

## IV.A.6 Electrochemical Reversible Formation of Alane

Ragaiy Zidan<sup>1</sup> (Primary Contact),  
Douglas A. Knight<sup>1</sup>, Scott Greenway<sup>2</sup>

<sup>1</sup>Savannah River National Laboratory  
999-2W Room 121  
Savannah River Site  
Aiken, SC 29808  
Phone: (803) 646-8876  
Email: ragaiy.zidan@srnl.doe.gov

<sup>2</sup>Greenway Energy

DOE Manager  
HQ: Ned Stetson  
Phone: (202) 586-9995  
Email: Ned.Stetson@ee.doe.gov

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TABLE 1. Alane Compared with 2015 Target

Storage Parameter	2015 Target	AlH <sub>3</sub>
Gravimetric Capacity	0.055 kg H <sub>2</sub> /kg System	0.1 kg H <sub>2</sub> /kg AlH <sub>3</sub>
Volumetric Capacity	0.04 kg H <sub>2</sub> /L System	0.149 kg H <sub>2</sub> /L AlH <sub>3</sub>

### FY 2012 Accomplishments

- Demonstrated the use of a hydrogen-pressurized electrochemical cell, producing alane at a higher rate and minimal amount of dendrites.
- Demonstrated the use of spent aluminum to produce alane and regenerate the starting material (LiAlH<sub>4</sub>-based electrolyte).
- Used saturated solutions to have solid aluminum adducts to precipitate, allowing efficient separation.
- Produced several of gram quantities of high purity alane at an improved energy efficiency.



### Fiscal Year (FY) 2012 Objectives

- Identify means for achieving energy efficiency improvements of over 50%.
- Perform electrochemical production of alane and alane adducts in a pressurized electrochemical cell and demonstrate production of  $\alpha$ -alane.
- Demonstrate the formation of alane and the regeneration of the starting materials, using spent aluminum and identify electro-catalytic additive.
- Produce larger quantities of alane (several grams).

### Technical Barriers

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

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (R) Regeneration Processes Scale Up

### Technical Targets

In this project studies are being conducted to lower cost and improve efficiency of the electrochemical method to form AlH<sub>3</sub>. This material has the potential to meet the 2015 technical target for on-board hydrogen storage as shown in Table 1.

### Introduction

The DOE is supporting research to demonstrate viable materials for onboard 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°C to 175°C (depending on particle size and the addition of catalysts) has the potential to meet the 2010 and 2015 DOE targets [1,2].

The main drawback for using alane as a hydrogen storage material is unfavorable thermodynamics towards hydrogenation. Past attempts to regenerate alane under mild conditions were reported, including attempts based on electrochemical methods [3,4]. However, recent results on the regeneration of alane reported by Zidan and others [5] 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 AlH<sub>3</sub> and the chemical reaction route of AlH<sub>3</sub> that leads to the formation of alkali halide salts, such as LiCl or NaCl, which become a thermodynamic sink because of their stability. During FY 2012, the electrochemical synthesis of alane described in Zidan and others [5] has been improved using a higher efficiency set up while increasing the alane production rate. Improvements are achieved by the use of LiAlH<sub>4</sub> etherates (e.g. Et<sub>2</sub>O and DME) and a hydrogen-pressurized

electrochemical cell. In the hydrogen-pressurized cell, electrochemical alane was formed at higher rate than in the ambient cell. Aluminum from dehydrogenated aluminum hydride (spent aluminum) was used to form alane as well as regenerate the starting electrolyte.

## Approach

Experimentally, the electrolysis was carried out as described in the electronic supplementary information of Zidan and others [3]. However,  $\text{LiAlH}_4$  was used instead of  $\text{NaAlH}_4$ . Both, tetrahydrofuran (THF) and diethyl ether ( $\text{Et}_2\text{O}$ ) were used as aprotic solvents for the alane regeneration. Research on the electrochemical properties of  $\text{MAlH}_4$  ( $\text{M} = \text{Na}, \text{Li}$ ) in THF and  $\text{Et}_2\text{O}$  has been reported [7,8] but these studies were not directed at the regeneration and characterization of alane. Also, the work of Senoh and others [7,8] was performed with Ni electrodes different to this work in which Al is used as working electrode. Our group work is aimed at advanced studies involve the use of a modified Parr reactor designed to perform the electrolysis under a moderate pressure of hydrogen in order to observe how this might affect both the production rate of alane and the formation of any byproducts such as  $\text{Li}_3\text{AlH}_6$  and aluminum dendrites that tend to foul the electrochemical cell. Similarly, further studies involve improved separation of alane from the alane-THF adduct and other alane-etherates adducts as well as an investigation of using spent aluminum to produce alane and regenerate the starting material to close the alane production cycle.

## Results

As mentioned above, a modified Parr reactor was used for electrochemical reactions under pressurized hydrogen. The Parr reactor used is shown in Figure 1. The factory sealed electrodes featured in this design along with the



**FIGURE 1.** The modified Parr reactor as a pressurized electrochemical cell shown as it looks in operation. With factory-sealed electrodes and Swagelok fittings, this reactor is rated to 2,500 psig operating pressure.

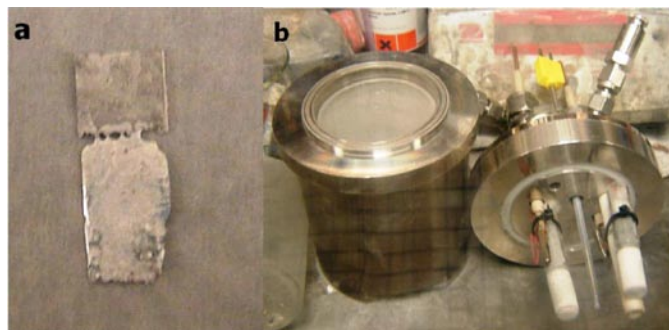
various selected Swagelok fittings allow for an operating pressure of up to 2,500 PSIG; well beyond our proposed pressures of 500-1,000 psig when used with hydrogen and only 70 psig when being used with the dimethyl ether solvent system.

A promising observation with the hydrogen-pressurized reactions was realized when aluminum anode in a cell at 500 psig hydrogen with a 1.5 V potential would be rapidly consumed. The Al electrode degradation after a 12 hour run is shown in Figure 2a. The majority of the electrode deterioration occurs at the surface of the solvent as is interfaces with the pressurized hydrogen. This should make it possible to design a cell that will accommodate electrodes that are made of spent alane (aluminum metal) and recycle this into the reaction. An early version of this electrode is pictured in Figure 2b, showing each electrode as a hollow glass frit that holds the aluminum powder and allows for the reaction solution to flow through.

The cathode also is fabricated from another fritted electrode. This time, the electrode is filled with catalyzed aluminum powder. With this type of set up, the catalyzed aluminum ( $\text{Al}^*$ ) is expected to react with the LiH byproduct (formed during the electrolysis of  $\text{LiAlH}_4$  and while under pressurized hydrogen) and reform  $\text{LiAlH}_4$  as per the reaction:  $\text{LiH} + \text{Al}^* + \text{H}_2 \rightarrow \text{LiAlH}_4$

This type of reaction has been recently reported as a process for regeneration of  $\text{LiAlH}_4$  [9].

We have shown this will fit with our proposed electrochemical cell using the spent alane. In our study, alane containing a catalytic amount (~0.2 mole %) of Ti-catalyst was thermally decomposed to remove all hydrogen, leaving the activated catalyzed aluminum. This activated catalyzed aluminum was then transferred into a Parr reactor containing LiH in THF. After 12 hours of stirring the spectrum of the Fourier transform infrared analysis of the solution had shown

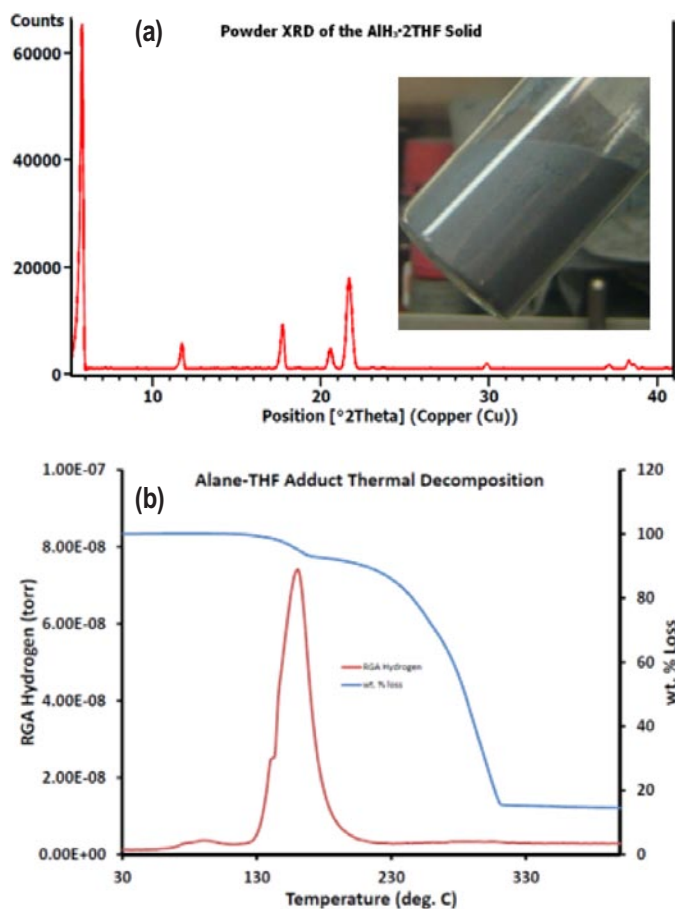


**FIGURE 2.** a) The aluminum anode from a hydrogen-pressurized cell showing the decomposition that occurs near the solvent/hydrogen interface. b) First generation of proposed fritted electrodes to house spent alane (aluminum powder) in the anode and activated spent alane (aluminum powder with Ti-catalyst) to recycle the alane as it is used in hydrogen delivery.

the appearance of an Al-H stretch at  $1,650\text{ cm}^{-1}$ , indicative of the presence of  $\text{LiAlH}_4$ .

Based on our initial results of this cycling reaction in the electrochemical cell more experimental work and cell design needs to be conducted to achieve a more efficient cycle. The initial porous frit electrode proved to be too small to be useful in this operation. None-the-less, this design was only the first of a new line of modified porous electrodes with the most recent and much larger porous electrodes ready now for future experiments.

The study on the economical isolation of the alane from the THF continues. Latest results show that the alane-THF adduct can be crystallized out of a toluene solution containing the electrolytic solution. It was found that the solid material  $\text{AlH}_3\cdot 2\text{THF}$  appears quite readily after this solution is heated to  $\sim 70^\circ\text{C}$ . The resulting solid, shown in Figure 3a, was found to be considerably stable, being insoluble in several solvents; including THF. This material demonstrates an easy route to isolate the solid alane material and is



**FIGURE 3.** a) A sample of the crystallized alane/THF adduct and the powder pattern indicative of alane-2THF adduct; still with the typical alane-grey appearance. This material shows added stability as it remains insoluble in several solvents, including THF. b) The TGA of this alane/THF adduct showing a combination release of hydrogen and THF.

currently being investigated as an intermediate to the alpha alane recovery. The thermal decomposition of this material (Figure 3b) shows an apparent release of hydrogen prior to the THF loss. Calculations of the recorded weight loss and residual gas analysis (RGA) indicate, however, that the THF release onset coincides with the release of hydrogen.

In a related study, electrochemical cells were run that contained saturated lithium aluminum hydride (LAH,  $\text{LiAlH}_4$ ) in THF. This concentrated LAH/THF electrolyte was obtained by gently heating and stirring a mixture of excess LAH in THF using a Parr pressure reactor set at  $75^\circ\text{C}$ . After filtering out the undissolved LAH, the resulting solution was somewhat viscous but relatively clear. The cell, shown in Figure 4a is fitted with an aluminum anode and a palladium cathode. The maximum current flow was the highest ever recorded for these types of reactions at some 200 mA, peaking at four hours into the experiment. After only around seven hours of applied current, the anode area in



**FIGURE 4.** a) Showing a glass frit-divided electrochemical cell with an aluminum anode and palladium cathode in place. b) The saturated LAH-THF solution forces the alane-THF adduct to precipitate at the anode as a grey-white solid.



the electrochemical cell, shown in Figure 4b, was filled with a grey solid. Analysis of this solid revealed it was composed mainly of alane-2THF. As suspected, the saturated solution forced the alane adduct to solidify as it was formed in the solution. The solution also contained a considerable amount of alane as the dissolved THF adducted material. The same saturated solution using etherates will be conducted in the future. While the aluminum anode remained unchanged (in the absence of pressurized hydrogen) the palladium cathode lacked any dendrite formation and, instead, was covered with a fine black coating of activated aluminum. Both of these results combined have shown great results in the advancement of the electrochemical generation of alane.

## Conclusions and Future Directions

- Perform electrochemical production of alane and alane adducts based on etherates in a pressurized solvent environment and demonstrate production of  $\alpha$ -alane.
- Investigate the recycling of LiH into LAH in situ during electrochemical production of alane.
- Work with industrial partners to lower the cost of alane production for use as high energy density storage materials in near term portable power systems.
- Continued production of gram quantities of alane with improving energy efficiency.

## Patents Issued

1. Two Steps Hydrogen System Based on Dehydrogenating and Hydrolysis Enhanced by Novel Additives to Alane and Activated Al, *Pending*.
2. Novel Method for Synthesizing Alane without the Formation of Adducts and Free of Halides, *Pending*.
3. Enhancing Electrochemical Methods for Producing and Regenerating Alane by Using Electrochemical Catalytic Additive, *Pending*.

## FY 2012 Publications [PU]/Presentations [PR]

1. Michael J. Martínez-Rodríguez, Brenda L. García-Díaz, Joseph A. Teprovich Jr., Douglas A. Knight, Ragaïy Zidan, "Advances in the Electrochemical Regeneration of Aluminum Hydride" *Applied Physics A*, 2011 Vol106, Issue 3, pp.545-550 [PU].
2. Long V. Dinh, Douglas A. Knight, Mark Paskevicius, Craig E. Buckley and Ragaïy Zidan "Novel methods for synthesizing halide-free alane without the formation of adducts" *Applied Physics A*, 2012 Vol. 107, No. 1, 173-181 [PU].

3. Joseph A. Teprovich Jr., Theodore Motyka, Ragaïy Zidan" Hydrogen system using novel additives to catalyze hydrogen release from the hydrolysis of alane and activated aluminum" *Int. J. of Hydrogen Energy* 2012 Vol. 3, Issue 2, 1594-1603 [PU].
4. "Advances in Materials and Methods for Hydrogen Storage" Gordon Research Conference July 17–22, 2011 Stonehill College Easton, MA Invited Speaker [PR].
5. "Progress in the Electrochemical Formation of Alane" MRS San Francisco, March 2011, Invited Speaker [PR].
6. "Development and Characterization of Novel Hydrogen Storage Materials" IEA January 16 2011 Fremantle, Copenhagen, Denmark, September 2011 [PR].

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8. H. Senoh, T. Kiyobayashi and N. Kuriyama, *Int. J. Hydrogen Energy*, 2008, 33, 3178-3181.
9. (a) Graetz, Jason; Wegrzyn, James; Reilly, James J.; *JACS* (2008), 130(52), 17790-17794. (b) Lacina, David; Yang, Liu; Chopra, Irinder; Muckerman, James; Chabal, Yves; Graetz, Jason; *Phys. Chem. Chem. Phys.*, (2012), 14(18), 6562-6569.