97% trans-ligation and 20–30%  $\alpha$ -alane conversion yield for NEM and 70% trans-ligation and 20–40%  $\alpha$ -alane conversion yield for  $\text{N}^i\text{PrMe}_2$ .
- Electrolyte regeneration. Showed that electrochemically generated, recovered cathode product could be converted to electrolyte salt with additional aluminum derived from de-hydrated alane under elevated  $\text{H}_2$  pressure and temperature. The regeneration yield was 92% after only 18 h.
- Hydrogen storage system performance. The alane fuel storage system energy densities based on the  $\text{H}_2$  produced were:
  - 0.98 kWh/kg (target was 1.0 kWh/kg)
  - 1.26 kWh/L (target was 1.3 kWh/kg)



### Overall Objective

Reduce production cost of  $\alpha$ -alane ( $\text{AlH}_3$ ) 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 (i.e., smart phones, tablets, laptops), back-up power, unmanned aerial vehicle, forklifts, and vehicles.

### Fiscal Year (FY) 2017 Objectives

- Demonstrate electrochemical alane adduct generation at high current density and product yield.
- Identify alane adducts suitable for trans-ligation from alane-tetrahydrofuran (THF) adduct. Characterize trans-ligation yields and yields of alane adduct conversion into alpha alane.
- Demonstrate high yield regeneration of  $\text{NaAlH}_4$  from the reaction of recovered cell cathode product, aluminum and hydrogen.
- Update process and economic models.

### 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.

**TABLE 1.** Progress towards Meeting Technical Targets for Hydrogen Storage

Storage System Costs		Chemical Route <sup>(1,2)</sup>	Electrochemical Route <sup>(3)</sup>		
			Baseline <sup>(1,4)</sup>	Cathode Recycle <sup>(1)</sup>	
		Commercial Scale	(80% AlH <sub>3</sub> from R1)	(80% AlH <sub>3</sub> from R1, 80% LiAlH <sub>4</sub> regenerated)	
Alane Fuel Costs	\$/kg alane	112	82	50	
Cartridge Cost	\$/kg alane	53	53	53	
Total	\$/kg alane	165	135	103	
<b>Storage System Cost</b>	<b>\$/g H<sub>2</sub></b>	<b>1.79</b>	<b>1.47</b>	<b>1.12</b>	
DOE Metrics		\$/g H <sub>2</sub>	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

<sup>1</sup> Chemical and electrochemical route productions costs are for a 320 MT/y process.

<sup>2</sup> Commercial scale estimate provided by industrial partner.

<sup>3</sup> Assumes 90% electrochemical utilization of NaAlH<sub>4</sub> and 90% adduct conversion.

<sup>4</sup> 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%)  $\text{LiAlH}_4 \rightarrow \text{AlH}_3 + 1/2 \text{ H}_2 + \text{Li}^+ + \text{e}^-$

## 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.

## APPROACH

To develop synthesis technology to reduce the cost of  $\alpha$ -alane to <\$5/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 focus on a continuous synthesis/regeneration reactor and process design that ideally only requires low-cost elemental aluminum (preferably spent alane) and hydrogen as input. This approach could greatly reduce fuel costs and accelerate the commercial acceptance of the alane-based fuel-cell technology. The cost of alane produced by the electrochemical route (Table 1) translates to a storage system costs of <\$1/g H<sub>2</sub>, achieving the DOE H<sub>2</sub> 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/kg and the recycling cost to \$2/kg. This will result in hydrogen costs that are competitive with the cost of gasoline.

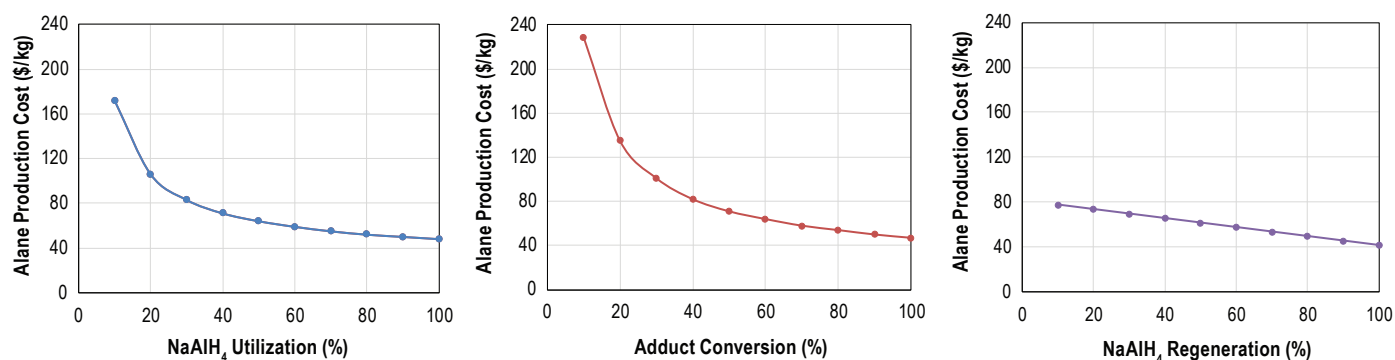
## RESULTS

During Phase 3, updates were made to the process and economic models for the electrochemical route for the synthesis of  $\alpha$ -alane. The costing included detailed estimates for material and utilities requirements and capital and manufacturing costs. The updated cost table above 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 electrochemical alane production cost is estimated to be <\$82/kg alane at 320 MT/year and an estimated storage system cost of <\$1.47/g H<sub>2</sub> for the worst-case scenario.

### Alane Manufacturing Cost: Process Yield Sensitivity

A major thrust of the current phase of this project was a determination of the likely yields of the various steps involved in the electrochemical process for alane. We have modeled process yield sensitivities for production at the 320 MT/y scale. At the outset, we have focused on the yields of three key elements of electrochemical alane production: NaAlH<sub>4</sub> utilization, adduct conversion, and NaAlH<sub>4</sub> regeneration.

Figure 1 shows our estimates of the cost-yield sensitivities for the three processes. In each case, a single sensitivity is plotted at the constant, nominal values of the remaining quantities. For reference, if nominal value of these quantities is chosen to be 90%, 90%, and 80%, respectively, the alane cost is predicted to be approximately \$50/kg at scale.



**FIGURE 1.** Cost-yield sensitivities for three aspects of alane production

### High Current Density Electrochemical Alane Adduct Generation

Thermodynamically, the soluble alane adduct formed at the anode in the electrochemical cell design is predicted to react with any electrically-disconnected, solid Na<sub>3</sub>AlH<sub>6</sub> or NaH present on the cathode which it encounters to regenerate the adduct-stabilized, soluble NaAlH<sub>4</sub> electrolyte.

Cells of the following general design: (-) Al (1 cm<sup>2</sup>)/1.3 M NaAlH<sub>4</sub> in THF/separator/1.3 M NaAlH<sub>4</sub> in THF/Al (approx. 24 cm<sup>2</sup>) (+) were operated at 100 mA cm<sup>-2</sup> referred to the anode area with a variety of porous separators. The highest yield of recovered alane-THF adduct, 61% referred to the total charge passed, was obtained with a 1–1.6 μm pore diameter, porous silica separator. Cells with less restricted anolyte/catholyte separations resulted in lower adduct yields. In recent work, a sodium-ion conducting, non-porous membrane was used as the separator. In this case, the adduct formation yield rose to 71% with a cathode product formation yield of 99%.

### Conversion

The conversion of Lewis acid-base adducts of alane (AlH<sub>3</sub>-L) into α-AlH<sub>3</sub> is determined in part by the strength of the Al-L interaction. A strong Al-L interaction requires forcing conditions for the conversion and can lead to AlH<sub>3</sub> decomposition, whereas weak binding leads to instability of the AlH<sub>3</sub>-L adduct. Our studies found that the MAIH<sub>4</sub>/THF (M = Li or Na) electrolyte is better suited for the electrochemical synthesis of AlH<sub>3</sub>-L due to its greater electrical conductivity compared to LiAlH<sub>4</sub>/Et<sub>2</sub>O. However, the use of the MAIH<sub>4</sub>/THF electrolyte generates AlH<sub>3</sub>-THF, which is not known to convert to α-AlH<sub>3</sub>.

We reasoned that post-electrosynthetic trans-ligation of THF for another Lewis base may be a promising synthetic strategy. We have characterized trans-ligation yields from alane-THF adduct and yields of adduct conversion to α-AlH<sub>3</sub> for several promising ligands. Our studies were performed in collaboration with Savannah River National Laboratory,

which has been calculating the Al-L interaction free energy using density functional theory methods on the national laboratory's computing resources. Among the tested ligands NEM and N<sup>i</sup>PrMe<sub>2</sub> had the highest overall conversion yields, 97% trans-ligation and 20–30% alpha alane conversion yield for NEM and 70% trans-ligation and 20–40% alpha alane conversion yield for N<sup>i</sup>PrMe<sub>2</sub>.

### Electrolyte Regeneration

In addition to electrochemical alane-adduct isolation and subsequent conversion efficiencies, the efficiency of electrolyte salt (MAIH<sub>4</sub>, where M = Li or Na) regeneration from the electrochemical cathode product, and supplemental aluminum and hydrogen, is an important component of the overall alane production cost reduction strategy. Using a high-pressure Parr reactor we have evaluated NaAlH<sub>4</sub> regeneration yields from aluminum and cathode reaction products generated at 100 mA/cm<sup>2</sup> current density.

In the most promising experiment, we have shown that electrochemically generated, recovered cathode product could be converted to electrolyte salt with additional aluminum derived from de-hydrated alane under elevated H<sub>2</sub> pressure and temperature. The regeneration yield was 92% after only 18 h. This result clearly indicates that cost-effective electrolyte regeneration may be achievable on a commercial scale.

## CONCLUSIONS AND UPCOMING ACTIVITIES

- 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.
- Optimize solvent swap methods for complete separation of alane adduct from the concentrated NaAlH<sub>4</sub> based electrolyte. Optimize thermal conversion to α-alane from amine adducts using crystallization aides and heating profiles.

## **SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED**

The following patents or inventions were reported to DOE:

- 1.** 7260US, Use of Fluidized-Bed Electrode Reactors for Alane Production.
- 2.** 7369PRV, Alane Production in an Electrochemical Process Utilizing Li Battery Cathode.
- 3.** Invention-Capillary Flow Cell for Use with Resistive Electrolyte for Alane Production.