

Review

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Aluminum hydride as a hydrogen and energy storage material: Past, present and future

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ABSTRACT

Aluminum hydride (AlH₃) and its associated compounds make up a fascinating class of materials that have motivated considerable scientific and technological research over the past 50 years. Due primarily to its high energy density, AlH₃ has become a promising hydrogen and energy storage material that has been used (or proposed for use) as a rocket fuel, explosive, reducing agent and as a hydrogen source for portable fuel cells. This review covers the past, present and future research on aluminum hydride and includes the latest research developments on the synthesis of α -AlH₃ and the other polymorphs (e.g., microcrystallization reaction, batch and continuous methods), crystallographic structures, thermodynamics and kinetics (e.g., as a function of crystallite size, catalysts and surface coatings), high-pressure hydrogenation experiments and possible regeneration routes.

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1. Introduction

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Aluminum hydride (AlH₃) is a metastable, crystalline solid at room temperature that has a volumetric hydrogen density (148 g H_2/L) greater than twice that of liquid hydrogen and a gravimetric hydrogen density that exceeds 10 wt.%. It also exhibits a low

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heat of reaction (7 kJ/mol H_2) and rapid hydrogen evolution rates at low temperature (<100 °C). Military research programs on aluminum hydride date back to the 1960s when independent groups in the United States and the Former Soviet Union first synthesized the crystalline form of α -AlH₃. Over the past half century it has been used as an explosive, a reducing agent, a solid rocket propellant, a hydrogen source for portable power systems and for the deposition of Al films. The recent renaissance in hydrogen storage research for automotive applications has generated renewed interest in AlH₃ due to its light weight and low decomposition temperature.

Over the years, research groups from around the world have led efforts to tackle the key challenges that limit the widespread use of aluminum hydride. This review covers the five primary areas of AlH₃ research: (i) synthesis and morphology – reviewing the early history of alane studies as an adduct and as a pure material along with the procedures to prepare the different AlH₃ polymorphs and the various morphologies of each phase; (ii) structures - covering the crystallographic structure of α -AlH₃ and the other polymorphs $(\alpha', \beta \text{ and } \gamma \text{-AlH}_3)$ and high pressure phases; (iii) thermodynamics and kinetics - covering decomposition pathways and H₂ release rates and methods to stabilize (by growing larger crystallites and applying surface coatings) to destabilize alane (by breaking up particles and incorporating catalysts); (iv) high pressure studies - reviewing efforts to hydrogenate Al metal under extreme pressure conditions and the $AlH_3/(Al+H_2)$ pressure-temperature phase diagram; (v) regeneration - covering the low-pressure chemical and electrochemical routes to reform the hydride from the elements.

2. Synthesis and morphology

One of the earliest published reports on the synthesis of AlH₃ appeared in 1942 when Stecher and Wiberg prepared AlH₃ in an impure and low yield form, as an alane amine complex AlH₃·2N(CH₃)₃ [1]. A few years later in 1947 Finholt et al. prepared an ethereal solution of aluminum hydride from a much simpler reaction between LiH (or LiAlH₄) and AlCl₃ in diethyl ether (Et₂O) [2].

$$3\text{LiH} + \text{AlCl}_3 + n\text{Et}_2\text{O} \rightarrow \text{AlH}_3 \cdot n\text{Et}_2\text{O} + 3\text{LiCl}$$
(1)

 $3\text{LiAlH}_4 + \text{AlCl}_3 + n\text{Et}_2\text{O} \rightarrow 4\text{AlH}_3 \cdot n\text{Et}_2\text{O} + 3\text{LiCl}$ (2)

At this time it was commonly believed that the ether could not be removed from the alane without loss of hydrogen. However, in 1955 Chizinsky prepared the non-solvated form of AlH₃ by first preparing the etherated alane solution, filtering into an inert liquid (e.g., pentane) followed by drying under high vacuum for at least 12 h [3]. This material was later identified as primarily γ -AlH₃ from a comparison of X-ray diffraction patterns [4].

After the mid 1950s there was very little work published in the open literature on pure aluminum hydride. However, a significant amount of classified work was ongoing in the Former Soviet Union and the United States (in latter case through a collaboration between the Air Force and the Dow Chemical Company). Approximately 20 years after Chizinsky's report on the preparation of non-solvated AlH₃, Brower et al. (of the Dow Chem. Co.) published a summary of their findings on non-solvated AlH₃ [4]. A total of seven different polymorphs of AlH₃ were prepared and investigated during this period including α , α' , β , γ , δ , ε , ζ . Their synthesis method was similar to that developed by Finholt and Chizinsky, namely an ethereal reaction between LiAlH₄ and AlCl₃ to form etherated AlH₃ (reaction (3)) followed by desolvation (reaction (4)) by heating the solution in a mixture of ether and benzene. Importantly, Brower et al. used excess LiAlH₄ and in some cases excess LiBH₄ in the alane–ether solution [5,6], which reduced the time and temperature of desolvation. The critical discovery that excess

LiAlH₄ lowered the desolvation temperature allowed Brower et al. to achieve a controlled and reproducible separation of the alane etherate. It is speculated that the successful desolvation by Finholt and Chizinsky was somewhat serendipitous due to the inadvertent use of excess LiAlH₄ [4].

The following is the typical synthesis procedure for preparing microcrystalline α -AlH₃ (100–200 nm):

$$4\text{LiAlH}_4 + \text{AlCl}_3 + \text{Et}_2\text{O} \rightarrow 4\text{AlH}_3 \cdot n\text{Et}_2\text{O} + 3\text{LiCl} \downarrow + \text{LiAlH}_4 + \text{Et}_2\text{O}$$
(3)

$$4\text{AlH}_{3} \cdot n\text{Et}_{2}\text{O} + \text{LiAlH}_{4} + \text{LiBH}_{4} + \text{Et}_{2}\text{O} \xrightarrow{65 \circ \text{C}}{5 \text{ h}} 4\text{AlH}_{3} + \text{Et}_{2}\text{O} \uparrow$$
$$+ \text{LiAlH}_{4} \downarrow + \text{LiBH}_{4} \downarrow \qquad (4)$$

In the final step the excess $LiAlH_4$ and $LiBH_4$ is removed by a wash with diethyl ether (AlH_3 is insoluble in Et_2O) and, in some cases, a wash in dilute acid.

The other polymorphs of AlH₃ are prepared through slight modifications of the above reactions for α -AlH₃. Generally γ -AlH₃ is the first polymorph to form and transforms into α -AlH₃ during the desolvation heat treatment. Therefore, at lower temperature ($\sim 60 \,^{\circ}$ C) and in the absence of excess LiBH₄, it is possible to isolate a pure phase of γ -AlH₃ before it transforms into α -AlH₃. The γ polymorph can also be prepared by carefully grinding a dry mixture of alane etherate (AlH₃·nEt₂O) with LiAlH₄ (4:1) and heating to 70-80 °C under dynamic vacuum. Using the standard synthesis procedure (with excess LiAlH₄ and LiBH₄), β -AlH₃ typically forms within the first 1–2 h along with γ -AlH₃ and rarely (never) appears in pure form. Brower et al. prepared α' -AlH₃ by performing the desolvation in a sealed pressure reactor [4], while Brinks et al. prepared an impure form of α' by reacting LiAlH₄ with AlCl₃ in a cryomill [7]. The other polymorphs (δ , ε and ζ) prepared by Brower et al., were formed either during the continuous reaction or in reactions using other solvents, but little information is known about these phases since no reproducible synthesis method has been established [4].

Brower et al. also describes a continuous method to prepare larger quantities of α -AlH₃ with larger crystallite sizes (50–100 μ m) [4]. In the continuous reaction the ethereal solution is prepared as in reaction (3), but the desolvation occurs in benzene (or toluene) using a crystallization flask equipped with a fractionation column. In this steady state reaction the ethereal AlH₃ solution (with excess LiAlH₄ and LiBH₄) is added continuously to the benzene (or toluene) and heated to ~77 °C to continuously distill off Et₂O and precipitate AlH₃. This procedure was used to produce many kilograms of α -AlH₃ at the Dow Chemical Company.

It was later discovered that AlH₃ (etherated or pure) could be synthesized using any of the binary hydrides or tetrahydroaluminates (alanates) from the 1st and 2nd groups through a reaction with a Brønsted–Lewis acid (e.g., AlCl₃) [5,8–15]. Regardless of the precursors, several conditions are necessary in order to achieve successful synthesis, including the use of the excess of lithium alanate, introduced in solution or as a solid mixture; the absence of any transition metals, especially titanium (maximum allowed content below 10^{-3} wt.%); and, in the case of the batch or continuous reactions, one of the liquid components must be non-solvating with a higher boiling point than ether (normally belonging to the group of aromatic hydrocarbons).

When these conditions are satisfied the crystallization process can be accomplished in different ways, including a process that avoids the formation alane etherate (Eq. (3)) as an independent step. The "direct" synthesis of non-solvated alane (any polymorph) occurs by a reaction between an alanate and aluminum bromide in an aromatic hydrocarbon in the absence of ether [16]. Another example is a high-temperature synthesis of α -AlH₃ similar to reaction (3), but performed by mixing the solutions of alanate and aluminum chloride in an ether-toluene solution at high temperature (>90 °C) [17]. It should be noted, however, that reactions (3) and (4) are the preferred synthesis methods for the preparation of α -AlH₃ and in most cases the use of other reactants and synthesis techniques results in a less dense material with a non-ideal morphology and a lower thermal stability.

Each polymorph of AlH₃ exhibits a unique morphology as shown in Fig. 1. α -AlH₃ prepared by the batch or continuous process forms single crystal cuboids (50–100 μ m). From the SEM image in Fig. 1, it is difficult to discern a distinct morphology for β -AlH₃, however α' -AlH₃ clearly adopts a pincushion or fuzzy ball morphology while γ -AlH₃ forms as a collection of fused needles. Previous work of Brower et al. indicated that the etherated AlH₃ forms translucent spheres after precipitating from solution. According to Bulychev et al. [18] the etherated material has a chemical composition close to AlH₃·0.25Et₂O and although it is generally amorphous, it may form a crystalline phase with an orthorhombic structure and unit cell parameters a = 9.90 Å; b = 8.54 Å, c = 12.05 (±0.01)Å.

Since the beginning of alane research in the early 40s and 50s a number of groups were successful in synthesizing and characterizing a variety of alane adducts. In fact, the first alane compound synthesized by Wiberg in 1942 was an amine adduct [1], bistrimethylamine alane. Many other amine alane adducts were prepared by Wiberg et al. in subsequent years [19] and a summary of their work on amine alane complexes was compiled in a review paper published in 1966 [5]. In 1964 Ashby identified a method of directly synthesizing an alane amine complex from Al, H₂ and triethylenediamine [20]. In 1966 another review paper by Semenenko et al. covered the synthesis of aluminum hydride and compounds of aluminum hydride with amines [21]. Although a number of different ways of forming alane complexes are covered, the authors identify a direct reaction between aluminum, hydrogen and an amine as one possible route. They also discuss the possibility of an amine exchange reaction where a simple amine group $(e.g., N(Me)_3)$ can be exchanged for another to form a new amine alane complex. Both of these reactions, the direct reaction with H₂ gas and the exchange reaction, are critical steps for the chemical regeneration of aluminum hydride, a pathway first described by Murib and Horvitz (discussed later) [22].

3. Structures

In 1969 Turley and Rinn determined the crystal structure of α -AlH₃, which crystallizes in the trigonal space group, $R\bar{3}c$, with a hexagonal unit cell and lattice parameters a = 4.449 Å and c = 11.804 Å [23]. The structure consists of corner connected AlH₆ octahedra with each H bridging two octahedra as shown in Fig. 2 (top left). The volume of each AlH₃ unit is 33.5 Å³ and the shortest bond distances are 1.715 Å (Al–H), 2.418 Å (H–H) and 3.236 Å (Al–Al) [7,23]. It is interesting to note that the geometry of the Al atoms in the Al layer is equivalent to Al metal (face centered cubic packing), but AlH₃ is half as dense as Al. Hydrogenation of Al metal increases the interatomic distances from 2.86 Å to 3.24 Å in AlH₃ resulting in a volume expansion of more than 100%.

With the exception of α -AlH₃, there was essentially no new structural information on the other AlH₃ polymorphs (α' , β , γ , δ , ε , and ζ) until 2005 when a theoretical study by Ke et al. identified the structures of two polymorphs (orthorhombic *Cmcm* and cubic *Fd*3*m*) that were predicted to be more stable than α -AlH₃ (trigonal $R\overline{3}c$) [24]. In 2006 Brinks et al. used X-ray and neutron diffraction techniques to determine the structure of α' -AlH₃, which crystallizes in an orthorhombic space group, *Cmcm*, with cell dimensions a = 6.470 Å, b = 11.117 Å and c = 6.562(2) Å [7]. The α' polymorph has two Al and four H crystallographic sites and consists of corner connected octahedra (each H shared with two octahedra) and forms an open 3D network with 3.9 Å channels (Fig. 2, top right) [7]. The

volume of each AlD₃ unit is 39.3 Å³ and the shortest bond distances are 1.68 (Al–D), 2.31 Å (D–D) and 3.22 Å (Al–Al).

In 2007 similar diffraction studies by Brinks et al., determined the structure of β -AlD₃, which crystallizes in a cubic ($Fd\bar{3}m$) structure with cell dimension a = 9.004 Å [25]. This structure consists of corner-connected octahedra forming a 3D network with 3.9 Å channels (similar to α') as shown in Fig. 2 (bottom left). The structure has one Al and one D crystallographic site. The volume of each AlD₃ unit is 45.6 Å³ and the shortest bond distances are 1.712 Å (Al–D), 2.358 Å (D–D) and 3.183 Å (Al–Al). It is interesting to note that the structures predicted by Ke et al. [24] are in good agreement with the structures (space group and cell dimensions) of α' -AlD₃ and β -AlD₃, however, both phases (α' and β) are less stable than α -AlH₃ at room temperature.

The structure of γ -AlH₃, determined by Yartys et al. [26] in 2007 and in an independent investigation of γ -AlD₃ by Brinks et al. [27], crystallizes with an orthorhombic unit cell (*Pnnm* space group). The hydride has cell dimensions a = 5.3806(1)Å. b = 7.3555(2)Å. c = 5.77509(5)Å and V = 228.561(7)Å³ [26], while the deuteride has a slightly contracted unit cell with dimensions a = 5.367 Å, b = 7.336 Å, c = 5.756 Å and V = 226.63 Å³ [27]. The crystal structure of γ -AlH₃, shown in Fig. 2 (bottom right), contains two types of AlH₆ octahedra building blocks. A prominent feature of the crystal structure is the formation of the bifurcated double-bridge bonds, Al-2H-Al (Fig. 3a), in addition to the normal bridge bonds, Al-H-Al (Fig. 3b), found in all other alane structures. The double-bridge bonds are only observed in γ -AlH₃ and their formation is a result of the edge sharing of the AlH₆ octahedra, as opposed to the normal corner sharing octahedral in α -, α' - and β -AlH₃. The geometry of the double-bridge bond has a short Al-Al (2.606 Å) and Al-H (1.68–1.70 Å) bonds compared to the Al–Al distances in Al metal (2.86 Å) and Al-H distances for Al atoms involved in the formation of normal bridge bonds (1.769-1.784 Å). The crystal structure of γ -AlH₃ contains large cavities between the AlH₆ octahedra and therefore, the density is 11% less than for α -AlH₃.

The list of the Al–Al and Al–H (or Al–D) bond distances for Al metal, the AlH₃ polymorphs and Al–H complex hydrides are shown in Table 1. A summary of the synthesis conditions and structural properties of the four primary polymorphs of AlH₃ and etherated AlH₃ are shown in Table 2. A general review of the structures of lightweight, aluminum-based hydrides (alane and alanates) can be found elsewhere [29].

Goncharenko et al. recently discovered two new phases of AlH₃ at high-pressures [30]. Above 72 GPa α -AlH₃ transforms from the hexagonal unit cell to a trigonal unit cell (*P*1) with dimensions a = 3.83 Å, b = 5.12 Å, c = 6.72 Å, $\alpha = 112.6^{\circ}$, $\beta = 111.9^{\circ}$ and $\gamma = 56.6^{\circ}$. A second high pressure transition was observed at around 100 GPa where the trigonal unit cell transformed into a metallic phase with a cubic unit cell (*Pm*3*n*) with cell dimension a = 3.08 Å. This high pressure phase was predicted to be superconductive, but no evidence of superconductivity was observed down to 4 K. It is interesting to note that the H-H distance in this phase (1.54 Å) is slightly smaller than the shortest observed H-H distance in any metal hydride (1.56 Å in NdNiIn_{1.19}) [84] and therefore, with the exception of the H₂ molecule, this high pressure cubic phase exhibits the shortest H–H distance ever measured [30].

4. Thermodynamics and kinetics

 α -AlH₃ decomposes to the elements (Al and H₂) in a single endothermic step: α -AlH₃ \rightarrow Al+(3/2)H₂. Experimentally determined (calorimetry) values for the formation enthalpy range from -6.0 to -7.6 kJ/molH₂ [31-33], with a formation entropy of -129 J/K molH₂ [31]. Based on these values the Gibbs formation energy for α -AlH₃ at 300 K is approximately 31 kJ/molH₂ [31,32]. α' , β and γ -AlH₃ are less stable than α -AlH₃ and undergo an



Fig. 1. Morphology of the various aluminum hydride polymorphs showing α -AlH₃, α' -AlH₃, β -AlH₃ and γ -AlH₃.



Fig. 2. Structures of AlH₃ polymorphs showing α -AlH₃, α' -AlH₃, β -AlH₃ and γ -AlH₃.



Fig. 3. (a) Two types of AlH₆ octahedra in γ -AlH₃ showing (Al1)(H2)₂(H4)₄ and (Al2)(H1)(H2)₂(H4)₂. A double bridge (edge sharing AlH₆ octahedra) bond Al2–2H3–Al2 and one type of single bridge (corner sharing) bond Al1–H4–Al2 are shown. In the Al1 octahedron, all Al–H distances are large (1.78–1.79 Å). In the Al2 octahedra the axial Al–H bonds are large (1.78 Å) while the Al–H distances in the double bridge bonds (H–2Al–H) are much shorter (1.68 and 1.72 Å), resulting in a short Al2–Al2 interatomic distance (2.61 Å) and a much shallow bond angle (101°) compared to the normal bridge bond angle of 125°. For comparison (b) shows the interconnection of the AlH₆ octahedra in the structure of α -AlH₃ composed of Al–H–Al bridge bonds with an angle of 141° [28].

Table 1

Al-H and Al-Al distances in Al-containing hydrides.

| Bond | Al metal | α -AlH ₃ | α'-AlH ₃ | β-AlH ₃ | γ-AlH₃ | [AlH ₄] ⁻ | $[AlH_6]^{3-}$ |
|-------|-------------------------|----------------------------|---------------------|--------------------|-----------|----------------------------------|----------------|
| Al-Al | 2.86 | 3.24 | 3.22 | 3.183 | 2.61–3.17 | - | >3 |
| Al-H | 1.75 (tetra)2.02 (octa) | 1.72 | 1.68(Al-D) | 1.712(Al–D) | 1.66–1.79 | 1.61-1.63 | 1.75–1.77 |

exothermic transition to the α phase at elevated temperatures $(\geq 100\ ^\circ C)$ [32,34,35]. The energies of the polymorph transitions are $-1.1\ kJ/mol\ H_2\ (\alpha'-AlH_3\rightarrow\alpha-AlH_3),\ -1.0\ kJ/mol\ H_2\ (\beta-AlH_3\rightarrow\alpha-AlH_3)\ and\ -1.9\ kJ/mol\ H_2\ (\gamma-AlH_3\rightarrow\alpha-AlH_3)\ [32,35].$ It is important to note that no hydrogen is lost during these transitions. At lower temperatures the decomposition of the less stable polymorphs is more complex with a fraction of the material decomposing directly to the elements (e.g., γ -AlH_3 \rightarrow Al+(3/2)H_2) while the

remaining material transforms to α -AlH₃ before decomposing (e.g., γ -AlH₃ $\rightarrow \alpha$ -AlH₃ $\rightarrow Al$ + (3/2)H₂).

The diffusion of hydrogen in metallic aluminum is fast. The temperature-dependent diffusion coefficient (cm^2/s) for hydrogen in polycrystalline aluminum is given below:

$$D = 1.75 \times 10^{-4} \exp\left[\frac{-E}{RT}\right]$$
(5)

Table 2

Properties of AlH₃ polymorphs showing synthesis conditions (mole ratios LiAlH₄:AlH₃:LiBH₄ and temperature/time of desolvation), structural properties (space group and lattice parameters), morphology and transition enthalpy (ΔH_{trans}).

| Polymorph | Synthesis conditions | | Structure | Morphology | $\Delta H_{\rm trans}$ (kJ/mol H ₂) | |
|---|----------------------|------------------------------|--|---------------------|---|--|
| | (LAH:AH:LBH) | Temp./time | | | | |
| α -AlH ₃ | 1:4:1 | 65 °C/6.5 h (micro) | R3c a = 4.449 Å c = 11.804 Å | Cubes | - | |
| α' -AlH ₃ | 1:4:0 | 75 °C/2–4 h (under pressure) | Cmcm a = 6.470 Å b = 11.117 Å c = 6.562 Å | Fuzzy balls | $-1.1(\alpha'\to\alpha)$ | |
| β -AlH ₃ | 1:4:1 | 65 °C/1 h (impure) | Fd3̄m a = 9.004 Å | Irregular | $-1.0(\beta{\rightarrow}\alpha)$ | |
| γ-AlH ₃ | 1:4:0 | 60 °C/4 h | Pnnm a = 7.336 Å b = 5.367 Å c = 5.756 Å | Needles | $-1.9(\gamma{\rightarrow}\alpha)$ | |
| AlH ₃ . <i>n</i> Et ₂ O | 0:4:0 | 25 °C/1 h | Amorphous | Translucent spheres | - | |



Fig. 4. Isothermal decomposition of α -AlH₃ (Dow) at 180 °C showing (I) induction period, (II) acceleratory period and (III) decay period [43].

where $E = 16.2 \pm 1.5 \text{ kJ/mol}$ [36]. In the temperature range of interest ($\sim 140 \,^{\circ}$ C) the diffusion coefficient is approximately 1×10^{-6} cm²/s [36,37], which suggests a diffusion time of seconds for 100 µm particles. However, desorption of H₂ from aluminum hydride is typically slow. Detailed kinetic studies of thermal and photolytic decomposition of α -AlH₃ were originally performed by Herley et al. using material prepared by the Dow Chemical Company $(50-100 \,\mu\text{m})$ [38-42]. The thermal decomposition curve has a sigmoidal shape consisting of an induction period, corresponding to nucleation, an acceleratory period, attributed to growth of the metal in two and three dimensions and a decay period (Fig. 4) [43]. Herley et al. measured an activation energy for the acceleratory and decay period of approximately 157 kJ/mol. Other studies by Herley et al. demonstrated a decrease in the induction period when the hydride was irradiated prior to thermal decomposition [40] likely due to an increase in the number of nucleation sites.

More recently Graetz and Reilly have investigated the thermal decomposition of α -, β - and γ -AlH₃ [44]. These materials were prepared via the microcrystallization route (discussed above) and are different than the Dow material (50–100 μ m) used by Herley et al. in that they consist of small particles (100–200 nm) and have a relatively oxide-free surface. At 100 °C and above the reaction rates for all three polymorphs are similar as shown in Fig. 5. A series of ex situ diffraction scans before, during and after decomposition revealed a rapid transformation from the less stable β and γ phases to the more stable α phase at these higher temperatures. Since this transformation occurs rapidly, prior to decomposition,



Fig. 5. Rate of H₂ release as a function of temperature during thermal decomposition of α , β and γ -AlH₃ [45,45] and α -AlH₃ prepared by the Dow Chemical Company [40]. The right axis shows the equivalent power based on the lower heating value of H₂ (120 kJ/g).

the rates from all three samples are similar. Below 100 °C, the rate curves begin to diverge revealing more rapid H₂ evolution from β and γ -AlH₃. At lower temperatures two decomposition pathways are observed with some of the material undergoing direct decomposition (e.g., γ -AlH₃ \rightarrow Al+(3/2)H₂) while the remaining material transforms to α -AlH₃ followed by decomposition (e.g., γ -AlH₃ $\rightarrow \alpha$ -AlH₃ \rightarrow Al+(3/2)H₂) [44,45]. *In situ* synchrotron X-ray diffraction studies of the thermal decomposition of γ -AlH₃ heated at 2 °C/min in vacuum performed by Maehlen et al. [46] showed that around 60% of the hydrogen is released in the direct decomposition process γ -AlH₃ \rightarrow Al+(3/2)H₂ (see Fig. 6a and b), while the remaining 40% of the γ -AlH₃ first transforms into the α -AlH₃ and then decomposes.

The divergence of the rate curves in Fig. 5 indicates that the fraction of material that undergoes direct decomposition increases with decreasing temperature. The activation energies for the three polymorphs were 102 kJ/mol (α -AlH₃), 92 kJ/mol (β -AlH₃) and 79 kJ/mol (γ -AlH₃) [44]. However, the energies for β and γ -AlH₃ should be considered averages over the two possible decomposition pathways. It is interesting to note that a similar study by Gabis et al. [47] on larger crystallites of α -AlH₃ (shown Fig. 7a) gave an activation energy of 104 kJ/mol, similar to the value measured from the smaller 100–200 nm particles (102 kJ/mol). However, these values were significantly lower than the ~157 kJ/mol activation energy measured for the stabilized α -AlH₃ prepared by Dow Chem-



Fig. 6. (a) In situ SR-XRD pattern of the thermal decomposition of γ -AlH₃ in the temperature range 50–105 °C and (b) the rates of the individual transformation pathways, γ -AlH₃ $\rightarrow \alpha$ -AlH₃ and γ -AlH₃ $\rightarrow Al+(3/2)H_2$ [46].



Fig. 7. Large single crystals of α -AlH₃ (a) before and (b) after H₂ desorption [47].

ical (50–100 μ m). This suggests that the enhanced stabilization observed in the Dow material is primarily attributed to a thick surface oxide, rather than the crystallite size (which has a smaller effect).

The general interest in using aluminum hydride as a rocket propellant in the 60s and 70s inspired a number of efforts to prepare an air-stable hydride with a long shelf life (years to decades). Therefore, a variety of stabilization methods were developed over the years, one example includes the addition of magnesium compounds, LiAlH₄·Mg(AlH₄)₂ and LiCl·Mg(AlH₄)₂ [17], which was shown to significantly increase the activation energy of decomposition. Probably the most successful and widely used method of alane stabilization is the application of a thick surface oxide and/or hydroxide layer [48–51]. The rate of hydrogen transport through a surface layer of Al₂O₃ was investigated by Wang et al., and was found to decrease rapidly with oxide thickness (1-3 nm) [52]. A recent study by Kato et al. clearly demonstrates that desorption of H₂ from the surface of AlH₃ requires the break-up of the oxide layer [53]. Once channels have formed in the oxide, small zones of metallic Al form on the hydride surface and act as nuclei for further desorption. The desorption creates a porous aluminum structure, as shown in Fig. 7, which provides short diffusion paths for hydrogen traveling from the metal-hydride boundary to the surface [47]. Efforts to further enhance the hydride stability typically involve additional coatings such as a thin organic layer (in addition to the oxide). Although their exact stabilization procedure remains unknown, the α -AlH₃ prepared by Dow was extremely stable and recent reports suggest that the original material lost little hydrogen despite being stored in air for over 30 years [54].

Recent interest in aluminum hydride for low temperature fuel cell applications has shifted the focus towards destabilizing (rather than stabilizing) the hydride and enhancing desorption rates. This has been motivated by the need for lightweight and compact hydrogen storage media for fuel cells that require rapid hydrogen evolution rates at low temperature ($\leq 100 \,^{\circ}$ C). The thermal stability of alane and its decomposition activation energy are both highly dependent upon the synthesis conditions and sample purity. For example, a post-synthesis thermal treatment has been shown to substantially increase in the desorption rates (Fig. 8) [47]. Similarly, alane is also sensitive to light [18,38,41,42] and even a few minutes of exposure to visible light decreases the activation energy by 15–20% compared to non-irradiated "fresh" samples [18]. Sandrock et al. [54] and Yartys [55] have demonstrated that simply ball milling AlH₃ results in an enhancement of the H₂ desorption rates (Fig. 9) likely due, in part, to an increase in clean (oxide free) surfaces. However, the primary reason for the enhanced desorption rates achieved with all of these methods (thermal, irradiation, ball milling) is the small amount of desorption that occurs during the treatment. The formation of metallic Al particles on the hydride surface act as a nucleation sites and reduces, or in some cases eliminates the incubation period (shown in region 1 of Fig. 4). Other studies have shown a destabilization effect with the addition of additives such as alkali hydrides [54,56] and transition metals [55], which catalyze the desorption of H_2 .

A decrease of the activation energy by at least 50% is possible with the addition of Ti, making the storage and even synthesis of catalyzed alane quite dangerous [58]. The effects of transition metal catalysts (e.g., Ti) on the decomposition kinetics are even more pronounced when the catalyst is added in solution during the AlH₃ synthesis. In the case of Ti, a measurable enhancement of the H₂ evolution rate was observed at levels of just a few parts-permillion when the Ti was introduced in solution (added as TiCl₃ in reaction (3)). Isothermal decomposition curves from Ti-catalyzed



Fig. 8. Temperature programmed desorption from (a) as-received and (b) thermally activated α -AlH₃ at various heating rates. The thermally activated material was heated to 170 °C at 0.1 K/s and rapidly cooled resulting in a hydrogen loss of 15–20%. The solid lines represent the fit to the experimental data (circles) [47].



Fig. 9. SEM images of AlH₃ prepared by Dow Chemical (a) after partial desorption (75%, TDS stopped at 170 °C), (b) enlarged area of white rectangle showing aluminum metal formed on the surface of the cubes and (c) ball-milled AlH₃ after processing for 120 min in Fritsch mill (H₂ atmosphere). Effect of ball milling on decomposition rate is shown in (d) at various milling times and (e) deconvolution of the TDS spectrum of the Dow Chemical sample ball milled for 480 min showing its significant destabilization and formation of two different fractions with reduced stabilities. The Arrhenius plots are shown in (f) revealing a decrease in activation energy with milling and the addition of Ti [57].

 α -AlH₃ (~10 ppm) and uncatalyzed α -AlH₃ at temperatures from 60 °C to 192 °C are shown in Fig. 10 [59]. 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 (evident at higher temperatures); the second is an increase in the slope or rate of H₂ release (evident at lower temperatures). Samples with higher Ti concentrations were prepared, but the material was extremely unstable and decomposed at room temperature before any observations could be made. These results clearly demonstrate that Ti has a dramatic destabilizing effect on α -AlH₃ especially when it is finely distributed throughout the material.



Fig. 10. Isothermal decomposition curves for catalyzed (circles) and uncatalyzed (thin line) α -AlH₃ [59].

5. High pressure studies

 α -AlH₃ is metastable at ambient conditions, but given the Gibbs formation energy of 31 kJ/mol H₂, α -AlH₃ becomes stable at high hydrogen pressure (~7 kbar at room temperature) [60]. A few papers have reported on the high-pressure synthesis of α -AlH₃ from Al powder produced by thermal decomposition of chemically prepared alane [61–63] and recently from a pristine Al foil [64]. With the exception of a few isolated points, little is known about the pressure and temperature conditions necessary to form AlH₃ from Al and H₂. Here we present the equilibrium curve for the reversible reaction, AlH₃ \leftrightarrow Al + (3/2)H₂, constructed at H₂ pressures up to 90 kbar and temperatures up to 600 °C using results from inelastic neutron scattering (INS) experiments and compare the calculated equilibria with experimental values [65].

 α -AlH₃ irreversibly decomposes upon heating and its non-Debye behavior suggests that extrapolating the heat capacity and standard thermodynamic properties to higher temperatures will be unreliable. To overcome this difficulty, the phonon density of states, *g*(*E*), of α -AlH₃ and α -AlD₃ were constructed from the INS spectra measured at helium temperatures [66] as shown in Fig. 11.

Aluminum hydride is dielectric, and therefore its heat capacity, $C_V(T)$, at constant volume is completely determined by g(E),

$$C_V(T) = k_B \int \left(\frac{E}{k_B T}\right)^2 g(E) n(E) \left[n(E) + 1\right] dE,$$
(6)

where n(E) is the Bose factor. The calculated heat capacities for α -AlH₃ and α -AlD₃ are shown in Fig. 12. The dashed lines in Fig. 12 show the $C_V(T)$ dependencies for α -AlH₃ and α -AlD₃ at a pressure of 1 atm and temperatures 0–1000 K calculated using the g(E) spectra presented in Fig. 11 [67]. The $C_P(T)$ dependencies at constant pressure (thin solid lines) were obtained from the $C_V(T)$ dependencies using the equation $C_P = C_V + \alpha^2 T V / \beta$, where the compressibilities (β) of α -AlH₃ and α -AlD₃ were taken from Baranowski et al. [68]



Fig. 11. Densities of phonon states g(E) for (a) AlD₃ and (b) AlH₃ obtained from the INS spectra [66].

and Goncharenko et al. [69] and the coefficients of thermal expansion (α) were determined from X-ray diffraction measurements at 80–370 K [67]. The $C_P(T)$ dependencies are in agreement with the experimental values [31,66,70] measured at temperatures up to 320 K. Using the calculated $C_P(T)$, the standard (at P = 1 atm) Gibbs energy of α -AlH₃ at temperatures 0–1000 K was determined [67] from:

$$G_{AIH_3}^{\circ}(T) = H_{AIH_3}^{\circ}(T) - TS_{AIH_3}^{\circ}(T) = \int_0^T C_P \, dT - T \int_0^T \frac{C_P}{T} dt \tag{7}$$

The standard free energy $\Delta G^{\circ}(T) = G_{AlH_3}^{\circ}(T) - G_{Al}^{\circ}(T) - (3/2)G_{H_2}^{\circ}(T)$ of the reaction AlH₃ \leftrightarrow Al + (3/2)H₂ was further calculated [65] using $G_{Al}^{\circ}(T)$ and $G_{H_2}^{\circ}(T)$ tabulated in Ref. [71] and the experimentally determined ΔG° (298 K) = 31 kJ/mol H₂ [31]. The temperature dependence of the equilibrium pressure, $P_{eq}(T)$, of this reaction was calculated based on the condition that $\Delta G(P_{eq},T) = 0$ written in the form $\Delta G^{\circ}(T) + \int_{P_0}^{P_{eq}} [V_{AlH_3} - V_{Al} - (3/2)V_{H_2}] \cdot dP = 0$. The pressure dependences of the molar volumes of AlH₃ and Al



Fig. 12. Heat capacities of α -AlH₃ and α -AlD₃ showing the experimental $C_P(T)$ data as triangles [31], circles [70] and thick solid lines [67]. The dashed curves and thin solid curves represent $C_V(T)$ and $C_P(T)$, respectively, calculated using Eq. (6) [67] and the g(E) spectra [66] displayed in Fig. 11.



Fig. 13. *T*–*P* phase diagram of the Al–H system showing a solid line representing the calculated equilibrium for AlH₃ \leftrightarrow Al+(3/2)H₂ [65]. The markers indicate the presence (filled) or absence (unfilled) of α -AlH₃ in the samples. Decomposition points from Tkacz et al. (triangles) [61], Baranowski and Tkacz (upside down triangles) [62] and Konovalov and Bulychev (squares) [63] are for alane powders stabilized by a surface oxide layer. Results from Sakharov et al. (stars) [65] were obtained using non-oxidized Al powder as the starting material (see text).

were taken from Baranowski et al. [68] and the equation of state, $V_{\text{H}_2}(P, T)$, for gaseous hydrogen from Hemmes et al. [72].

Fig. 13 shows the calculated equilibrium line for $AlH_3 \leftrightarrow Al+(3/2)H_2$ along with the results from various experimental studies [61–63] on the formation and decomposition of α -AlH₃ under high hydrogen pressure. The calculated equilibrium line predicts a consistently lower temperature than the early experimental results of Tkacz et al. [61], Baranowski and Tkacz [62] and Konovalov and Bulychev [63].

The early (de)hydrogenation experiments [62.63] were carried out using Al powder obtained from decomposed AlH₃ (stabilized form). Sakharov et al. [65] conjectured that the α -AlH₃ decomposition and formation temperatures in these experiments might be artificially high (compared to the equilibrium values) due to a thick and ruggedized oxide layer virtually impermeable to hydrogen. The reaction of hydrogen with non-oxidized Al particles was therefore investigated by filling a Cu capsule with AlH₃ and decomposing at 300 °C and 10 kbar H₂ pressure. By forming the Al powder in situ (via AlH₃ decomposition), the subsequent hydrogenation was performed on relatively oxide-free Al particles (or particles with a fragmented oxide shell). The results in Fig. 13 show solid stars representing the formation of AlH₃ (under the given conditions) and open stars representing no AlH₃ formation. The calculated line lies exactly in between two sets of points for the non-oxidized Al at pressures 30–90 kbar, suggesting that the line rather accurately represents the AlH₃ \leftrightarrow Al+(3/2)H₂ equilibrium at pressures up to 90 kbar.

The baric hysteresis of the AlH₃ \leftrightarrow Al+(3/2)H₂ transformation rapidly increases at temperatures below 150 °C. The minimum hydrogen pressure necessary for the formation of α -AlH₃ is about 20 kbar at temperatures 50–100 °C. The oxidized Al foils also exhibited a large temperature hysteresis for the Al+(3/2)H₂ \leftrightarrow AlH₃ transformation (not shown)[64]. It is interesting to note that points corresponding to the formation of α -AlH₃ are closest to the calculated equilibrium line [64]. This distinguishes dielectric AlH₃ from metallic hydrides, which typically decompose near the equilibrium line [73].

6. Regeneration

Extremely high pressures are required to hydrogenate aluminum and therefore the utility of this material is dependent upon the development of a low cost recycling or regeneration process to reform the hydride from the spent fuel and H₂ gas. The key requirement is to maintain a low energy input relative to the amount of chemical energy stored in the material. Based on the lower heating value of hydrogen (LHV_{H2} = 120 kJ/g) one mole of AlH₃ contains approximately 360 kJ of fuel energy or, equivalently, the energy density of AlH₃ is 12 kJ/g. Using the free energy of formation of ΔG° (298 K) = 31 kJ/mol H₂ (46.5 kJ/mol AlH₃), the direct hydrogenation of aluminum to form AlH₃ requires a minimum of 13% of the fuel energy contained within the hydride. Although the hydrogenation enthalpy is slightly exothermic, the free energy is positive due to the large entropy change associated with forming the hydride from H₂ gas.

Some have speculated that one method of reducing the synthesis cost might be to form AlH_3 using the existing chemical synthesis procedure (reactions (3) and (4)) and simply recycle the byproducts (e.g., LiCl). However, the energy required to overcome the thermodynamic barrier to split the salt is high. It is useful to estimate the minimum energy necessary to transform the byproducts (LiCl and Al) into the reaction precursors (AlCl₃ and LiH) in a hypothetical reaction with perfect efficiency:

$$3\text{LiCl} + \text{Al} + (3/2)\text{H}_2 \rightarrow \text{AlCl}_3 + \text{LiH}$$
(8)

Even in this ideal scenario the cost to reform the precursors is 167 kJ/mol H_2 , which amounts to $\sim 70\%$ of the fuel energy contained within the hydride giving a maximum regeneration efficiency of 30%. Therefore, a recycling approach to regeneration that involves the conventional chemical synthesis (or a variation thereof) is unlikely to meet the well-to-tank efficiency targets of 60%.

6.1. Electrochemical

Electrochemical hydrogenation of aluminum is an alternative method that allows the formation of the hydride at low pressures. Since the potential required to drive hydrogen into a metal scales as the logarithm of the pressure ($E \propto -\ln[P]$), the application of even a low electrochemical potential results in a high hydrogen fugacity. Investigations of electrochemical hydrogenation of aluminum date back to the early 60s when Classen et al. used an aluminum anode and an iron/mercury cathode with an electrolyte of NaAlH₄ in THF [74,75] to form AlH₃. In the late 90s Birnbaum et al. used aqueous solutions of H₂SO₄ and HCl along with a recombination poison (NaAsO₄) to achieve high hydrogen fugacities for cathodic charging of aluminum [76]. They demonstrated hydrogen enters vacancies in the Al structure and achieved concentrations of >1000 ppm, but no transformation to α -AlH₃ was observed.

More recently Zidan et al. [77] have demonstrated the feasibility of electrochemically charging Al with H using a cell similar to that of Classen et al. with an Al anode, platinum cathode and an electrolyte of NaAlH₄ in THF. In this reaction three AlH₄⁻ ions (from NaAlH₄) combine with one Al³⁺ ion (from anode) to generate four moles of solvated AlH₃ at the anode and Na metal at the cathode. The anode reaction is shown below:

$$3AlH_4^- + Al^{3+} + nTHF \rightarrow 4AlH_3 \cdot nTHF + 3e^-$$
(9)

The remaining steps involve separating AlH₃ from THF, which is achieved by exchanging the THF ligand with an amine group (triethylamine, TEA) and heating the liquid AlH₃. TEA under vacuum to recover pure α -AlH₃. A survey of the available reference data on adducts of aluminum hydride with amines and cyclic ethers support a claim that separation of the ligands and alane is generally not possible without cracking (decomposing) the AlH₃ [5]. Murib and Horvitz suggest that the tertiary amine groups that form stable (nondecomposable) amine alane adducts have four or less carbons per nitrogen atom. However, amine alane adducts with more than four carbons per nitrogen are less stable and in some cases (e.g., TEA) can be separated at low temperature to recover AlH₃ [22].

It is interesting to note that the above reaction (9) is similar to the conventional chemical synthesis reaction (2) where the Al⁻ ions from AlCl₃ are replaced by Al⁻ from the anode. Removing the chloride from the reaction is an important step towards achieving a low energy regeneration process since it eliminates the need to break up a salt (e.g., LiCl). The regeneration efficiency is further improved by bubbling H₂ gas through the electrolyte during the reaction, to deposit NaH (rather than Na metal) at the cathode. In this case, the full regeneration process involves reacting the NaH (recovered from the cathode) with the spent Al and H₂ gas to reform NaAlH₄ using the well-known process of Bogdanovic and Schwickardi [78].

6.2. Regeneration using alane adducts

Efforts to form alane amine complexes date back to early work of Wiberg et al. and Ashby et al. in late 50s and early 60s [19,20]. However, the first example of using an amine alane as an intermediate in a process to form α -AlH₃ dates back to 1972 when Murib et al. used various tertiary amine alane adducts and TEA to form AlH₃ [22]. More recently, Graetz et al. have used a three-step regeneration process, which involves initially forming a stabilized alane amine from catalyzed Al, H₂ and an amine, followed by transamination and adduct separation [79–81]. A similar low energy regeneration process was demonstrated for LiAlH₄, which was formed by initially forming LiAlH₄.*n*THF from catalyzed Al, LiH and THF, followed by desolvation and recovery of pure LiAlH₄ [82].



Fig. 14. Regeneration pathway for AlH₃ showing hydrogenation of Al and dimethylethylamine (DMEA= $C_4H_{11}N$) to form DMEA-AlH₃, followed by transamination to form TEA-AlH₃, and separation to recover AlH₃.

The first step of AlH₃ regeneration involves the low-pressure hydrogenation of catalyzed Al and an amine (NR₃) in a liquid medium to form an amine alane (AlH₃·NR₃) [79]. A number of different tertiary amines are suitable including trimethylamine (TMA), triethylenediamine (TEDA), dimethylethylamine (DMEA), quinuclidine and hexamine [20–22,79,80]. However, the more stable alane amines (e.g., AlH₃·TEDA) that form readily at low pressures tend to decompose at high temperatures where AlH₃ is unstable. Therefore, the direct separation and recovery of AlH₃ has proven to be difficult [79,80]. A transamination step is necessary to exchange the amine with one that forms a less stable adduct, such as TEA, which forms AlH₃·TEA. This adduct is a liquid at room temperature and can be separated into AlH₃ and TEA by heating to 75 °C under a nitrogen sweep [22]. The three steps of the regeneration procedure are shown below:

Hydrogenation:
$$Al + NR_3 + (3/2)H_2 \rightarrow AlH_3 \cdot NR_3$$
 (10)

 $\textit{Transamination}: \quad AlH_3 \cdot NR_3 + TEA \rightarrow AlH_3 \cdot TEA + NR_3 \uparrow \qquad (11)$

Separation :
$$AIH_3 \cdot TEA \rightarrow AIH_3 \downarrow +TEA \uparrow$$
 (12)

A schematic showing the regeneration process using dimethyethlyamine (DMEA) and the molecules formed at each stage of the reaction is shown in Fig. 14. It is interesting to note that this simple regeneration procedure may be broadly applicable to other kinetically stabilized hydrides (e.g., $Mg(AlH_4)_2$ and $Ca(AlH_4)_2$).

7. Future directions

Although funding for automotive hydrogen storage research has declined recently, there remains a need for a low pressure (e.g., solid state) option for onboard vehicular hydrogen storage and AlH₃ has been identified as one of only a few "near term materials" [83]. In addition, there is an increasing demand for innovative energy storage at all scales (from microelectronics to the grid). AlH₃ is especially well suited for high value portable electronics that require lightweight and compact energy storage systems. There is currently considerable demand for power systems built into backpacks, jackets and clothing for military, industrial and recreational use. Although lithium ion batteries are typically used to power these types of devices, a substantial improvement may be possible with an AlH₃-fuel cell system. This is because the energy density of a typical lithium battery is around 300 Wh/L and 150 Wh/kg, whereas an aluminum hydride-fuel cell system operating at 50% efficiency might offer up to four times the energy density (1200 Wh/L and 850 Wh/kg assuming a 50% penalty for the fuel cell system).

The high energy density of an AlH_3 -fuel cell system will likely continue to drive interest in aluminum hydride in the near future. Ultimately, the success of an AlH_3 -fuel cell system will depend upon improvements in alane synthesis (increasing yield and reducing cost) and the development of a compact and efficient storage system suitable for low temperature fuel cells. A simple, but useful system would utilize a single-use cartridge of AlH_3 that could supply H_2 by low temperature thermolysis and be easily replaced when the hydrogen was exhausted.

8. Conclusions

Aluminum hydride is a fascinating and technologically important material that exhibits a high volumetric and gravimetric energy density, a low decomposition enthalpy and rapid hydrogen release rates at low temperature. It is a rather unusual metal hydride in that it is metastable at room temperature and the release of hydrogen is kinetically limited (as opposed to thermodynamically limited) by an activation barrier set by particle size, surface coatings, additives, etc. Therefore, the hydride stability and decomposition rate can be tailored to a variety of applications, which make it a suitable hydrogen source for low temperature, portable fuel cells for small sensors, portable (e.g., backpack) power systems, vehicles along with other applications.

AlH₃ can be prepared in a variety of metastable polymorphs and morphologies at room temperature. A number of different synthesis routes have been used to prepare solvent-free AlH₃ including the conventional organometallic (ethereal) reaction, direct high-pressure hydrogenation, electrochemical charging and low-pressure hydrogenation using stabilizing ligands (e.g., amines). Although the ethereal reaction developed in the 60s and 70s remains the preferred synthesis route, recent developments in chemical and electrochemical regeneration offer promising low energy alternatives to the conventional route.

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