

## IV.A.7 Electrochemical Reversible Formation of Alane

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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 2011 Accomplishments

- Developed a pressurized dimethyl ether (DME)-based synthesis for alane that eliminates need for vacuum drying of alane and yield  $\alpha$ -alane crystallites.
- Demonstrated electrochemically active compounds and used electrochemical impedance spectroscopy (EIS) to show that kinetic improvements were due to more than increased ionic conductivity.
- Continued production of gram quantities of alane with improving energy efficiency.



### Introduction

The 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°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 draw back 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 et al. [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 2011, the electrochemical synthesis of alane described in Zidan et al. [5] has been improved allowing higher cell efficiency while increasing the alane production rate. Improvements are achieved by the use of LiAlH<sub>4</sub> and the introduction of LiCl [6] which acts as an electro-catalytic additive (ECA) and greatly enhanced the electrochemical process. A pressurized solvent electrochemical method for alane production has also been developed and demonstrated that reduces the need for parasitic vacuum processing of the alane to remove solvents.

### Fiscal Year (FY) 2011 Objectives

- Identify energy efficiency improvements for the alane production process of over 50%.
- Characterize new electrochemical additives for alane production.
- Improve production process and properties of alane adducts.

### Technical Barriers

This project addresses the following technical barriers from the Technical Plan - 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

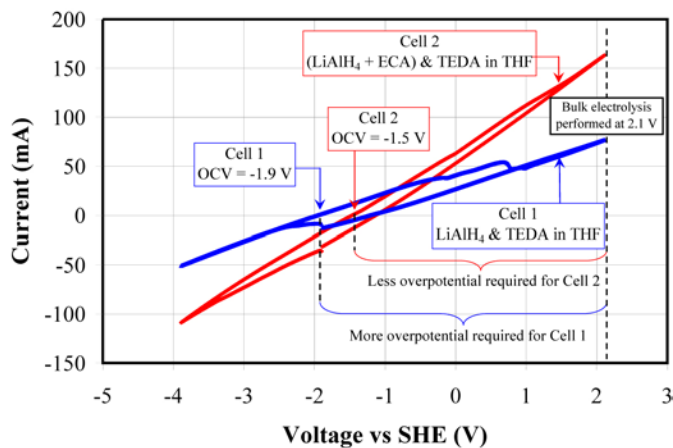
In this project studies are being conducted to lower cost and improve efficiency of the electrochemical method to form AlH<sub>3</sub>. This material has the potential to meet the 2015 technical target for on-board hydrogen storage as shown in Table 1.

## Approach

Experimentally, the electrolysis was carried out as described in the electronic supplementary information of Zidan et al [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 et al [7, 8] was performed with Ni electrodes different to this work in which Al is used as working electrode. The use of Al is essential to the alane regenerative process and the reaction with the ECA as discussed later.

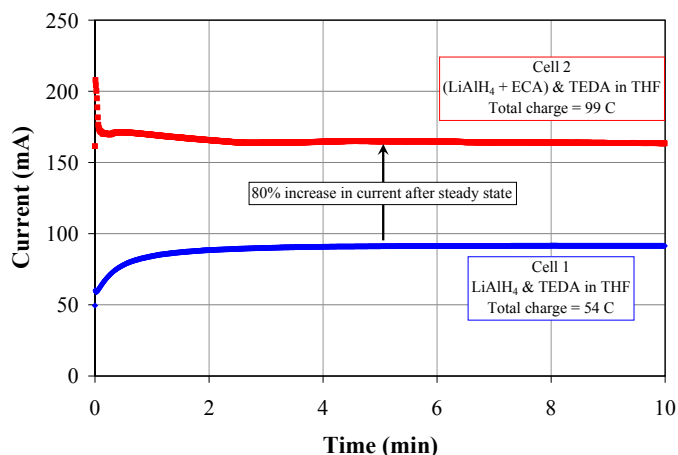
## Results

To test the effect of the LiCl two cells were prepared using  $\text{LiAlH}_4$  and triethylenediamine (TEDA) in THF and LiCl was added to one of the cells. TEDA was incorporated in the solution to easily detect and visualize the formation of alane as  $\text{AlH}_3\text{-TEDA}$  (white precipitate [3]) during the experimental test. Figure 1 shows 10 min of the bulk electrolysis at 2.1 V for the alane production using the two cells described above. The high potential used during the electrolysis was applied to produce enough alane in those 10 min for visualization purpose and comparison. Alane-TEDA is not expected to decompose during the conditions of these tests. Figure 2 shows an increase of 80% in the current when LiCl was used. The total charge for cell 2 was two times the total charge obtained with cell 1. Since the charge is proportional to the moles of product produced, the amount of  $\text{AlH}_3\text{-TEDA}$  was doubled when the ECA was used in cell 2. The precipitated alane-TEDA was separated from solution and weighted. Consistently, Cell 2 was found to produce twice as much  $\text{AlH}_3\text{-TEDA}$ .

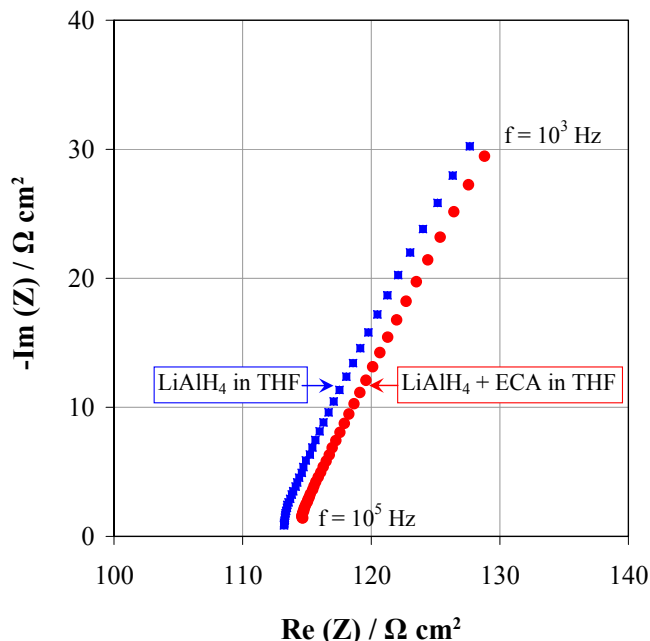


**FIGURE 1.** Cyclic voltammograms at 50 mV/s for the formation of  $\text{AlH}_3\text{-TEDA}$  using identical electrochemical cells with 1 M of  $\text{LiAlH}_4$  and TEDA in THF without LiCl (Cell 1) and with LiCl (Cell 2).

EIS was performed on the cells with and without the LiCl. Figure 3 shows that the high frequency value, which represents the resistance of the cells, is about 113 and 114  $\Omega\text{-cm}^2$  for the cells without and with LiCl, respectively. This shows that LiCl does not have a significant effect in the resistance (or conductivity) of the solution. That is, the LiCl is not acting as an electrolyte. Consequently, the increase in current and efficiency discussed above are an electro-catalytic effect of the added species.



**FIGURE 2.** Bulk Electrolysis for the Production of  $\text{AlH}_3\text{-TEDA}$  using two Identical Electrochemical Cells with 1 M of  $\text{LiAlH}_4$  in and THF without LiCl (Cell 1) and with LiCl (Cell 2)



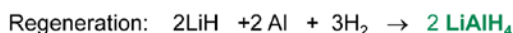
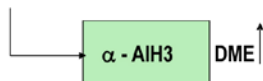
**FIGURE 3.** Nyquist Diagram for Identical Electrochemical Cells with 1 M of  $\text{LiAlH}_4$  and TEDA in THF without LiCl (Cell 1) and with LiCl (Cell 2)

## Minimizing the use vacuum pump

Anode:



Cathode:



**FIGURE 4.** Pressurized Solvent System to Improve Overall Energy Efficiency of Alane Production

Therefore, the electrochemical synthesis of alane has been improved by adding LiCl to a solution of  $\text{LiAlH}_4\text{-THF}$ . We have shown that LiCl function as an electro-catalytic additive in a cyclic process that increases the current. This process lead to a higher cell efficiency and higher amount of alane produced.

Analysis from the DOE Hydrogen Storage Team and has shown that the main energy losses in the production of alane will be the energy required to run the vacuum pump during product separation. Therefore, a pressurized solvent system (similar to work reported earlier by Shane et al. on  $\text{LiAlH}_4$  [9]) was developed to increase the energy efficiency of alane production and purification. Figure 4 outlines the concept for alane synthesis using a system with pressurized DME. The DME solvent is polar, aprotic and has good safety characteristics. Using this method, alane can be purified and crystallized just through the release of the DME solvent from the system. X-ray diffraction data from alane produce in DME shows a relatively pure crystalline alpha phase.

### Conclusions and Future Directions

- 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.
- Perform electrochemical production of alane and alane adducts in a pressurized solvent environment and demonstrate production of  $\alpha$ -alane using these methods.

### Patents Issued

1. Improving Electrochemical Methods for Producing and Regenerating Alane by the Addition of Halides to Electrolyte, Patent pending.

### FY 2011 Publications/Presentations

1. “Progress in the Electrochemical Formation of Alane” MRS San Francisco, March 2011, *Invited Speaker*.
2. Ragaizy Zidan “Electrochemical Reversible Formation of Alane” 2011 Annual Merit Review Washington, D.C., May 2011.
3. Ragaizy Zidan “Electrochemical Reversible Formation of Alane” Hydrogen storage tech team meeting March 17, 2011 USCAR, Southfield, Michigan.
4. Ragaizy Zidan “Development and Characterization of Novel Hydrogen Storage Materials” IEA HIA Task 22 Meeting – Fundamental and Applied Hydrogen Storage Material Development January 16, 2011 Fremantle, Australia.
5. Ragaizy Zidan “Advances in Electrochemical Formation of Alane” Pacificchem December 15, 2010 - Honolulu, Hawaii Invited Speaker.

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6. Improving Electrochemical Methods for Producing and Regenerating Alane by the Addition of Halides to Electrolyte, *Patent pending*.
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