Aluminium hydride: a reversible material for hydrogen storage†

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Aluminium hydride has been synthesized electrochemically, providing a synthetic route which closes a reversible cycle for regeneration of the material and bypasses expensive thermodynamic costs which have precluded AlH$_3$ from being considered as a H$_2$ storage material.

Discovering efficient and economic methods for storing hydrogen is critical to realizing the hydrogen economy. The US Department of Energy (DOE) is supporting research to demonstrate viable materials for on-board hydrogen storage. The DOE goals are focused on achieving a storage system of 6 mass% H$_2$ and 45 kg H$_2$ m^{-3} by 2010 and developing a system reaching 9 mass% H$_2$ and 81 kg H$_2$ m^{-3} by 2015.[1]

Researchers worldwide have identified a large number of compounds with high hydrogen capacity that can fulfill these gravimetric and volumetric requirements. Unfortunately, the majority of these compounds fail to meet the thermodynamic and kinetic requirements for on-board storage systems. Alane has the gravimetric (10.1 mass% H$_2$) and volumetric (149 kg H$_2$ m^{-3}) density needed to meet the 2010 DOE goals.[2,3] In addition, rapid hydrogen release from alane can be achieved using only the waste heat from a fuel cell or a hydrogen internal combustion engine.[4] The main drawback to using alane in hydrogen storage applications is unfavorable hydriding thermodynamics. The direct hydrogenation of aluminium to alane requires over 10^5 bars of hydrogen pressure at room temperature as shown in eqn (1). The impracticality of using high hydriding pressure has precluded alane from being considered as a reversible hydrogen storage material.

$$Al + \tfrac{3}{2}H_2 \xrightarrow{\text{10}^5 \text{ bar 25 °C}} AlH_3 \qquad (1)$$
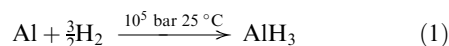
The typical formation route of alane is through the chemical reaction of lithium alanate with aluminium chloride in diethyl ether. This reaction yields dissolved alane etherate, AlH$_3$·Et$_2$O, and precipitates lithium chloride. Alane can then be separated from the ether by heating *in vacuo*.[3,5–7] The synthesis of AlH$_3$ by this method results in the formation of alkali halide salts such as LiCl. The formation of these salts becomes a thermodynamic sink because of their stability.

For a cyclic process, lithium metal must be recovered from lithium chloride by electrolysis of a LiCl–KCl melt at 600 °C and costing at least −429 kJ mol^{-1} of energy equivalent to the

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heat of formation and heat of fusion of LiCl.[8] In addition, −117 kJ mol^{-1} is required to regenerate LiAlH$_4$. The large amount of energy required to regenerate AlH$_3$ from spent aluminium and the alkali halide makes this chemical synthesis route economically impractical for a reversible AlH$_3$ storage system.

For these reasons, our research has pursued a more economically and thermodynamically cost effective synthetic and regeneration route to produce alane. We believe our findings will not only impact the hydrogen storage community but will also have broad influence on the synthetic endeavors of others, especially those looking to bypass unfeasible thermodynamics. We present a cycle that uses electrolysis and catalytic hydrogenation of spent Al$_{(s)}$ to avoid both the high hydriding hydrogen pressure of aluminium and the formation of stable by-products such as LiCl. The cycle, shown in Fig. 1, utilizes electrochemical potential to drive the formation of alane and alkali hydride (*e.g.* LiH, NaH and KH) from an ionic alanate salt. The starting alanate is regenerated by direct hydrogenation of spent aluminium with the byproduct alkali hydride (*e.g.* NaH) in the presence of a titanium catalyst under moderate hydrogen pressure (∼100 bars), a well-studied reaction.[9–13] In comparison to chemical methods, using the electrochemical cycle should, in principle, cost the heat of formation of NaAlH$_4$, which is −115 kJ mol^{-1}.

The electrolysis reaction is carried out in an electrochemically stable, aprotic, polar solvent such as THF or ether. NaAlH$_4$ is dissolved in this solvent, forming the ionic solution (Na$^+$–AlH$_4^-$–THF) which is used as an electrolyte. Though not directed at the regeneration of alane, elaborate research
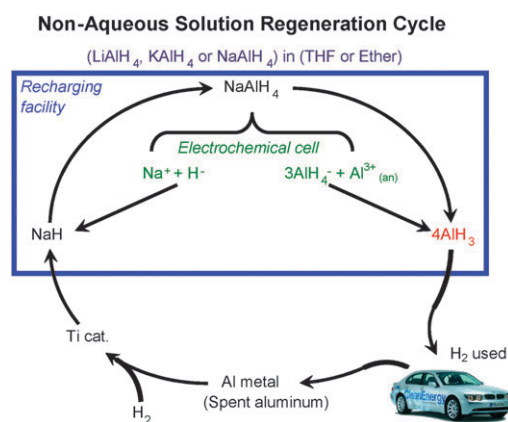

Fig. 1 Proposed reversible fuel cycle for alane. All components of the electrochemical process can be recycled to continually afford a viable solid state storage material for the hydrogen economy.
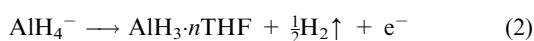
and extensive studies on the electrochemical properties of this type of electrolyte have been reported.[14,15] Although attempts in the past were made to synthesize alane electrochemically,[16–18] none have shown isolated material or a characterized alane product.

Thermodynamic properties of the above electrolyte, along with cyclic voltammetry were the basis for conducting this electrochemical process. Thermodynamic calculations were made to determine the reduction potentials for possible electrochemical reactions of $NaAlH_4$ in an aprotic solution (THF) with an aluminium electrode. From the half reaction potentials, the cell voltage for alane formation was calculated and a theoretical cyclic voltammogram was constructed (see Fig. 2).

The onset potential of the $NaAlH_4$ decomposition reaction to Al is shifted to approximately -2.05 V vs. SHE indicating greater than 250 mV of overpotential. A limiting current of 9.7 mA was reached near -1.5 V. At least two separate reaction mechanisms can produce alane at the aluminium electrode. One possible mechanism is the oxidation of the alanate ion to produce alane, an electron, and hydrogen as shown in eqn (2):

$$AlH_4^- \longrightarrow AlH_3 \cdot n\text{THF} + \tfrac{1}{2}H_2\uparrow + e^- \qquad (2)$$

Another possible mechanism is the reaction of AlH_4^- with the aluminium anode to form alane. In this reaction route, the

Fig. 3 Aluminium electrode before (left) and after reaction (right) in $NaAlH_4$–THF. The electrode is consumed when the voltage is held at $+1.5$ V versus SHE.

evolution of hydrogen is suppressed and the reaction is expected to consume the Al electrode as in eqn (3):

$$3AlH_4^- + Al \longrightarrow 4AlH_3 \cdot n\text{THF} + 3e^- \qquad (3)$$

The different conditions of reactions (2) and (3) depend on their Gibbs free energy (ΔG). ΔG for reaction (2) is -167.1 kJ mol^{-1} AlH_3 and for reaction (3) is -113.7 kJ mol^{-1} AlH_3. Since Na$^+$ is the counter-ion of AlH_4^-, the respective equilibrium potentials are -1.73 for reaction (2) and -1.57 V for reaction (3) vs. SHE. Experimental observations confirm that under the conditions of reaction (3), the anode is consumed as shown in Fig. 3.

Once the correct operating voltage for the formation of alane was calculated, constant voltage experiments were performed. During these experiments, the current was steady and increased slightly with time. The electrochemical production of alane is found not to be slowed by the formation of AlH_3. The surface area of the electrodes and the cell current are observed to be the rate limiting factors. In contrast to previous reports, no visible signs of alane formation are observed and the alane produced by our method is completely dissolved in solution as a THF adduct.[18] During electrolysis, dendritic material was deposited on the platinum counter electrode. This material was collected and determined to be Na_3AlH_6 from XRD data.

Experiments were conducted to determine the feasibility of plating sodium at the platinum cathode to complete the cycle. The platinum cathode and aluminium anode potentials were -2.89 V and -1.31 V, respectively. Plating of Na metal was observed at the cathode while alane was produced at the aluminium anode. In this case, no dendrites were observed at the platinum cathode as sodium was reduced. Furthermore, bubbling hydrogen at the platinum cathode can form NaH and increase the efficiency by eliminating dendrite formation and the need to reduce Na$^+$ to sodium metal.

With an over potential of ~ 0.3 V the alane process is 25% of the H_2 value gained from alane. This value is less than that required in compression and liquefaction of H_2 gas (30–35%). Once our understanding of the electrochemical processes took shape, our attention turned to harvesting AlH_3 from the solution. Alane recovered from the electrochemical cells was characterized by powder X-ray diffraction, Raman spectroscopy, and TGA. The methods of chemical separation and results of characterization are discussed herein.
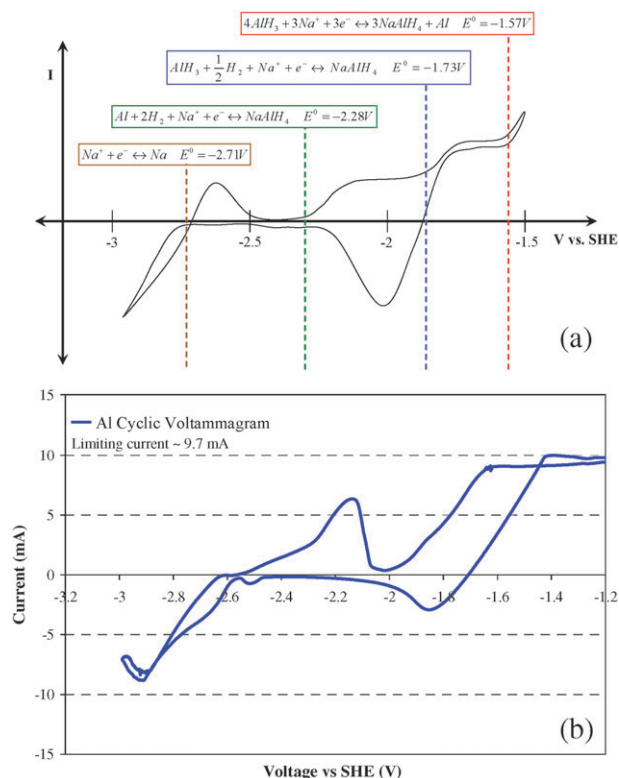

Fig. 2 Experimental and hypothetical cyclic voltammograms for the electrochemical formation of alane. (a) A hypothetical cyclic voltammogram was formulated from the equilibrium potential data for possible reactions and the anticipated state of each species generated. (b) Bulk electrolysis experiment at an aluminium wire electrode for a cell containing a 1.0 M solution of $NaAlH_4$ in THF at 25 °C.
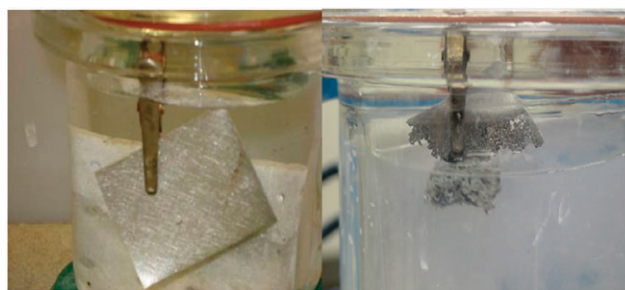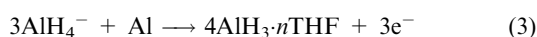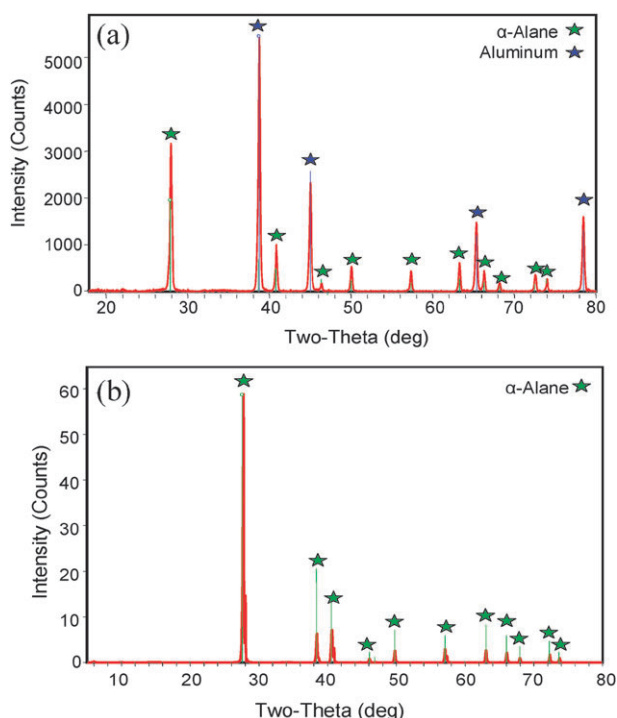
Fig. 4 XRD patterns for products recovered from an electrochemical cell. (a) Alane separated from reaction mixture as the THF adduct. When heated under vacuum to remove THF, the solid partially decomposes, losing hydrogen and affording aluminium. (b) Alane is recovered using triethylamine.

The separation of alane from the etherate adduct is well established and affords the pure AlH_3 compound. Separation of the $AlH_3 \cdot THF$ adduct is however not as straight forward as that of the etherate and has proven more sensitive to decomposition if isolated in the same manner as the etherate. For this reason we have explored the used of adducts in purifying the product obtained from the cell. The procedure involves precipitation of the unconsumed sodium alanate using a non-polar hydrocarbon followed by filtration and introduction of triethylamine (TEA). The adduct free alane is then recovered by heating the neat liquid $AlH_3 \cdot TEA$ *in vacuo*.

Powder X-ray diffraction pattern data for two different separation methods are shown in Fig. 4. When alane is separated by simply heating the $AlH_3 \cdot THF$ product after removing left over starting materials, the diffraction pattern shows the presence of aluminium metal as well as α-alane. The TEA adduct is more stable and less susceptible to thermal degradation. Separation using the TEA method affords only the pure α-alane phase as seen in the diffraction pattern; no aluminium is present. Indexing of this pattern was performed and the unrefined unit cell parameters were found to be $a = 4.446$ Å and $c = 11.809$ Å. Based on the systematic absences, the space group was assigned as $R\bar{3}c$ which is consistent with α-alane.[19]

In conclusion, we have demonstrated the feasibility of a recyclable and reversible hydrogen storage material. We have used the nature of the alane molecule and its tendency to form complexes to our advantage, helping in the isolation of a pure, highly crystalline compound. This generation cycle of alane provides a clean, facile route to a high capacity H_2 storage material while avoiding unrecoverable thermodynamic costs. We anticipate this work will impact other fields including those of thin films, adduct based syntheses, and the recycling and regeneration of other materials.

Notes and references

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