

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

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- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates

### Technical Targets

Our aim is to produce high hydrogen content compounds that can be used for onboard hydrogen storage systems. Our effort utilizes a novel method of forming  $\text{AlH}_3$ , based on the fundamental thermodynamic characteristics of materials and electrochemical techniques. The targeted material, alane, is an attractive candidate with gravimetric capacity of 10 wt% and volumetric capacity of 149 g/L  $\text{H}_2$  and desorption temperature of  $\sim 60^\circ\text{C}$  to  $175^\circ\text{C}$  (depending on particle size and use of catalyst). The reversible energy requirement for the regeneration of alane is targeted not to exceed 30% of the hydrogen content energy value. The result of this research work is expected to meet DOE 2010 and 2015 targets such as:

### Objectives

- Develop a novel process to produce low-cost rechargeable hydrogen storage materials with cyclic stability and favorable thermodynamics and kinetics fulfilling the DOE onboard hydrogen transportation goals.
- Reversibly generate aluminum hydride (alane,  $\text{AlH}_3$ ), having 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), meets the 2010 DOE targets for desorption.

### Specific Objectives

- Avoid the impractical high pressure needed to form  $\text{AlH}_3$  and other possible high capacity hydrides.
- Utilize electrolytic potential to increase hydrogen activity and/or drive chemical reactions to recharge high capacity hydrides such as  $\text{AlH}_3$ .
- The process used is electrochemical, based on employing Gibbs free energy and Faraday's equations to drive the formation of  $\text{AlH}_3$  under practical conditions.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage Technical Challenges section (3.3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) Regeneration Cost

- System Gravimetric Capacity and Volumetric Density
- Charging/Discharging Rates
- Fuel Purity
- System Fill Time
- Minimum Hydrogen Delivery Rate

### Accomplishments

- Modified electrochemical cell design and materials to achieve larger quantities of  $\text{AlH}_3$ .
- Demonstrated feasibility of electrolytically forming  $\text{AlH}_3$  (larger quantities).
- Devised and conducted experiments to understand the mechanism of any reactions taking place and showed theoretical production capability.
- Characterized reaction products with X-ray diffraction (XRD) and other methods.
- Quantified yield and efficiencies of recharging reaction.



### Introduction

Discovering efficient and economic methods for storing hydrogen is a critical issue for realizing the hydrogen economy. The DOE is supporting research to demonstrate viable hydrogen storage technology with the specific objectives of developing and verifying onboard hydrogen storage systems. The DOE goals are focused

on achieving a storage system (not just material) of 6 mass%  $H_2$  (2.0 kWh/kg) and 45 kg  $H_2/m^3$  (1.5 kWh/L) by 2010 and developing a system reaching 9 mass%  $H_2$  (2.7 kWh/kg) and 81 kg  $H_2/m^3$  (2.7 kWh/L) by 2015. In order to meet these goals, DOE's primary investment focuses on exploratory research of new system concepts and materials. Under the material discovery effort, directed by the DOE, researchers have identified a large number of compounds with high hydrogen capacity that can fulfill the gravimetric and volumetric requirements. Unfortunately, the majority of these compounds fail to fulfill the thermodynamic and kinetic requirements for onboard storage system. However,  $AlH_3$  not only has the needed gravimetric and volumetric density but also has thermodynamic and kinetic conditions of operation compatible with the use of waste heat from proton exchange membrane fuel cells or hydrogen burning internal combustion engines. The problem with this hydrogen storage material ( $AlH_3$ ) is the re-hydrogenation of the material. Direct hydrogenation of aluminum to form  $AlH_3$  requires  $10^5$  bars of hydrogen pressure at room temperature. This requirement of such high pressure had precluded  $AlH_3$  in the past from being considered as a hydrogen storage material. For this reason our research work is focused on developing a novel technique that can cost effectively achieve the hydrogenation or regeneration of aluminum hydride under practical condition.

## Approach

In order to avoid the impractical hydrogen high pressure in charging and recharging aluminum to form aluminum hydride, a novel electrochemical technique was used. This electrochemical scheme utilizes electrolytic potential,  $E$ , to increase hydrogen activity to hydrogenate Al or drive a chemical reaction to regenerate aluminum hydride. Based on Gibbs free energy and Faraday equations the above concept can be expressed as:

$$\Delta G = -nFE$$

$n$  = number of moles of electrons transferred  
 $F$  = Faraday's constant, the charge on a mole of electrons = 95,484.56 C/mol

$$E = -\frac{RT}{nF} \ln(f),$$

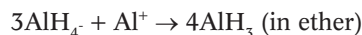
where  $R$  = gas constant and  $f$  = fugacity of reacting ions.

Since Al and  $AlH_3$  will be oxidized in an aqueous environment we had to come up with a novel route to use non-aqueous solvents. A polar conductive solution acts as an electrolyte, made of ionic complex hydride (such as  $LiAlH_4$ ,  $NaAlH_4$  and  $KAlH_4$ ) dissolved in tetrahydrofuran (THF) or ether. The electrochemical cell has an aluminum anode and a platinum cathode where hydrogen could be bubbled out.

Example:



At the anode,



The above equation indicates that aluminum electrode is expected to dissolve as  $AlH_3$  is formed.

At the cathode, hydrogen is bubbled out resulting in atomic hydrogen, which reacts with Na as:

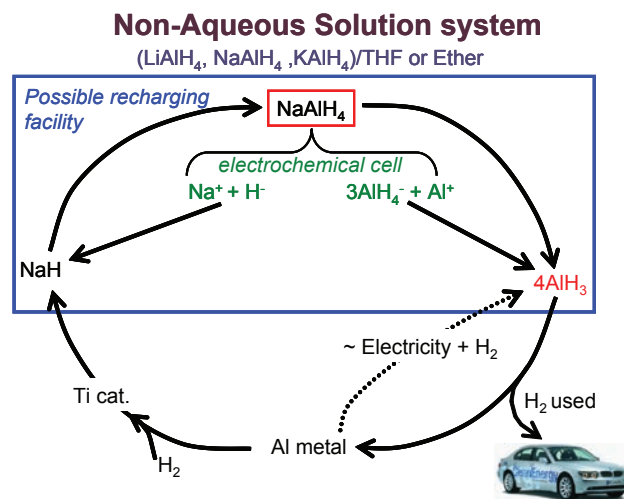


As shown in Figure 1, aluminum hydride is produced. Once hydrogen is used spent aluminum is reacted back with sodium hydride to form sodium aluminum hydride in a closed loop.

## Results

Cyclic voltammetry was conducted and the regions of voltage needed to form alane were identified. Alane was observed at the aluminum electrode in the region above -1.6 volts. The reduction of sodium ions to sodium metal was observed to occur at the expected voltage of 2.72 V. White film formed at the aluminum electrode was identified by XRD as  $\alpha$ -alane ( $\alpha$  phase  $AlH_3$ ) as shown in Figure 2.

Efficiency calculations of alane formation were also made and, at this point, kinetics of formation are still slow. Subsequently other organic solvents, forming adduct with  $AlH_3$ , have been identified. And preliminary results showed ten gram quantities of  $AlH_3$ -adduct can be generated using the electrochemical technique.



**FIGURE 1.** Closed Cycles of Electrochemically Forming and Regenerating Alane

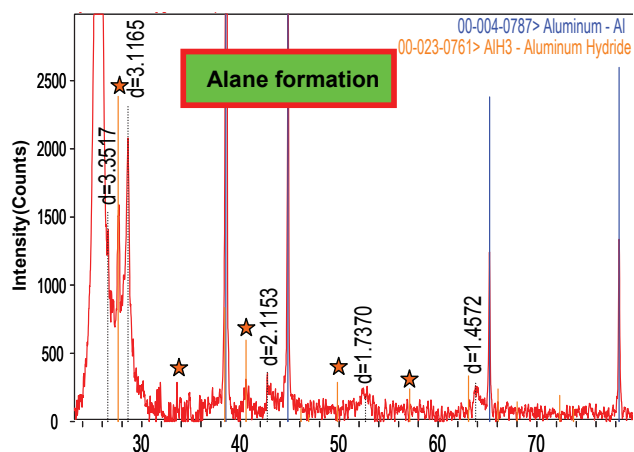


FIGURE 2. Peaks of  $\alpha$  Phase Alane

## Conclusions

- A novel electrochemical methods was developed to reversibly form alane ( $\text{AlH}_3$ ).
- Bulk  $\text{AlH}_3$  formed during electrochemical regeneration.
- The aluminum electrode dissolved as expected.
- The needed energy was found not to exceed 30% of the energy values of  $\text{H}_2$  stored.
- 0.37 mg of  $\text{AlH}_3$  was formed in 10 minutes.
- Other  $\text{AlH}_3$ -adducts forming solvent were identified to increase the  $\text{AlH}_3$  yield.

## Future Directions

- Upgrade the electrochemical cell with larger surface area working and counter electrodes.
- Examine the use of catalysts (Ti) in accelerating the electrochemical regeneration.
- Use the several identified adducts that form bonds with  $\text{AlH}_3$  to increase the efficiency and yield.
- Use other techniques (e.g. nuclear magnetic resonance and Raman) to quantify and characterize  $\text{AlH}_3$ .
- Optimize all parameters needed for producing several grams of  $\text{AlH}_3$  efficiently.
- Design and construct a larger electrochemical cell capable of producing larger quantities of  $\text{AlH}_3$ .
- Develop efficient methods of extracting  $\text{AlH}_3$  from the electrochemical cell.
- Work closely with other  $\text{AlH}_3$  partners Brookhaven National Laboratory and the University of Hawaii.