Supplementary Material (ESI) for Chemical Communications

Aluminium Hydride: A Reversible Material for Hydrogen Storage

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Supplementary Information

Expanded Discussion. For the electrochemical cell, the equilibrium potential is determined from the Gibbs' free energy change using the relation:

$$\Delta G = -nFE \tag{1}$$

If hydrogen ions are directly used to form alane as in a metal hydride battery the equilibrium hydriding potential can be related to the equilibrium hydriding fugacity:

$$E = -\frac{RT}{nF}\ln(f_{H_2}) \tag{2}$$

If that was practically possible the alane formation would only require 0.16 V of potential difference to achieve the equivalence of the needed 270,000 bar of hydrogen fugacity. In a conventional hydriding electrochemical cell such as a nickel metal hydride battery, a basic aqueous solution is used as the electrolyte. Nevertheless, activated Al and AlH_3 are extremely reactive in water and air, forbidding the use of all protic solvents. For this reason, a novel route using a non-aqueous solvent system is needed. Polar aprotic solvents such as tetrahydrofuran (THF) or diethyl ether with dissolved ionic compounds such as $NaAlH_4$ or $LiAlH_4$ form a conductive electrolyte that can be used in the electrochemical cell to form alane. The electrochemical cell has an aluminum anode and a platinum cathode.

In the electrolytic solution we have sodium alanate dissolved in THF which can be expressed in terms of ions as.

$$NaAlH_4 / THF\ (solution) \rightarrow Na^+ / AlH_4^- / THF \tag{3}$$

When the appropriate voltage is applied, alane is produced at the anode. Two separate reaction mechanisms can produce alane at an aluminum electrode. The desired half-reaction at the anode for alane production is:

$$AlH_4^- \rightarrow AlH_3 + \frac{1}{2}H_2 + e^- \qquad (4)$$

This reaction mechanism has the lower reduction potential and thus requires less energy input to drive the oxidation in an electrolytic cell. The second mechanism for alane production is by the equation:

$$3AlH_4^- + Al \rightarrow 4AlH_3\left(in\ THF\right) + 3e^- \qquad (5)$$

The Gibbs free energy for reactions (2) and (3) are -167.1 and -113.7 kJ/mol AlH_3, respectively, when Na^+ is used as the counter-ion of AlH_4^-. The respective equilibrium potentials are -1.73 and -1.57 V vs. SHE. Reaction (2) has a more negative Gibbs free energy, indicating a more favorable reaction and resulting in a lower equilibrium potential. Consequently, if the electrode potential is higher than -1.73 V but lower than -1.57 V only reaction mechanism (2) will take place. At electrode potentials higher than -1.57 V both reactions will take place.

In the route of equation (5) the aluminum electrode is expected to be consumed, which is consistent with experimental observations. This reaction also has a higher reduction potential and will require slightly more energy, however, it produces more moles of AlH_3.

At the cathode sodium ions can be reduced to elemental sodium as,

$$Na^+ + e^- \xrightarrow{Pt} Na$$

The plating of sodium at the cathode is slightly more energy intensive than formation of sodium hydride, but can directly be used to regenerate the starting material. At the proper voltage sodium can be collected from the cathode. Once in elemental form, sodium is easily converted to its hydride by direct hydrogenation at 100°C.

Sodium hydride can also be directly formed to precipitate in the cell when hydrogen is bubbled at the Pt cathode, resulting in atomic hydrogen, to form NaH.

$$\begin{aligned} &Na + \frac{1}{2}H_2 \rightarrow NaH \quad \text{or} \quad Na^+ + H^- / Pt \quad \rightarrow NaH \quad \text{or} \\ &Na^+ + \frac{1}{2}H_2 + e^- \rightarrow NaH \end{aligned} \qquad (7)$$

$NaAlH_4$ can be regenerated by reacting sodium and aluminum or sodium hydride and aluminum at 150°C under moderate hydrogen pressure (100 bars) in the presence of Ti catalysts as shown in equation (8)

$$Na + Al + 2H_2 \rightleftarrows NaH + Al + 3/2H_2 \overset{Ti}{\rightleftarrows} NaAlH_4 \qquad (8)$$

In this paper, it is shown that alane forms in the electrochemical cell complexes with the solvent and does not precipitate in a solid form in contrast to earlier reported attempts to make alane, electrochemically.

Feasibility Study. To determine the feasibility of producing alane and to determine if an advantage was gained over current standard methods of making alane, the following calculations were performed.

The thermodynamic cost of producing alane from the elements was determined to be, ΔG = 61.2 kJ/mol. Given the amount of hydrogen in alane, we derive 5.66 kWh per kg of hydrogen.

$$\mathit{Ideal\ Cost} = \frac{61.2\ \text{kJ}}{\text{mol AlH}_3}\left|\frac{33.3\ \text{mol AlH}_3}{\text{kg AlH}_3}\right|\frac{10\ \text{kg AlH}_3}{\text{kg H}_2}\left|\frac{1\ \text{kWh}}{3{,}600\ \text{kJ}}\right. = 5.66\frac{\text{kWh}}{\text{kg H}_2}:$$

Based on the lower heating value of hydrogen (33.3 kWh/kg), the energy from hydrogen to be used in the electrochemical process is 17% of that which is generated, making the process 83% energy efficient. With the added over-potential, the cost of making alane electrochemically is 25%, making the process 75% efficient. The method presented in this paper is much more efficient than recycling AlH_3 by splitting LiCl or NaCl in the chemical method, which requires a minimum of 0.7J for every 1J of fuel (requiring 70% of fuel energy for regeneration and resulting in maximum 30% efficiency).

Electrochemical Preparation of AlH_3. Electrochemical experiments were performed with a CH Instruments 660C potentiostat. After assembly of the cell and before cell characterization or bulk electrolysis, the working electrode was held at a constant potential of +1.3 V vs. SHE. Cyclic voltammograms provided diagnostic information of the electrolytic processes to define the constant voltage applied for bulk electrochemical AlH_3 formation. Cyclic voltammograms were performed between -3.0 V and -1.0 V vs. SHE. Bulk electrolysis experiments were carried out at -1.5 V vs. SHE.

Cell preparation and electrochemical experiments were performed in an argon environment, using traditional air sensitive techniques and were carried out at standard temperature and pressure. Electrochemical alane generation experiments were performed using an air-tight three electrode electrochemical cell. The working electrode was an aluminum sheet or coiled aluminum rod (Aldrich). A “leak-free” 3M KCl Ag/AgCl reference electrode (Warner Instruments) was used to measure the potential of the working electrode.

A typical electrochemical cell contains the following starting materials: ~75-300mL of 1.0M $NaAlH_4$ in THF, Aluminum anode (sheet of Al approximately 1.0g and 1.5” square), Platinum cathode (Pt foil approximately 1.5” square). Prior to experiments, the aluminum electrode was sanded and rinsed with acetone in an inert environment to remove as much of the oxide layer as possible. Voltage was applied for approximately 24 hours.

Chemical Separation and Isolation of Alane. The resulting solution was decanted from the cell apparatus and filtered. An equal volume of pentane was added to the above solution. The solution was stirred over night and the resulting precipitate was filtered on a frit over celite. To the resulting solution, 100 mL of a 4:1 mixture of triethylamine and pentane was added. This solution was stirred over night and again filtered on a frit over celite. The solvent was removed *en vacuo* leaving a clear viscous liquid. This liquid was heated in a sand bath at 65°C for 2 hours in an effort to remove the remaining triethylamine. Unable to remove all of the triethylamine, approximately 15 mL of benzene was added to the flask and stirred. The solution was placed under vacuum and heated again at 65°C. After another 2 hours the product rendered was a fine powder. This powder was rinsed 3 times with 20 mL portions of THF and dried under vacuum. From a cell with a starting volume of 200mL, 1.0M $NaAlH_4$, the average yield is approximately 2.0 grams of alane.

Materials Characterization. X-ray diffractions analysis was performed on a Bruker D8 system with Bragg-Brentano geometry, using Copper Kα1 radiation and a NaI scintillation detector. Source voltage and tube current were 45 kV and 40 mA, respectively. Scans were performed using a 2θ range of 5 to 80 degrees with a step size of 0.02° and a scan speed of 1.0 seconds per step. Patterns were indexed with the Fullprof Suite of programs utilizing TREOR and DICVOL methods. Space group determination was performed using the program Chekcell.

Raman spectra were obtained using a holographic spectrometer (HoloSpec, Kaiser Optical Systems) and CCD detector (DV420-BV-133, Andor, -55 C) with 532 nm excitation (Verdi, Coherent, Inc., 25 mW at sample). The wavelength response of the spectrometer was calibrated with a neon arc lamp; the intensity response was calibrated with a NIST-traceable halogen lamp. Peak positions for a 50/50 acetonitrile/toluene mixture matched accepted values within +/- 1 cm^{-1}. Spectra were obtained using a 180-degree backscattering geometry with a fiber optic imaging probe (MultiRxn, Kaiser Optical Systems, Inc., 5 mm focal length, ~200 micron spot size at focus). Samples were sealed inside glass vials under an inert atmosphere and measured outside containment. There was little evidence of sample decomposition at this laser power.

Thermal gravimetric analysis was conducted on a Netzsch TG-DTA 409 PC LUXX. The sample heating ramp was 2°C per minute while using an atmosphere of argon with a flow rate of 25 $cm^3 \bullet s^{-1}$.

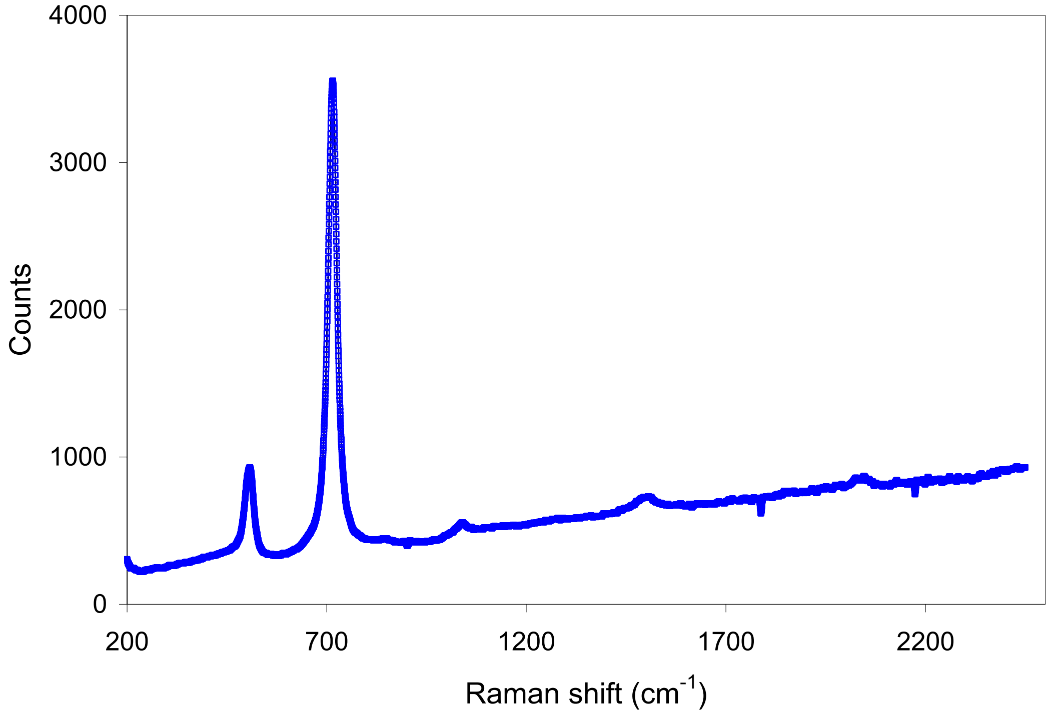

Figure 1. Raman spectrum of material isolated from an electrochemical cell showing α-phase alane.

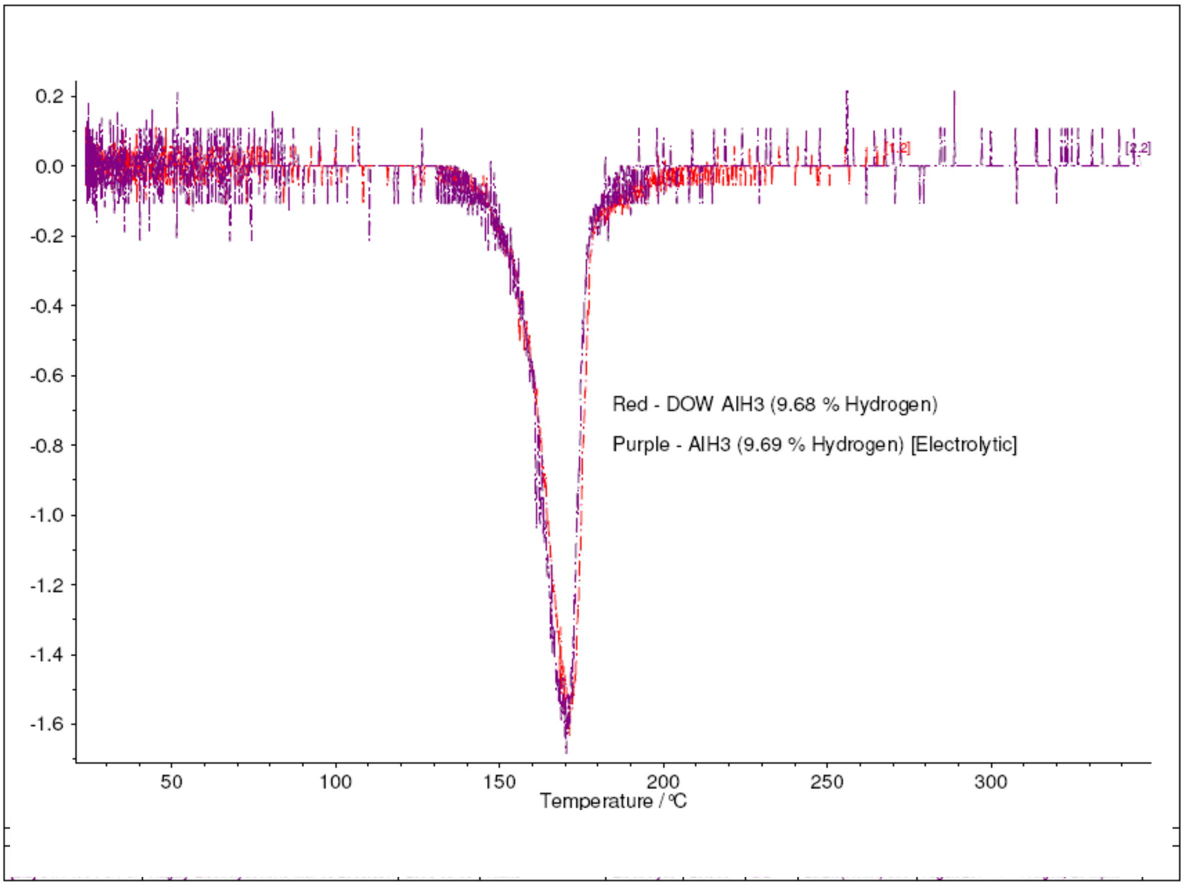

Figure 2. Differential weight loss of alane synthesized electrochemically and a commercial sample procured from Dow. The onset temperature of the electrochemically prepared alane and H_2 content is identical to that of the Dow product.