

IV.C.11 Electrochemical Reversible Formation of α -Alane

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

The research performed as part of this contract is equally applicable to both areas.

- By 2020, develop and verify a single-use hydrogen storage system for portable power applications achieving 1.3 kWh/kg system (4.0 wt% hydrogen) and 1.7 kWh/L system (0.050 kg H₂/L) at a cost of \$0.03/Wh net (\$1/g H₂ stored).

FY 2016 Accomplishments

- Demonstrated recovery and recycling of 99.9% of crystallization additives.
- Demonstrated transamination of alane-tetrahydrofuran (THF) adduct to alane-triethylamine adduct,
- Improved ambient pressure crystallization of α -alane to 88% yield without producing unwanted phases.



Objectives

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

Technical Barriers

This project addresses the following technical barriers from the Hydrogen 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
- (Q) Regeneration Processes

Technical Targets

In this project studies are being conducted to lower cost and improve efficiency of the electrochemical method to form α -AlH₃. This material has the potential to meet long-term and near-term target for portable power applications [1,2].

INTRODUCTION

The U.S. Department of Energy (DOE) is supporting research to demonstrate viable materials for hydrogen storage. Aluminum hydride (alane [AlH₃]), having a gravimetric capacity of 10 wt% and volumetric capacity of 149 g H₂/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 2020 DOE system-level targets for portable power applications. The main barrier for using alane as a hydrogen storage material is the high material cost and unfavorable thermodynamics towards (re)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 α -AlH₃ and the chemical reaction route of α -AlH₃ 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 2016, SRNL focused on advanced alane-etherate crystallization strategies that will allow efficient and low cost conversion to α -alane. The project focused on improving processes for alane synthesis and regeneration that have been developed by SRNL in prior years including: (1) electrochemical synthesis of alane from commercial Al and spent alane, and (2) solid state alane production. The goals the FY 2016 efforts were to exceed 85% yield

of α -alane through advanced crystallization. SRNL also continued to develop recovery and recycling methods to recover and reuse over 75% of the solvents and additives during the crystallization process.

APPROACH

The electrochemical generation of α -alane has been shown 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 methods to enhance the practicality of utilizing the electrochemical method for the large scale production of alane etherate as well as the crystallization of the etherate to stable crystals of α -alane. The focus this year has been to refine the crystallization process to reduce costs and produce high quality material with only the alpha phase at a high yield. Additionally, focus has been placed on moving to the crystallization of the alane-THF adduct that has high ionic conductivity and will enable the electrochemical process. The crystallization has focused on ambient pressure crystallization of alane-etherate in toluene due to lower toxicity and lower required energy input compared to performing the crystallization at reduced pressure.

RESULTS

In collaboration with Ardica and SRI, SRNL identified that the use of LiBH_4 and LiAlH_4 as crystallizing aids was a significant additional cost for alane crystallization if the products were not recycled between batches. Although the recycling of these compounds has been assumed as a cost savings, the ability to isolate them in high yield from product rinses and show that they are not changed in the crystallization process had never been done. To demonstrate the recovery, SRNL collected the product ether rinses from batches of alane. The ether rinses were then evaporated to remove the solvent on a Schlenk line with heating. The dried product was weighed and X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were performed on the product. The 99.9% recovery of the theoretical amount of LiAlH_4 and LiBH_4 in the washes was obtained. The XRD of the recovered product (Figure 1) only has peaks from LiAlH_4 and LiBH_4 . The TGA of the recovered product (Figure 2) has weight loss peaks from LiAlH_4 and

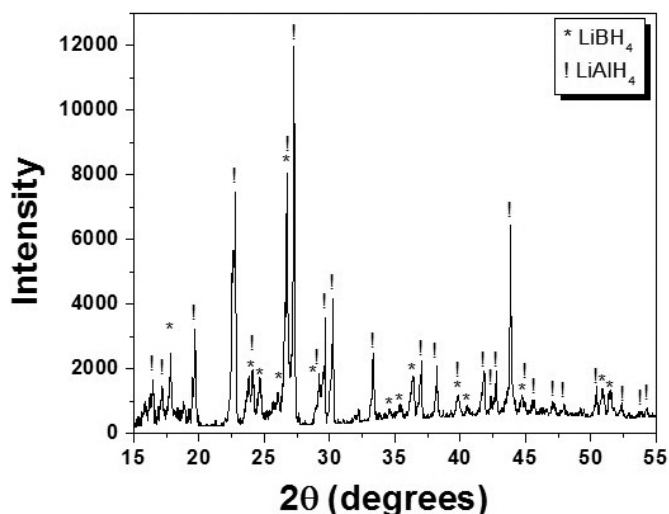
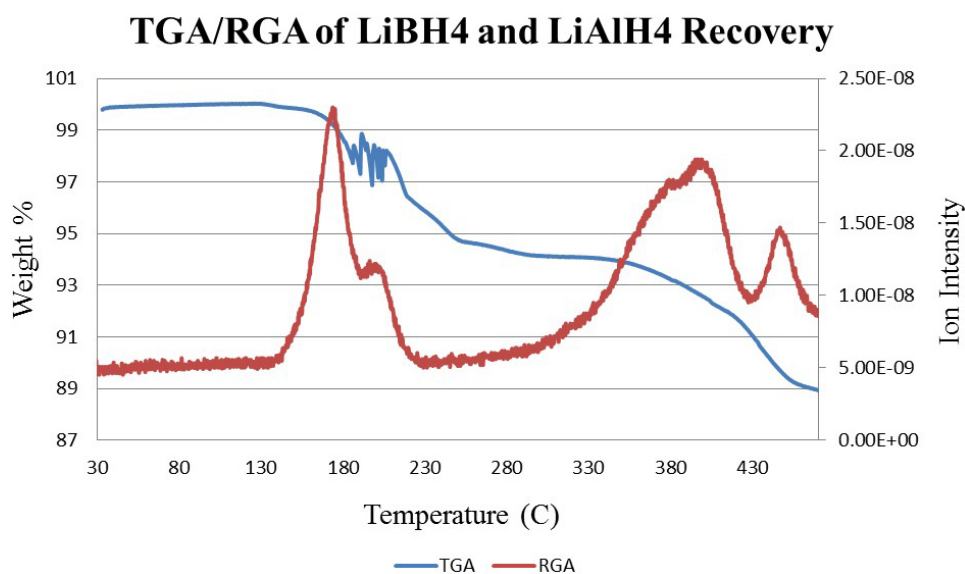


FIGURE 1. XRD showing LiAlH_4 and LiBH_4 recovered from the ether washes

LiBH_4 . These results demonstrate fulfillment of the first two milestones for the year and validate that recovery of LiAlH_4 and LiBH_4 crystallizing aids is very feasible.

The SRNL team was successful in reproducibly synthesizing α -alane with 9.8 wt% hydrogen content during synthesis runs at the 15 g scale as measured by TGA, but the yield during these runs was low due to difficulties with recovering the product from the glassware. Figure 3 shows a scanning electron micrograph of the alane produced on the 15 g scale and it can be seen that there are square crystallites. Figure 4 shows a TGA of the material produced at the 15 g scale with >9.8 wt% H_2 . Crystallization at the 150 g scale



RGA – Residual gas analysis

FIGURE 2. TGA showing dehydrogenation of LiBH_4 and LiAlH_4 recovered from ether washes



FIGURE 3. Scanning electron micrograph image of α -alane agglomerates synthesized at the 15 g scale

reproducibly yielded 88% α -alane with >9.8 wt% H_2 . The yield was enhanced due to the lower surface area to volume ratio for the vessels. This demonstrated that large scale alane crystallization at ambient pressure with high yield is possible. The stability of the α -alane produced through this set-up is excellent and behaves exactly like former Soviet Union samples. The passivated α -alane is inert to direct exposure to oxygen, water, and impacts. This was confirmed by experiments at Ardica/SRI.

The SRNL team has demonstrated the crystallization of alternative adducts such as triethylamine -alane formed by transamination reactions with THF-alane adducts. Research is continuing to increase the yield of the adduct and to identify the optimal conditions for crystallization.

CONCLUSIONS AND FUTURE DIRECTIONS

- Increasing the current of the electrochemical cell is one of the last critical issues related to alane adduction production.
- Investigate alternative crystallization pathways which may be suitable for the use of higher ionic conductivity solvent.
- Investigate additives and other solvents that may increase the conductivity of the electrochemical cell for increase alane adduct production rates.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Ragaïy Zidan, Joseph A. Teprovich, Ted Motyka; Two step novel hydrogen system using additives to enhance hydrogen release from the hydrolysis of alane and activated aluminum, US9,199,844B2, December 2015.

2. Ragaïy Zidan; High energy density battery based on complex hydrides, US9,325,030B2, April 2016.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. Patrick Ward, Joseph Teprovich, Scott Greenway, Ragaïy Zidan. "Current Progress in the Low-cost Production of Alane." PacifiChem. December 2015.

2. Ted Motyka. "Investigation of Metal and Chemical Hydrides for H_2 Storage in Fuel Cell Systems." 2016 ONR Undersea Energy and Propulsion Review. April 2016.

3. Ragaïy Zidan. "Reversible Formation of Alane." Department of Energy Annual Merit Review 2016.

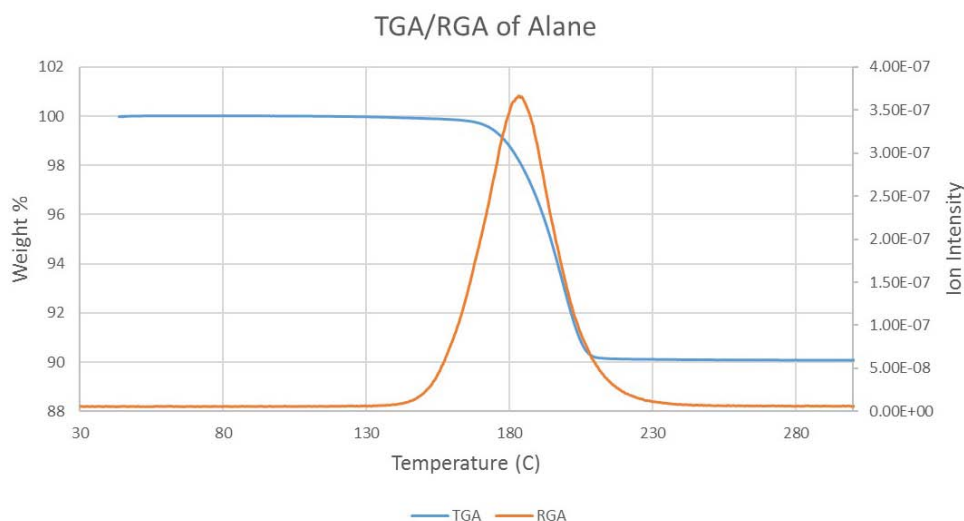


FIGURE 4. TGA and RGA data showing dehydrogenation of AlH_3 obtained from the 15 g batch that contains greater than 9.8 wt% H_2

4. Ragaiy Zidan, Patrick Ward, and Joseph Teprovich. “Current Progress in the Low-cost Production of Alane.” MH Conference. August 2016.

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1. Teprovich, J.A., T. Motyka, and R. Zidan, International Journal of Hydrogen Energy, 2012. **37**(2): p. 1594–1603.
2. Graetz, J. and J.J. Reilly, J. Phys. Chem. B, 2005. **109**(47): p. 22181–22185.
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.