IV.A.1k 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 material with hydrogen storage capacities 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 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 values listed in Table 1 under the column for 2008 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 BNL. Argonne's analysis assumes a 70-wt% aluminum

hydride slurry, and uses trimethylamine as the harvesting agent for regenerating aluminum hydride in determining the 55% well-to-wheels efficiency. The reactor temperature listed in the row for full flow rate is the most recent value measured by BNL that achieves nearly complete hydrogen release from aluminum hydride at a space velocity of 60 h^{-1} (see Figure 4).

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

Storage Parameter	Units	2010/2015 Target	2008 Status
Gravimetric	wt% H_2	0.06/0.09	0.045
Volumetric	kg H_2/L	0.045/0.081	0.05
Full Flow Rate (temperature)	(g/s)/kW °C	0.02 80	0.02 192
Well-to-Wheels Efficiency	kW-H_2/kW	60%	55%
Refueling Time	min	3/2.5	TBD

TBD - to be determined

Accomplishments

- Achieved nearly 100% aluminum hydride decomposition in 80 seconds at a temperature of 192°C.
- Identified lithium hydride as a harvesting agent for replacing trimethylamine.
- Quantified titanium catalyst loadings for AlH_3-synthesis kinetics.

✧   ✧   ✧   ✧   ✧

Introduction

A cornerstone of the Hydrogen Economy is the hydrogen fuel cell car. A key barrier to realizing hydrogen cars 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_3, $LiAlH_4$, $Mg(AlH_4)_2$) offers some new hope with high volumetric (>80 g-H_2/L) and gravimetric (8 wt%) energy densities and with low decomposition temperatures (150°C). However, these materials typically have very high hydrogenation pressures (>1 kbar) and are generally prepared from costly organo-metallic 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 aluminum hydride (AlH_3). Reports of molecular alane (*e.g.* AlH_3, Al_2H_6 and Al_4H_6) 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 "harvesting" the transient alane formed on the catalyzed aluminum surface [2]. In this study the amine alane (AlH_3-TEDA) was directly synthesized from aluminum and hydrogen gas in solution at low pressures and temperatures. In Fiscal Year 2008 we have expanded this concept to regenerate lithium alanate ($LiAlH_4$) from aluminum and hydrogen using lithium hydride (LiH) as the harvesting agent, and are currently investigating pathways for recovering aluminum hydride (AlH_3) from lithium alanate.

Approach

The research direction being pursued by BNL is to make hydride material on the aluminum particle surface, and then harvest the surface hydride with chemical agents such as amines 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 harvesting 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 "harvesting" 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 compound.

Besides regeneration studies, the work also investigates aluminum hydride decomposition kinetics as a function of temperature, particle size, surface coatings, 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 efficiency to above 60%, the aluminum hydride decomposition temperature needs to be lowered and more energy efficient regeneration schemes are needed.

Results

In FY 2008 we demonstrated a low-energy route to regenerate $LiAlH_4$ at low pressure without the need for mechanical milling. This process involves the direct hydrogenation of catalyzed Al and LiH in a tetrahydrofuran (THF) slurry followed by a low-temperature desolvation step to recover crystalline $LiAlH_4$. The initial hydrogenation step was found to be reversible:

$$LiH + Al + 3/2H_2 \overset{THF}{\longleftrightarrow} LiAlH_4 \cdot 4THF \qquad (1)$$

The hydrogenation procedure (reaction 1) is similar to that used to directly hydrogenate Al to form an alane amine (AlH_3-NR_3) where the AlH_3 is stabilized by an Al-N bond [2]. Here we are using an analogous procedure to stabilize the metastable $LiAlH_4$ as a THF adduct ($LiAlH_4 \cdot 4THF$) using an Al-O bond. The solid-state decomposition of tetrahydride ($LiAlH_4$) is known to occur in a two-step process. The first step is the tetrahydride decomposing to the hexahydride and then to the binary hydride in the following reactions:

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2 \rightarrow 3LiH + 3Al + 9/2H_2 \qquad (2)$$
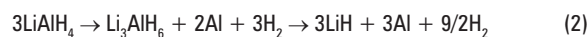
It has been suggested that the hydrogenation/dehydrogenation reactions of $LiAlH_4$ in THF follow a different pathway and bypass the hexahydride (Li_3AlH_6) phase [3]. Since Li_3AlH_6 is completely insoluble in THF the formation of this phase should immediately precipitate out of solution. Based on the reactant concentrations (2LiH + Al) and the amount of hydrogen uptake, the hexahydride phase should be the dominant solid reaction product after hydrogenation if the formation of this phase occurs in THF. However, X-ray diffraction analysis of the reaction products at both ends of the (de)hydrogenation cycle and after partial hydrogenation revealed no evidence of the Li_3AlH_6 phase. Therefore, we conclude that the reversible (de)hydrogenation reaction cycles between LiH + Al and $LiAlH_4$, as shown in reaction 1. The strong heat of solvation, which makes the direct formation of $LiAlH_4$ in THF possible at low pressure, is also responsible for preventing the formation of the Li_3AlH_6 phase. The high solvation energy of $LiAlH_4 \cdot 4THF$ is much greater than the small thermodynamic driving force to form crystalline Li_3AlH_6 [3].

The (de)hydrogenation isotherms of Figure 1 were acquired near equilibrium, but do not exhibit the flat plateaus characteristic of many metal hydrides [4] and some organic-metal hydride systems [2]. This may be attributed to the high solubility of the product, which increases the number of degrees of freedom and allows the pressure to vary as the concentration changes (i.e. the pressure does not need to be fixed to establish the intensive state of the system). It is also possible that
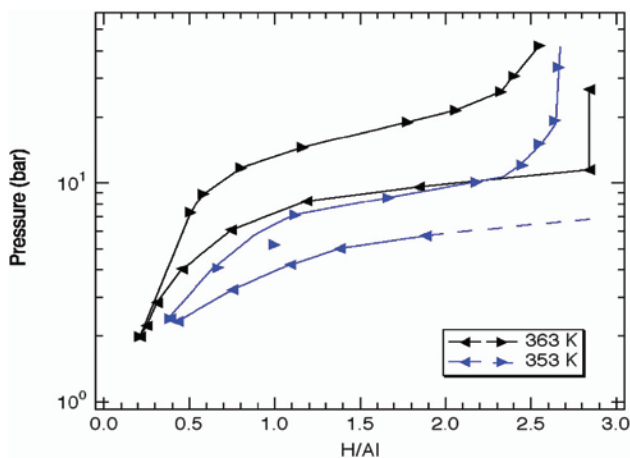
FIGURE 1. Equilibrium Pressure-Composition Isotherms for LiH + Al* in THF at 353 K and 363 K (The equilibrium pressures represent the actual pressure in the reactor and include contributions form H₂ and the THF vapor pressure.)

the sloping shape of the plateau and the large hysteresis observed in the pressure, composition, temperature (PCT) isotherms are simply a consequence of slow kinetics. Slow reaction kinetics are not surprising since the LiH hydride is nearly insoluble in THF and hydrogenation (reaction 1) requires the interaction between two solids (LiH and Al*), a liquid (THF) and a gas (H₂).

Two (de)hydrogenation PCT isothermal experiments were performed at 353 K and 363 K (Figure 1). The isotherms at 363 K were initiated in the dehydrogenated state (LiH + Al*) while the 353 K isotherms were initiated in the hydrogenated state (LiAlH₄). Since the composition of the starting material is well-known the dehydrogenation isotherm in Figure 1 is extrapolated (dashed line) back to the stoichiometric value (H/Al = 3.0). The pressures shown represent the actual equilibrium pressures measured in the reactor and include contributions from H₂ gas and the THF vapor pressure (1.56 bar at 353 K and 2.08 bar at 363 K). Equilibrium times varied somewhat but were typically around 1 day per point. The hydrogen concentrations were determined from the pressure change at each step (298 K) and corrections were made for the dissolution of H₂ in THF based on Henry's Law and data of Gibanel et al. [5]. It is interesting to note that a large hysteresis is observed on both cycles which is 3-8 bar at a composition of H/Al (≈1.5).

Hydrogenation isotherms collected at 298 K, 353 K and 363 K were used to construct a van't Hoff plot (Figure 2) using equilibrium pressure values taken at the midpoint of hydrogenation (H/Al = 1.5). The thermodynamic parameters for the formation of LiAlH₄·4THF were determined from the van't Hoff equation:

$$Ln[P(H_2)] = (\Delta H_f/RT) - \Delta S/R \qquad (3)$$

Using this equation and the linear fit to the equilibrium pressures (Figure 2), the formation enthalpy was determined from the slope: $\Delta H_f = -40.4 \pm 5.7$ kJ/mol H₂ and the formation entropy was determined from the y-intercept: $\Delta S_f = -132 \pm 17$ J/mol H₂ K. Similar to metal hydride reactions, the entropy change is nearly equivalent to the entropy of the hydrogen gas ($S_{H2} = 131$ J/mol K). Using the thermodynamic equation $\Delta G = \Delta H - T\Delta S$, the free energy for this reaction is $\Delta G = -1.1$ kJ/ mol H₂.

The PCT isotherms (Figure 1) and the van't Hoff plot (Figure 2) yield a free energy of formation of $\Delta G = -1.1$ kJ/mol H₂ (-1.65 kJ/mol LiAlH₄) for LiAlH₄·4THF suggesting that the equilibrium pressure is just under 1 bar at room temperature. This implies that hydrogenation will occur at H₂ pressures >1 bar at 300 K and equivalently, dehydrogenation will occur at temperatures just above 300 K at 1 bar pressure. As a comparison, the free energy to form unsolvated LiAlH₄ directly from LiH, Al and H₂ gas (no THF) can be approximated from the decompositon energy $\Delta G_{decomp} = 23$ kJ/mol H₂ (34 kJ/mol LiAlH₄) [6], giving an equilibrium pressure of around 10.9 kbar at 300 K. If we consider the direct formation of LiAlH₄ starting from the hexahydride phase (Li₃AlH₆ rather than LiH) the estimated free energy is somewhat lower, $\Delta G_{decomp} = 19$ kJ/mol H₂ (28 kJ/mol LiAlH₄) [6], but the equilibrium pressure is still extremely high, 2.2 kbar at 300 K. Regardless of the reaction precursors (LiH or Li₃AlH₆), the direct formation of LiAlH₄ in the solid
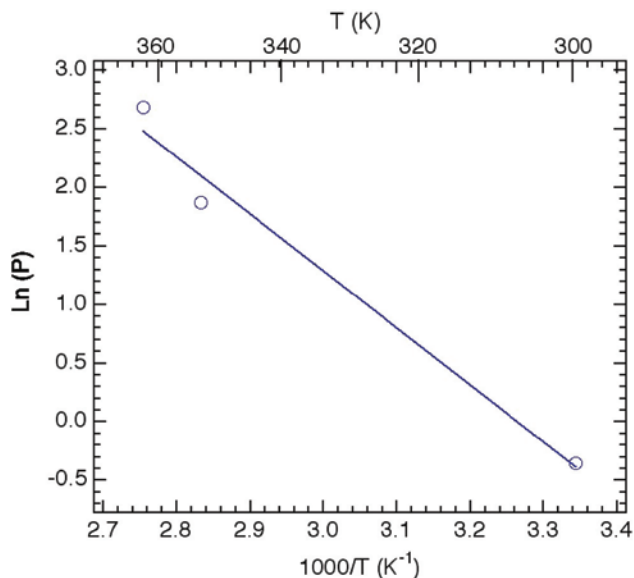

FIGURE 2. A van't Hoff Plot Taken from the Hydrogenation Isotherms (The isosteric formation enthalpy ($\Delta H_f = -40.4$ kJ/mol) and entropy ($\Delta S_f = 132$ J/mol K) were determined from the slope and y-intercept, respectively.)

state requires thousands of bars H_2 pressure whereas direct hydrogenation in THF requires ~1 bar pressure at room temperature.

The pure crystalline $LiAlH_4$ is metastable at ambient pressure and temperature (similar to AlH_3 [7]) whereas the THF solvated phase is stable. The results of our thermodynamic study suggest the difference in free energy between $LiAlH_4$ and $LiAlH_4·4THF$ is approximately 35 kJ/mol $LiAlH_4$. It is interesting to note that this difference in free energy is approximately equal to the enthalpy difference between solvent separated ions and contact ions (32 kJ/mol $LiAlH_4$) [8]. It should also be noted that the direct formation of $LiAlH_4$ also occurs in diglyme [9], which forms an even stronger solvate with $LiAlH_4$ and therefore may form at even lower pressures.

This year we also demonstrated that even a very small Ti content in activated Al is still very effective as a catalyst for the synthesis of the alane adduct of triethylenediamine (TEDA). This is illustrated in Figure 3 in which the uptake of hydrogen is plotted as a function of time for four different Ti concentrations. It should be noted that these are nominal concentrations and reflect the actual amount of Ti added (as $TiCl_3$) in the preparation of the activated Al component. It is known that not all the Ti additive is incorporated into the activated Al. In the present instance, while the rates were essentially same for all nominal Ti contents, the conclusion can still be drawn that even a very small Ti content acts as an effective catalyst. In this connection we have previously shown that in a blank experiment involving no Ti there is no reaction [2].

Likewise, studies on the effects of a Ti catalyst on decomposition kinetics have revealed a measurable enhancement of H_2 evolution rates with only parts-per-million levels of Ti. In this study Ti was introduced in a wet chemical process as $TiCl_3$. Isothermal
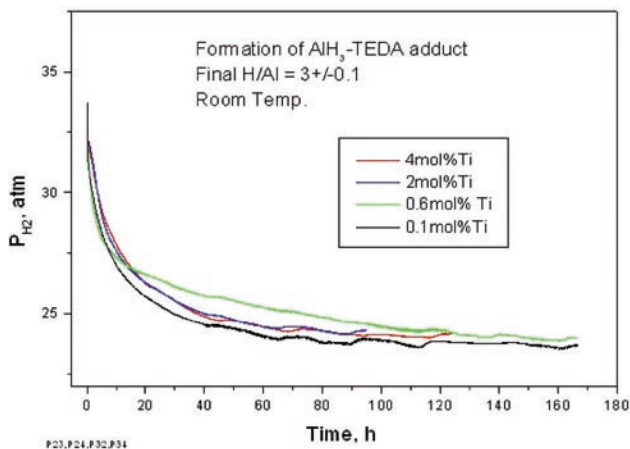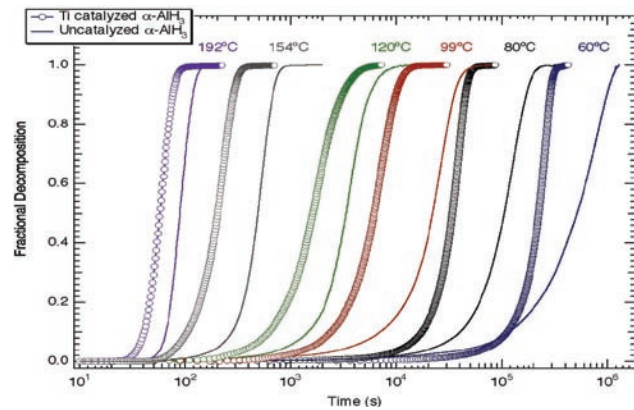
FIGURE 4. Isothermal Decomposition Rates of Dry Aluminum Hydride Particles as a Function of Time at Different Temperatures with and Without Catalysts

decomposition curves from Ti-catalyzed α-AlH_3 and un-catalyzed α-AlH_3 at temperatures from 60°C to 192°C are shown in Figure 4. Preliminary analyses of these results suggest there may be two kinetic enhancements; the first is a reduction in the induction period at the onset of decomposition; the second is an increase in the slope or rate of H_2 release (seen best at the lower temperatures). Samples with higher Ti concentrations were prepared, however the material was found to decompose to Al metal before any observations could be made. These results clearly show that Ti has a dramatic destabilizing effect on α-AlH_3.

Conclusions and Future Directions

This year's findings help identify the trade-offs when using aluminum hydride for meeting DOE's hydrogen storage targets. There are many very challenging engineering questions yet to be solved for designing and building a complete aluminum hydride storage system for fuel cell cars. However, on balance, kinetically stabilized hydrides offer promise and the energy requirement for aluminum hydride regeneration should not be considered prohibitive in the further development of this approach to hydrogen storage.

Next year's research effort will focus on the following activities:

- Further explore LiH as an effective harvesting agent for aluminum hydride.
- Investigate the role of the Ti catalyst and surface coatings for regenerating aluminum hydride.
- Gather decomposition kinetic data on 70% by wt aluminum hydride slurries.
- Continue working with Argonne National Laboratory and the Metal Hydride Center of Excellence.

FIGURE 3. The Effect of Ti Loading on AlH_3-Synthesis Kinetics using TEDA as Harvesting Agent

FY 2008 Publications/Presentations

1. J. Graetz, "New Approaches to Hydrogen Storage" Chemical Society Reviews, Invited article, submitted (2008).

2. M. Tkacz, T. Palasyuk, J. Graetz, S. Saxena, "High-pressure Raman spectroscopy study of α and γ polymorphs of AlH_3" J. Raman Sprectrosc. DOI: 10.1002/jrs.1936 (2008).

3. J. Graetz, S. Chaudhari, J. Wegrzyn, Y. Celebi, J.R. Johnson, W. Zhou, J.J. Reilly, "The Direct and Reversible Synthesis of AlH_3: Triethylenediamine from Al and H_2" J. Phys. Chem. C, 111 19148 (2007).

4. "Synthesis and Characterization of Alanes for Automotive Applications", DOE Hydrogen Program Annual Merit Review, Washington, DC, 2008.

5. "Direct Formation of Al Hydrides and Effects of Ti", International Energy Agency (IEA)Task 22 Experts Meeting, St.-Alexis-des-Monts, Canada, 2008.

6. "Direct Alane Formation under Mild Conditions", Materials Innovations in an Emerging Hydrogen Economy conference, Cocoa Beach, Florida, 2008.

7. "Metal Hydrides for Hydrogen Storage", Materials Research Society Fall Meeting, Boston, MA, 2007.

8. "New Approaches to Hydrogen Storage" High Significance Energy R&D Lecture presented at the Laboratory Energy R&D Working Group (LERDWG), Washington, DC, November 7, 2007.

9. "Aluminum Hydride", International Energy Agency (IEA) Task 22 Experts Meeting, Petten, Netherlands, 2007.

10. " Hydrogenation of Aluminum at Low Pressures", 234th American Chemical Society Meeting, Boston, MA, 2007.

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