

Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Aluminum Hydride: A Reversible Storage Material for Hydrogen Storage

Ragaiy Zidan^{1*}, Brenda L. Garcia-Diaz¹, Christopher S. Fewox¹, Ashley C. Stowe^{1,2},
Andrew G. Harter¹, Joshua Gray¹

¹ *Energy Security Directorate, Savannah River National Lab, P. O. Box A, Aiken, SC
29808, United States of America*

² *B&W Y-12 National Security Complex, 1 Bear Creek Road, Oak Ridge, TN 37831 (865)
241-0675*

*e-mail: Ragaiy.Zidan@srnl.doe.gov

Abstract

One of the challenges of implementing the hydrogen economy is finding a suitable solid H₂ storage material. Aluminium (alane, AlH₃) hydride has been examined as a potential hydrogen storage material because of its high weight capacity, low discharge temperature, and volumetric density. Recycling the dehydride material has however precluded AlH₃ from being implemented due to the large pressures required (>10⁵ bar H₂ at 25°C) and the thermodynamic expense of chemical synthesis. A reversible cycle to form alane electrochemically using NaAlH₄ in THF been successfully demonstrated. Alane is isolated as the triethylamine (TEA) adduct and converted to unsolvated alane by heating under vacuum. To complete the cycle, the starting alanate can be regenerated by direct hydrogenation of the dehydrided alane and the alkali hydride (NaH) This novel reversible cycle opens the door for alane to fuel the hydrogen economy.

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% H₂ and 45 kg H₂/m³ by 2010 and developing a system reaching 9 mass% H₂ and 81 kg H₂/m³ 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 fulfill the thermodynamic and kinetic requirements for on-board storage systems. Alane has the gravimetric (10.1 mass% H₂) and the volumetric (149 kg H₂/m³) 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 10⁵ bars of hydrogen pressure at room temperature as shown in equation(1). The impracticality of using high hydriding pressure has precluded alane from being considered as a reversible hydrogen storage material.



The typical formation route for alane is through the chemical reaction of lithium alanate with aluminium chloride in diethyl ether:



This reaction yields dissolved alane etherate, $\text{AlH}_3 \cdot \text{Et}_2\text{O}$, and precipitates lithium chloride. Alane can then be separated from the ether by heating *en vacuo*.^{3, 5-7} The synthesis of AlH_3 by this methods also 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 of energy equivalent to the heat of formation and heat of fusion of LiCl .⁸ In addition, -117 kJ/mol is required to regenerate LiAlH_4 . The large amount of energy required to regenerating 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 focused on developing a novel cycle to cost effectively regenerate AlH_3 under practical conditions. The proposed cycle uses electrolysis and catalytic hydrogenation of products to avoid both the high hydriding pressure for aluminium and the formation of stable by-products such as LiCl . The cycle, shown in [Figure 1](#), utilizes electrochemical potential to drive the formation of alane and alkali hydride from an ionic alanate salt. The starting alanate is regenerated by reacting spent aluminium with the byproduct alkali hydride in the presence of titanium catalyst under moderate hydrogen pressure.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.

Non-Aqueous Solution Regeneration Cycle

(LiAlH₄, KAlH₄ or NaAlH₄) in (THF or Ether)

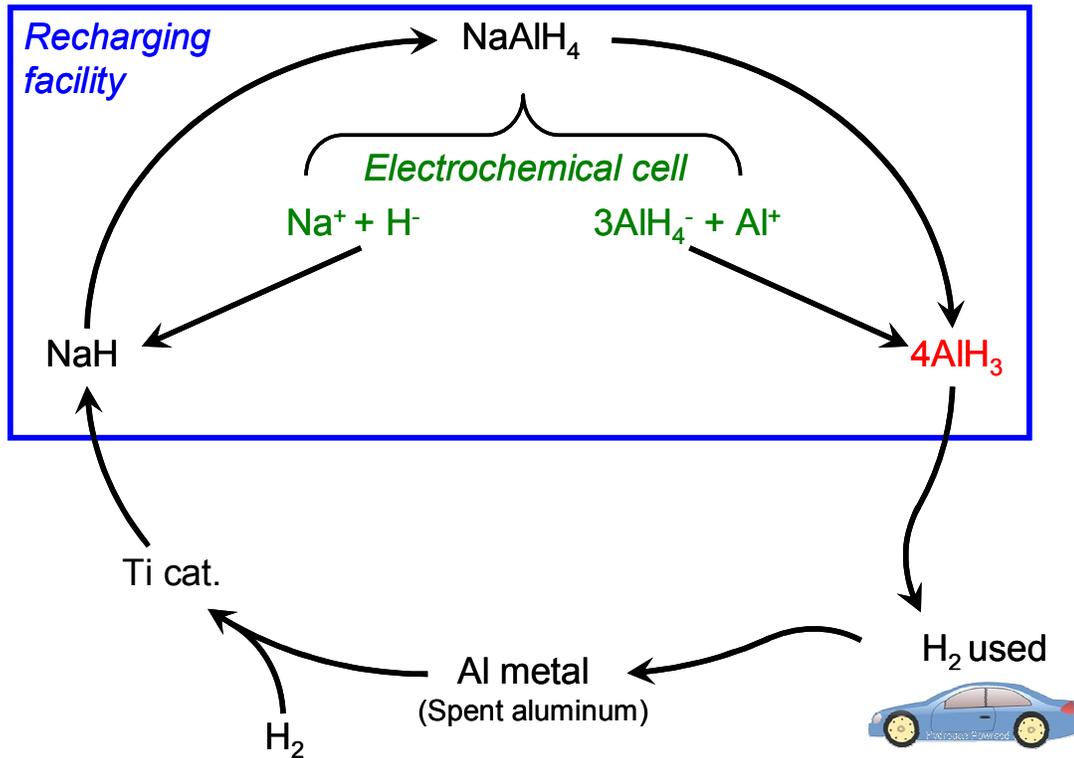


Figure 1. Proposed reversible fuel cycle for alane. All components of the electrochemical process can be recycled to continually afford a viable solid state storage material for the hydrogen economy.

The electrolysis reaction is carried out in an electrochemically stable, aprotic, polar solvent such as THF or ether. NaAlH₄ is dissolved in this solvent, forming the ionic solution (Na⁺/AlH₄⁻/THF) which is used as an electrolyte. Though not directed at the regeneration of alane, elaborate research and extensive studies on the electrochemical properties of this type of electrolyte has 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 calculations were made to determine the reduction potentials for possible electrochemical reactions of NaAlH₄ 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 [Figure 2](#)). Materials and methods are available as supporting material on *Science Online*. The onset potential of the NaAlH₄ 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 equation (4):

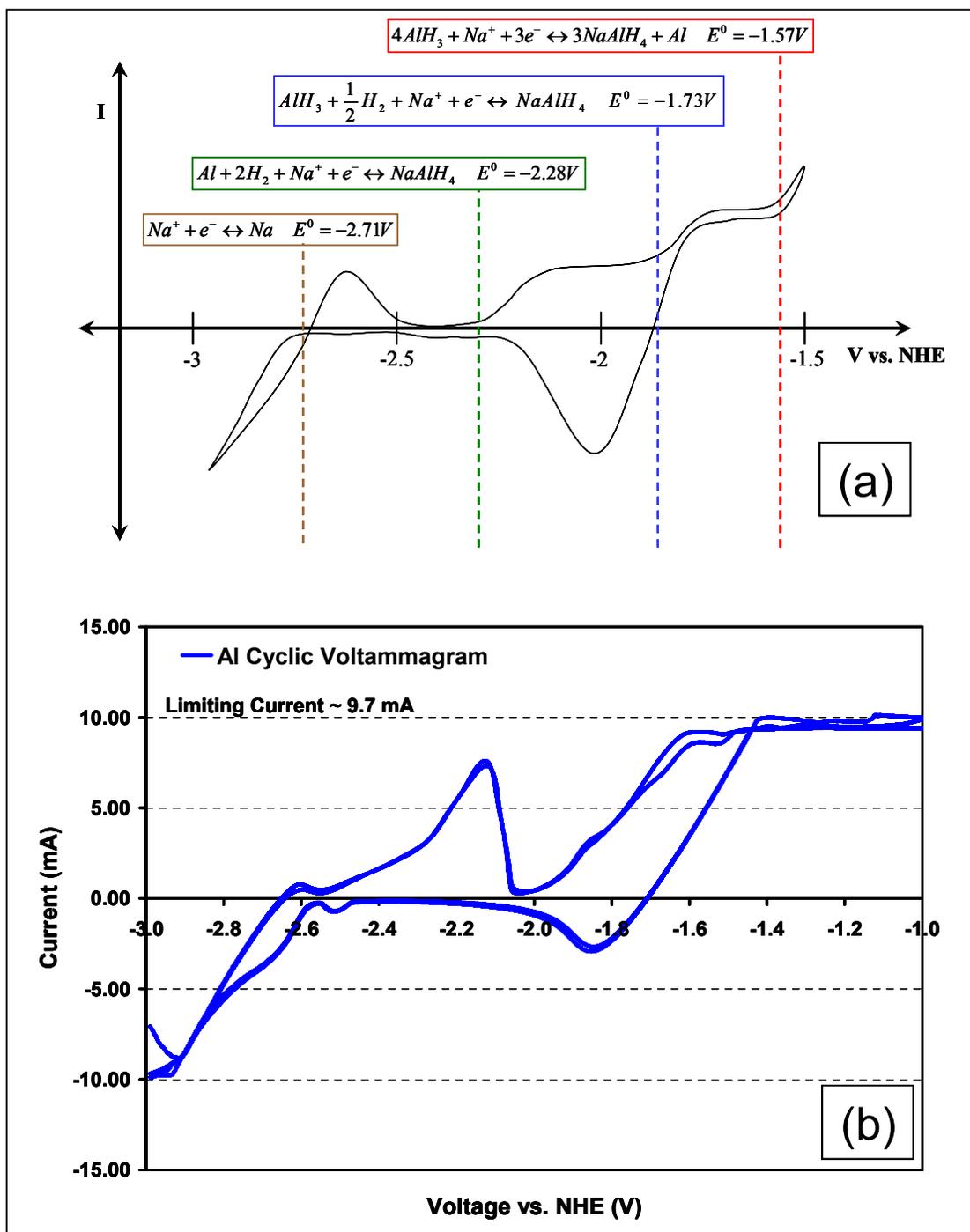
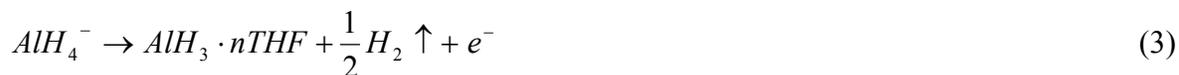


Figure 2. Experimental and hypothetical cyclic voltammograms for the electrochemical formation of alane. (a) A hypothetical cyclic voltammogram was formulated from the equilibrium potential data for possible reactions and the anticipated state of each species generated. (b) Bulk electrolysis experiment at an aluminum wire electrode for a cell containing a 1.0 M solution of NaAlH_4 in THF at 25°C .



Another possible mechanism is the reaction of AlH_4^- with the aluminium anode to form alane. In this reaction route, the evolution of hydrogen is suppressed and the reaction is expected to consume the Al electrode as in equation(5).



Experimental observations confirm that under certain conditions the anode is consumed as shown in **Error! Reference source not found.** as discussed below.

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 not slowed by the formation of AlH_3 . 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. Reacting sodium with aluminium from used

alane under moderate hydrogen pressure (~100 bars) in the presence of a Ti catalyst will regenerate the starting material, NaAlH_4 , leading to a reversible cycle.

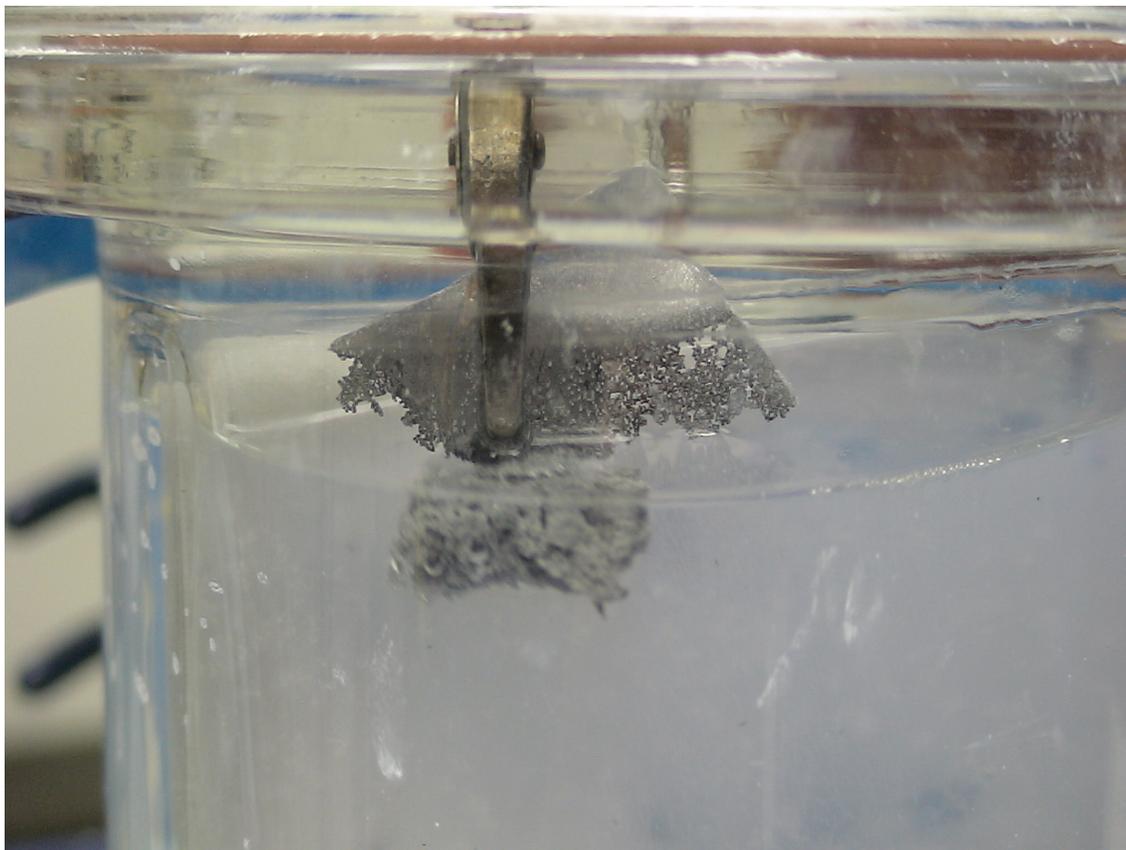


Figure 3. The aluminum electrode is consumed during the reaction when voltage is held at +1.5 V versus SHE.

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.

The separation of alane from the etherate adduct is well established and affords the pure AlH_3 compound.⁶⁻⁸ Separation of the $\text{AlH}_3\cdot\text{THF}$ adduct is however not as straightforward 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 use 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 $\text{AlH}_3\cdot\text{TEA}$ *en vacuo*.

Powder X-ray diffraction patterns data for two different separation methods are shown in [Figure 4](#). When alane is separated by simply heating the $\text{AlH}_3\cdot\text{THF}$ product after removing left over starting materials, the diffraction pattern shows the presence of a large amount of aluminum 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 aluminum is present. Indexing of this pattern was performed and the unrefined unit cell parameters were found to be $a = 4.446 \text{ \AA}$ and $c = 11.809 \text{ \AA}$. Based on the systematic absences, the space group was assigned as R-3c which is consistent with α -alane.¹⁹

Raman spectra and thermal gravimetric data were collected for AlH_3 isolated from an electrochemical cell are available in the supporting online material. Raman

modes present at 510, 715, 1050, and 1515 cm^{-1} are consistent with the literature.²⁰ The representative weight loss onset temperature of approximately 160°C was identical to that of a standard sample purchased from Dow which was performed on the same apparatus.

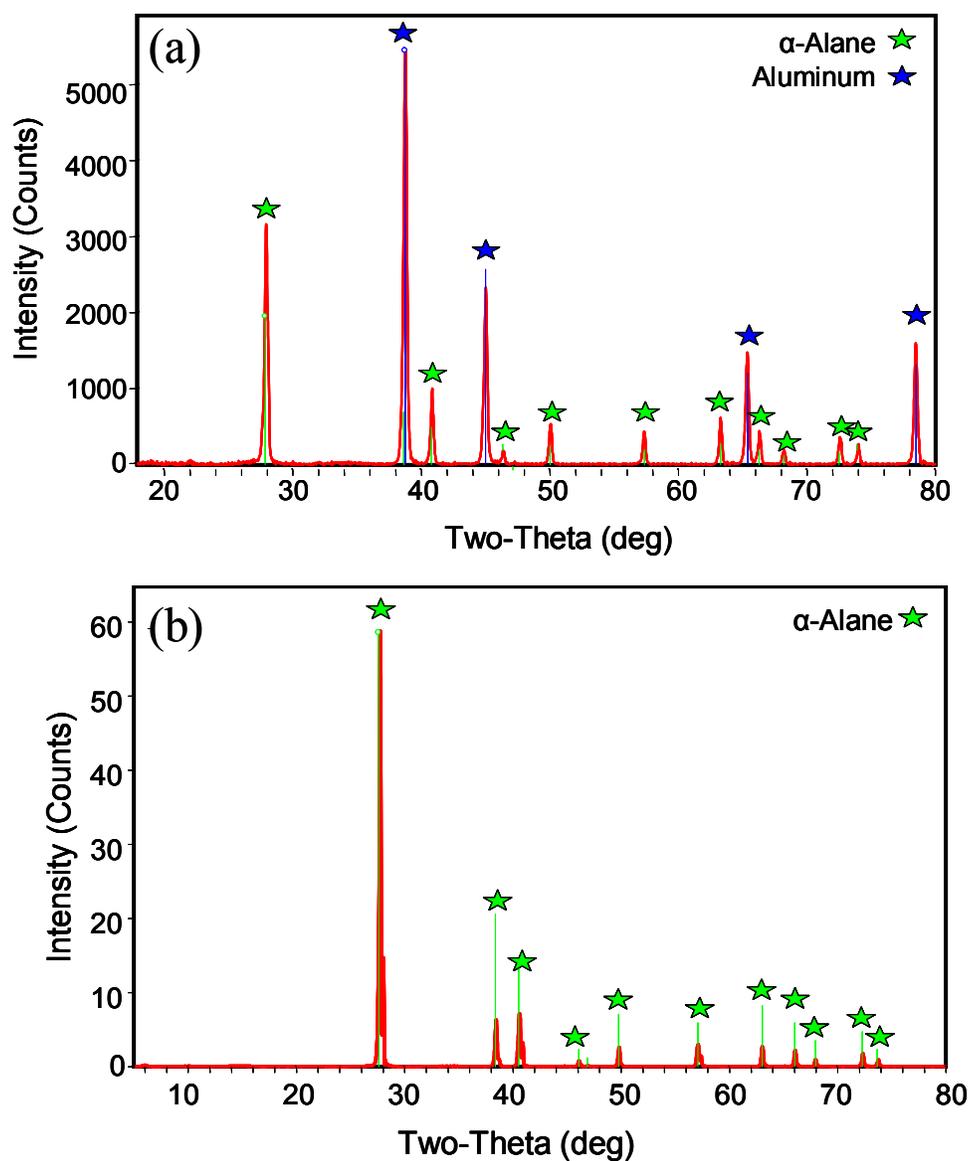


Figure 4. XRD patterns for products recovered from an electrochemical cell. (a) Alane separated from reaction mixture as the THF adducts. When heated under vacuum to remove THF, the solid partially decomposes, losing hydrogen and affording aluminum. (b) Alane is recovered using triethylamine.

References

1. Hydrogen, Fuel Cells & Infrastructure Technologies Program. Multi-Year Research, Development and Demonstration Plan: Planned Program Activities for 2005-2015. <http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/> (2007).
2. Beattie, S., Humphries, T., Weaver, L. & McGrady, S. Watching the dehydrogenation of alane (AlH₃) in a TEM. American Physical Society, 2008 APS March Meeting, New Orleans, Louisiana March 10-14, 2008, Abstract # L36.004.
3. Graetz, J. & Reilly, J. J. Decomposition kinetics of the AlH₃ polymorphs. *Journal of Physical Chemistry B*, **109**, 22181-22185 (2005).
4. Sandrock, G. et al. Alkali metal hydride doping of alpha-AlH₃ for enhanced H₂ desorption kinetics. *J. Alloys Compd.*, **421**, 185-189 (2006).
5. Finholt, A. E., Bond, A. C. & Schlesinger, H. I. Lithium aluminum hydride, aluminum hydride and lithium gallium hydride, and some of their applications in organic and inorganic chemistry. *Journal of the American Chemical Society*, **69**, 1199-1203 (1947).
6. Brower, F. M. et al. Preparation and properties of aluminum-hydride. *Journal of the American Chemical Society*, **98**, 2450-2453 (1976).
7. Kato, T., Nakamori, Y., Orimo, S., Brown, C. & Jensen, C. M. Thermal properties of AlH₃-etherate and its desolvation reaction into AlH₃. *J. Alloys Compd.*, **446**, 276-279 (2007).
8. Wietelmann, U. & Bauer, R. J. in *Ullmann's Encyclopedia of Industrial Chemistry 2005* (Wiley-VCH, Weinheim, 2005).
9. Bogdanovic, B. & Schwickardi, M. Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials. *J. Alloys Compd.*, **253**, 1-9 (1997).
10. Zidan, R. A., Takara, S., Hee, A. G. & Jensen, C. M. Hydrogen cycling behavior of zirconium and titanium-zirconium-doped sodium aluminum hydride. *J. Alloys Compd.*, **285**, 119-122 (1999).
11. Jensen, C. M., Zidan, R., Mariels, N., Hee, A. & Hagen, C. Advanced titanium doping of sodium aluminum hydride: segue to a practical hydrogen storage material? *Int. J. Hydrogen Energy*, **24**, 461-465 (1999).

- 12 Bogdanovic, B., Brand, R. A., Marjanovic, A., Schwickardi, M. & Tolle, J. Metal-doped sodium aluminium hydrides as potential new hydrogen storage materials. *J. Alloys Compd.*, **302**, 36-58 (2000).
- 13 Sandrock, G., Gross, K. & Thomas, G. Effect of Ti-catalyst content on the reversible hydrogen storage properties of the sodium alanates. *J. Alloys Compd.*, **339**, 299-308 (2002).
- 14 Senoh, H., Kiyobayashi, T., Kuriyama, N., Tatsumi, K. & Yasuda, K. Electrochemical reaction of lithium alanate dissolved in diethyl ether and tetrahydrofuran. *J. Power Sources*, **164**, 94-99 (2007).
- 15 Senoh, H., Kiyobayashi, T. & Kuriyama, N. Hydrogen electrode reaction of lithium and sodium aluminum hydrides. *Int. J. Hydrogen Energy*, **33**, 3178-3181 (2008).
- 16 Adhikari, S., Lee, J. J. & Hebert, K. R. Formation of aluminum hydride during alkaline dissolution of aluminum. *J. Electrochem. Soc.*, **155**, C16-C21 (2008).
- 17 Alpatova, N. M. Kessler, Y. M., Dymova, T. N. & Osipov, O. R. Physicochemical properties and structure of complex compounds of aluminum hydride. *Russ. Chem. Rev.*, **37**, 99-114 (1968).
- 18 Clasen, H., German P. 1141 623 (1962).
- 19 Turley, J. W. & Rinn, H. W. Crystal Structure of Aluminum Hydride. *Inorganic Chemistry*, **8**, 18-& (1969).
- 20 Wong, C. P. & Miller, P. J. Vibrational spectroscopic studies of alane. *J. Energetic Mat.*, **23**, 169-181 (2005).
21. Work presented here is supported by the DOE office of EERE (Energy Efficiency and Renewable Energy) Contract Number EB4202000. Our gratitude is extended to Dr. Robert Lascola for his expertise in characterizing materials using Raman spectroscopy. Special thanks are given to Joseph G. Wheeler for whose assistance and guidance we are extremely grateful.

Supporting Online Material

Methods and Materials

Figures S1 and S2

Supporting Online Material

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 charging. 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.

Chemical Separation and Isolation of Alane. A typical electrochemical cell for the preparation of alane 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 any oxide layer on the electrode. Voltage was applied for approximately 24 hours. The resulting solution was decanted from the cell apparatus and filtered. To this solution was added an equal volume of pentane. 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 in vacuo leaving a viscous clear liquid. This liquid was heated at 65°C in a sand bath 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 blue grey powder. This powder was rinsed with 3 times with 20 mL portions of THF and dried under vacuum.

Materials Characterization. X-ray diffractions analysis was performed on a Bruker D8 system with Bragg-Brentano geometry using Copper K α 1 radiation and a NaI scintillation detector. Source voltage and tube current were 45 kV and 40 mA, respectively. Scans were performed using a 2 θ 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 cm³•s⁻¹.

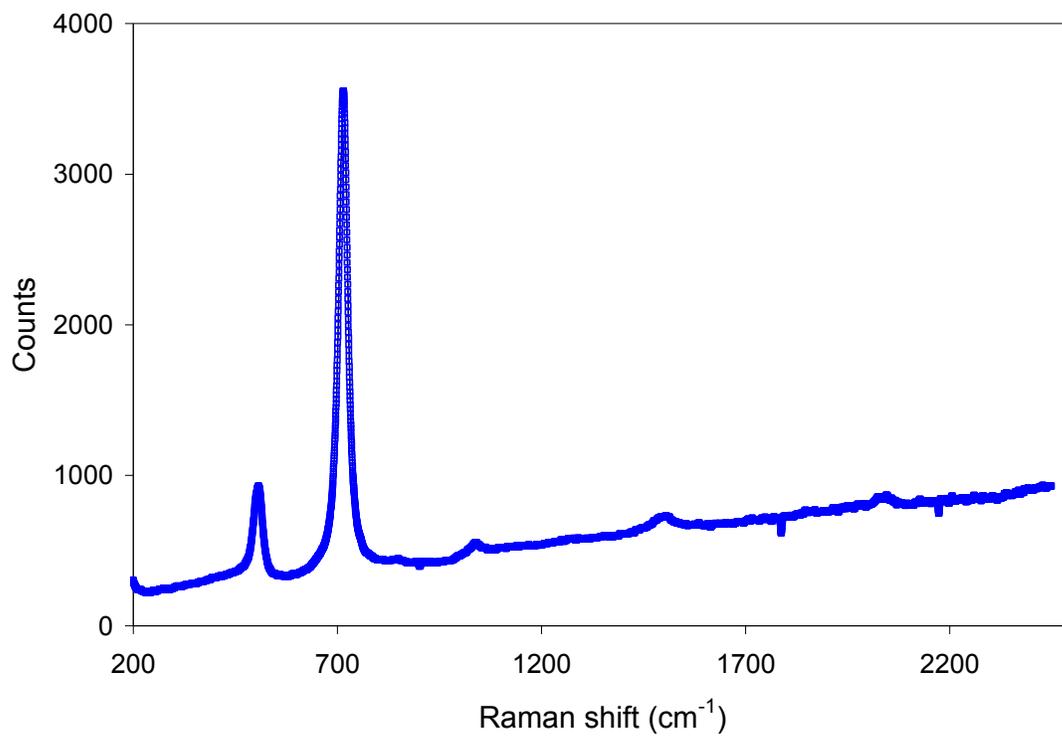


Figure S5. Raman spectrum of alane isolated from an electrochemical cell.

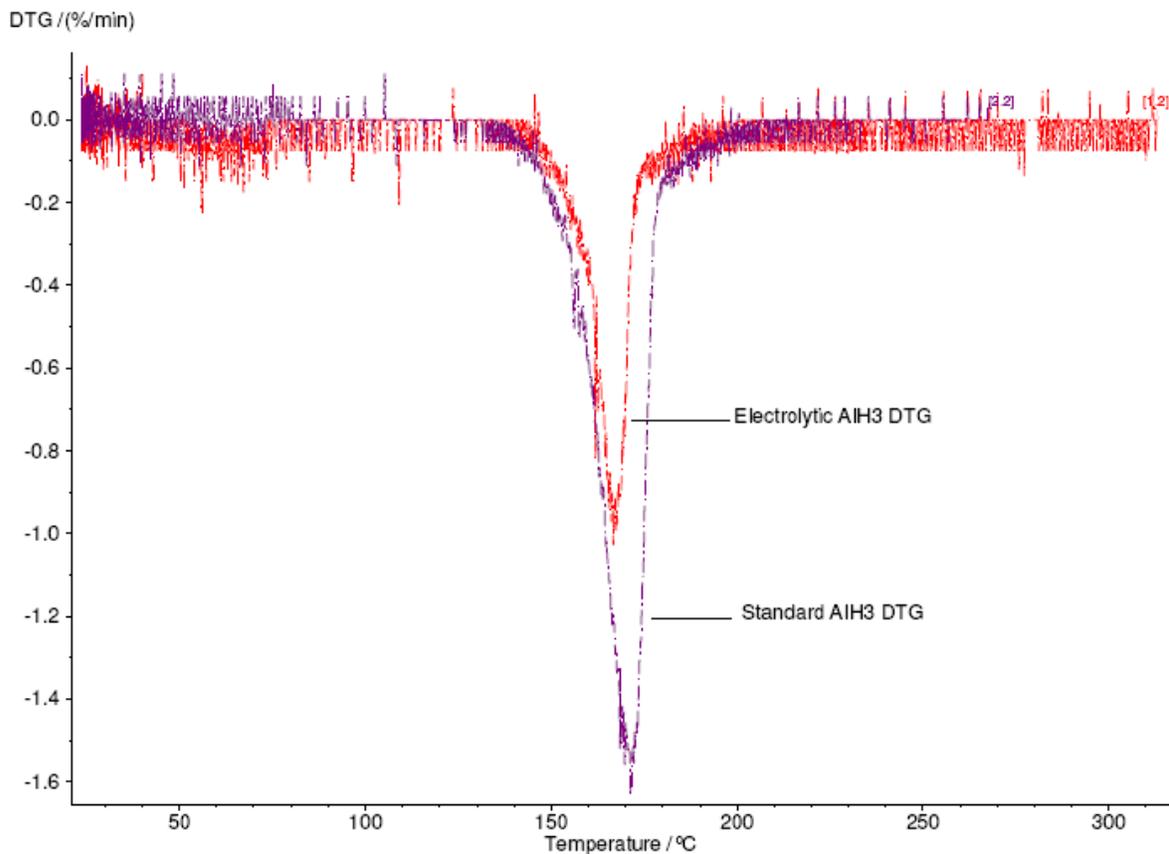


Figure S6. Differential weight loss of alane synthesized electrochemically and a commercial sample procured from Dow. The onset temperature of the electrochemically prepared alane is identical to that of the Dow product.