

## IV.A.1g Electrochemical Reversible Formation of Alane

Ragaiy Zidan (Primary Contact),  
Michael Martínez-Rodríguez, Joseph Teprovich  
Savannah River National Laboratory (SRNL)  
999-2W Room 121  
Savannah River Site  
Aiken, SC 29808  
Phone: (803) 646-8876  
E-mail: ragaiy.zidan@srnl.doe.gov

DOE Technology Development Manager:  
Ned Stetson  
Phone: (202) 586-9995  
E-mail: Ned.Stetson@ee.doe.gov

Project Start Date: October 1, 2006  
Project End Date: October 1, 2011

### Objectives

- Develop a low-cost rechargeable hydrogen storage material with cyclic stability and favorable thermodynamics and kinetics fulfilling the DOE onboard hydrogen transportation goals. Alane  $\text{AlH}_3$  was identified as material of potential to meet the DOE targets.
- Avoid the impractical high pressure needed to form  $\text{AlH}_3$ .
- Avoid the chemical reaction route of  $\text{AlH}_3$  that leads to the formation of alkali halide salts such as  $\text{LiCl}$  or  $\text{NaCl}$ .
- Utilize electrolytic potential to translate chemical potential into electrochemical potential and drive chemical reactions to form  $\text{AlH}_3$ .

### 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

### Technical Targets

In this project studies are being conducted to lower cost and improve efficiency of the electrochemical method to form  $\text{AlH}_3$ . This material has the potential to

meet the 2015 technical target for on-board hydrogen storage as shown in Table 1.

TABLE 1. Alane Compared With 2015 Target

Storage Parameter	2015 Target	$\text{AlH}_3$
Gravimetric Capacity	0.055 kg $\text{H}_2$ /kg System	0.1 kg $\text{H}_2$ /kg $\text{AlH}_3$
Volumetric Capacity	0.04 kg $\text{H}_2$ /L System	0.149 kg $\text{H}_2$ /L $\text{AlH}_3$

### Accomplishments

- Continued to produce gram quantities of alane with high purity.
- $\text{LiAlH}_4$  was also used to produce alane.
- The amount of dendrites was reduced by using  $\text{LiAlH}_4$ .
- Yield was increased and higher electrochemical cell efficiency was achieved.
- An electro-catalytic additive was discovered and found to greatly enhance the electrochemical process.
- Started improving efficiencies in every step of the regeneration method and achieved success.
- A pressurized electrochemical cell is being constructed for close material regeneration cycle and the use of more efficient separation.



### Introduction

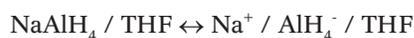
The DOE is supporting research to demonstrate viable materials for on-board hydrogen storage. Aluminum hydride (alane, or  $\text{AlH}_3$ ), having a gravimetric capacity of 10 wt% and volumetric capacity of 149 g  $\text{H}_2$ /L and a desorption temperature of  $\sim 60^\circ\text{C}$  to  $175^\circ\text{C}$  (depending on particle size and the addition of catalysts) has the potential to meet the 2010 and 2015 DOE targets.

In this report improvements to the electrochemical method to produce alane are discussed. Although many attempts in the past were made to make alane electrochemically [1-3] none of these attempts have isolated or characterized alane. These attempts were not directed at hydrogen storage. Our group is the first to demonstrate a reversible cycle utilizing electrochemistry and direct hydrogenation, where gram quantities of alane are produced, isolated and characterized [4]. Our regeneration method is based on a complete cycle that uses electrolysis and catalytic hydrogenation of spent aluminum  $\text{Al}(s)$ .

## Approach

Electrochemical methods have been developed at SRNL to produce alane [4]. These methods avoid the impractical high pressure needed to form  $\text{AlH}_3$  and the chemical reaction route of  $\text{AlH}_3$  that leads to the formation of alkali halide salts such as  $\text{LiCl}$ . The process utilizes an electrolytic potential to drive the chemical reaction to form  $\text{AlH}_3$ . However,  $\text{AlH}_3$  will be oxidized in an aqueous environment, forbidding the use of all protic solvents. For this reason, the use of a non-aqueous solvent system is required.

The electrolysis is carried out in an electrochemically stable, aprotic, and polar solvent such as tetrahydrofuran (THF) or ether.  $\text{MAlH}_4$  ( $\text{M} = \text{Li}, \text{Na}$ ) is dissolved in a polar solvent, forming an ionic solution. For example, sodium alanates dissolved in THF is used as an electrolyte.



Though not directed at the regeneration of alane, elaborate research and extensive studies on the electrochemical properties of this type of electrolyte have been reported [5-6].

In addition ways to improve the electrochemical methods were considered, leading to the addition of chemicals that accelerate alane production. At this moment this species is referred as the electrocatalytic additive (ECA). Electrochemical techniques such as electrolysis, cyclic voltammograms (CV), and electrochemical impedance spectroscopy (EIS) were used to evaluate the effect of the ECA.

## Results

Alane has continued to be produced in grams quantities, using the electrochemical method described in Zidan et al [4]. This method was improved by modifying the electrochemical cell setup and the electrochemical process. Increase in the alane production was obtained by increasing cell size, electrode size, minimizing resistance (by reducing electrode distance), and prolonging the electrolysis. Dendrites formation at the counter electrode has been reduced by the use of  $\text{LiAlH}_4$  instead of  $\text{NaAlH}_4$ . Both solutions of  $\text{NaAlH}_4$  in THF and  $\text{LiAlH}_4$  in THF contain triple ions complexation. However, solutions of  $\text{NaAlH}_4$  in THF produce more tightly solvated ions ( $\text{Na}^+$  and  $\text{AlH}_4^-$ ) than solvent separated ion pairs ( $\text{Na}^+[\text{AlH}_4^-]$ ) whereas solutions of  $\text{LiAlH}_4$  in THF contains more solvent separated ion pairs ( $\text{Li}^+[\text{AlH}_4^-]$ ) than solvated ions ( $\text{Li}^+$  and  $\text{AlH}_4^-$ ) [6-7]. Consequently, there are less free ions in the solution of  $\text{LiAlH}_4$  than in the solution of  $\text{NaAlH}_4$  which can lead to less formation of  $\text{Li}_3\text{AlH}_6$  and Al (dendrites). A new modified system is being developed to further reduce the dendrites formation. This system consists of a pressurized electrochemical cell

in which a higher  $\text{H}_2$  pressure is used to increase the  $\text{H}_2$  in the solution in order to displace the reaction of Li to  $\text{LiH}$  avoiding in this way the reaction to form  $\text{Li}_3\text{AlH}_6$ . In addition, the electrochemical method was improved by the use of an ECA.

To test the effect of the ECA two cells were prepared using  $\text{LiAlH}_4$  and triethylenediamine (TEDA) in THF and including the ECA in one of the cells. TEDA was incorporated in the solution to visually detect the formation of alane as  $\text{AlH}_3$ -TEDA (white precipitate) during the experimental test.  $\text{AlH}_3$ -TEDA was easily separated by filtering and weighted. Figure 1 shows the initial state of each cell and after 10 min of electrolysis. This figure clearly shows that cell 2 (cell with ECA) contains a larger amount of  $\text{AlH}_3$ -TEDA. Also, it should be notice that a minimal amount or no dendrites were produced in the counter electrode in either cell.

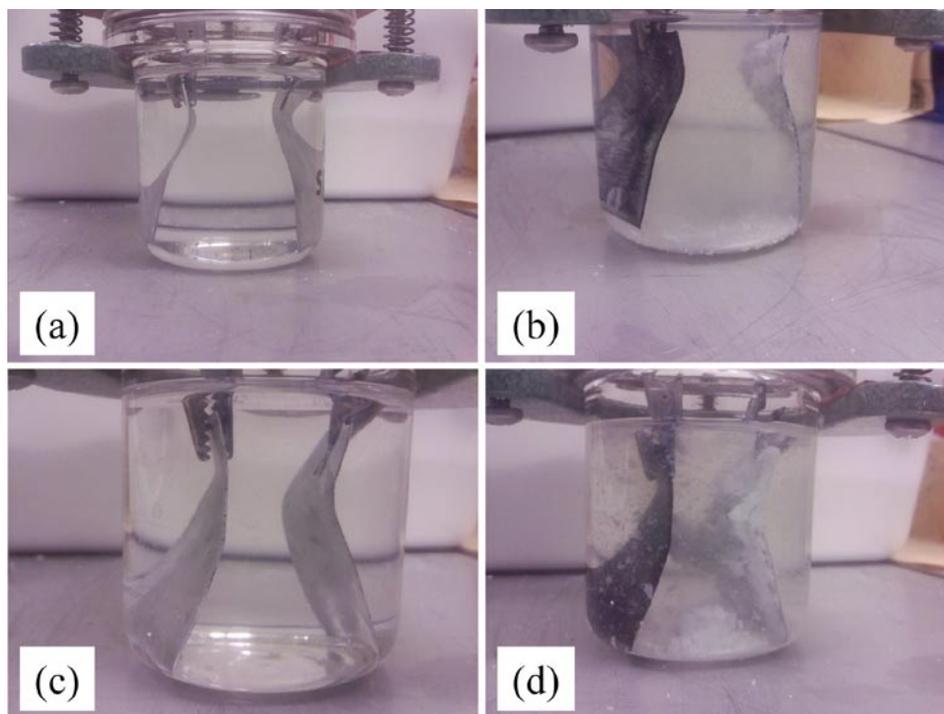
Figure 2 shows 10 min of bulk electrolysis at 2.1 V for alane production using the two comparative cells described above. The high potential used during the electrolysis was required to produce enough alane in those 10 min for visualization purpose and eventually yield comparison. This figure shows an increase of 80% in the current when the ECA was used. The total charge for cell 2 was twice the total charge obtained with cell 1. The amount of yield of  $\text{AlH}_3$ -TEDA was doubled when the ECA was used on cell 2. CVs for both cells are presented in Figure 3. It should be noted that the open circuit voltage (OCV) for cell 2 is shifted to -1.5 V from the original cell #1 ( $\text{OCV} = -1.9$ ). This means that the overpotential required for cell 2 is less when performing the electrolysis at 2.1 V. Consequently, lower energy is required for cell 2 to produce  $\text{AlH}_3$ -TEDA, which implies that cell 2 is more efficient because it has more current with less energy input.

EIS was performed on the cells with and without the ECA. Figure 4 shows that real part of the impedance, which represents the resistance of the cells, is about  $112 \text{ Wcm}^2$  for both cells. This shows that the ECA does not have a significant effect in the resistance (or conductivity) of the solution. That is, the ECA is not acting as an electrolyte. Consequently, the increase in current and efficiency discussed above are an electrocatalytic effect of the added species.

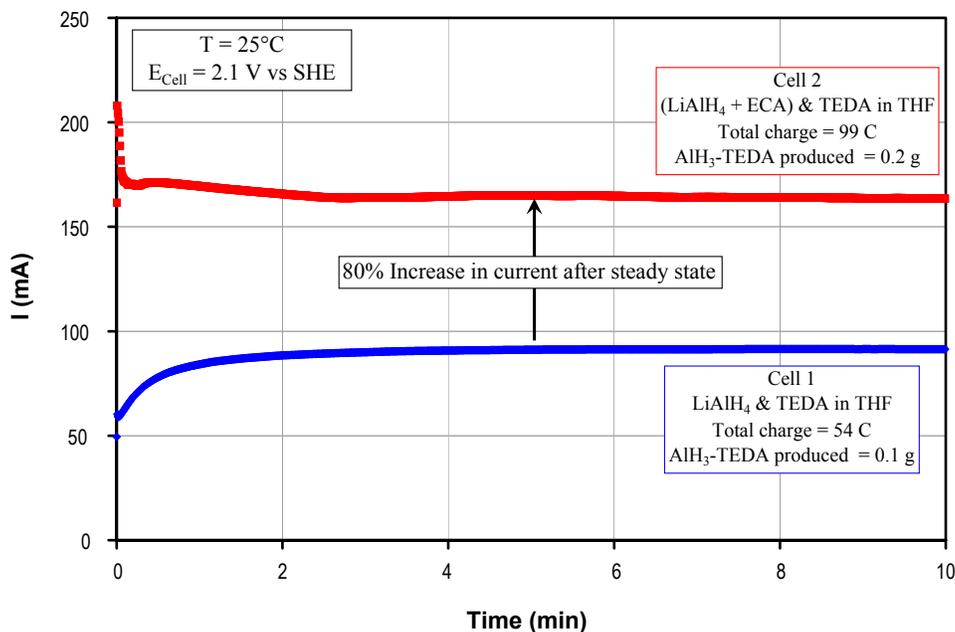
In additions to the improvements described above methods have been developed to extract alane from THF. These methods involve the heating and vacuum distillation of THF adducted alane solutions with subsequent crystallization of alane in toluene or other non coordinating solvents.

## Conclusions and Future Directions

- The electrochemical cell setup was modified and larger quantities (grams) of alane were produced.



**FIGURE 1.** Two electrochemical cells showing the formation of  $\text{AlH}_3\text{-TEDA}$ . Cell 1 without the ECA (a) before and (b) after 10 min of electrolysis; and cell 2 with the ECA (c) before and (d) after the 10 min of electrolysis.



**FIGURE 2.** Comparison of the bulk electrolysis for the production of  $\text{AlH}_3\text{-TEDA}$  using two electrochemical cells: with and without the ECA.

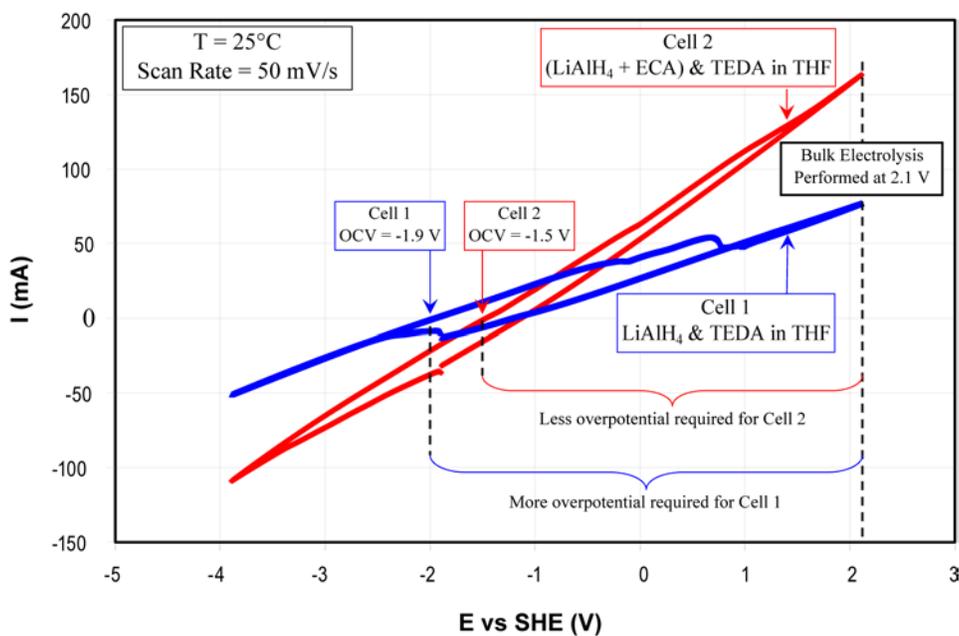


FIGURE 3. Comparison of the CV performed on the two electrochemical cells: with and without the ECA.

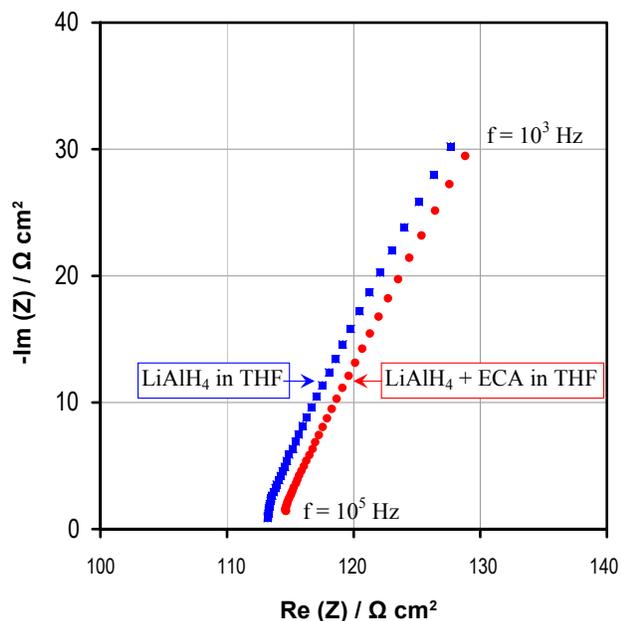


FIGURE 4. Comparison of the EIS performed on the two electrochemical cells: with and without the ECA.

- The use of  $\text{LiAlH}_4$  helped to reduce the dendrites formation.
- An electro-catalytic additive was discovered and found to greatly enhance the electrochemical process by increasing the cell efficiency and the alane production.
- Ongoing work and future direction include:

- Use of a pressurized electrochemical cell to further reduce the dendrites formation.
- Examine catalysts in accelerating formation and regeneration.
- Use other techniques (e.g. nuclear magnetic resonance, prompt gamma activation analysis and Raman) to quantify and characterize  $\text{AlH}_3$ .
- Design and construct a larger electrochemical cell capable of producing larger quantities of  $\text{AlH}_3$ .
- Develop closed and efficient  $\text{AlH}_3$  extracting system based on new solvents.
- Optimize all parameters needed for producing several grams of  $\text{AlH}_3$  efficiently.
- Explore, reversibly, forming other high capacity complex hydrides such as Mg and Ca-based complex hydrides using electrochemical methods.

### Special Recognitions & Awards/Patents Issued

1. 2010 DOE Hydrogen Program Team Award in Storage. This award recognizes Dr. Ragaiy Zidan and his team at SRNL for their outstanding contribution to the development of electrochemical methods to regenerate alane.

### FY 2010 Publications/Presentations

1. R. Zidan, *Aluminum Hydride (Alane)*, in M. Hirscher (Ed.), *Handbook of Hydrogen Storage: New Materials for*

*Future Energy Storage*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, DE, pp. 249-278 (2010).

2. R. Zidan, Invited Speaker, “Developing Novel Materials and Methods for Hydrogen Storage” International Symposium on Metal-Hydrogen Systems Moscow, Russia July 19–24, 2010.
3. R. Zidan, Invited Speaker-Chair and Advisor Board Member, “Electrochemical Formation and Reversibility of Aluminum Hydride” CIMTEC2010-, Montecatini Term, Italy, June 2010.
4. R. Zidan, B. L. García-Díaz, M. J. Martínez-Rodríguez, J. Teprovich, “Electrochemical Reversible Formation of Alane” 2010 DOE Annual Merit Review, Washington, D.C., June 2010.
5. R. Zidan, “Electrochemical Reversible Formation of Alane” International Energy Agency Meeting, Death Valley, CA, April 2010.
6. R. Zidan, Invited Speaker-Chair and Committee Advisor, “Electrochemical Generation and Reversibility of Alane” Material Challenges in Alternative & Renewable Energy, American Ceramic Society, Cocoa Beach, FL, February 2010.

## References

1. S. Adhikari, J.J. Lee and K.R. Hebert, *J. Electrochem. Soc.*, 2008, **155**, C16–C21.
2. N.M. Alpatova, T.N. Dymova, Y.M. Kessler and O.R. Osipov, *Russ. Chem. Rev.*, 1968, **37**, 99–114.
3. H. Clasen, *Ger. Pat.*, 1141 623, 1962.
4. R. Zidan, B.L. Garcia-Diaz, C.S. Fewox, A.C. Stowe, J.R. Gray and A.G. Harter, *Chem. Commun.*, 2009, 3717–3719.
5. H. Senoh, T. Kiyobayashi, N. Kuriyama, K. Tatsumi and K. Yasuda, *J. Power Sources*, 2007, **164**, 94–99.
6. H. Senoh, T. Kiyobayashi and N. Kuriyama, *Int. J. Hydrogen Energy*, 2008, **33**, 3178–3181.
7. E.C. Ashby, F.R. Dobbs, and H.P. Hopkins, Jr., *J. Am. Chem Soc.*, 1973, **95**, 2823–2829.