

IV.E.2 Aluminum Hydride: the Organic-Metallic Approach

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Project End Date: September 30, 2014

Technical Targets

Table 1 is a listing of the 2015 EERE hydrogen storage targets along with BNL's current aluminum hydride project status. The well-to-wheels efficiency listed in the table under the column for Status was taken from an independent analysis by Argonne National Laboratory on the alane adduct (AlH_3 ; triethylamine) storage system. The 0.0582 gravimetric storage parameter listed in Table 1 was a measured value obtained by decomposing 60-wt% alane slurries. The slurries consisted of aluminum hydride particles having a hydrogen content of 9.7 wt% that were suspended in liquid glycol. The gravimetric storage parameter was hydrogen material weight only, and did not take into account the balance of plant weight.

TABLE 1. Progress in Meeting Technical Hydrogen Storage Targets

Storage Parameter	Units	Target	Status
Gravimetric	wt% H_2	0.055	0.0582
Volumetric	kg- H_2 /L	0.040	0.070
Fuel Flow Rate (temperature)	(g/s)/kW $^\circ\text{C}$	0.02 80	0.02 80
Well-to-Wheels Efficiency	kW- H_2 /kW	60%	>55%
Refueling Time	min	3.3	To be determined

Overall Objectives

Develop onboard vehicle storage systems using aluminum hydride that meets all of DOE's targets for the proton exchange membrane fuel cell vehicle.

- Produce aluminum hydride material with a hydrogen gravimetric storage capacity greater than 9.7% (kg- H_2 /kg) and volumetric storage capacity of (0.13 kg- H_2 /L).
- Identifying solvent substitutions in the chemical synthesis of aluminum hydride.

Fiscal Year (FY) 2014 Objectives

Develop practical and economical processes for regenerating aluminum hydride.

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

FY 2014 Accomplishments

- The chemical synthesis of the alane adduct (2-MeTHF: AlH_3) by directly reacting γ - AlH_3 in a solution of 2-MeTHF.
- Recovery of donor-free alpha aluminum hydride in high yields by combining vacuum distillation with thermal drying methods, starting with a solution of 2-MeTHF: AlH_3 .



INTRODUCTION

Past research on developing hydrogen storage materials for proton exchange membrane fuel cells have focused primarily on stable-reversible metal hydrides. However all reversible metal hydrides with high hydrogen content also have reaction enthalpies greater than 30 kJ/ H_2 -mol. Therefore they require operating temperatures greater than 150 $^\circ\text{C}$ when delivering hydrogen at acceptable fueling rates (>0.02 g H_2 /s/kW). Kinetically stabilized (metastable) hydrides, on the other hand, represent a class of hydrogen storage materials receiving much less attention. This lack of attention, placed on metastable hydrides, can be attributed to the technical and cost challenges of achieving chemical

reversibility. However, if the regeneration-reversibility problem could be solved, metastable hydrides would have clear hydrogen delivery advantages over more stable reversible metal hydrides. Of the many metastable hydrides, aluminum hydride is of interest because its volumetric hydrogen density of 148 g H₂/L is twice that of liquid hydrogen, and its gravimetric hydrogen density exceeds 10 wt%. Aluminum hydride also exhibits a low heat of reaction (7 kJ/mol H₂) and has demonstrated acceptable hydrogen delivery rates at temperatures much less than 100°C. Since aluminum hydride is not thermodynamically but instead kinetically stable, previous studies were focused mainly on stabilizing the material (tailoring particle size and coatings) to extend its shelf life from months to decades. Figure 1 shows four electron microscope slides of aluminum hydride. These samples have been prepared by either a wet or dry synthesis using diethyl ether as the solvent. The dry method of making aluminum hydride results in nanometer size particles, and the wet crystal growth procedure yields micron size particles. Micron-size particles are preferred over the nanometer size material. Shown in Figure 1 are micron size donor free aluminum hydride particles produced by DOW, ATK and BNL by wet crystal growth in a diethyl ether-toluene mixture. In FY 2014 the work focuses on investigating various solvent substitutions for replacing the use of diethyl ether as the solvent in the synthesis of donor free aluminum hydride.

APPROACH

The main challenge of using alane as a storage medium is finding methods for the cost- and energy-effective hydrogenation of aluminum back to donor-free AlH₃. Several synthetic methods that include reaction of AlCl₃ with alkali alanates, electrochemical synthesis from LiAlH₄ and NaAlH₄,

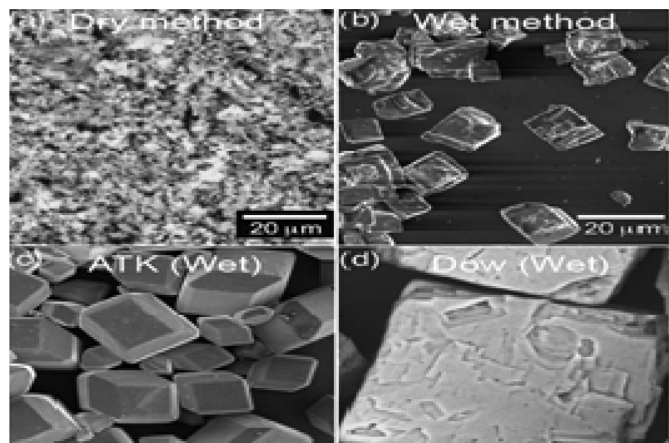


FIGURE 1. Figure 1 shows four electron microscope pictures of donor-free AlH₃; a) dry BNL, b) wet BNL, c) wet ATK, d) wet DOW. The wet samples are from crystal growth, dry samples are from vacuum distillation and thermal drying.

and direct hydrogenation of Al metal all involve either expensive materials or very high H₂ pressures. All these methods for producing materials are very challenging when manufacturing aluminum hydride on a large commercial scale. In addressing this challenge, work at Brookhaven has shown a three-step alane regeneration pathway. This regeneration procedure involves hydrogenating titanium catalyzed aluminum metal under moderate hydrogen pressure using tertiary amines to form various amine:alane adducts in diethyl ether and tetrahydrofuran (THF) solvents. The approach for FY 2014 is to further improve the synthesis of donor free aluminum hydride by replacing the use of diethyl ether or THF solvent/electrolyte with 2-MeTHF.

RESULTS

Alane formation, using the organo-metallic approach, requires the use of aprotic solvents. In past studies we have exclusively used either THF or diethyl ether as the aprotic solvents of choice. This year we have explored the advantages of using 2-MeTHF as a replacement solvent for THF and/or Et₂O. The solvent properties of 2-MeTHF is between THF and Et₂O in solvent polarity and Lewis base strength. Table 2 lists these solvent properties [1].

TABLE 2. Solvent Properties

Property	MeTHF	THF	Et ₂ O
Dielectric constant	6.97	7.5	4.42
Dipole moment, Debye	1.38	1.69	1.11
Water solubility, g/100g	4	miscible	1.2
Hildebrand parameter	16.9	18.7	15.5
Solvation energy, kcal/mol	0.6	0	2.3
Donor number	18	20.5	19.2

Attractive features of 2-MeTHF are that it is available in bulk and derivable from renewable resources. Another important feature is its solubility decreases with increasing temperature. This fact allows for a 70% reduction in energy requirements for drying 2-MeTHF compared to THF. It also has received DOE approval as an additive to gasoline. To our knowledge, 2-MeTHF:Alane is a newly synthesized compound whose properties are now being tabulated at BNL. However the alane adduct (THF:Alane) has been previously studied [2], and its crystal structures and infrared spectrum are available in the open literature. However, there appears to be no consistent terminology for alane adducts. Figure 2 shows the three accepted structures for alane adducts. They are referred to as 1:1 (for both Structures I and II) and the 1:2 bis-compounds (Structure III). For THF:Alane the 1:2 bis-compound is formed when THF is in excess. As the excess THF is removed the 1:2 bis-compound is converted to the 1:1 dimer compound. Some confusion arises because the 1:1 compound has two types of structures (I and II).

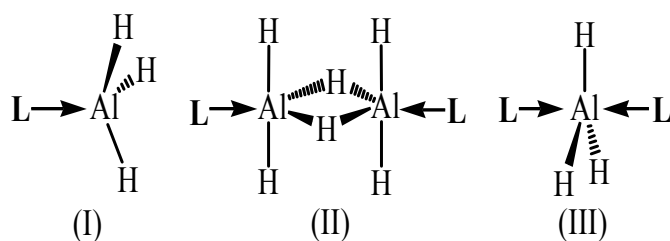


FIGURE 2. Figure 2 shows the three structure types of mono-dentate Lewis base alane compounds; (I) mono, (II) dimer, (III) bis.

To avoid this confusion we prefer to discuss the Fourier transform infrared spectrum for alane compound in terms of either terminal or bridging hydrogen bonds. The Type III bis-compound has three terminal hydrogen bonds and an absorption peak at 1727 wavenumber, while the Type II dimer compound having two bridging hydrogen bonds and an absorption peak at 1803 wavenumber. This year work has been towards evaluating 2-MeTHF as the adduct in forming 2-MeTHF:Alane, and comparing its structure and properties against other ether adducts such as; THF:Alane and Et₂O:Alane. Figure 3 is a section of the FTIR spectrum for 2-MeTHF:Alane. The spectrum shows two absorption peaks at wavenumbers 1727 and 1803. These peaks overlap with the THF:Alane peaks, and confirms that 2-MeTHF:Alane compound has similar structures as THF:Alane. These two structures are the hydrogen bridging dimer-compound and a bis-compound consisting of three terminal hydrogen bonds. Figure 4 is the X-ray diffraction spectrum of donor-free aluminum hydride by recovery from 2-MeTHF:Alane.

CONCLUSIONS AND FUTURE DIRECTIONS

The result of this year study on the properties of 2-MeTHF identified its usefulness both as a solvent and an electrolyte in the synthesis of donor-free aluminum hydride. Future work will investigate the conditions for producing micron size donor free aluminum hydride by the crystal growth method in a saturated 2-MeTHF:Alane/Toluene mixed solution. Also during this year the research application has shifted to portable power because of the selection of compressed hydrogen storage as the fuel cell vehicle storage system of choice. The future direction of this work therefore will address a different set of targets than those associated with hydrogen storage (Table 1) for the fuel cell vehicle. Instead, the new challenge is developing aluminum hydride storage systems that meets DOE's 2015 hydrogen cost target of \$6.7/g-H₂ (primary) and \$33/g-H₂ (rechargeable) for medium portable power applications.

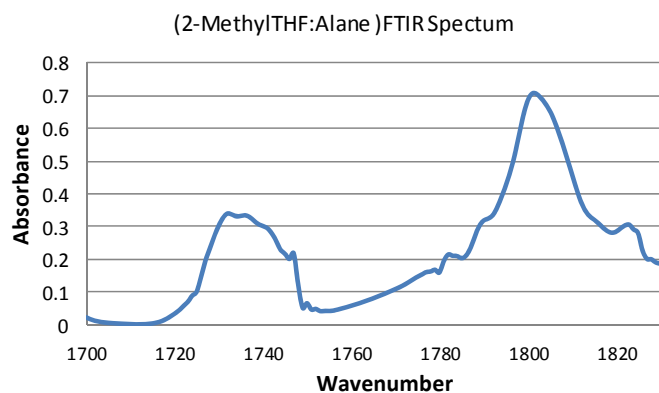


FIGURE 3. Figure 3 is the Fourier transform infrared spectrum of 2-MeTHF:Alane showing the 1727 wavenumber peak for the bis-compound and the 1803 wavenumber for the mono or dimer compound.

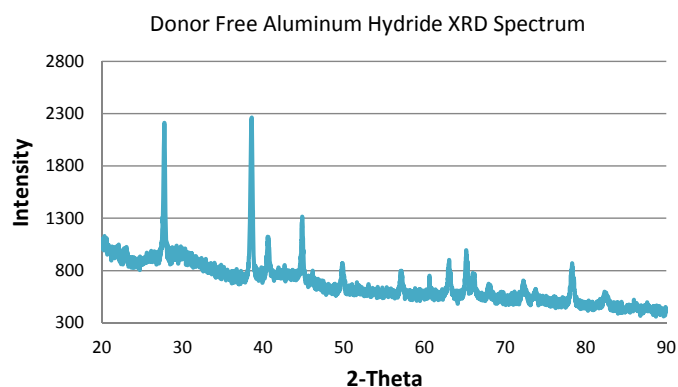


FIGURE 4. Figure 4 is the X-ray diffraction spectrum of donor free alane recovered from 2-MeTHF:Alane.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. Ni, Chengbao; Yang L.; 'Reaction pathways and roles of N-Alkylmorphine in amine-alane transamination: A mechanistic study', *Int. J Hydrogen Energy*, March (2014), p 5003.

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1. Aycock, D. F., *Organic Processes R&D*, Vol 11, 2007.
2. I.B. Gorrell. *et. al.*, *J. Chem. Soc., Chem. Commun.*, 1993.