

IV.A.6 Aluminum Hydride

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direction determined annually by DOE

Fiscal Year (FY) 2011 Objectives

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

- Produce aluminum hydride material with a hydrogen storage capacity greater than 9.7% gravimetric ($\text{kg-H}_2/\text{kg}$) and 0.13 $\text{kg-H}_2/\text{L}$ volumetric.
- Develop practical and economical processes for regenerating aluminum hydride.
- Assist in developing aluminum hydride slurry storage systems for better than 6% hydrogen gravimetric material density, 0.07 $\text{kg-H}_2/\text{L}$ volumetric hydrogen storage capacity, 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
- (B) System Cost
- (E) Charging/Discharging Rates

Technical Targets

Listed in Table 1 are the 2015 Hydrogen Storage targets along with BNL's current 2011 aluminum hydride project status. The well-to-wheels efficiency listed in the table under the column for 2011 Status was taken from an independent analysis of an aluminum hydride storage system by Argonne

National Laboratory. The Argonne analysis assumes 70-wt% aluminum hydride slurry, uses trimethylamine as the stabilizing agent for regenerating aluminum hydride and assumes the availability of low grade heat in determining the 55% efficiency. The tank's operating temperature of 80°C was the lowest temperature measured by BNL for AlH_3 slurries that meets the DOE fuel flow target of 0.02 (g/s)/kW. The criteria for meeting this flow target is 96% hydrogen release in 60 minutes or less from a 10 liter tank. The 0.0582 gravimetric storage parameter listed in Table 1 is a measured value from a 60-wt% slurry consisting of 9.7-wt% aluminum hydride particles and does not take into account the balance of plant weight.

TABLE 1. Progress in Meeting Technical Hydrogen Storage Targets

Aluminum Hydride Regeneration			
Storage Parameter	Units	2015 Target	2011 Status
Gravimetric	wt% H_2	0.055	0.0582
Volumetric	kg H_2/L	0.040	0.070
Full Flow Rate (temperature)	(g/s)/kW °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

FY 2011 Accomplishments

- Demonstrated 6 wt% H_2 slurries using mineral oil and glycols as the liquid carrier.
- In the aluminum hydride synthesis process identified diphenyl methane as a safe solvent substitute for toluene.
- Demonstrated that aluminum hydride slurries can meet DOE's fuel flow targets at temperatures less than the fuel cell operating temperature of 100°C.



Introduction

The FY 2011 objective was to achieve DOE's 2015 system fill target of 5 kg of H_2 in 3.3 minutes. Since aluminum hydride exists only as a solid, this objective was redirected towards formulating a 'pumpable' 6% by H_2 wt AlH_3 slurry. In order to meet this 1.5 kg H_2 per minute target, the slurry had to be stable against phase separation and sedimentation with a viscosity less than 1,000 centipoise. This type of slurry could be made, however the condition of remaining "pumpable" after the

release of hydrogen at temperatures of 120°C was not met by using either mineral oil or glycol as the liquid carriers.

Approach

AlH_3 is classified as a kinetically stabilized material. In the past we have used a nucleation and growth chemistry model to describe the stability of AlH_3 . This chemical model was useful in defining an induction period (nucleation) along with a kinetic decomposition period (growth). However recently, we found that a statistical approach (hyperbolic secant probability distribution function, Eqn. [1]) is very useful in describing the AlH_3 decomposition rate under isothermal conditions:

$$f(t) = (1/2t_k) \text{sech}[(\pi/2)(t-t_m)/t_k] \quad [1]$$

In Eqn. [1], t_m is the time when the decomposition rate reaches its peak value and $(1/2t_k)$ is the peak kinetic decomposition rate. The integration of the probability distribution function $f(t)$ over time yields the cumulative distribution function $F(t)$. This function is more convenient to work with than the probability density function, since it is the percent loss of hydrogen as a function of time. Integrating over time Eqn. [1] yields the following expression for the cumulative distribution function $F(t)$:

$$F(t) = (2/\pi) \tan^{-1}(\exp[(\pi/2)(t-t_m)/t_k]). \quad [2]$$

The induction period (IP) is now defined as the time when $F(t) = 0.02$. In other words, the time it takes for 2% decomposition. Setting $F(t) = 0.02$, replacing (t) with IP and solving for IP gives the following:

$$\text{IP} = t_m + (2t_k/\pi) \ln\{\tan(0.01\pi)\} = t_m - (2t_k/\pi)3.4601. \quad [3]$$

The time required for 96% release of hydrogen after the induction period is:

$$\Delta t(96\%) = (2t_k/\pi) \ln\{\tan(0.49\pi)\} - (2t_k/\pi) \ln\{\tan(0.01\pi)\} = (4t_k/\pi)3.4601. \quad [4]$$

Note that $\ln\{\tan(0.49\pi)\} = 3.4601$ and $\ln\{\tan(0.01\pi)\} = -3.4601$.

This model implies that surface coatings can increase the induction period by increasing t_m (see Eqn. [3]). Eqn. [4] shows that the time release of hydrogen $\Delta t(96\%)$ depends only on t_k and not t_m . Recall that $(1/2t_k)$ is the peak decomposition rate. Thus, the increase in IP, that results from increasing t_m , will essentially have no effect on the time it takes to release the remainder (96%) of the hydrogen. The results of this study support this model, since it shows that surface coatings can improve the stability of AlH_3 against decomposition; but once decomposition has started, the rate is then controlled by catalysts and the sample temperature.

Results

A 6% (or larger) by weight slurry is best achieved by using micron-sized particles. The preferred method

for making micron-sized AlH_3 particles is by nucleating and growing these particles from an alane-etherate in an inert solvent solution. The inert solvent can be benzene or toluene; and just recently, we found that diphenyl methane is also a suitable medium. In simple terms, AlH_3 solubility decreases with increasing temperatures so by raising the temperature one would expect aluminum hydride to precipitate out of solution. The complication is that aluminum hydride decomposes at temperatures above 100°C. Thus far, only the alane etherate compounds have yielded aluminum hydride by this method. Attempts to recover aluminum hydride from alane-amine complexes have not yet been successful by this approach. We are, however, able to control particle size by controlling the rate at which the diethyl ether is removed from the reactor. Controlling the particle morphology is more challenging. Figure 1 shows individual particles and clusters of particles with aspect ratios close to 1, yet Figure 2 shows that under very similar conditions rod-shaped particles can also be produced. These particles are formed in batch and semi-continuous reactors. The batch reactor is 1 liter in size and makes 1.25 gram of product per batch. The recovered AlH_3 is then washed in either diethyl ether or hydrochloric acid. The semi-continuous method has a port connection for introducing the alane-etherate to a 1.5 liter reactor and we have used this method to produce up to 5 grams of AlH_3 . After the wash, a milliliter of diethylene dibutyl ether glycol (density 0.80 g/ml) is mixed with the 1.25 grams of AlH_3 to make a nominally 60% aluminum hydride-glycol slurry. A similar procedure was used to prepare a mineral oil slurry where 4 milliliters of mineral oil and 0.15 grams of dispersant (Triton x-100) was used along with the AlH_3 .

A series of isothermal kinetic decomposition experiments were performed on these aluminum hydride glycol and mineral oil slurries. Figure 3 shows plots of

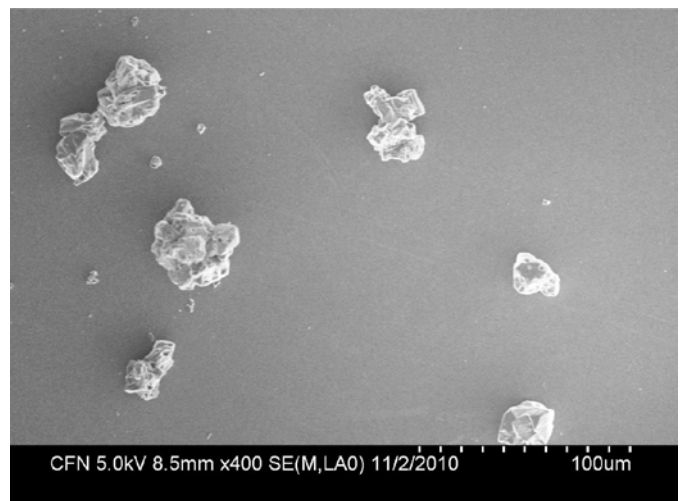


FIGURE 1. Electron micrograph of 97% pure alpha aluminum hydride particles in cluster shapes precipitated from an alane-etherate/toluene solution (sample AH-3390).

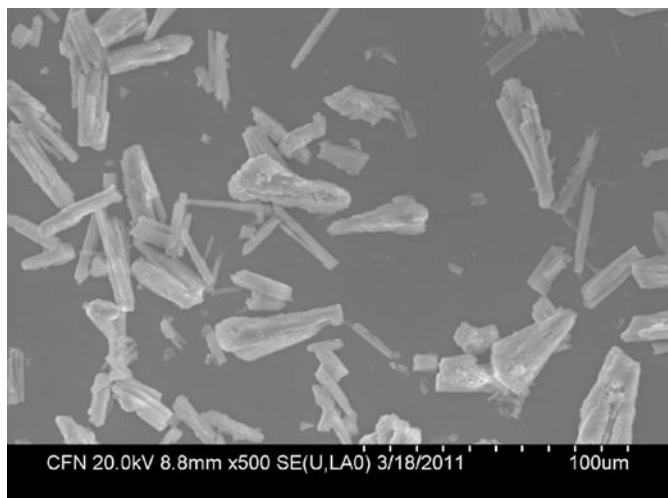


FIGURE 2. Electron micrograph of 97% pure rod shaped alpha aluminum hydride particles precipitated from an alane-etherate/toluene solution (Sample AH-3399).

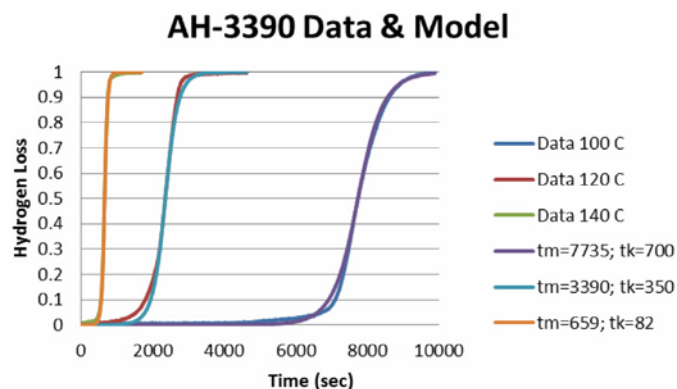


FIGURE 3. Fractional decomposition of AlH_3 at the three temperatures of 100, 120 and 140°C showing experimental data and fit using the statistical model.

the hydrogen loss as a function of time for the aluminum hydride-glycol slurry at three temperatures: 100, 120 and 140°C. Also plotted on this figure are the results from the statistic model with the corresponding two parameter fit (t_m , t_k). The good fit between the experimental data and model allows us to discuss the data in terms of t_m and t_k . For the catalyzed glycol slurries $t_k \sim 250$ ($T = 120^\circ\text{C}$), while this parameter is much greater for the mineral oil slurries $t_k \sim 700$ ($T = 120^\circ\text{C}$). At this point we can only speculate why the catalyzed glycol slurries have better decomposition kinetics than the mineral oil slurries. Figure 4 shows how the acid wash affects the IP. Incorporating a wash at the end of the synthesis increases the IP by applying an oxide/hydroxide coating on the surface of the AlH_3 particle. In this experiment one half the particles were acid washed and the other half were only washed in diethyl ether. Note that even though the IP increased after the acid wash, the peak

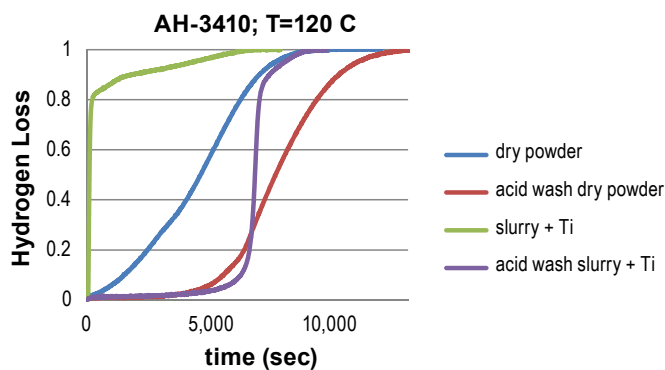


FIGURE 4. AlH_3 decomposition data for particles with and without acid wash as a function of time.

decomposition rate t_k remained essentially constant ($t_k = 100$ & 300 for the two Ti-catalyzed samples; $t_k = 2,100$ and $2,400$ for the two samples without catalysts). The non-symmetric result (green line) for the catalyzed slurry in Figure 4 has been attributed to non-uniform mixing of the catalyst in the slurry.

Conclusions and Future Directions

- 6 wt% H_2 AlH_3 slurries were prepared and performed satisfactory at temperatures less than 100°C .
- Determined that surface coatings can stabilize AlH_3 against the start of decomposition. We also found that using a hydrochloric acid wash is an effective means of applying surface coatings on one micron or larger AlH_3 particles.
- The AlH_3 decomposition rates after the induction period are controlled mainly by temperature and catalyst loading. Morphology, particle size and the type of liquid carrier also affect decomposition kinetics, but to a lesser extent.
- The future direction is to develop the procedure and hardware to increase AlH_3 production from 5 grams/week to 50 grams/week.

FY 2011 Publications

1. B.M. Wong, D. Lacina, I.M.B. Nielsen, J. Graetz, and M.D. Allendorf, "Thermochemistry of Alane Complexes for Hydrogen Storage: A Theoretical and Experimental Investigation" *J. Phys. Chem. C*, **115** 7778 (2011).
2. D. Lacina, J. Wegrzyn, J. Reilly, J. Johnson, Y. Celebi and J. Graetz, Regeneration of Aluminum Hydride using Trimethylamine" *J. Phys. Chem. C*, **115** 3789 (2011).
3. J. Graetz, J.J. Reilly, V.A. Yartys, J.P. Maehlen, B.M. Bulychev, V.E. Antonov, B.P. Tarasov, I.E. Gabis, "Aluminum hydride as a hydrogen and energy storage material: past, present and future" *J. Alloys Compd.* doi:10.1016/j.jallcom.2010.11.115 (2010).

4. D. Lacina, J. Reilly, J. Johnson, J. Wegrzyn and J. Graetz "The Reversible Synthesis of Bis(Quinuclidine) Alane" *J. Alloys Compd.* DOI: 10.1016/j.jallcom.2010.10.010. (2010).
5. D.D. Graham, J. Graetz, J. Reilly, J. Wegrzyn, I.M. Robertson, "Location of Ti Catalyst in the Reversible AlH₃ Adduct of Triethylenediamine" *J. Phys. Chem. C*, **114** 15207–15211 (2010).
6. F.S. Manciu, L. Reza, W.G. Durrera, A. Bronson, D. Lacina and J. Graetz, "Spectroscopic and structural investigations of α -, β -, and γ -AlH₃ phases," *J. Raman Spectrosc.*, **42** 512-516 (2011).
7. D. Lacina, J. Wegrzyn, J. Reilly, Y. Celebi, J. Graetz "Regeneration of Aluminum Hydride using Dimethylethylamine" *Energy Env. Science, Energy Environ. Sci.*, **3** 1099 (2010).
3. "Aluminum hydride as an energy and hydrogen storage material: past present and future" Plenary Lecture, International Symposium on Metal-Hydrogen Systems (MH2010), Moscow, Russia, July, 2010.
4. "Regeneration of Aluminum Hydride", *International Energy Agency (IEA) Task 22 Experts Meeting*, Death Valley, CA, April, 2010.
5. "Regeneration of AlH₃ studied with Raman and Infrared Spectroscopy", *Materials Research Society Spring Meeting*, San Francisco, CA, April, 2010.
6. "Regeneration of Aluminum Hydride", *International Forum for Hydrogen Storage 2010*, Tokyo, Japan, March, 2010.
7. "Structural Properties of Aluminum Hydride", *Symposium on Synchrotron Radiation Research 2010 - Materials Science on Metal Hydrides*, Hyogo, Japan, February, 2010.
8. "New Approaches to Hydrogen Storage", *Materials Science Colloquium*, Stony Brook, New York, February, 2010.

FY 2011 Presentations

1. "Regeneration of Aluminum-Based Hydrides", *International Energy Agency (IEA) Task 22 Experts Meeting*, Fremantle, WA, Australia, January, 2011.
2. "Regeneration of aluminum-based hydrides" *The International Chemical Congress of Pacific Basin Societies*, Honolulu, HI, December, 2010.