IV.E.3 Electrochemical Reversible Formation of Alane

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Project Start Date: October 1, 2011
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Develop methods of alane (AlH_3) production and regeneration that lower the cost of alane production to less than $10/kg
- Demonstrate and characterize alane production system that lower the cost of alane production with the lowest possible capital and operating costs
- Identify and quantify fundamental properties of alane production chemistry and physics that will lead to improved design and modeling of systems for alane production and use

Fiscal Year (FY) 2014 Objectives

- Demonstrate improved synthesis of alane using the dry method, and identify improved reaction conditions for improved yield and crystal size.
- Demonstrate $NaAlH_4$ electrolyte recycling with a reaction yield above 70% in a system where at least 5 g of $NaAlH_4$ can be produced.
- Synthesis of AlH_3 in a divided cell with an electrolyte containing $NaAlH_4$. Synthesis will produce at least 1 g of AlH_3 that can be isolated and products at the sodium electrode will be characterized to demonstrate the potential for electrolyte recycling.
- $NaAlH_4$ and $LiAlH_4$ electrolyte recycling. Identification of low-cost catalyst formulations and catalyst loadings necessary to achieve yields above 80%.

Technical Barriers

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

(A) System Weight and Volume

(B) System Cost

(C) Efficiency

(Q) Regeneration Processes

Technical Targets

In this project studies are being conducted to lower cost and improve efficiency of the electrochemical method to form AlH_3. This material has the potential to meet long-term and near-term targets for automotive and portable power applications [1,2]. The research performed as part of this contract is equally applicable to both areas.

- By 2015, develop and verify a single-use hydrogen storage system for portable power applications achieving 0.7 kWh/kg system (2.0 wt% hydrogen) and 1.0 kWh/L system (0.030 kg hydrogen/L) at a cost of $0.09/Whnet ($3/g H_2 stored).
- By 2017, develop and verify onboard automotive hydrogen storage systems achieving 1.8 kWh/kg system (5.5 wt% hydrogen) and 1.3 kWh/L system (0.040 kg hydrogen/L) at a cost of $12/kWh ($400/kg H_2 stored).

FY 2014 Accomplishments

- Developed projections for AlH_3 cost
- Demonstrated synthesis of AlH_3 by the dry method with $NaAlH_4$ precursors
- Demonstrated regeneration of $NaAlH_4$ electrolyte for electrochemical alane generation is possible with a cheaper catalyst to enable low cost alane recycling
- Synthesized alane by the electrochemical method and developing novel adduct removal techniques
- Demonstrated improved $NaAlH_4$ recycling with yields above 80% and production of over 5 grams of material.

INTRODUCTION

The DOE is supporting research to demonstrate viable materials for onboard hydrogen storage. Aluminum hydride (alane, AlH_3), having a gravimetric capacity of 10 wt% and volumetric capacity of 149 g H_2/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 2015 and 2017 DOE targets for automotive and portable power applications. The main draw back for using alane as a hydrogen storage material is unfavorable thermodynamics towards hydrogenation. Zidan et al. [3] 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_3 and the chemical reaction route of AlH_3 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 2014, research has continued to demonstrate methods that will improve the generation of alane. This work has been done in collaboration with Ardica Technologies and has focused on improving dry methods of alane synthesis that can reduce costs from solvent removal and product recovery along with improvements in the electrochemical method that will allow more efficient generation of alane. This research seeks to solve real-world problems in using alane as a hydrogen carrier and make it a more cost effective material for transportation and portable power systems.

APPROACH

The electrochemical generation of alane has been show by Zidan et al. [3,4] to be capable of generating high purity material using methods that can be developed into a fueling cycle for hydrogen vehicles, portable power systems, or other applications. This research has demonstrated the system electrochemistry and improvements have been made to improve the efficiency of the electrochemical alane production reactions. The regeneration of the electrolyte from spent materials and improvements in the separations process are equally as important in developing overall alane production and reprocessing schemes. SRNL has developed and demonstrated a method to regenerate the electrolyte for the electrochemical cell with materials present in electrochemical cell cathode, dehydrogenated alane, and hydrogen gas. Improvements to the electrochemical cell design have also been realized to allow improved separation of the cell products to enable electrolyte generation and separation of alane.

RESULTS

SRNL has investigated the use of $NaAlH_4$ in the dry method for the synthesis of alane in order to achieve cost reductions in its manufacture. Figure 1 displays an X-ray

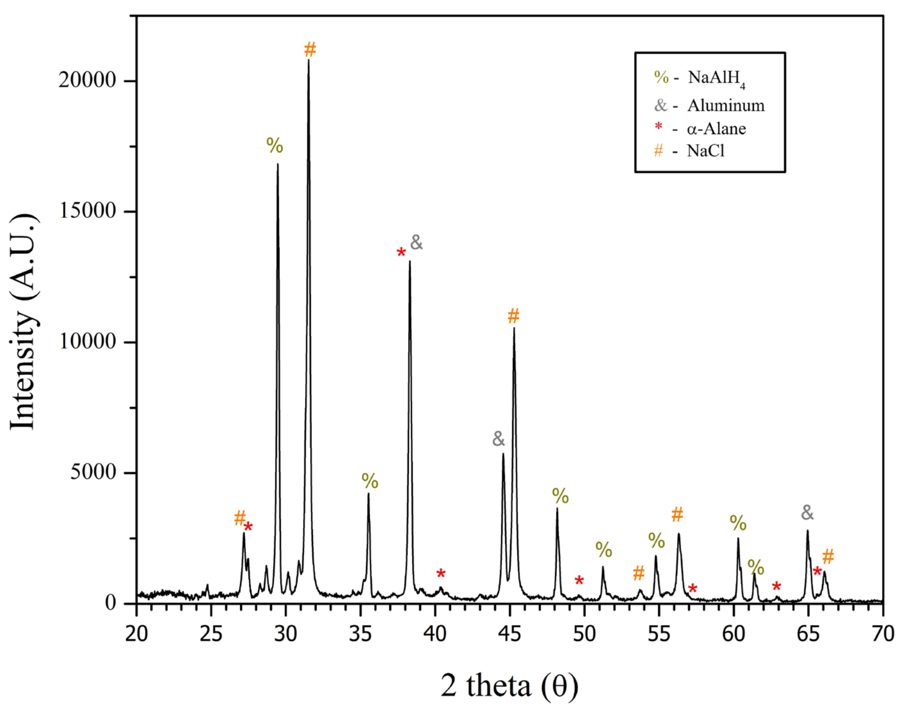

FIGURE 1. XRD spectrum of the unwashed product formed from annealing $NaAlH_4$ and $AlCl_3$ in the solid state.

diffraction (XRD) measurement of the crude reaction product from the dry method synthesis using $NaAlH_4$. A diffraction pattern confirming the production of α-alane is observed. A novel variation of the dry method to produce alane with $NaAlH_4$ has also been accomplished. This process is currently being optimized to increase yields.

Recycling the $NaAlH_4$ electrolyte in tetrahydrofuran can potentially reduce the cost of the electrolyte that is used in the electrochemical cell. $NaAlH_4$ regeneration resulting in a percent yield over 80% was conducted by lengthening the reaction time and the hydrogen pressure in the reactor. This reaction was conducted on a scale to produce more than 5 grams of material. Table 1 shows the $NaAlH_4$ yield for various operating conditions and using two different catalysts. $TiCl_3$ is a well-known catalyst for this reaction and displays the highest regeneration yields, but the new catalyst is nearly two orders of magnitude cheaper than $TiCl_3$. Figure 2 shows the diffraction pattern for regenerated $NaAlH_4$ with no detectable impurities from both catalysts used. These results demonstrate that high purity $NaAlH_4$ can be regenerated from spent alane using both catalysts. These experiments were conducted in a Parr vessel with simple hydrogen overpressure. In this reactor configuration, the slow step in the reaction is the diffusion of hydrogen into the solution because it is limited by Henry's law. The results suggest that if a reactor with better two-phase mixing of the hydrogen would likely be able to lower the hydrogen pressure that is needed and reduce the reaction time. The yield can likely be further increased, while retaining high purity, by developing a flow reactor with better gas, liquid, solid mixing.

TABLE 1. Percent yield of $NaAlH_4$ at different pressures, temperatures and catalyst utilization. The highest percent yield of 84.2% was acquired by increasing the duration of the reaction to 42.5 hours

Temperature and H_2 Pressure	Percent Yield with New Catalyst (5 mol%)	Percent Yield with $TiCl_3$ (5 mol%)
70°C, 1,400 psi	17.0%	31.8%
120°C, 1,400 psi	28.2%	56.6%
150°C, 1,400 psi	55.5%	65.5%
150°C, 1,800 psi	57.1%	84.2%

Crystallization of the product from the electrochemical reaction of alane is important for being able to get the desired storage lifetime and hydrogen release characteristics. Left over electrolyte from the electrochemical cell containing AlH_3 product after the reaction was used to crystallize over 1 g of alane. $LiAlH_4$ assists in the adduct removal process by thermal decomposition. This electrolyte can be easily separated by washing with diethyl ether and then reused for alane production. The alane can then be washed with dilute hydrochloric acid solution to passivate the surface

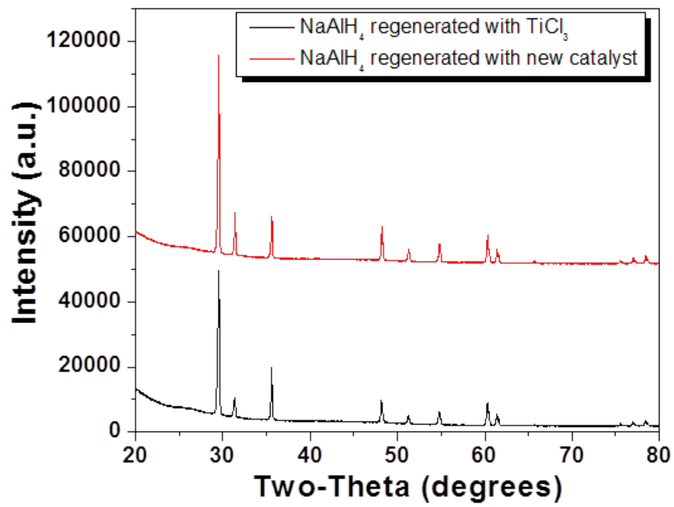

FIGURE 2. XRD pattern of regenerated $NaAlH_4$ from utilization of both catalysts displaying a pure product in both cases.

and remove residual aluminum. This passivation process increases the shelf life of the material. Alternative adduct removal techniques have been theorized and the equipment necessary to conduct these experiments has been constructed. This theoretical adduct removal approach could result in further cost reductions for the synthesis of alane.

CONCLUSIONS AND FUTURE DIRECTIONS

- Improved dry methods that work with $NaAlH_4$ and allow simple product separation.
- Regeneration of $NaAlH_4$ electrolyte for the electrochemical cell was demonstrated with a yield greater than 80% producing more than 5 grams of material.
- The recycled $NaAlH_4$ electrolyte was produced without detectable impurities and it is hypothesized that optimization of the reactor can increase the yield while lowering the reaction time and pressure.
- Crystallization of alane from the electrolyte of the electrochemical cell has shown control of crystal size and demonstrated that a product with desirable storage and hydrogen release characteristics can be synthesized from the electrochemical cell product.
- Characterization of the electrode material is currently underway and its composition should be confirmed soon.
- Optimization of the regeneration conditions for $LiAlH_4$ to produce yields above 80% is currently being investigated.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Ragaiy Zidan, Douglas A. Knight, Long V. Dinh; Novel Methods for Synthesizing Alane without the Formation of Adducts and Free of Halides US20120141363 Feb 2013.

2. Ragaiy Zidan; Electrochemical Process and Production of Novel Complex Hydrides US8,470,156B2 Jun 2013.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. Ragaiy Zidan" Development and characterization of novel hydrogen storage materials", Oct 27 2012 International Energy Agency (IEA) HIA Task 22 Meeting Kyoto Japan. [PR]

2. Novel Materials and New Methods for Hydrogen Storage" International Symposium on Metal-Hydrogen Systems 2012, Oct 21 Kyoto, Japan Invited Speaker. [PR]

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3. Zidan, R., et al., Chemical Communications, 2009(25): p. 3717-3719.

4. Martinez-Rodriguez, M.J., et al., Appl. Phys. A-Mater. Sci. Process., 2012. **106**(3): p. 545-550.