

## IV.A.1e Aluminum Hydride Regeneration

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### Objectives

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

- Produce aluminum hydride ( $\text{AlH}_3$ ) material with a hydrogen storage capacity greater than 9% 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.
- Provide assistance in designing onboard fuel tank storage system for better than 6% gravimetric, 0.07  $\text{kg-H}_2/\text{L}$  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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (D) Durability/Operability
- (E) Charging/Discharging Rates

### Technical Targets

The 2010 and 2015 hydrogen storage targets are listed in Table 1 along with our 2009 status using  $\text{AlH}_3$ . The well-to-wheels efficiency listed in Table 1 under the column for 2009 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 (BNL). Argonne's analysis assumes a 70 wt% aluminum hydride slurry, and uses trimethylamine 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 a 40 wt% aluminum hydride slurry (see Figure 4). The gravimetric storage parameter of 0.036 is a measured value from a 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	2009 Status
Gravimetric	wt% $\text{H}_2$	0.06/0.09	0.036
Volumetric	$\text{kg H}_2/\text{L}$	0.045/0.081	0.05
Full Flow Rate (temperature)	(g/s)/kW °C	0.02 80	0.02 120
Well-to-Wheels Efficiency	kW- $\text{H}_2$ /kW	60%	55%
Refueling Time	min	3/2.5	TBD

TBD - to be determined

### Accomplishments

Progress was realized in Fiscal Year 2009 towards meeting DOE's storage targets with the following four findings:

- (1) Several new pathways were identified to form  $\text{AlH}_3$  adducts from  $\text{H}_2$  and catalyzed aluminum ( $\text{Al}^*$ ):
  - Quinuclidine alane:  
 $\text{C}_7\text{H}_{13}\text{N} + \text{Al}^* + 3/2\text{H}_2 \rightarrow \text{C}_7\text{H}_{13}\text{N-AlH}_3$
  - Dimethylethylamine alane:  
 $\text{C}_4\text{H}_{11}\text{N} + \text{Al}^* + 3/2\text{H}_2 \rightarrow \text{C}_7\text{H}_{13}\text{N-AlH}_3$
  - Hexamine alane:  
 $\text{C}_6\text{H}_{12}\text{N}_4 + \text{Al}^* + 3/2\text{H}_2 \rightarrow \text{C}_6\text{H}_{12}\text{N}_4\text{-AlH}_3$
  - Trimethylamine alane:  
 $\text{C}_3\text{H}_9\text{N} + \text{Al}^* + 3/2\text{H}_2 \rightarrow \text{C}_3\text{H}_9\text{N-AlH}_3$
- (2) Improved adduct separation by introducing triethylamine (TEA) transamination step for the recovery of  $\text{AlH}_3$  from  $\text{AlH}_3$  adducts.
- (3) Two low energy pathways identified for complete regeneration of  $\text{AlH}_3$  using trimethylamine (TMA) and dimethylethylamine (DMEA) (each step verified independently).

- (4) Initial results on H<sub>2</sub> evolution rates from AlH<sub>3</sub> in slurries showed promising results for Ti catalyzed AlH<sub>3</sub> in C<sub>10</sub>H<sub>22</sub>O<sub>2</sub>.



## Introduction

A cornerstone of the hydrogen economy is the hydrogen fuel cell car. Although there are many barriers before consumers fully accept the fuel cell car, a key barrier is the poor volumetric energy densities of conventional hydrogen storage media. Solid-state storage in metal hydrides or complex hydrides offers enhanced volumetric hydrogen densities, however they have either poor gravimetric capacity (<4 wt%) or release hydrogen at temperatures (>300°C) that are impractical for a fuel cell car. A class of kinetically stabilized hydrides (e.g. AlH<sub>3</sub>, LiAlH<sub>4</sub>, Mg(AlH<sub>4</sub>)<sub>2</sub>) offers some new hope with high volumetric (>80g H<sub>2</sub>/L) and gravimetric (>10 wt%) energy densities and with low decomposition temperatures (<120°C). However, these materials typically have very high hydrogenation pressures (>1 kbar) and are generally prepared from costly organometallic reactions. Therefore, Brookhaven has been interested in developing new low-cost methods to regenerate these kinetically stabilized hydrides from spent (hydrogen depleted) material and hydrogen gas. Of the high capacity, kinetically stabilized hydrides one of the most promising storage materials is AlH<sub>3</sub>. Reports of molecular alane (e.g. AlH<sub>3</sub>, Al<sub>2</sub>H<sub>6</sub> and Al<sub>4</sub>H<sub>6</sub>) formation from aluminum and hydrogen under a variety of conditions support the recent suggestion that transient alane species form on the surface of catalyzed aluminum in the presence of hydrogen gas [1]. Based on this hypothesis, last year we developed a method to prepare alane and alane adducts by “stabilizing” the transient alane formed on the catalyzed aluminum surface [2]. In Fiscal Year 2009 various amine alanes were directly synthesized from aluminum and hydrogen gas in solution at low pressures and temperatures, and we began investigating aluminum hydride slurries.

## Approach

The research direction under the Metal Hydride Center of Excellence (MHCoe) 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 alane 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 way to meet the three minute refueling target. However, to improve the well-to-wheel efficiencies to above 60%, the aluminum hydride decomposition temperature needs to be lowered to less than 100°C, and more energy efficient regeneration schemes are still required.

## Results

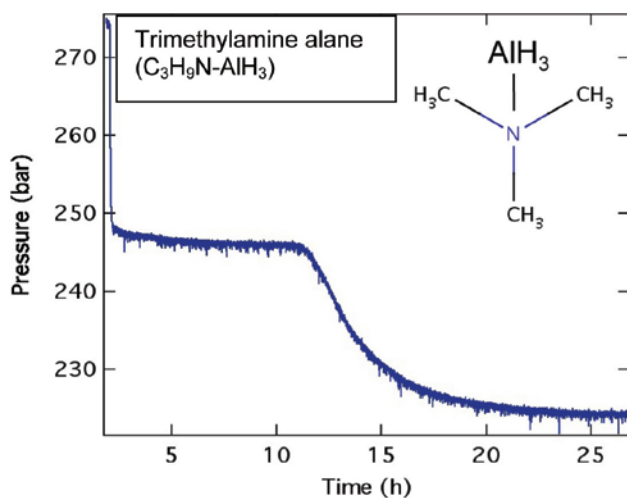
**Regeneration of AlH<sub>3</sub> – Stabilization.** The Ti-catalyzed Al (henceforth denoted as Al\*) was prepared by first synthesizing AlH<sub>3</sub> in an ethereal reaction between LiAlH<sub>4</sub> and AlCl<sub>3</sub>. The TiCl<sub>3</sub> catalyst was added to the diethyl ether solution and filtered to remove the LiCl precipitate. The filtrate (AlH<sub>3</sub> + Ti + Et<sub>2</sub>O) was dried and decomposed under vacuum at 373 K for one hour to remove the ether and decompose the hydride. The addition of Ti significantly destabilized the hydride (AlH<sub>3</sub>) and decomposition occurred readily at room temperature using a nominal concentration of 2 mol% Ti. Powder X-ray diffraction of the dried and decomposed material showed no evidence of the hydride phase and confirmed that the final product was pure Al\*.

Hydrogenation experiments were performed in a 300 ml Parr Instruments (P <100 bar) and a PPI (P >100 bar) stainless steel stirred reactor. The reactors were loaded and sealed in an Ar-filled glove box with typically between 1-1.5 g of Al\*. Thermocouples were used to monitor the internal and external temperatures and the gas pressure in the reactor was measured using a pressure transducer.

Figure 1 shows the formation of AlH<sub>3</sub>-TMA occurring at moderate pressures (~250 bar) in toluene after a 10-12 hour incubation period. The hydrogenation reaction is shown in equation (1):

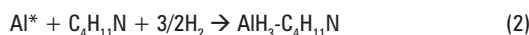


This reaction occurs more quickly in ether solvents such as diethyl ether and tetrahydrofuran (THF) and exhibits a shorter incubation period. TMA is a gas under ambient conditions, while the TMA-AlH<sub>3</sub> product is a crystalline solid that appears to be soluble in toluene, diethyl ether and THF.



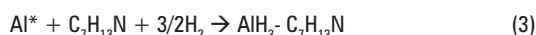
**FIGURE 1.** Formation of Trimethylamine Alane as a Function of Time at 298 K in THF

Figure 2 shows that the formation of  $\text{AlH}_3$ -DMEA occurring readily at low pressures (<60 bar) after an 8-10 hour incubation period. The hydrogenation reaction is shown in equation (2):



In this case the amine precursor ( $\text{C}_4\text{H}_{11}\text{N}$ ) and the amine alane product ( $\text{AlH}_3\text{-C}_4\text{H}_{11}\text{N}$ ) are both liquids.

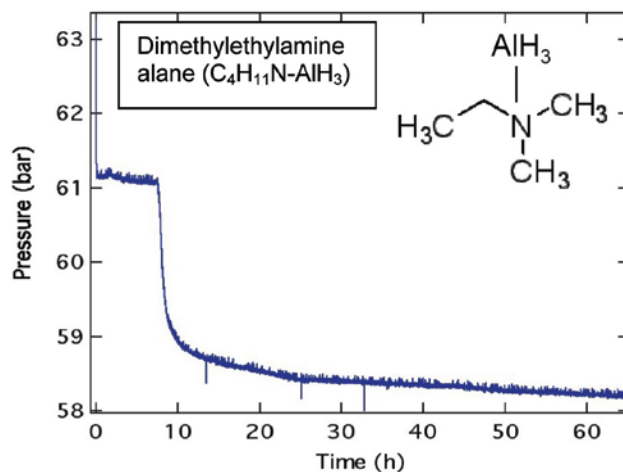
Figure 3 shows that the formation of  $\text{AlH}_3$ -quinuclidine occurring at low pressures (<62 bar) with an incubation period of around 5 hours. The hydrogenation reaction is shown in equation (3):



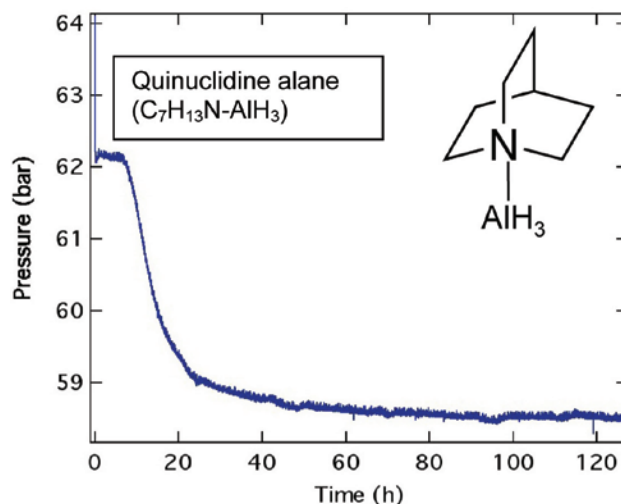
Both  $\text{AlH}_3$ -TMA and  $\text{AlH}_3$ -quinuclidine are solids at room temperature.  $\text{AlH}_3$ -quinuclidine and  $\text{AlH}_3$ -TMA are at least partially soluble in the ether solvents, but the solid product can easily be distilled from the solution.

**Regeneration of  $\text{AlH}_3$  – Adduct Separation.** The previous results demonstrate that a number of different ligands can be used to stabilize  $\text{AlH}_3$ . A second step, where the alane adduct is separated and  $\text{AlH}_3$  is recovered, is required to complete the regeneration cycle. Despite numerous attempts most of the alane amines that form readily by direct hydrogenation can only be separated at high temperatures where  $\text{AlH}_3$  is unstable.

The challenge of recovering intact  $\text{AlH}_3$  from the alane amine can be overcome by introducing a transamination step. In this process the more stable alane amine is displaced by a second alane amine that is less thermally stable. One example of a less stable alane amine is  $\text{AlH}_3$ -TEA (TEA = triethylamine).  $\text{AlH}_3$ -TEA is a liquid at room temperature and can be separated into

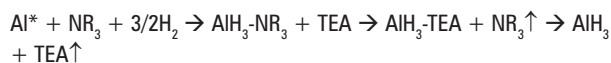


**FIGURE 2.** Formation of Dimethylethylamine Alane as a Function of Time at 296 K in THF



**FIGURE 3.** Formation of Quinuclidine Alane as a Function of Time at 298 K in THF

$\text{AlH}_3$  (solid) and TEA (liquid) by heating to  $75^\circ\text{C}$  under a nitrogen sweep. The full regeneration procedure for  $\text{AlH}_3$  can be envisioned as shown below where  $\text{NR}_3$  represents an amine:

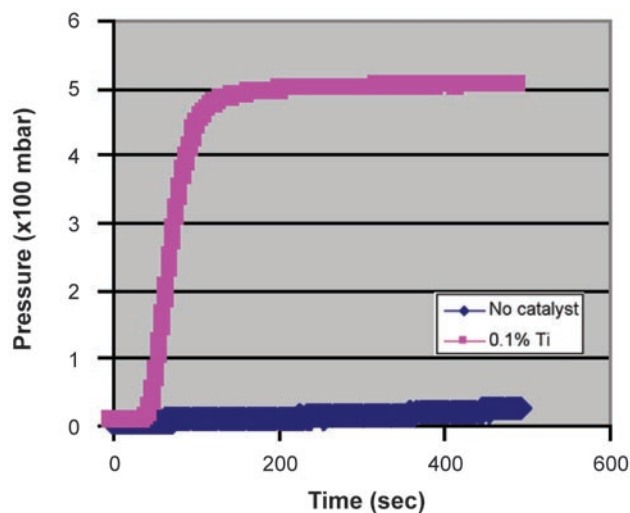


**Alane Slurries.** A constant volume Sieverts apparatus with a controlled temperature ( $30\text{-}150^\circ\text{C}$ ) oil bath was used to determine the hydrogen release rates of alane slurries. The liquid carrier used for the slurry tests was diethylene glycol dibutyl ether (DEGDBE). DEGDBE was initially selected because it is water immiscible, has a very low vapor pressure, and mixes well with (wets) aluminum hydride particles. At the reactor temperature of  $150^\circ\text{C}$  the

vapor pressure of DEGDBE was measured to be less than 1 mbar in the Sieverts. For reference, 0.3 g of dry aluminum hydride, consisting of 9 wt% hydrogen upon decomposition, raises the pressure in the Sieverts to just over 500 mbar(s). The experiment consisted of testing three samples; 1) dry 0.3 g  $\text{AlH}_3$ , 2) 0.3 g of  $\text{AlH}_3$  in 40 wt% slurry with no catalyst, and 3) 0.3 g of  $\text{AlH}_3$  in 40 wt% slurry with 0.1% Ti catalyst addition. All samples tested raised the pressure in the Sieverts to 500 mbar which indicates complete decomposition. The major difference in this test was the time to reach complete decomposition. Figure 4 plots the hydrogen release at 120°C for the two slurries tested, and shows the significant increase in decomposition rates with the use of 0.1% Ti catalyst. Further tests will be directed towards slurries consisting of larger sized aluminum hydride particles to increase the allowable solid mass loading of the slurry. Furthermore, the inert DEGDBE liquid carrier will be replaced by a liquid that also releases hydrogen. The target is to formulate an alane slurry with greater than 8 wt% hydrogen release at 100°C.

## Conclusions and Future Directions

At this point we have concluded that many alanes of tertiary amines may be synthesized at relatively modest hydrogen pressures using activated Al, provided steric effects are not inhibiting. Thus simple amines such as DMA and DMEA react readily, as well as more complex, cyclic amines such as TEDA, quinuclidine and hexamine where the functional N atom is exposed and in a constrained spatial configuration. In conclusion, this year's research has reinforced the concept of using alane as a hydrogen storage material for fuel cell vehicles. However several technical barriers need to be overcome before an alane storage system becomes viable. These



**FIGURE 4.**  $\text{H}_2$  Release at 120°C from 40 wt%  $\text{AlH}_3$  Slurry With/Without Ti Catalyst

barriers define the future direction of alane research at BNL, and are listed as follows.

- High yield, regeneration of  $\text{AlH}_3$  with  $E$  penalty  $\leq 73$  kJ/ $\text{H}_2$  (30% of fuel energy).
- Continue investigation of alane slurries and liquid carriers for 8 wt%  $\text{H}_2$  storage at temperatures around 100°C.
- Work with partners (Argonne National Laboratory) to determine mass balance and energy cost for alane recovery from spent aluminum.
- Work with partners (MHCoe) on safety and engineering of alane regeneration and slurry systems.

## Special Recognitions & Awards/Patents Issued

1. J. Graetz, J. Wegrzyn, J. Reilly, "Regeneration of Aluminum Hydride" US Patent application No. 11/831,297 filed July 31, 2007, and issued as US Patent No. 7,521,037 on April 21, 2009.
2. G. Sandrock, J. Reilly, J. Graetz, J. Wegrzyn, "Activated aluminum hydride hydrogen storage compositions and uses thereof" US Patent application No. 20070025908, filed July 29, 2005. (patent pending)

## FY 2009 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. J. Graetz, J. Wegrzyn and J.J. Reilly, "Regeneration of lithium aluminum hydride ( $\text{LiAlH}_4$ )", *J. Amer. Chem. Soc.* **130** 17790 (2008).
4. M. Tkacz, T. Palasyuk, J. Graetz, S. Saxena, "High-pressure Raman spectroscopy study of polymorphs of  $\text{AlH}_3$  and  $\alpha 3$ " *J. Raman Spectrosc.* **39** 922-927 (2008).
5. J. Graetz "Regeneration of Aluminum Hydride" *International Energy Agency (IEA) Task 22 Experts Meeting*, Jeju, South Korea, 2009.
6. D. Lacina, "Regeneration of Aluminum Hydride Studied with Raman Microscopy", *March Meeting of American Physical Society*, 2008.
7. J. Graetz, "Overview of U.S. Department of Energy Hydrogen Storage Activities", *Norwegian Hydrogen Seminar*, Bergen, Norway, 2008.
8. J. Graetz, "Regeneration of Metastable Hydrides", *LANL-AIST/NEDO Workshop on Hydrogen Storage and Fuel Cells*, San Diego, CA, 2008.
9. J. Graetz "Catalyzed (De)Hydrogenation Reactions in Al Hydrides", *International Symposium on Metal-Hydrogen Systems*, Reykjavik, Iceland, 2008.

10. J. Graetz “Direct Alane Formation under Mild Conditions”, *American Ceramics Society - Materials Innovations in an Emerging Hydrogen Economy conference*, Cocoa Beach, Florida, 2008.

## References

1. S. Chaudhuri, J. Graetz A. Ignatov, J.J. Reilly and J.T. Muckerman, *J. Amer. Chem. Soc.* **2006**, 128 11404.
2. Graetz, J.; Chaudhari, S.; Wegrzyn, J.; Celebi, Y.; Johnson, J.R.; Zhou, W.; Reilly, J.J., *J. Phys. Chem. C* **2007**, 111 19148-19152.