

## IV.C.5 Electrochemical Reversible Formation of $\alpha$ -Alane

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determined annually by DOE

### Overall and Fiscal Year (FY) 2015 Objectives

- Develop methods of  $\alpha$ -aluminum hydride ( $\alpha$ -alane or  $\alpha$ -AlH<sub>3</sub>) production and regeneration that lower the cost of  $\alpha$ -alane production to less than \$10/kg
- Demonstrate and characterize alane production system that lowers the cost of  $\alpha$ -alane production with the lowest possible capital and operating costs
- Identify and quantify fundamental properties of  $\alpha$ -alane production chemistry and physics that will lead to improved design and modeling of systems for  $\alpha$ -alane production and use

### 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
- (Q) Regeneration Processes

### Technical Targets

In this project studies are being conducted to lower cost and improve efficiency of the electrochemical method to form  $\alpha$ -AlH<sub>3</sub>. This material has the potential to meet long-term and near-term targets for various applications such as portable

power [1,2]. The research performed as part of this contract is equally applicable to both areas.

- By 2015, develop and verify a single-use hydrogen storage system for portable power applications achieving 0.7 kWh/kg system (2.0 wt% H<sub>2</sub>) and 1.0 kWh/L system (0.03 kg H<sub>2</sub>/L) at a cost of \$0.09/Wh net (\$3/g hydrogen stored)
- By 2020, develop and verify a single-use hydrogen storage system for portable power applications achieving 1.3 kWh/kg system (4.0 wt% H<sub>2</sub>) and 1.7 kWh/L system (0.05 kgH<sub>2</sub>/L) at a cost of \$0.03/kWh net (\$1.0/g hydrogen stored).

### FY 2015 Accomplishments

- Developed reverse pulsing technique capable of significant reduction of dendrites formed during the electrochemical generation of  $\alpha$ -alane etherate
- Investigated the use of spent  $\alpha$ -alane for the production of aluminum electrodes
- Optimized crystallization process to produce pure  $\alpha$ -alane with particle sizes >4  $\mu$ m



## INTRODUCTION

DOE is supporting research to demonstrate viable materials for on-board hydrogen storage. Aluminum hydride (alane - AlH<sub>3</sub>), having a gravimetric capacity of 10 wt% and volumetric capacity of 149 g H<sub>2</sub>/L and a desorption temperature of ~60–175°C (depending on particle size and the addition of catalysts), has the potential to meet the 2015 and 2020 DOE system-level targets for portable power applications, as well as the requirements for other hydrogen storage applications. The main barrier for using alane as a hydrogen storage material is the high material cost and unfavorable thermodynamics towards (re)hydrogenation. Zidan et al. [3] were the first to show a reversible cycle utilizing electrochemistry and direct hydrogenation, where gram quantities of alane were produced, isolated, and characterized. This regeneration method is based on a complete cycle that uses electrolysis and catalytic hydrogenation of spent Al(s). This cycle avoids the impractical high pressure needed to form  $\alpha$ -AlH<sub>3</sub> and the chemical reaction route of  $\alpha$ -AlH<sub>3</sub> that leads to the formation of alkali halide salts, such as LiCl or NaCl, that become a thermodynamic sink because of their stability.

During FY 2015, research was continued to demonstrate methods that will improve the generation of alane. This work

was performed in collaboration with Ardica Technologies and focused on increasing the efficiency and reducing the costs of the manufacturing unit operations including the following key steps: (1) electrochemical alane etherate production, (2) crystallization of the alane etherate to  $\alpha$ -alane, and (3) stabilization of the  $\alpha$ -alane. This research is paving a path forward for the large scale continuous production of lower cost  $\alpha$ -alane for portable power and transportation applications.

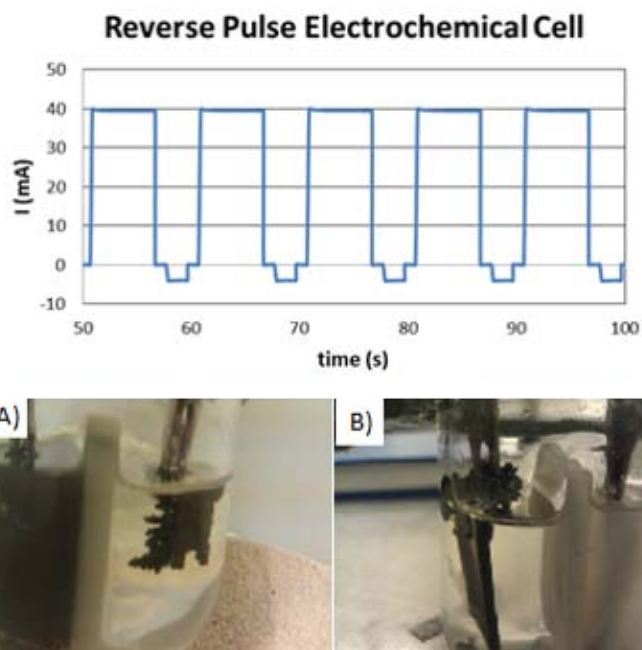
## APPROACH

The electrochemical generation of  $\alpha$ -alane has been shown [3,4] to be capable of generating high purity material using methods that can be developed into a fueling cycle for hydrogen vehicles, portable power systems, or other applications. This research has demonstrated methods to enhance the practicality of utilizing the electrochemical method for the large scale production of alane etherate as well as the crystallization of the etherate to stable crystals of  $\alpha$ -alane. By reinvestigating the Dow method for alane crystallization, conditions required to produce large crystals of pure  $\alpha$ -alane have been determined. The understanding of this process has provided direction to a path utilizing cheaper and less hazardous crystallizing solvents under reasonable conditions. Improvements to the electrochemical cell voltages patterns have also resulted in a method to nearly eliminate the dendrite formation that limits the time for which an electrochemical process can run continuously without interruptions.

## RESULTS

The electrochemical generation of alane etherate has been improved by utilization of a reverse pulse technique where the voltage is briefly reversed to reduce  $\text{Li}_3\text{AlH}_6$  (dendrite material) back into  $\text{LiAlH}_4$  (electrolyte). While this method reduces the overall amount of time that alane is being produced, the production rates can still be increased due to the ability to have the electrodes in closer proximity without shorting the electrochemical cell. The reserve pulsing timing sequence demonstrating the best results for this particular electrochemical cell and the electrodes are shown in Figure 1. In the figure, dendrites formation, which is a consequence of evaporating solvent, can be observed at the top of the electrode (anode). The dendrites cannot be converted back to  $\text{LiAlH}_4$  unless they are submerged in the solvent. This effect can easily be accounted for by insulating the electrode at the surface of the electrolyte solution.

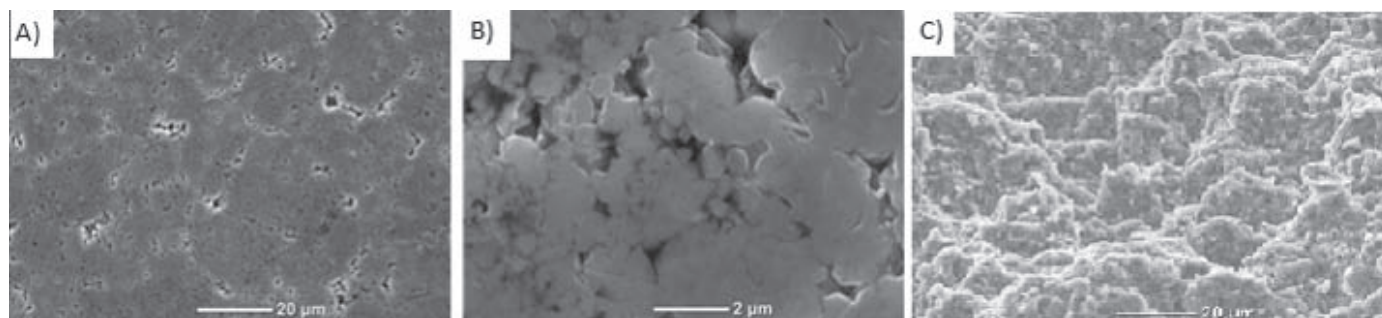
The use of spent alane in electrode production was also investigated. It was found that spent alane pellets pressed at 4 tons could be used as electrodes, but did not perform as well as commercial aluminum electrodes. Scanning electrode microscopy (SEM) images revealed that this was controlled by the contact resistance between the particles within the



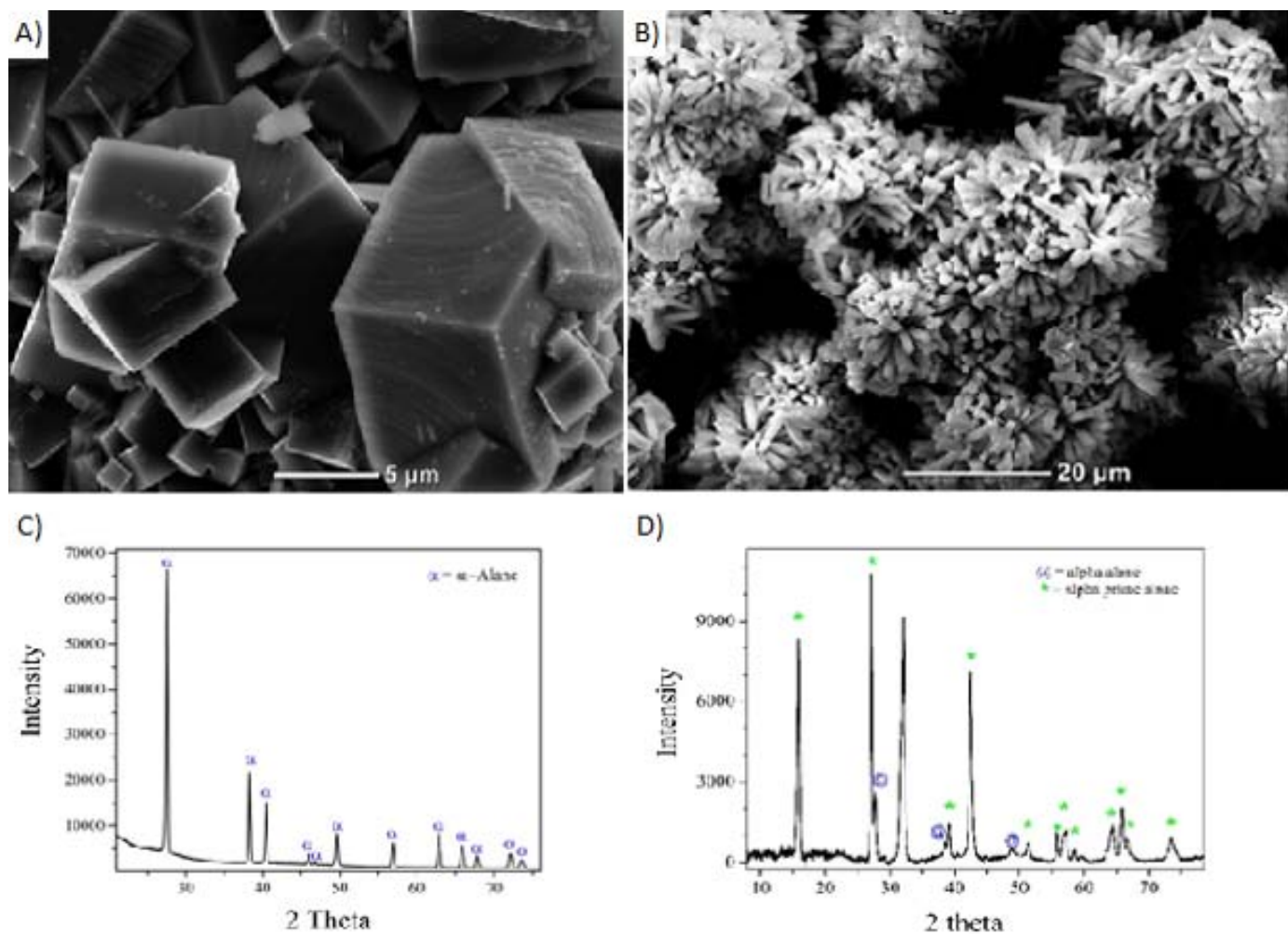
**FIGURE 1.** Plot of the current vs. time for the reverse pulsing technique used for dendrite formation reduction: (A) anode without reverse pulsing technique and (B) anode with reverse pulsing technique

pressed pellets. This hypothesis was evidenced by charging observed in cracks and certain regions of the pellets as shown in Figure 2. Furthermore, the spent alane pellets were brittle compared to the malleable commercial aluminum electrodes. SEM images of the inside of a spent alane pellet displayed an array of particles sandwiched together that cause the higher electrical resistance observed and the brittle nature of the pellets. Our observations conclude that spent alane pellets may be used as electrode, but optimal electrode design would require pressing pellets and much higher pressures or melting the spent alane to produce aluminum electrodes.

In order to produce stable, high-capacity  $\alpha$ -alane, crystallization techniques based on the Dow method were explored. The most significant parameters for crystallization were determined to be solvent removal rate, temperature, and time. These parameters must be meticulously controlled to achieve pure  $\alpha$ -alane with particle sizes above 4  $\mu\text{m}$ . Of those factors the ether removal rate was determined to be the most influential for  $\alpha$ -alane phase formation. Figure 3 displays the X-ray diffraction (XRD) patterns and SEM images for two crystallizations that were carried out under the same conditions with the exception of ether removal rate. Figures 3B and 3D show that alpha prime is primarily formed when the rate of ether removal is very slow. Figures 3A and 3C show that pure  $\alpha$ -alane can be formed when the rate of ether removal is higher; however, the optimum rate of ether removal is highly dependent on thermal control and crystallizer vessel design and is currently a point of emphasis for our studies. Thermogravimetric analysis/



**FIGURE 2.** (A) SEM image of the surface of a spent alane pellet pressed at 4 tons, (B) increased magnification of the same spent alane pellet, and (C) SEM image of the inside of a broken spent alane pellet



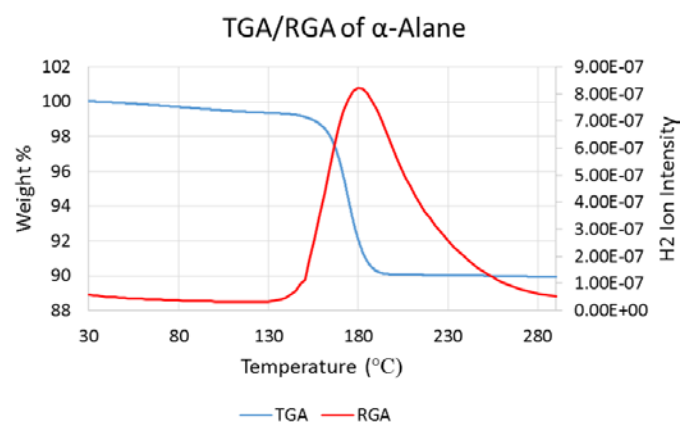
**FIGURE 3.** (A) SEM image of alpha-alane crystals, (B) SEM image of alpha prime crystals, (C) XRD pattern of pure alpha alane, and (D) XRD pattern of alpha prime alane with trace alpha alane

residual gas analysis (TGA/RGA) results (Figure 4) from the pure  $\alpha$ -alane show that this material contains  $>9$  wt%  $H_2$ . Also, XRD results confirm the absence of any aluminum in the final product. Altogether, this work provides important information required for the production of stable  $\alpha$ -alane.

## CONCLUSIONS AND FUTURE DIRECTIONS

The following conclusions were drawn:

- Further work on the crystallization is required to make large-scale, continuous production practical.



**FIGURE 4.** TGA/RGA of  $\alpha$ -alane displaying >9 wt% H<sub>2</sub>

- Increasing the current of the electrochemical cell is one of the last critical issues related to alane adduction production.

Future work includes the following:

- Investigate additives and other solvents that may increase the conductivity of the electrochemical cell for increasing alane adduct production rates.
- Develop recycling techniques for the crystallization process including the use of removed ether for the final product wash and the recovery of toluene, LiBH<sub>4</sub>, and LiAlH<sub>4</sub> for subsequent crystallizations.
- Investigate alternative crystallization pathways that may be suitable for the crystallization of other adducts of alane.
- Develop ambient pressure toluene crystallization technique to reduce the overall cost of alane crystallization.

## SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

- Ragaiy Zidan, Douglas A. Knight, Long V. Dinh; Novel Methods for Synthesizing Alane without the Formation of Adducts and Free of Halides US20120141363 February 2013.
- Ragaiy Zidan; Electrochemical Process and Production of Novel Complex Hydrides US8,470,156B2 June 2013.

## FY 2015 PUBLICATIONS/PRESENTATIONS

- Patrick Ward, Joseph Teprovich, Scott Greenway, Ragaiy Zidan. Current Progress in the Low-cost Production of Alane. Gordon Research Conference Metal-Hydrogen Systems. July 2015.
- Ragaiy Zidan (PI), Joseph Teprovich, Patrick Ward, Ted Motyka, Scott McWhorter, Scott Greenway, Héctor R. Colón-Mercado. Tech to Market Presentation 2015.
- Ragaiy Zidan. Reversible Formation of Alane. Department of Energy Annual Merit Review 2015.

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- Graetz, J. and J.J. Reilly, J. Phys. Chem. B, 2005. **109**(47): p. 22181–22185.
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