

IV.C.16 Electrochemical Reversible Formation of Alane

Ragaiy Zidan (Primary Contact), Patrick Ward,
Joseph Teprovich, Scott McWhorter, Scott Greenway
Savannah River National Laboratory (SRNL)
Bldg. 999-2W
Aiken, SC 29808
Phone: (803) 646-8876
Email: ragaiy.zidan@srnl.doe.gov

DOE Manager: Ned Stetson
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov

Subcontractor:
Savannah River Consulting, Aiken, SC

Project Start Date: October 1, 2006
Project End Date: September 30, 2017

Overall Objectives

- Develop novel methods to reduce production costs of alane.
- Demonstrate scalable low-cost alane etherate production methods which can be translated into a suitable crystallization process.
- Develop a crystallization process to produce high quality α -alane.
- Develop passivation methods to produce alane which is stable over time.
- Demonstrate a process to regenerate α -AlH₃ from spent alane.

Fiscal Year (FY) 2017 Objectives

- Develop methods to utilize lower cost precursor NaAlH₄ in order to significantly reduce the overall cost of alane production.
- Improve operational conditions of electrochemical alane production with a primary focus on the conductivity of the solvent.
- Utilize density functional theory (DFT) calculations to gain deeper insight into the potential crystallization of alane from alternative adducts.
- Determine ligands which can exchange with the AlH₃•THF (tetrahydrofuran) adduct, so THF can be used in the electrochemical cell to improve electrical conductivity.
- Demonstrate crystallization of alane from alternative adducts.

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

- Acquire DFT data on various alane adducts to gain insight into the parameters which influence the production of alane from these adducts.
- Develop methods to produce alane from lower cost precursors.
- Demonstrate a lower cost crystallization method for the production of high quality α -alane.
- Demonstrate ligand exchange with AlH₃•THF to produce alternative adducts.
- Demonstrate the crystallization of alternative adducts of alane.

FY 2017 Accomplishments

- Crystallization method developed which significantly lowers the cost of production of high quality α -alane.
- DFT calculations were performed on a series of alane adducts to gain a deeper understanding of the variables which affect the production of alane.
- Novel method for the production of alane from NaAlH₄ was developed.



INTRODUCTION

The main objective at SRNL is to develop a low-cost hydrogen storage material with favorable thermodynamics and kinetics capable of fulfilling various portable power applications. Our specific goal is to develop an economical method to regenerate aluminum hydride (alane - AlH₃) from aluminum metal, since aluminum hydride has a gravimetric capacity of 10 wt%, volumetric capacity of 149 g/L H₂, and a desorption temperature range of ~60°C to 175°C (depending on particle size and the addition of catalysts). Direct synthesis of alane from hydrogen and aluminum is

unfeasible due to the enormously high pressure of hydrogen required thermodynamically to drive direct hydrogenation. Conventional chemical methods for alane synthesis react alkaline metal or alkali-earth metal hydrides or alanates with aluminum chloride to produce an alane adduct using significant quantities of polar aprotic solvents such as THF or ether that form complexes with the alane product. The high energy required for significant solvent separation, product purification, and the large energy required to recycle reaction byproducts (primarily LiCl) makes production of alane prohibitively expensive for hydrogen storage applications. It is currently estimated that production of alane by the conventional chemical route costs between \$3,000/kg and \$5,000/kg. Electrochemical alane production methods have promise for significant cost reduction for the synthesis of alane. This method has been developed and demonstrated by SRNL to have the potential to reduce alane production costs by over 100 times, which would make alane cost effective for various applications. However, technical challenges still remain to improve and optimize these methods.

APPROACH

The electrochemical generation of α -alane has been shown by Zidan et al. [1,2] 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 produce stable crystals of α -alane. By reinvestigating the traditional DOW method for alane crystallization, conditions required to produce large crystals of pure α -alane have been demonstrated in an enhanced process intensified chemical method. The understanding of this process has provided direction in a path to utilizing cheaper and less hazardous crystallizing solvents under more industrially viable conditions. Improvements to the electrochemical cell voltage patterns have also resulted in a method to nearly eliminate the dendrite formation which limits the time that an electrochemical process can run continuously without interruptions. Another opportunity for enhancement of the electrochemical process lies in the poor ionic conductivity of diethyl ether. The ionic conductivity of LiAlH_4 in diethyl ether is significantly lower than the ionic conductivity of alanates in THF. Furthermore, the lack of solubility of NaAlH_4 in diethyl ether restricts the use of NaAlH_4 in an electrochemical method to directly produce the alane diethyl etherate adduct. Unfortunately, attempts to crystallize the $\text{AlH}_3 \cdot \text{THF}$ adduct have not been successful in producing pure α -alane. Therefore, investigation into ligands which can exchange with the $\text{AlH}_3 \cdot \text{THF}$ adduct and produce an adduct capable of being crystallized to high purity α -alane would bypass the conductivity and higher expense issue associated with operation of the electrochemical cell with diethyl ether.

RESULTS

Previously, we reported a method to eliminate the issue related to dendrite formation in the electrochemical process which limits continuous operational time of the process on an industrial scale [3]. The other primary roadblock in this electrochemical method is the limited ionic conductivity in diethyl ether. To circumvent this limitation, the electrochemical cell can be operated in THF, but a ligand exchange process would be required afterwards. In order to gain insight into the capability to exchange ligands in the $\text{AlH}_3 \cdot \text{THF}$ adduct, bond dissociation energies were calculated for 18 various alane adducts using the hybrid DFT functional B3LYP and the triple zeta Pople basis set G6-311 with polarization functions on all atoms. Predicted bond dissociation enthalpies of various adducts are given in Table 1. There are two definitive trends apparent from the computational results. The first trend is that asymmetry of the ligand around the bonded atom tends to result in lower bond dissociation enthalpies than a symmetric adducting ligand. The second trend noticed is that steric hindrance plays a role in destabilizing the adduct bond as graphically illustrated in Figure 1. These calculations give insight into the adduct exchange reaction because ligands which form a stronger bond with alane will undergo the exchange reaction more rapidly and with a higher yield. Unfortunately, the bond dissociation energy calculated here does not provide a full picture for alane crystallization (adduct removal). This is because many of these adducts form an intermediate species before crystallizing into α -alane. This is known for the diethyl ether adduct and we recently determined intermediate adduct species ($\text{AlH}_3 \cdot \text{L}_{x<1}$) to be present during the crystallization of the triethyl amine and dimethyl ethyl amine adducts. Since there is an intermediate adduct species, the bond dissociation energy is actually the sum of energy required to go from the initial adduct to the intermediate adduct and then to alane. Because these intermediate adducts were only recently discovered in the less common adducts

TABLE 1. Bond Dissociation Enthalpies for Various Alane Adducts Calculated at the B3LYP Level of Theory

Adduct	Bond Dissociation Enthalpy (kJ/mol)	Bond Dissociation Enthalpy (kcal/mol)
$\text{AlH}_3 \cdot \text{Me}_2\text{EtN}$	110.27	26.36
$\text{AlH}_3 \cdot \text{Me}_2\text{O}$	85.40	20.41
$\text{AlH}_3 \cdot \text{Et}_2\text{MeN}$	73.13	17.48
$\text{AlH}_3 \cdot \text{IsoproMe2N}$	92.35	22.07
$\text{AlH}_3 \cdot \text{Et3N}$	98.23	23.48
$\text{AlH}_3 \cdot \text{DiisoproMeN}$	87.51	20.92
$\text{AlH}_3 \cdot \text{MeButylO}$	77.70	18.57
$\text{AlH}_3 \cdot \text{MTBE}$	73.16	17.49
$\text{AlH}_3 \cdot \text{MeProO}$	81.18	19.40
$\text{AlH}_3 \cdot \text{MeEtO}$	81.00	19.36

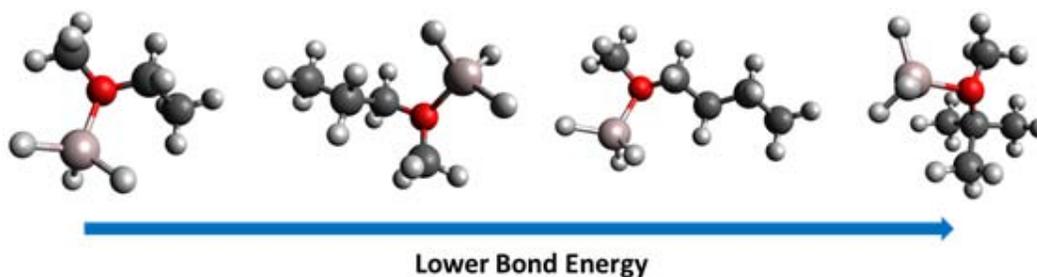


FIGURE 1. Effect of steric hindrance on adducts bond energy

of alane, the crystal structure is unknown and the bond dissociation energies cannot be modeled without first solving the crystal structures for each intermediate adduct species. Nonetheless, this set of calculations still provides valuable insight into the influences associated with the alane-ligand bond.

Another alternative to the electrochemical process, which is capable of utilizing the lower cost NaAlH_4 precursor, was recently developed by SRNL and a patent was filed. This process involves the production of alane diethyl etherate from the milling of NaAlH_4 and AlCl_3 in diethyl ether under particular temperature and pressure conditions. The presence of alane diethyl ether adduct was confirmed by thermal-gravimetric analysis (TGA)/residual gas analysis (RGA), as shown in Figure 2, and then a dry method crystallization was carried out to convert the material to α -alane. This milling process significantly reduces the cost of alane production by avoiding the use of LiAlH_4 , which costs nearly an order of magnitude greater. The advantage of producing the diethyl ether adduct of alane lies in the known crystallization methods to produce pure α -alane. While other adducts can produce α -alane, the control of particles size, purity, and morphology is difficult. Previously

reported alane production methods from alane diethyl ether adduct required the use of the more expensive LiAlH_4 precursor. The production of alane can be compartmentalized into three primary steps: front end adduct production, crystallization, and passivation. While the electrochemical process and newly patented process address the production of the alane adduct, crystallization of this adduct is still the critical step of the production of stable and high purity α -alane. Recently, SRNL has developed a process intensified chemical process to crystallize the diethyl ether adduct of alane which significantly reduces solvent requirements under less energy intensive conditions. This increases the production capacity and reduces the cost of the material. The newly developed crystallization process produces stable high purity α -alane as determined by X-ray diffraction shown in Figure 3. The importance of the production of α -alane without the presence of other phases lies in the significantly higher stability of the α -phase, but even α -phase alane can decompose over time if not properly passivated. The alane produced via the new crystallization process was passivated and demonstrated to have no loss in capacity (Figure 4) over 6 months of storage in air.

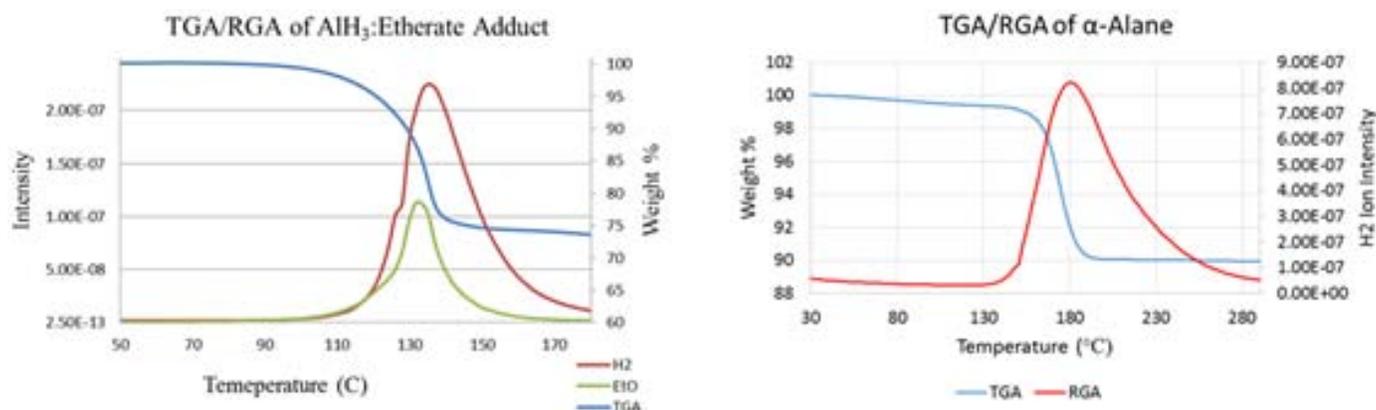


FIGURE 2. TGA/RGA of alane diethyl ether adduct produced by milling process (left) and TGA/RGA of alane adduct converted to α -alane via the dry method (right)

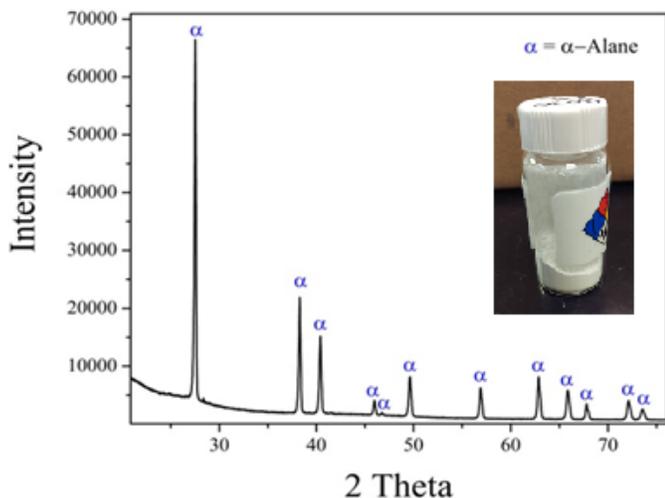


FIGURE 3. X-ray diffraction pattern of alane obtained from the process intensified crystallization process

CONCLUSIONS AND UPCOMING ACTIVITIES

Advancements in the low-cost production of alane were achieved with respect to both the etherate production process and the alane crystallization process. A novel ball milling method to produce alane etherate from NaAlH_4 was developed which reduces the cost of chemical precursors required. Furthermore, a process intensified method to crystallize alane etherate under ambient pressure in toluene was developed which is capable of producing more than seven times more alane per unit volume than the previously

reported DOW method. The newly developed crystallization method produced high purity α -alane, reduced the required solvent (by nearly an order of magnitude), and was found to produce α -alane which was stable in air and demonstrated no observable degradation over 6 mo. To evaluate alternative adducts for the electrochemical process, a large number of amine and ether adducts of alane were evaluated by DFT methods to determine the viability of adduct exchange from the $\text{AlH}_3 \cdot \text{THF}$ ligand to an adduct more suitable for crystallization. It was determined that the bond dissociation energy of the adduct is affected by both symmetry and steric hindrance contributions from the binding ligand. The improvements for alane production techniques demonstrated during the course of the project have defined a feasible path forward for the low-cost production of high quality α -alane.

SPECIAL RECOGNITIONS & AWARDS/PATENTS ISSUED

1. Zidan, Ragaiy; Ward, Patrick A. MECHANOCHEMICAL SOLID/LIQUID REACTION IN FORMATION OF ALANE Patent: U.S. Application No.: 15/482,913.

REFERENCES

1. Zidan, R., et al., Chemical Communications, 2009(25): p. 3717–3719.
2. Martinez-Rodriguez, M.J., et al., Appl. Phys. A-Mater. Sci. Process., 2012. 106(3): p. 545–550.
3. Zidan, R. et al. SRNL FY 2016 Report.

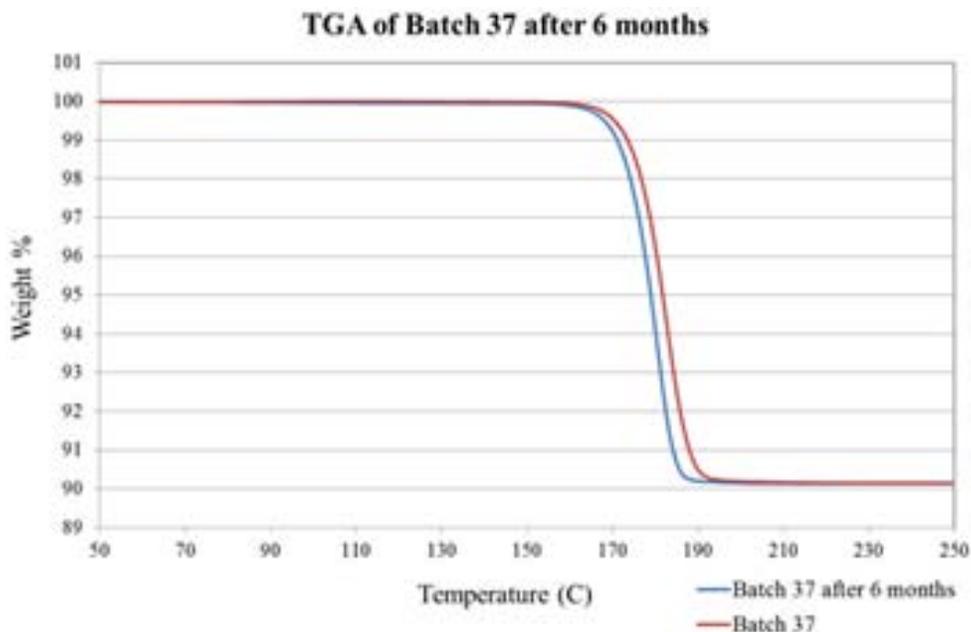


FIGURE 4. TGA of alane obtained from the process intensified crystallization process after production (red) and after being stored six months in air (blue)