IV.A.1e Aluminum Hydride Regeneration

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Project Start Date: October 1, 2005
Project End Date: June 30, 2010

Objectives

Develop an onboard vehicle storage system meeting DOE's targets that uses aluminum hydride for storing hydrogen:

- Produce aluminum hydride material with a hydrogen storage capacity greater than 9% gravimetric (kg-H_2/kg) and 0.13 kg-H_2/L volumetric.
- Develop practical and economical processes for regenerating aluminum hydride.
- Provide assistance in designing onboard fuel tank storage system for better than 6% gravimetric, 0.07 kg-H_2/L volumetric hydrogen storage capacities and well-to-wheels efficiencies greater than 60%.

Technical Barriers

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

(A) System Weight and Volume

(D) Durability/Operability

(E) Charging/Discharging Rates

Technical Targets

The current 2010 and 2015 hydrogen storage targets are listed in Table 1 along with our 2010 status using AlH_3. The well-to-wheels efficiency listed in Table 1 under the column for 2010 Status were taken from an independent analysis of an aluminum hydride storage system by R. K. Ahluwalia of Argonne National

Laboratory. This analysis was presented at the 2008 Hydrogen Annual Program Review and was based, in part, on data supplied by Brookhaven National Laboratory. Argonne's analysis assumes 70-wt% aluminum hydride slurry, and uses trimethylamine (TMA) as the stabilizing agent for regenerating aluminum hydride in determining the 55% well-to-wheels efficiency. The reactor temperature of 120°C listed in the row for full flow rate is the most recent value measured by Brookhaven that meets the DOE fuel flow target, and is for 40-wt% aluminum hydride slurry. The 0.036 gravimetric storage parameter listed in Table 1 is a measured value from 40-wt% slurry consisting of 9-wt% aluminum hydride particles.

TABLE 1. Progress in Meeting Technical Hydrogen Storage Targets Aluminum Hydride Regeneration

Storage Parameter	Units	2010/2015 Target	2010 Status
Gravimetric	wt% H_2	0.045/0.055	0.036
Volumetric	kg H_2/L	0.028/0.040	0.05
Full Flow Rate (temperature)	(g/s)/kW °C	0.02 80	0.02 100
Well-to-Wheels Efficiency	kW-H_2/kW	60%	55%
Refueling Time	min	3/2.5	To Be Determined

Accomplishments

Progress was realized in Fiscal Year (FY) 2010 towards meeting DOE's hydrogen storage targets by demonstrating the following three steps for the synthesis of AlH_3:

Step 1: formation of NR_3-AlH_3 by direct hydrogenation

- Five alane adducts formed by direct hydrogenation under mild conditions.
- Alane adducts also formed by reacting amine directly with alane.

Step 2: transamination exchange NR_3 for triethylamine (TEA)

- Transamination demonstrated starting with dimethlethylamine (DMEA) and TMA.

Step 3: separation of TEA-AlH_3

- Separation of TEA-AlH_3 successful with ~70% AlH_3 recovery (additional optimization is necessary to improve yields to achieve the target).

✦   ✦   ✦   ✦   ✦

Approach

The research direction under the Metal Hydride Center of Excellence being pursued by Brookhaven is to form hydride materials on the aluminum particle surfaces, and then stabilize these surface hydrides with chemical agents such as amines, ethers and/or lithium hydride. This approach is very similar to the well-studied cycling of sodium alanate with aluminum, where sodium hydride functions as the stabilizing agent. The main difference being that this research focuses on forming the hydride on the aluminum surface in a liquid phase rather than a high-pressure hydrogen gaseous environment. The advantages are that surface alane formation lowers considerably the hydrogenation pressure, and the liquid phase offers better thermal management and mass transport. The research plan therefore calls for first identifying the appropriate adduct(s), solvents, catalysts, and temperature and pressure conditions for making and "stabilizing" the aluminum hydride adduct in an effective and energy efficient manner. The second step, necessary to complete the regeneration cycle, is hydride recovery from the newly formed hydride-adduct. In addition to the regeneration studies, we have recently started to investigate slurry aluminum hydride decomposition kinetics as a function of temperature, catalysts and slurry type. The use of slurries is one approach towards meeting the three-minute refueling target.

Results

In FY 2010 we continued to explore low-energy methods to regenerate AlH_3 from Ti-catalyzed aluminum and hydrogen gas. In the past we demonstrated, in the presence of hydrogen gas and an inert solvent, the direct reaction of catalyzed aluminum with many tertiary amines to form amine-alane adducts. The practice of Ti doping to catalyze the reversible formation of aluminum-based hydrides has been the subject of many studies. These catalyzed materials are known to possess improved reaction kinetics in regards to the formation of alane complexes and reversibility when compared with those formed with un-doped materials. Our currrent model suggests that arrangements of Ti atoms on the surface of Al promote the chemisorption of hydrogen and the formation of transitory alane species. Based upon these calculations, it is believe that any alane formed on the surface of titanium-doped aluminum, survives long enough to react with a Lewis base, such as DMEA, to form an alane adduct. The alane adduct detaches from the aluminum surface and is significantly more stable than molecular AlH_3. Previously, we demonstrated the formation of dimethlethylamine alane (DMEAA) through the direct hydrogenation of Al* and
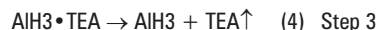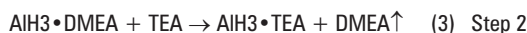
DMEA in one of three solvents (Et_2O, tetrahydrofuran or toluene) using the following reaction:

$$DMEA + Al^* + 3/2H2 \rightarrow AlH3 \cdot DMEA \quad (1) \; Step \; 1$$
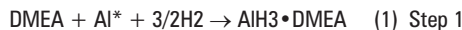
Attempts to produce a pure DMEAA adduct through direct hydrogenation without a solvent were not successful. DMEAA can also be synthesized by a direct reaction between AlH_3 and DMEA in a number of solvents including excess DMEA, Et_2O, tetrahydrofuran or toluene using the following reaction:

$$DMEA + AlH3 \rightarrow AlH3 \cdot DMEA \quad (2)$$
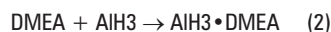
This year the focus was placed on recovering the alane from the amine-alane adduct with particular attention given to the (DMEAA) adduct. The recovery of intact AlH_3 from most amine-alane adducts is difficult since the temperatures required for adduct separation are typically greater than the AlH_3 decomposition temperature (~100ºC). The one known exception is triethylamine-alane (TEAA), which can be separated under a partial vacuum at 70ºC. In this effort, we demonstrate that although TEAA is not easily formed by direct hydrogenation, it can be formed by an amine exchange reaction (transamination) using DMEAA and TEA. This gives us a low-energy regeneration reaction which initially involves the direct formation of DMEAA from DMEA, catalyzed aluminum (Al*), and H_2 gas under moderate conditions (Eq. 1). This step is followed by transamination with TEA (Figure 1), and then finally the separation of TEAA for the recovery of alane (Figure 2):

$$AlH3 \cdot DMEA + TEA \rightarrow AlH3 \cdot TEA + DMEA\uparrow \quad (3) \; Step \; 2$$

$$AlH3 \cdot TEA \rightarrow AlH3 + TEA\uparrow \quad (4) \; Step \; 3$$

Step 2: amine exchange (transamination)

Transamination reaction to form TEA- AlH_3 from DMEA-AlH_3

AlH_3-DMEA + TEA $\xrightarrow[3hrs]{50ºC}$ AlH_3-TEA + DMEA↑

DMEA-AlH_3 + 4TEA
T = 50ºC
Pi = 1 bar
Pf = 26 mbar
time = 4.5 hrs

Al-H stretch in FTIR used to identify type of adduct:
DMEA-AlH_3: ~1710 cm⁻¹
TEA-AlH_3: ~1780 cm⁻¹

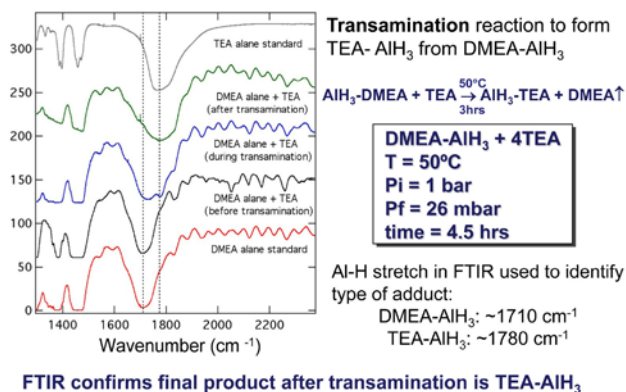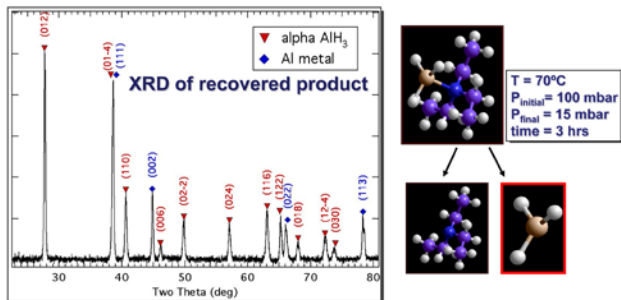FTIR confirms final product after transamination is TEA-AlH_3

FIGURE 1. Fourier Transform Infrared (FTIR) Spectra Confirming the Exchange of DMEA with TEA

Step 3: Separation of TEA-AlH₃

- TEA-AlH$_3$ successfully separated at 70ºC under vacuum (<100 mbar)
- Analysis of recovered AlH$_3$ (XRD and decomposition) suggests ~70% AlH$_3$ with 30% Al

FIGURE 2. X-Ray Diffraction (XRD) Spectrum Showing 70% Recovery of Aluminum Hydride from TEAA

Figure 3 shows the recovery of aluminum hydride by starting with DMEAA synthesized using Equation 2, and then combining steps 2 and 3 together for the recovery of aluminum hydride.

Conclusions and Future Directions

At the close of this project we have concluded that many alanes of tertiary amines may be synthesized at relatively modest hydrogen temperatures and pressures. However, the technical barriers of improving yields and slurry mass loadings need to be addressed before an alane storage system can meet all of DOE's hydrogen storage targets. These barriers define the future direction of alane research at BNL, and are listed as follows.

- Improve the well-to-tank efficiency from the estimate of 40-55% with TMA to the target efficiency of 70% with DMEAA.

Combining step 2 + 3: Separation of DMEA-AlH₃
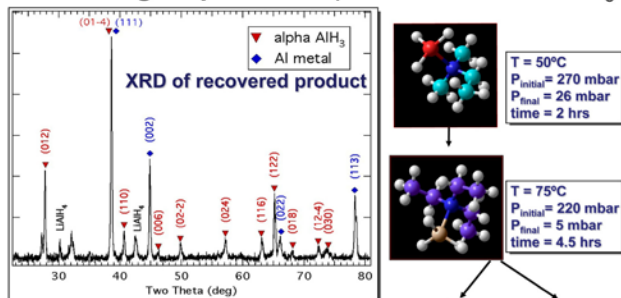
- DMEA-AlH$_3$ separated by combining steps 1 & 2
- Analysis of recovered AlH$_3$ (XRD) suggests ~35% AlH$_3$ with 65% Al when steps 1 & 2 are combined
- Improvements expected with optimization & washes to remove unwanted material

FIGURE 3. XRD Spectrum Showing 35% Recovery of Aluminum Hydride from DMEAA

- Work with private partners Aspen and University of Texas at El Paso on the synthesis of micron-sized alane particles.
- Investigate different slurry formulations with micron-sized alane particles for up to 8 wt% H$_2$ delivery at temperatures around 100ºC.
- Work with DOE's Hydrogen Engineering Center of Excellence on supplying alane material for the testing of onboard alane storage systems suitable for the proton exchange membrane fuel cell.

Special Recognitions & Awards/Patents Issued

1. Jason Graetz was awarded the "Presidential Early Career Award for Scientists and Engineers" (PECASE) for innovative research in hydrogen storage for automotive fuel-cell applications, 2009.

FY 2010 Publications/Presentations

1. J. Graetz, S. Chaudhuri, T.T. Salguero, J.J. Vajo, M.S. Meyer, F.E. Pinkerton, "Local bonding and atomic environments in Ni-catalyzed complex hydrides" *Nanotechnology*, **20** 204007 (2009).

2. J. Graetz, "New Approaches to Hydrogen Storage" *Chem. Soc. Rev.*, **38** 73 (2009).

3. Lacina, D.; Wegrzyn, J.; Reilly, J.J.; Celebi, Y; Graetz, J. "Characterization of Dimethylethylamine-alane and the Regeneration of Aluminum Hydride", *Energy Environ. Sci.*, DOI: 10.1039/c002064h (2010).

4. F.S. Manciua, L. Rezaa, W.G. Durrera, A. Bronsonb, D. Lacina, J. Graetz, "Spectroscopic and structural investigations of α-, β-, and γ-AlH$_3$ phases", J. Raman Spectrosc, DOI 10.1002/jrs.2722 (2010).

5. Graham, D.D.; Graetz, J.; Reilly, J.; Wegrzyn, J.; Robertson, I. M. "Location of Ti Catalyst in the Reversible AlH$_3$ Adduct of Triethylenediamine" *J. Phys. Chem. C*, Submitted (2010).

6. Lacina, D., Reilly, J., Celebi, Y., Johnson, J., Wegrzyn J., Graetz J., "The Reversible Synthesis of Bis(Quinuclidine) Alane via the Direct Reaction of Quinuclidine with Ti catalyzed Al and H$_2$", Chemical Engineering Journal, Submitted (2010).

7. "Regeneration of Aluminum Hydride studied with Raman and Infrared Spectroscopy", American Physical Society March Meeting 2010, Portland, Oregon, March, 2010.

8. "Regeneration of Aluminum Hydride studied with Raman and Infrared Spectroscopy", Materials Research Society Spring Meeting 2010, San Francisco, California, April, 2010.

9. "Regeneration of Aluminum Hydride", *International Forum for Hydrogen Storage 2010*, Tokyo, Japan, March, 2010.

10. "Structural Properties of Aluminum Hydride", *Symposium on Synchrotron Radiation Research 2010 - Materials Science on Metal Hydrides*, Hyogo, Japan, February, 2010.

11. "New Approaches to Hydrogen Storage", *Materials Science Colloquium*, Stony Brook, New York, February, 2010.

12. "Direct Hydrogenation of Aluminum to form Alane and Alanate Adducts" *Materials Research Society Fall Meeting*, Boston, MA, December, 2009.

13. "New Approaches to Hydrogen Storage", *China-America Frontiers of Engineering (CAFOE) Symposium*, Changsha, China, October, 2009.