

IV.A.5 Aluminum Hydride

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 direction determined annually by DOE

Fiscal Year (FY) 2012 Objectives

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

- Produce aluminum hydride material with a hydrogen storage capacity greater than 9.7% gravimetric (kg-H₂/kg) and 0.13 kg-H₂/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 kg-H₂/L volumetric hydrogen storage capacity, and well-to-wheels efficiencies greater than 60%.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen 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

Table 1 is a listing of the 2015 DOE hydrogen storage targets along with BNL's current 2012 aluminum hydride project status. The well-to-wheels efficiency listed in the table under the column for 2012 Status was taken from an

independent analysis of an aluminum hydride storage system by Argonne National Laboratory. The 0.0582 gravimetric storage parameter listed in Table 1 is a measured value from decomposing 60-wt% slurry consisting of 9.7-wt% aluminum hydride particles. It does not take into account the balance-of-plant weight. In FY 2012 progress was realized in meeting the refueling target by formulating 60-wt% alane slurry using di-ethylene glycol as the liquid carrier. At 25°C the slurry viscosity was measured to be 1,500 centipoise.

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

Storage Parameter	Units	2015 Target	2012 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	TBD

TBD – to be determined

FY 2012 Accomplishments

- Measured the viscosities for four different ATK/solvent slurries as a function of composition, shear rate and temperature.
- Identified the 60% by wt. ATK in a 40% by wt. di-ethylene glycol di-butyl ether (DGDE) slurry as having viscosities less than 1,500 centipoise at 25°C.
- Demonstrated 96% hydrogen release in 88 seconds at 180°C for a catalyzed 60% by wt. ATK in a 40% by wt. DGDE slurry.
- Demonstrated 96% hydrogen release in 2,860 seconds at 100°C for a catalyzed 60% by wt. ATK in a 40% by wt. DGDE slurry.



Introduction

The FY 2012 objective was to achieve DOE's 2015 system fill target of 5 kg of H₂ in 3.3 minutes. Since aluminum hydride exists only as a solid, this objective was directed towards formulating a "pumpable" 6% by H₂ wt. AlH₃ slurry. In order to meet this 1.5 kg H₂ per minute target, the slurry had to be stable against phase separation and sedimentation with a viscosity less than 1,500 centipoise (cP). This year a pumpable 6% by H₂ wt. AlH₃ slurry was formulated with viscosities less than 1,500 cP; however,

further work is needed to improve these slurries against phase separation due to particle sedimentation.

Approach

AlH_3 can be classified as a kinetically stabilized material. A nucleation and growth chemistry model was used in the past to describe the decomposition rates of AlH_3 . This chemical model was useful in defining both an induction period (IP) along with a kinetic decomposition period. However, under isothermal conditions, a statistical approach was also found to be helpful in describing the AlH_3 decomposition rate. The statistic of choice is the hyperbolic secant probability distribution function, which can be written as:

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

In the above equation 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 however 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 Equation [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 IP is now defined as the time when $F(t) = 0.02$. In other words, the time it takes for the first 2% decomposition. Setting $F(t) = 0.02$, replacing (t) with IP and solving for IP gives the following:

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

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 Equation [3]). Eqn. [4] shows that the time release of hydrogen Δt (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 from increasing t_m essentially has 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

This year's results were the measurements the viscosities and decomposition rates of several different types of 6-wt% H_2 alane slurries. The primary goal was to formulate 6-wt% H_2 alane slurries with viscosities around 1,500 centipoise. Another goal was to determine changes in aluminum hydride decomposition rates because of the slurry form. The aluminum hydride used in this study was supplied by Savannah River National Laboratory. It goes by the name of the company who made the material—ATK. The reason for using ATK-alane was that this was the alane material under consideration by DOE's Hydrogen Storage Engineering Center of Excellence. Figure 1 is an electron micrograph of the as-received ATK-alane material. No attempt was made to improve slurry properties by optimizing particle size distributions. The aluminum hydride particles were mixed (as-received) with the liquid carriers without changing their particle size.

Tests were conducted on the 6-wt% H_2 slurries by blending as-received ATK particles with several different types of liquid carriers. However, both the viscosities and kinetics of the slurry were modified by various chemical additive packages. The chemical additives tested this year were triton based ionic surfactants (X-10 and X-100), as well as the known alane de-stabilizers (LiH and/or Ti). The use of surfactants did lower the slurry's viscosities at low temperatures ($T < 25^\circ\text{C}$), but had little effect at higher temperatures. Since the surfactant study is considered preliminary, more data is needed before any conclusion

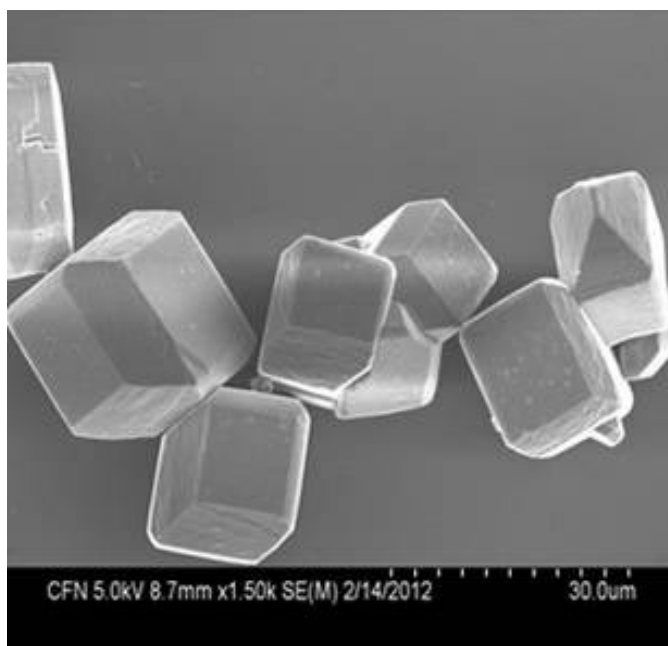


FIGURE 1. Electron micrograph of the as-received ATK aluminum hydride particles

can be reached. On the other hand, the addition of LiH and Ti increased quite significantly the alane's decomposition rate. This was most noticeable for the DGDE-based slurry. Figure 2 shows the per cent loss of hydrogen as a function of time. In this experiment the test reactor is lowered into a constant temperature 180°C oil bath. The liquid carrier in the test was (DGDE) with Ti and LiH additions. The figure lists both the experimental data along with the model as given by equation 2. The half-life was 74 seconds ($t_m=74$ sec) and where the maximum decomposition rate was $1/(2 \cdot t_k)$ where $t_k=20$ sec). One reason for the deviation between model and experiment is shown by Figure 3. This figure gives the internal temperature as a function of time of the test reactor as it's lowered into the temperature 180°C bath. One sees a

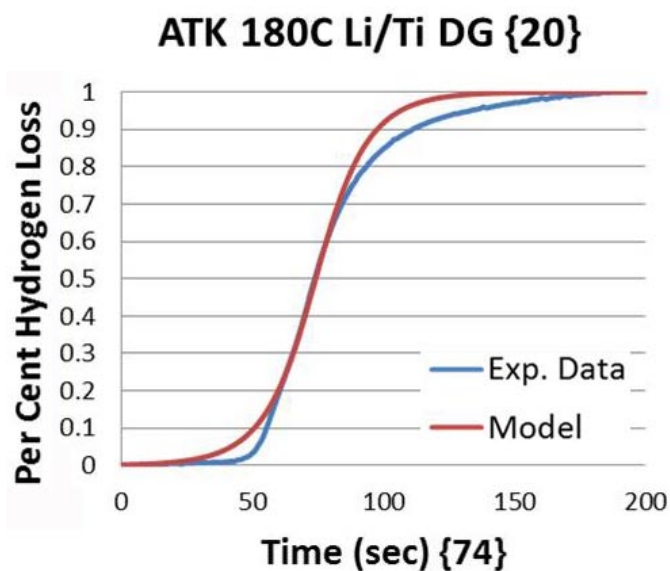


FIGURE 2. Comparison of the model (Eqn. 2; with $t_k=20$ seconds and $t_m=74$ seconds) against the experimental data of the time release of hydrogen at 180°C for a 60% by wt. ATK slurry in DGDE that was activated with Ti and LiH.

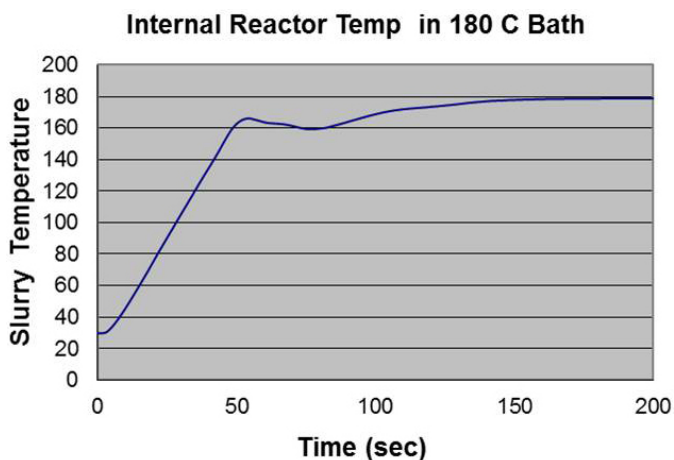


FIGURE 3. Slurry temperature as a function of time when placed in a 180°C oil bath

nearly linear increase in the alane sample temperature for the first 50 seconds. After the first 50 seconds, the sample cooling due to its endothermic nature is clearly evident. The isothermal model of Equation 2 does not account for the endothermic cooling, and thereby predicts higher hydrogen losses than actually measured.

Figure 4 shows the probability distribution of hydrogen loss for 6-wt% H₂ slurries with four different liquid carriers (DGDE, H350, C50S, and mineral oil); as well as the hydrogen loss for dry ATK particles (ATK-Ref). H350 and C50S are both high temperature, heat transfer fluids that were purchased from Julabo USA, Inc. The common material name for H350 is di-benzltoluene, and for C50S the common material name is di-methylsiloxane. The most notable fact about the data of Figure 4 is that the (DGDE) slurry showed increased alane decomposition in relation to powdered ATK-Ref. dry particles. All other slurries had slower kinetic decomposition rates than ATK-Ref. These tests were run without the addition of any catalysts. More tests are needed to understand these results. It is speculated that the higher decomposition rates with DGDE slurries are related to surface/solvent chemistry, since DGDE completely wets aluminum hydride. Since neither H350, C50S and mineral oil completely wet the aluminum hydride particles, these slurries appear to be more stable against decomposition than the dry ATK particles. The effect of changing particle/solvent surface tension on alane decomposition rates is at this time an open question. Also, at 120°C these measured decomposition rates are such that endothermic effects (as seen in Figure 3 at 180°C) were not observed, and the isothermal model is appropriate.

Figure 5 lists the viscosity data as function of shear rate for four different 6-wt% H₂ slurries. The data was taken at 25°C using a Brookfield DV-E viscometer. No surfactants

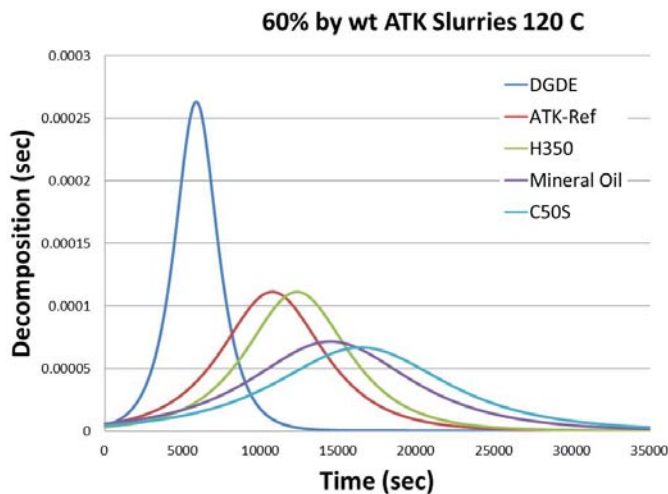


FIGURE 4. Plots at 120°C of the decomposition probability distribution functions (Eqn. 1) as function of time for four ATK slurries and dry material

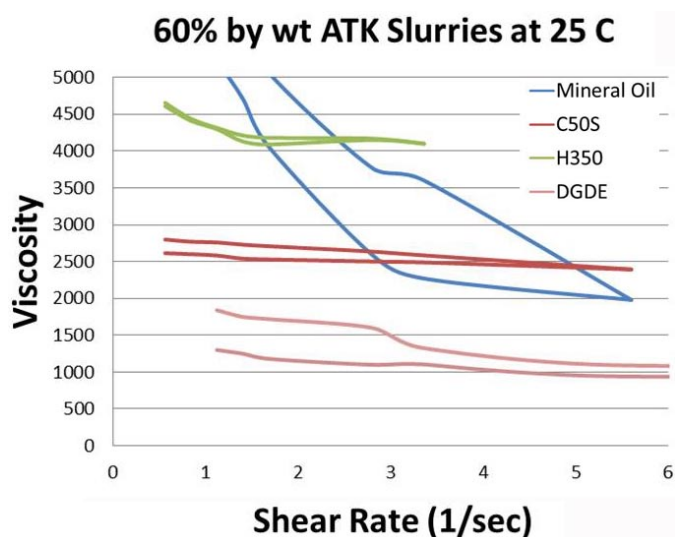


FIGURE 5. Viscosity measurements of four different 60% by wt ATK slurries at 25°C

were used to reduce the slurry's viscosity in these tests. The data presented in Figure 5 shows that the 60% by wt. DGDE alane slurry had the lowest viscosity tested. It had measured viscosities below 1,500 cP over all the test range of shear rates. Although the viscosity target can be met, further research is needed to improve the stability of these slurries. This research would entail reducing the aluminum hydride particle size, and also employ liquid carriers with densities above 1.20 gm/cm³. This combination would significantly improve slurry stability by reducing particle sedimentation velocity.

Conclusions and Future Directions

- Develop a 100 gram/week capability for synthesizing 1-10 micron AlH₃ particles.
- Improve the stability of AlH₃ slurries by lowering slurry sedimentation rate by reducing particle sizes and increase the liquid carrier density.
- For the lower temperature range ~0°C maintain slurries viscosities <1,500 cP.
- Optimize procedures for activating AlH₃ slurries for enhanced hydrogen release.

FY 2012 Presentations

1. "Tailoring aluminum hydride for mobile hydrogen storage systems" World Hydrogen Energy Conference, Toronto, June, 2012.
2. "Synthesis and Regeneration of Aluminum Hydride", *International Energy Agency (IEA) Task 22 Experts Meeting*, Heidelberg, Germany, May, 2012.
3. "Conversion Electrodes for Lithium Batteries" 243rd of the *American Chemical Society Meeting*, San Diego, March, 2012.
4. "Recent Developments with Aluminum Hydride", *Materials Challenges in Alternative and Renewable Energy (MCARE)*, Clearwater, Florida, February, 2012.