

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

Ragaiy Zidan

Savannah River National Laboratory (SRNL)  
999-2W Room 121  
Savannah River Site  
Aiken, SC 29808  
Phone: (803) 646-8876; Fax: (803) 652-8137  
E-mail: ragaiy.zidan@srnl.doe.gov

DOE Technology Development Manager:  
Ned Stetson

Phone: (202) 586-9995; Fax: (202) 586-9811  
E-mail: Ned.Stetson@ee.doe.gov

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### Objectives

- Develop a low-cost rechargeable hydrogen storage material with cyclic stability and favorable thermodynamics and kinetics fulfilling the DOE onboard hydrogen transportation goals.
- Develop an economical method to regenerate aluminum hydride (alane -  $\text{AlH}_3$ ) from aluminum metal, since aluminum hydride has a gravimetric capacity of 10 wt% and volumetric capacity of 149 g/L  $\text{H}_2$  and desorption temperature:  $\sim 60^\circ\text{C}$  to  $175^\circ\text{C}$  (depending on particle size and the addition of catalysts) meeting the 2010 DOE targets.

### Technical Barriers

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

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

### Technical Targets

- Develop a low-cost rechargeable hydrogen storage material fulfilling the DOE transportation goals.
- $\text{AlH}_3$  is a viable system that fulfills the DOE 2010 transportation goals.
- Avoid the impractical high pressure needed to form  $\text{AlH}_3$ .

- Avoid chemical reaction route of  $\text{AlH}_3$  that leads to the formation of alkali halide salts such as  $\text{LiCl}$ .
- Utilize electrolytic potential to translate chemical potential into electrochemical potential and drive chemical reactions to form  $\text{AlH}_3$ .

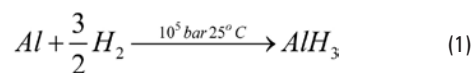
### Accomplishments

- Continued multiple electrochemical cells systematic study.
- Developed a methodology to confirm the generation of  $\text{AlH}_3$  in the cell.
- Succeeded in producing large quantities of  $\text{AlH}_3$ -triethylenediamine (TEDA) complex, electrochemically.
- Recovered alane from alane-tetrahydrofuran (THF) adduct.
- Developed ways to recover pure alane from solvent.
- Produced gram quantities of alane, electrochemically.
- Working on the efficiency aspects of the cycle.



### Introduction

Discovering efficient and economic methods for storing hydrogen is critical to advancing the hydrogen economy. The DOE is supporting research to demonstrate viable materials for on-board hydrogen storage. Researchers worldwide have identified a large number of compounds with high hydrogen capacity that can fulfill these gravimetric and volumetric requirements. Unfortunately, the majority of these compounds fail to meet the thermodynamic and kinetic needs for on-board storage systems. Alane has the gravimetric (10.1 mass%  $\text{H}_2$ ) and volumetric (149 kg  $\text{H}_2/\text{m}^3$ ) density. In addition, rapid hydrogen release from alane can be achieved using only the waste heat from a fuel cell or a hydrogen internal combustion engine [1]. The main drawback to using alane in hydrogen storage applications is unfavorable hydriding thermodynamics. The direct hydrogenation of aluminum to alane requires over  $10^5$  bars of hydrogen pressure at room temperature as shown in equation (1). The impracticality of using high hydriding pressure has precluded alane from being considered as a reversible hydrogen storage material.



The typical formation route of alane is through the chemical reaction of lithium alanate with aluminum chloride in diethyl ether. This reaction yields dissolved

alane etherate,  $\text{AlH}_3 \cdot \text{Et}_2\text{O}$ , and precipitates lithium chloride. Alane can be separated from the ether by heating *en vacuo* [2-5]. The synthesis of  $\text{AlH}_3$  by these methods result in the formation of alkali halide salts such as  $\text{LiCl}$ . The formation of these salts becomes a thermodynamic sink because of their stability. For a cyclic process, lithium metal must be recovered from lithium chloride by electrolysis of a  $\text{LiCl}/\text{KCl}$  melt at  $600^\circ\text{C}$  and costing at least  $-429 \text{ kJ/mol}$  of energy equivalent to the heat of formation and heat of fusion of  $\text{LiCl}$  [6].

## Approach

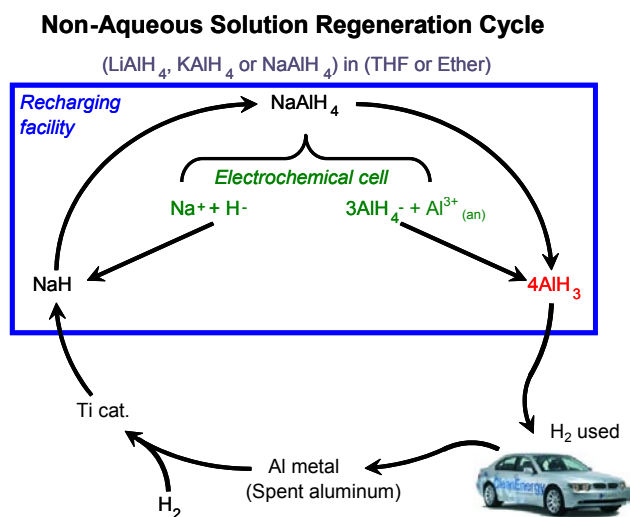
Our approach has pursued a more economically and thermodynamically cost-effective formation and regeneration route of alane than conventional chemical methods. Our process utilized electrolytic potential,  $E$ , to drive chemical reactions to form  $\text{AlH}_3$ . The equilibrium potential ( $E$ ) is determined from the Gibbs' free energy change ( $\Delta G$ ) using equation 2:

$$\Delta G = -nFE \quad (2)$$

Where  $n$  is number of electrons transferred and  $F$  is the Faraday constant of 96,485 coulombs.

However,  $\text{AlH}_3$  is extremely reactive in water and air, forbidding the use of all protic solvents. For this reason, a novel route using a non-aqueous solvent system is needed. Polar aprotic solvents such as THF or diethyl ether with dissolved ionic compounds such as  $\text{NaAlH}_4$  or  $\text{LiAlH}_4$  were used to form a conductive electrolyte that can be used in the electrochemical cell to form alane. For example,  $\text{NaAlH}_4$  is dissolved in this solvent, forming the ionic solution ( $\text{Na}^+/\text{AlH}_4^-/\text{THF}$ ) which is used as an electrolyte. The cycle, shown in Figure 1, utilizes electrochemical potential to drive the formation of alane and alkali hydride (e.g.  $\text{LiH}$ ,  $\text{NaH}$  and  $\text{KH}$ ) from an ionic alanate salt. The starting alanate is regenerated by direct hydrogenation of spent aluminum with the byproduct alkali hydride (e.g.  $\text{NaH}$ ) in the presence of titanium catalyst under moderate hydrogen pressure ( $\sim 100 \text{ bars}$ ), a well studied reaction [7-10].

Though not directed at the regeneration of alane, elaborate research and extensive studies on the electrochemical properties of this type of electrolyte has been reported [11,12]. Although attempts in the past were made to synthesize alane electrochemically, none have shown isolated material or a characterized alane product [13-15]. Thermodynamic properties of the above electrolyte, along with cyclic voltammetry were the basis for conducting this electrochemical process. Thermodynamic calculations were made to determine the reduction potentials for possible electrochemical reactions of  $\text{NaAlH}_4$  in an aprotic solution (THF) with an aluminum electrode. From the half reaction potentials, the cell voltage for alane formation was

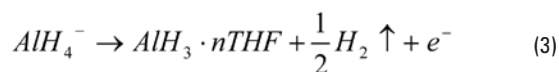


**FIGURE 1.** Reversible alane regeneration cycle. All components of the electrochemical process can be recycled to continually afford a viable solid state storage material for the hydrogen economy.

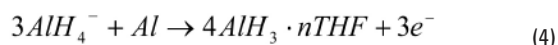
calculated and a theoretical cyclic voltammogram was constructed.

## Results

At least two separate reaction mechanisms can produce alane at the aluminium electrode. One possible mechanism is the oxidation of the  $\text{AlH}_4^-$  ion to produce alane, an electron, and hydrogen as shown in equation (3):



Another possible mechanism is the reaction of  $\text{AlH}_4^-$  with the aluminium anode to form alane. In this reaction route, the evolution of hydrogen is suppressed and the reaction is expected to consume the Al electrode as in equation (4):



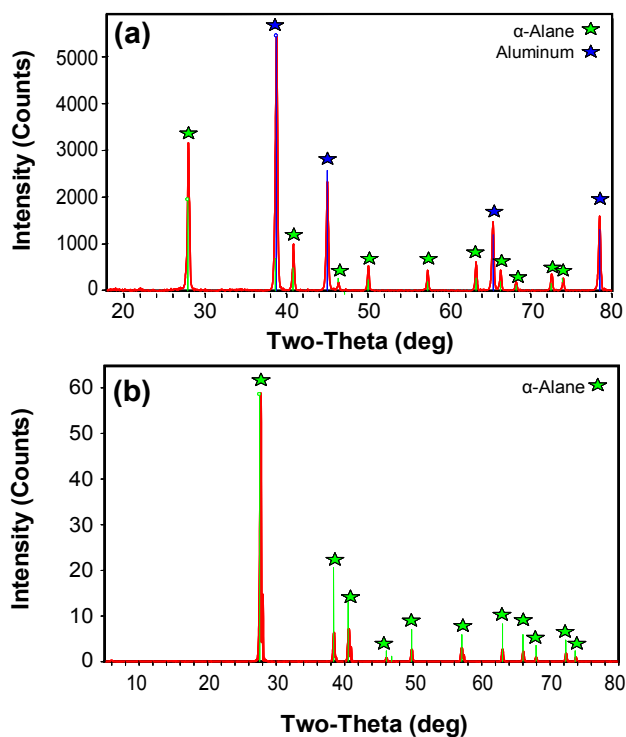
The different conditions of reactions 3 and 4 depend on their Gibbs free energy ( $\Delta G$ ).  $\Delta G$  for reactions (3) is  $-167.1 \text{ kJ/mol} \cdot \text{AlH}_3$  and for reactions (4) is  $-113.7 \text{ kJ/mol} \cdot \text{AlH}_3$ . Since  $\text{Na}^+$  is the counter ion of  $\text{AlH}_4^-$  the respective equilibrium potentials are  $-1.73$  for reaction (3) and  $-1.57 \text{ V}$  for reaction (4) vs. standard hydrogen electrode. Experimental observations confirmed that under the conditions of reaction 4, the anode is consumed.

During these experiments, the current was steady and increased slightly with time. The electrochemical production of alane is found not to be slowed by the formation of  $\text{AlH}_3$ . The surface area of the electrodes and the cell current are observed to be the rate limiting

factors. In contrast to previous reports, no visible signs of alane perception in solution were observed [15] and the alane produced by our method is completely dissolved in solution as a THF adduct. During electrolysis, dendritic material was deposited on the platinum counter electrode. This material was collected and determined to be  $\text{Na}_3\text{AlH}_6$  and Al from X-ray diffraction (XRD) data.

Experiments were conducted to determine the feasibility of plating sodium at the platinum cathode to complete the cycle. The platinum cathode and aluminium anode potentials were -2.89 V and -1.31 V, respectively. Plating of Na metal was observed at the cathode while alane was produced at the aluminium anode. In this case, no dendrites were observed at the platinum cathode as sodium was reduced. Furthermore, bubbling hydrogen at the platinum cathode can form NaH and increase the efficiency by eliminating dendrite formation and the need to reduce  $\text{Na}^+$  to sodium metal. With an over potential of  $\sim 0.3$  V the alane process costs 25% of the value of  $\text{H}_2$  stored in the alane. This value is less than that required in compression and liquefaction of  $\text{H}_2$  gas (30–35%). Alane recovered from the electrochemical cells was characterized by powder XRD, Raman spectroscopy, and thermal gravimetric analysis (TGA). The methods of chemical separation and results of characterization are discussed herein. The separation of alane from the etherate adduct is well established and affords the pure  $\text{AlH}_3$  compound. Separation of the  $\text{AlH}_3 \cdot \text{THF}$  adduct is however not as straight forward as that of the etherate and has proven more sensitive to decomposition if isolated in the same manner as the etherate. For this reason we have explored the use of other adducts in purifying the product obtained from the cell. The procedure involves precipitation of the unconsumed sodium alanate using a non-polar hydrocarbon followed by filtration and introduction of triethylamine (TEA). The adduct free alane is then recovered by heating the neat liquid  $\text{AlH}_3 \cdot \text{TEA}$  en vacuo.

XRD analysis was performed on a Bruker D8 system with Bragg-Brentano geometry, using Copper  $\text{K}\alpha 1$  radiation and a NaI scintillation detector. Source voltage and tube current were 45 kV and 40 mA, respectively. Scans were performed using a  $2\theta$  range of 5 to 80 degrees with a step size of 0.02° and a scan speed of 1.0 seconds per step. Patterns were indexed with the Fullprof Suite of programs utilizing TREOR and DICVOL methods. Space group determination was performed using the program Chekcell. Powder XRD patterns data for two different separation methods are shown in Figure 2. When alane is separated by simply heating the  $\text{AlH}_3 \cdot \text{THF}$  product after removing left over starting materials, the diffraction pattern shows the presence aluminum metal as well as  $\alpha$ -alane. Separation using the TEA method affords only the pure  $\alpha$ -alane phase as seen in the diffraction pattern; no aluminum is present. Indexing of this pattern was performed and

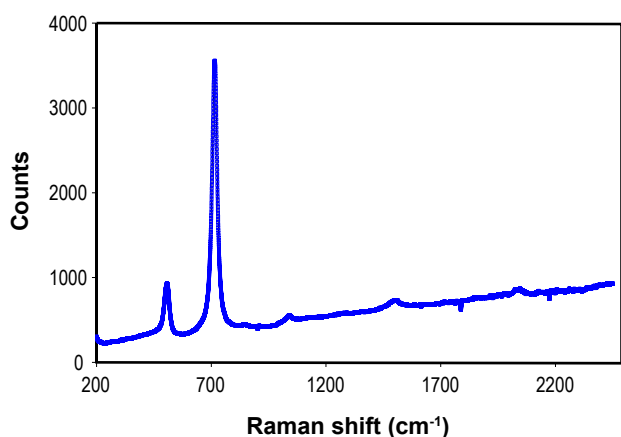


**FIGURE 2.** XRD patterns for products recovered from an electrochemical cell. (a) Alane separated from reaction mixture as the THF adducts. When heated under vacuum to remove THF, the solid partially decomposes, losing hydrogen and affording aluminium. (b) Alane is recovered using TEA.

the unrefined unit cell parameters were found to be  $a = 4.446 \text{ \AA}$  and  $c = 11.809 \text{ \AA}$ . Based on the systematic absences, the space group was assigned as R-3c which is consistent with  $\alpha$ -alane [16].

Raman spectra were obtained using a holographic spectrometer (HoloSpec, Kaiser Optical Systems) and charge-coupled device detector (DV420-BV-133, Andor, -55 C) with 532 nm excitation (Verdi, Coherent, Inc., 25 mW at sample). The wavelength response of the spectrometer was calibrated with a neon arc lamp; the intensity response was calibrated with a National Institute of Standards and Technology-traceable halogen lamp. Peak positions for a 50/50 acetonitrile/toluene mixture matched accepted values within  $\pm 1 \text{ cm}^{-1}$ . Spectra were obtained using a 180-degree backscattering geometry with a fiber optic imaging probe (MultiRxn, Kaiser Optical Systems, Inc., 5 mm focal length,  $\sim 200$  micron spot size at focus). Samples were sealed inside glass vials under an inert atmosphere and measured outside containment. There was little evidence of sample decomposition at this laser power (see Figure 3).

As part of this work we found that  $\text{AlH}_3$ -TEDA could be easily produced, using the electrochemical method reported here without the use of catalysts. Producing  $\text{AlH}_3$ -TEDA was used as a mean to confirm the formation of  $\text{AlH}_3$  molecules in the electrochemical



**FIGURE 3.** Raman spectrum of material isolated from an electrochemical cell showing  $\alpha$ -phase alane.



**FIGURE 4.** TEDA is known to complex with  $\text{AlH}_3$ , appearance of precipitate signals alane molecule formation.

cell. Although  $\text{AlH}_3$  can not be separated from  $\text{AlH}_3$ -TEDA it was selected because it precipitates as white solid and its formation can be observed visually (see Figure 4). The visual observation of the formation of relatively large quantities of TEDA- $\text{AlH}_3$  was good qualitative indication of the high rate of producing  $\text{AlH}_3$  in electrochemical cell. The formation of  $\text{AlH}_3$ -TEDA adduct indicates that a whole range of adducts could be formed, using the electrochemical route.

Thermal gravimetric analysis was conducted on a Netzsch TG-DTA 409 PC LUX. The sample heating ramp was  $2^\circ\text{C}$  per minute while using an atmosphere of argon with a flow rate of  $25\text{ cm}^3\cdot\text{s}^{-1}$ .

### Conclusions and Future Directions

This generation cycle of alane presented in this work provides a clean, facile route to a high capacity  $\text{H}_2$  storage material alane, while avoiding unrecoverable thermodynamic costs. This work is anticipated to impact other fields including those of thin films, adduct based syntheses, and the recycling and regeneration of other materials. This work can be concluded as:

- Conducted systematic study to achieve a closed generation cycle of alane.

- Developed a methodology to confirm the generation of  $\text{AlH}_3$  using this cycle.
- Succeeded in using this cycle to produce large quantities of  $\text{AlH}_3$ -TEDA.
- Produced gram quantities of alane, electrochemically.
- Identified other solvents to be tried for more efficient separation process.
- Started working on the efficiency aspects of the cycle and will continue in the future.
- Identified other complex hydrides that can be regenerated in similar manner and will be tried in the near future.
- A closed system cell is assembled and will be used in the future for higher efficiency.
- Other solvents forming alane adducts will be tried for higher efficiency of separation.

### Special Recognitions & Awards/Patents Issued

1. Electrochemical process and production of novel complex hydrides, IPC8 Class: AC25B100FI USPC Class: 205477, patent pending.

### FY 2009 Publications/Presentations

1. **Aluminum Hydride: A Reversible Material for Hydrogen Storage**, *Chem. Commun.*, 2009, DOI: 10.1039/b901878f, Ragaiy Zidan, Brenda L. Garcia-Diaz, Christopher S. Fewox, Ashley C. Stowe, Joshua R. Gray and Andrew G. Harter.

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