

**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 Material for Hydrogen Storage

Ragaiy Zidan\*, Brenda L. Garcia-Diaz, Christopher S. Fewox, Andrew Harter, Ashley C. Stowe, Joshua R. Gray

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

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

**Hydrogen storage is one of the challenges to be overcome for implementing the ever sought hydrogen economy. Here we report a novel cycle to reversibly form high density hydrogen storage materials such as aluminium hydride. Aluminium hydride ( $\text{AlH}_3$ , alane) has a hydrogen storage capacity of 10.1 wt%  $\text{H}_2$ , 149 kg  $\text{H}_2/\text{m}^3$  volumetric density and can be discharged at low temperatures ( $< 100\text{ }^\circ\text{C}$ ).<sup>1, 2</sup> However, alane has been precluded from use in hydrogen storage systems because of the lack of practical regeneration methods. The direct hydrogenation of aluminium to form  $\text{AlH}_3$  requires over  $10^5$  bars of hydrogen pressure at room temperature and there are no cost effective synthetic means. Here we show an unprecedented reversible cycle to form alane electrochemically, using alkali metal alanates (e.g.  $\text{NaAlH}_4$ ,  $\text{LiAlH}_4$ ) in aprotic solvents. To complete the cycle, the starting alanates can be regenerated by direct hydrogenation of the dehydrided alane and the alkali hydride being the other compound formed in the electrochemical cell. The process of forming  $\text{NaAlH}_4$  from  $\text{NaH}$  and  $\text{Al}$  is well established in both solid state and solution reactions.<sup>3-7</sup> The use of adducting Lewis bases is an essential part of this cycle, in the isolation of alane from the mixtures of the electrochemical cell. Alane is isolated as**

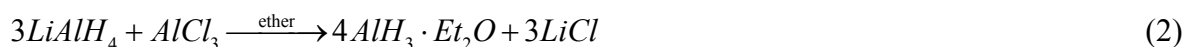
**the triethylamine (TEA) adduct and converted to pure, unsolvated alane by heating under vacuum.**

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<sub>2</sub> and 45 kg H<sub>2</sub>/m<sup>3</sup> by 2010 and developing a system reaching 9 mass% H<sub>2</sub> and 81 kg H<sub>2</sub>/m<sup>3</sup> by 2015.<sup>8</sup>

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% H<sub>2</sub>) and the volumetric (149 kg H<sub>2</sub>/m<sup>3</sup>) density needed to meet the 2010 DOE goals. 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.<sup>9</sup> The main drawback to using alane in hydrogen storage applications is unfavorable hydriding thermodynamics. The direct hydrogenation of aluminium to alane requires over 10<sup>5</sup> bars of hydrogen pressure at room temperature as shown in equation (1). The impracticality of high hydriding pressures has precluded alane from being considered as a reversible hydrogen storage material.



The typical formation route for alane is through the chemical reaction of an alanate compound (e.g. - LiAlH<sub>4</sub>) 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*.<sup>2, 10-12</sup> The synthesis of  $\text{AlH}_3$  by this methods also results in the formation of alkali halide salts such as  $\text{LiCl}$ . 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  $\text{LiCl}/\text{KCl}$  melt at  $600\text{ }^\circ\text{C}$  and requires at least  $-429\text{ kJ/mol}$  of energy equivalent to the heat of formation and heat of fusion of  $\text{LiCl}$ .<sup>13</sup> In addition,  $-117\text{ kJ/mol}$  is required to regenerate  $\text{LiAlH}_4$ . The large amount of energy required to regenerate  $\text{AlH}_3$  from spent aluminium and the alkali halide makes this chemical synthesis route economically impractical for a reversible  $\text{AlH}_3$  storage system.

For these reasons, our research focused on developing a novel cycle to cost effectively regenerate  $\text{AlH}_3$  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  $\text{LiCl}$ . The cycle, shown in Figure 1, utilizes electrochemical potential to drive the formation of alane and alkali hydride from an ionic alanate salt (e.g. sodium alanate,  $\text{NaAlH}_4$ ). The starting alanate is regenerated by reacting spent aluminium with the byproduct alkaline hydride in the presence of a titanium catalyst under moderate hydrogen pressure. In comparison to chemical methods, using the electrochemical cycle should, in principle, cost the heat of formation of  $\text{NaAlH}_4$ , which is  $-115\text{ kJ/mol}$ .

The electrolysis reaction is carried out in an electrochemically stable, aprotic, polar solvent such as THF or ether.  $\text{NaAlH}_4$  is dissolved in this solvent, forming the ionic solution ( $\text{Na}^+/\text{AlH}_4^-/\text{THF}$ ) 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.<sup>14, 15</sup> Although attempts in the past were made to synthesize alane electrochemically,<sup>16-18</sup> none have shown isolated material or a characterized alane product.

Thermodynamic calculations were made to determine the reduction potentials for possible electrochemical reactions with NaAlH<sub>4</sub> in an aprotic solution (THF) with an aluminium electrode. From the half reaction potentials of all possible reactions in solution (shown in the supplementary information), the cell voltage for alane formation was calculated and a theoretical cyclic voltammogram was constructed (see Figure 2). The onset potential of the NaAlH<sub>4</sub> 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. AlH<sub>3</sub> formation is confirmed by observing the rapid precipitation of the insoluble AlH<sub>3</sub>•TEDA complex when triethylenediamine (TEDA) is added to the electrochemical cell. AlH<sub>3</sub>•TEDA was identified by Powder XRD. Two separate reaction mechanisms can produce alane at the aluminium electrode. One mechanism is the oxidation of the alanate ion to produce alane, an electron, and hydrogen as shown in equation (3):



The other possible electrochemical reaction is the reaction of the alanate ion with the aluminium anode to form alane. In this reaction, no hydrogen is evolved and the reaction will consume the Al electrode as in equation (4).



Experimental observations confirm that under certain conditions the anode is consumed as shown in Figure 3 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  $\text{AlH}_3$ . 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.<sup>17</sup> During electrolysis, dendritic material was deposited on the platinum counter electrode. This material was collected and determined to be  $\text{Na}_3\text{AlH}_6$  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,  $\text{NaAlH}_4$ , leading to a reversible cycle.

In addition to determining the electrochemical processes for producing  $\text{AlH}_3$ , recovering  $\text{AlH}_3$  from the solution is a major step of this cycle. The separation of alane from  $\text{AlH}_3 \cdot \text{Et}_2\text{O}$  is well established and affords pure  $\text{AlH}_3$ .<sup>10-12</sup> However, separation of the  $\text{AlH}_3 \cdot \text{THF}$  adduct is more complicated because it decomposes when heated under vacuum. Therefore, adducts such as triethylamine (TEA) were added to the reaction product to

stabilize the alane during purification. Adduct free alane is recovered by heating the neat liquid  $\text{AlH}_3 \cdot \text{TEA}$  *en vacuo*.

Alane recovered from the electrochemical cells was characterized by powder X-ray diffraction, Raman spectroscopy, and thermal gravimetric analysis (TGA). Powder X-ray diffraction patterns data for two different separation methods are shown in Figure 4. Heating the  $\text{AlH}_3 \cdot \text{THF}$  product after removing left over starting materials (Figure 4a) showed the presence of a large amount of aluminum as well as  $\alpha$ -alane. Separation using the TEA (Figure 4b) yields only  $\alpha$ -alane. The unrefined unit cell parameters from indexing of this pattern were  $a = 4.446 \text{ \AA}$  and  $c = 11.809 \text{ \AA}$ . Based on the systematic absences, the space group was assigned as R-3c and is consistent with  $\alpha$ -alane.<sup>19</sup>

Raman spectra and TGA data collected for  $\text{AlH}_3$  isolated from the electrochemical cell are available in the supplementary information. Raman modes present at 510, 715, 1050, and  $1515 \text{ cm}^{-1}$  are consistent with the literature for  $\alpha$ -alane.<sup>20</sup> The TGA weight loss onset temperature was identical to that of a standard sample obtained from Dow analyzed on the same equipment.

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  $\text{H}_2$  storage material while avoiding unrecoverable thermodynamic costs.

## Methods

**Electrochemical Preparation of  $\text{AlH}_3$ .** Cell preparation and electrochemical experiments were performed in an argon environment using traditional air sensitive techniques. Electrochemical alane generation experiments were performed using an air-tight three electrode electrochemical cell. The working electrode was an aluminum sheet. Prior to experiments, the aluminum electrode was sanded and rinsed with acetone in an inert environment to remove any oxide layer on the electrode. A “leak-free” 3M KCl Ag/AgCl reference electrode (Warner Instruments) was used to measure the potential of the working electrode. A platinum foil counter electrode was used. The electrolyte was 1.0M  $\text{NaAlH}_4$ .

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 were performed between -3.0 V and -1.0 V vs. SHE. Bulk electrolysis experiments were carried out at -1.5 V vs. SHE and experiments to investigate aluminium consumption were performed at +1.5 V vs. SHE.

**Chemical Separation and Isolation of Alane.** The product solution was decanted from the cell apparatus and filtered. An equal volume of pentane was added to this solution and stirred overnight. The resulting precipitate was filtered on a frit over celite. To the filtrate, 100 mL of a 4:1 mixture of triethylamine and pentane was added, stirred overnight and filtered over celite. The solvent was removed *en vacuo* leaving a viscous clear liquid. This liquid was heated at 65°C in a sand bath for 2 hours to remove the remaining 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.

## References

1. Beattie, S., Humphries, T., Weaver, L. & McGrady, S. Watching the dehydrogenation of alane ( $\text{AlH}_3$ ) in a TEM. American Physical Society, *2008 APS March Meeting*, New Orleans, Louisiana March 10-14, 2008, Abstract # L36.004.
2. Graetz, J. & Reilly, J. J. Decomposition kinetics of the  $\text{AlH}_3$  polymorphs. *Journal of Physical Chemistry B*, **109**, 22181-22185 (2005).
3. Bogdanovic, B. & Schwickardi, M. Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials. *J. Alloys Compd.*, **253**, 1-9 (1997).
4. 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).
5. 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).
6. 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).
7. 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).
8. 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).
9. Sandrock, G. et al. Alkali metal hydride doping of  $\alpha$ - $\text{AlH}_3$  for enhanced H<sub>2</sub> desorption kinetics. *J. Alloys Compd.*, **421**, 185-189 (2006).
10. 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. *J. Am. Chem. Soc.*, **69**, 1199-1203 (1947).

11. Brower, F. M. et al. Preparation and properties of aluminum-hydride. *J. Am. Chem. Soc.*, **98**, 2450-2453 (1976).
12. Kato, T., Nakamori, Y., Orimo, S., Brown, C. & Jensen, C. M. Thermal properties of  $\text{AlH}_3$ -etherate and its desolvation reaction into  $\text{AlH}_3$ . *J. Alloys Compd.*, **446**, 276-279 (2007).
13. Wietelmann, U. & Bauer, R. J. in *Ullmann's Encyclopedia of Industrial Chemistry 2005* (Wiley-VCH, Weinheim, 2005).
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).

Supplementary Information is linked to the online version of the paper at [www.nature.com/nature](http://www.nature.com/nature).

**Acknowledgements** We would like to thank 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.

**Contribution of Authors** R.Z. was responsible for the idea of the reversible cycle of the regeneration of alane using organic solvent and complex hydride salt and directing the project.

B.L.G-D. was responsible for the design of electrochemical cells and experiments as well as the analysis of experimental results. She was also responsible for the coordination of laboratory operations and interpretation of analytical experiments.

C.S.F. was responsible for chemical isolation and wet chemistry treatment of the electrochemical cells. He has also assisted in conducting and interpreting powder x-ray diffraction data.

R.Z., B.L.G-D and C.S.F. were responsible for writing the manuscript.

A. H. Started preliminary studies, conducted experiments, and characterized resultant products of the electrochemical experiments

A. S. helped in designing several parts of the apparatus, conducted experiments, and characterized resultant products of the electrochemical experiments.

J.R.G. contributed to experimental design and execution, as well as data analysis and interpretation.

**Author Information** Reprints and permissions information is available at [www.natute.com/reprints](http://www.natute.com/reprints). Correspondence and requests for materials should be addressed to R.Z. ([ragaiy.zidan@srnl.doe.gov](mailto:ragaiy.zidan@srnl.doe.gov)).

## Non-Aqueous Solution Regeneration Cycle

( $\text{LiAlH}_4$ ,  $\text{KAlH}_4$  or  $\text{NaAlH}_4$ ) in (THF or Ether)

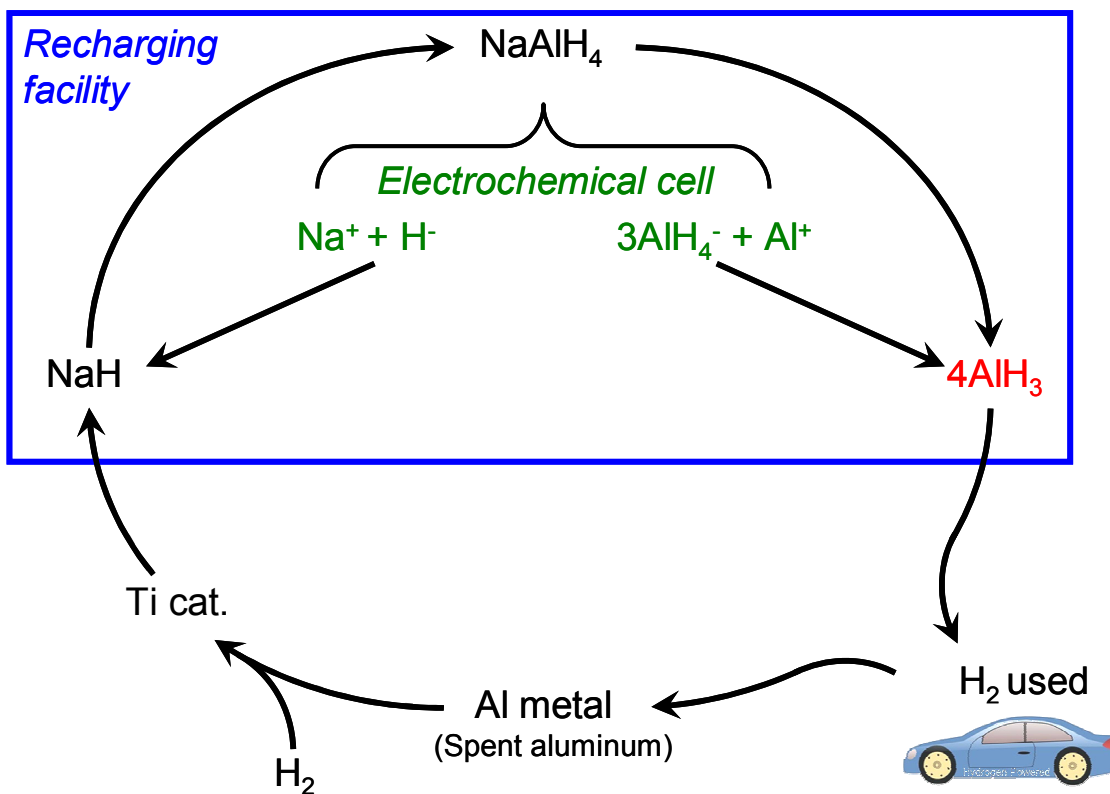


Figure 1. Proposed reversible fuel cycle for alane. All components of the electrochemical process can be recycled to continually afford a viable solid state storage material for the hydrogen economy.

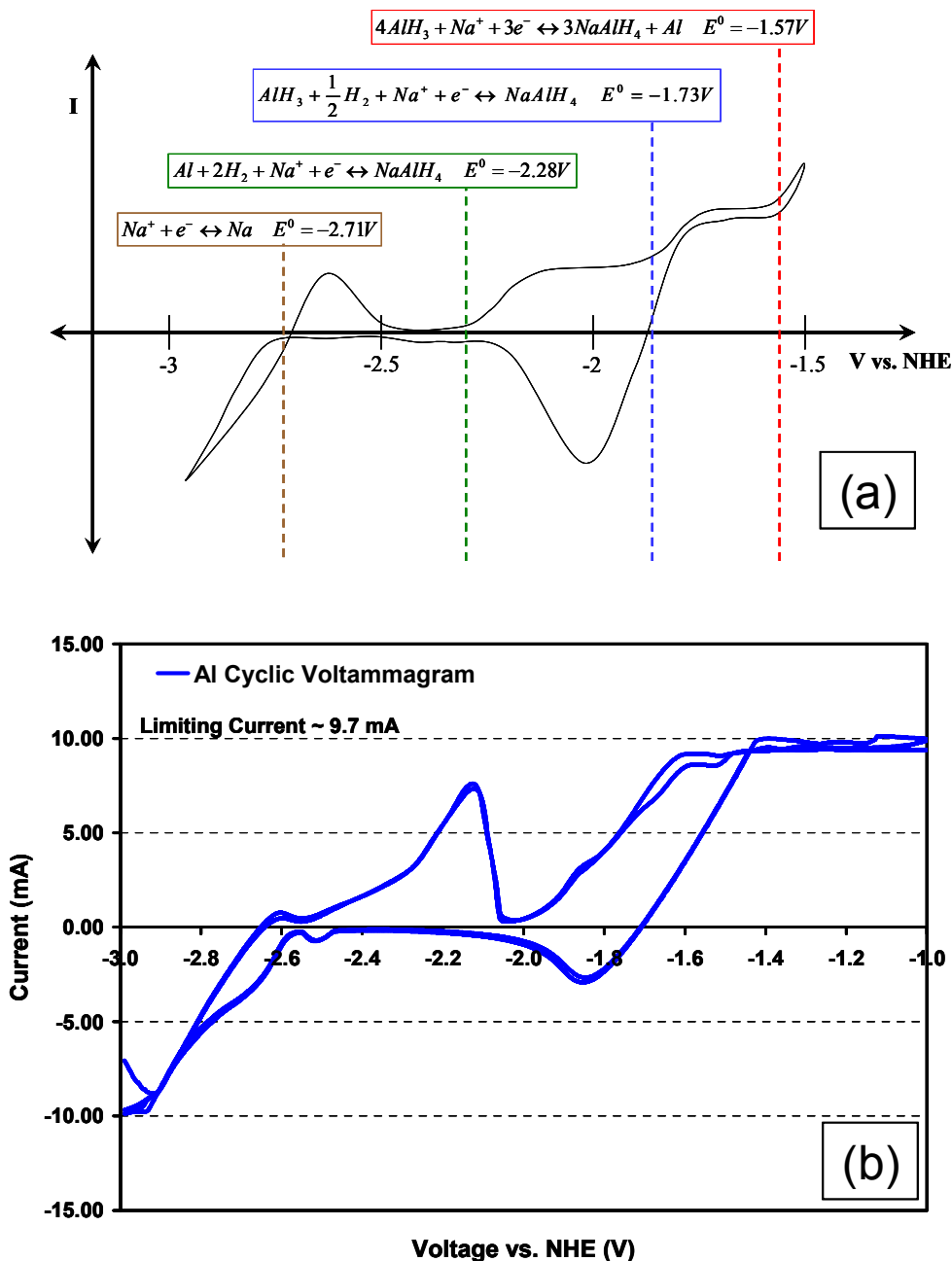


Figure 2. Experimental and hypothetical cyclic voltammograms for the electrochemical formation of alane. (a) A hypothetical cyclic voltammogram was formulated from the equilibrium potential data for possible reactions and the anticipated state of each species generated. (b) Bulk electrolysis experiment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

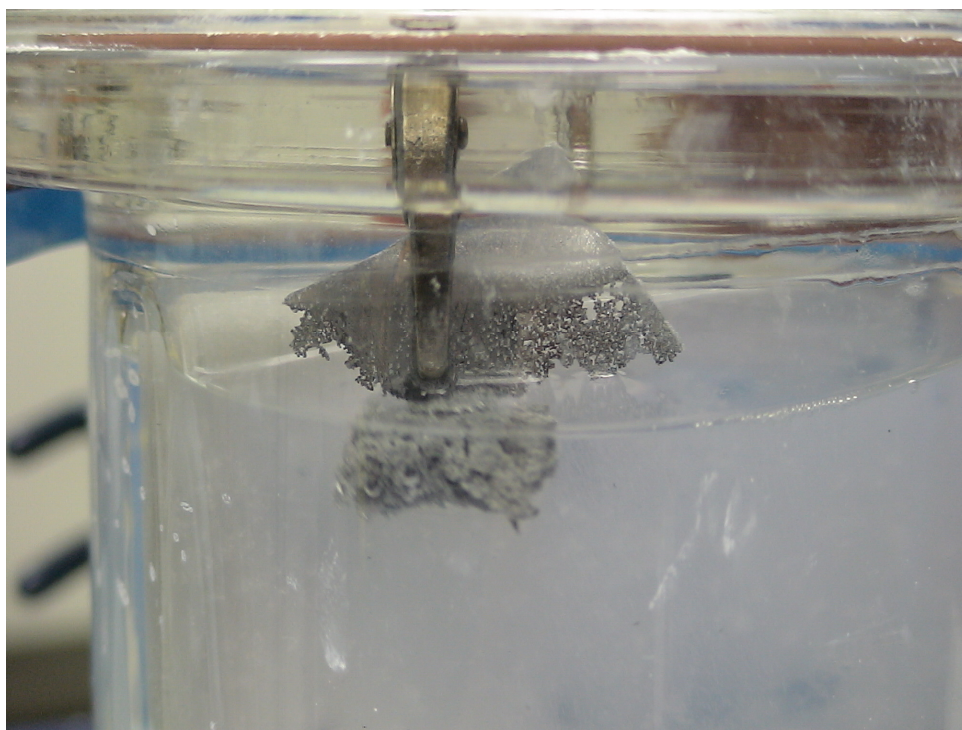


Figure 3. The aluminum electrode is consumed during the reaction at +1.5 V vs. SHE.

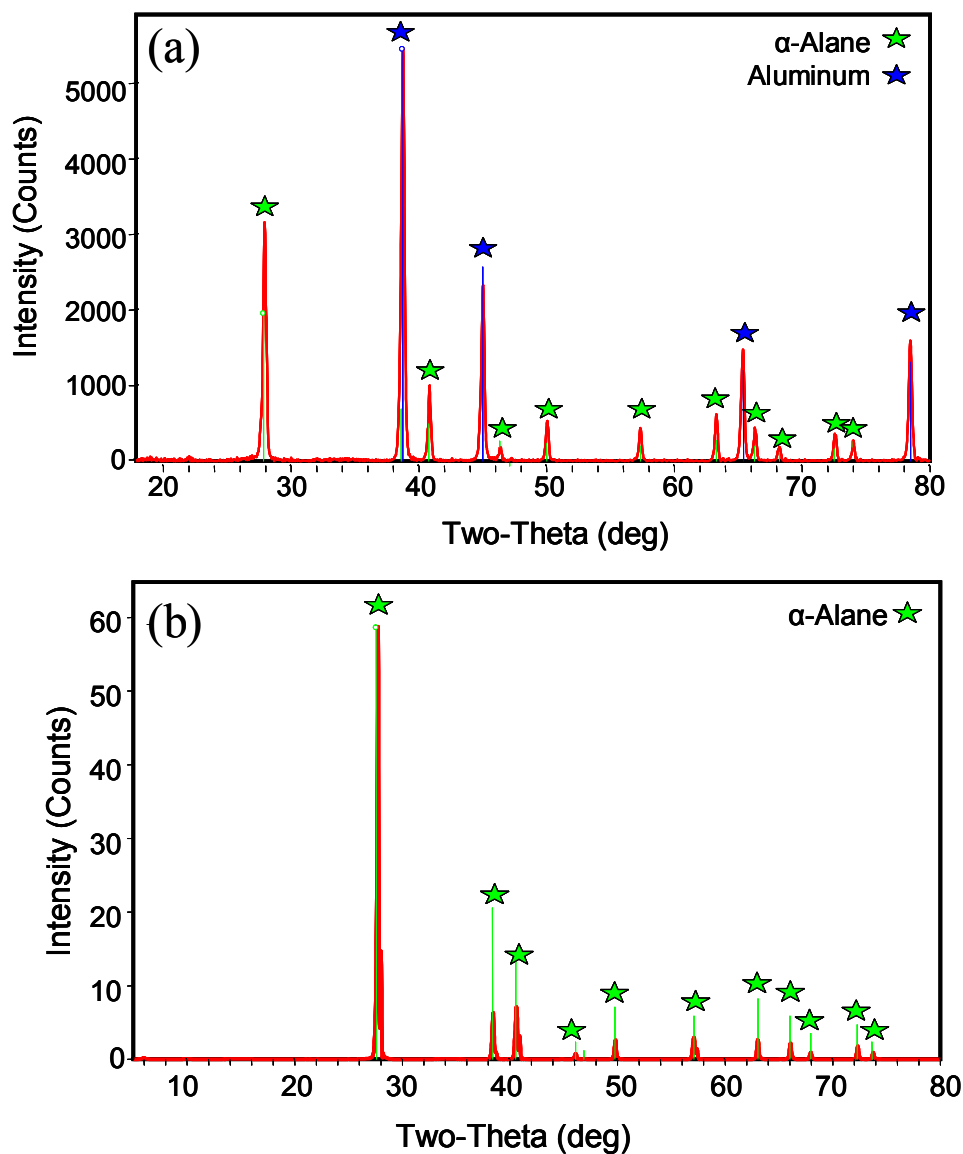


Figure 4. XRD patterns for products recovered from an electrochemical cell. (a) Alane separated from reaction mixture as the THF adducts. When heated under vacuum to remove THF, the solid partially decomposes, losing hydrogen and affording aluminum. (b) Alane is separated using triethylamine to stabilize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



## Supplementary Information for

# Aluminium Hydride: A Reversible Storage Material for Hydrogen Storage

Ragaiy Zidan\*, Brenda L. Garcia-Diaz, Christopher S. Fewox, Andrew Harter, Ashley C. Stowe, Joshua R. Gray

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

\*e-mail: Ragaiy.Zidan@srl.doe.gov

### Supplementary Discussion

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

$$\Delta G = -nFE \quad (5)$$

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:

$$E = -\frac{RT}{nF} \ln(f_{H_2}) \quad (6)$$

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<sub>3</sub> 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  $\text{NaAlH}_4$  or  $\text{LiAlH}_4$  form a conductive electrolyte that can be used in the electrochemical cell to form alane. The electrochemical cell has an aluminium 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.



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

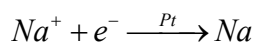


This reaction mechanism has the lower reduction potential and thus requires less energy input to drive the oxidation in an electrolytic cell. The second mechanism for alane production is by the equation:



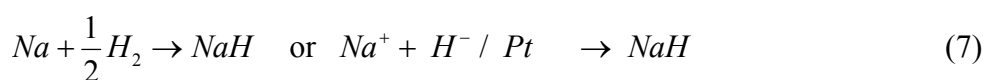
In this mechanism the aluminium electrode is consumed, which is consistent with experimental observations. This reaction also has a higher reduction potential and will require more energy to drive in an electrolytic cell, producing more moles of  $\text{AlH}_3$ .

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

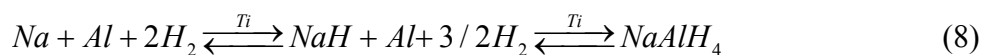


The plating of sodium at the cathode is slightly more energy intensive than formation of sodium hydride, but can directly be used to directly regenerate the starting material.

Once in elemental form, sodium is easily converted to its hydride either by direct hydrogenation or hydrogen can be bubbled at the Pt cathode, resulting in atomic hydrogen to form NaH.



NaAlH<sub>4</sub> Can be regenerated by reacting sodium and Al under moderate hydrogen pressure (100 bar) at 150°C in the presence of Ti catalysts as in equation (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.<sup>1</sup>

Separation of the alane from the electrochemical cell is not trivial. Alane is soluble in both THF and diethyl ether, yet when precipitated at room temperature, polymeric solvent adducts form which are insoluble in the mother liquor.<sup>2, 3</sup> The introduction of a more stable Lewis base has been suggested to retard this process thereby facilitating separation and quantitative recovery of the target species. However, care must be taken when introducing strongly adducting electron donors as separation of the adduct may require temperatures exceeding the stability of the aluminum hydride itself.<sup>4</sup> Finding a middle ground between stability and lability is essential. Triethylenediamine (TEDA) was used to test for alane formation during the electrochemical process. The TEDA scavenges AlH<sub>3</sub> as it is produced

forming a white solid alane adduct which has been verified by powder X-ray diffraction. Alane is easier to recover from the triethylamine adduct than from TEDA adduct and affords pure alane when the complex is heated under vacuum. The pure alane has been characterized by Raman, Figure 5, and by TGA, Figure 6.

Table 1 lists possible reactions (A-E) for the experimental system and the reduction potential for each reaction. Reactions A and B involve only sodium and hydrogen species and are likely to be reductions that take place at the cathode of an electrolytic cell. Reactions C, D, and E are likely to be oxidation reactions that occur at the anode of an electrolytic cell. The oxidation for reaction C, the electrochemical decomposition of  $\text{NaAlH}_4$  to aluminium and hydrogen, is the most favoured oxidation reaction in the system. The electrochemical oxidation reactions to form alane, D and E, are less favourable than C, but have kinetic advantages that allow high selectivity toward alane.

One factor that points to low kinetics for oxidation reactions C and D is the production of gaseous hydrogen. In aqueous solutions, the hydrogen evolution reaction has a low exchange current density relative to other many metals. The low activity toward hydrogen evolution in aqueous solutions similarly gives it low activity toward electrochemical reactions where hydrogen gas is formed. If the aluminium anode has low activity toward reactions that evolve hydrogen, the electrochemical oxidation reaction E will dominate at the anode. If oxidation reaction E is dominant at the anode, the aluminium anode will be consumed in the reaction. The low activity of hydrogen evolution on aluminium electrodes would be advantageous since the desired goal of the project is to design an electrochemical system that is selective to the production of  $\text{AlH}_3$  over possible by products.

### Supplementary Information References

1. Alpatova, N. M., Dymova, T. N., Kessler, Y. M. & Osipov, O. R. Physicochemical Properties and Structure of Complex Compounds of Aluminium Hydride. *Russ. Chem. Rev.*, **37**, 99-114 (1968).
2. Wibreg, E. & Uson, I. R. Properties of aluminum hydride. *Rev. Acad. Cienc. Exact. Fis. Quim. Nat. Zaragoza*, **10**, 35 (1955).; Clasen, H., German P. 1141 623 (1962).
3. Wiberg, E. & Gosele, W. Tetrahydrofuranate of aluminum hydride. *Z. Naturforsch. B*, **11**, 485 (1956).
4. Graetz, J., Wegrzyn, J. & Reilly, J. J. Regeneration of lithium aluminum hydride. *J. Am. Chem. Soc.*, **130**, 17790–17794 (2008).

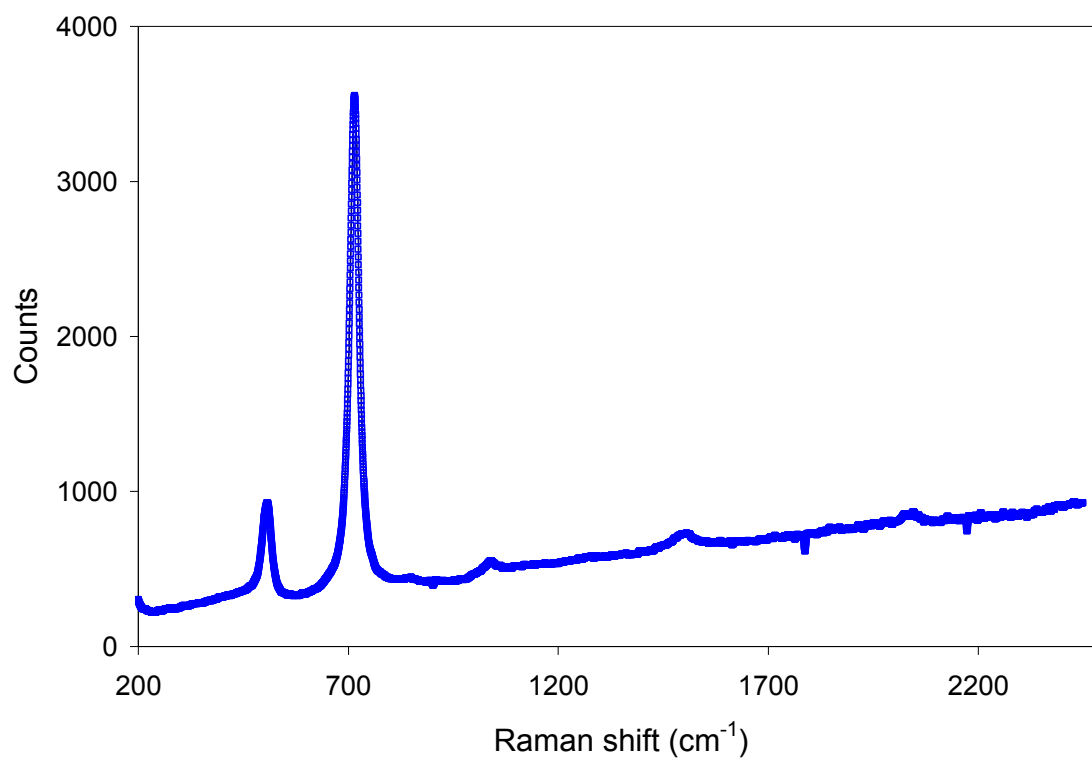


Figure 5. Raman spectrum of alane isolated from an electrochemical cell.

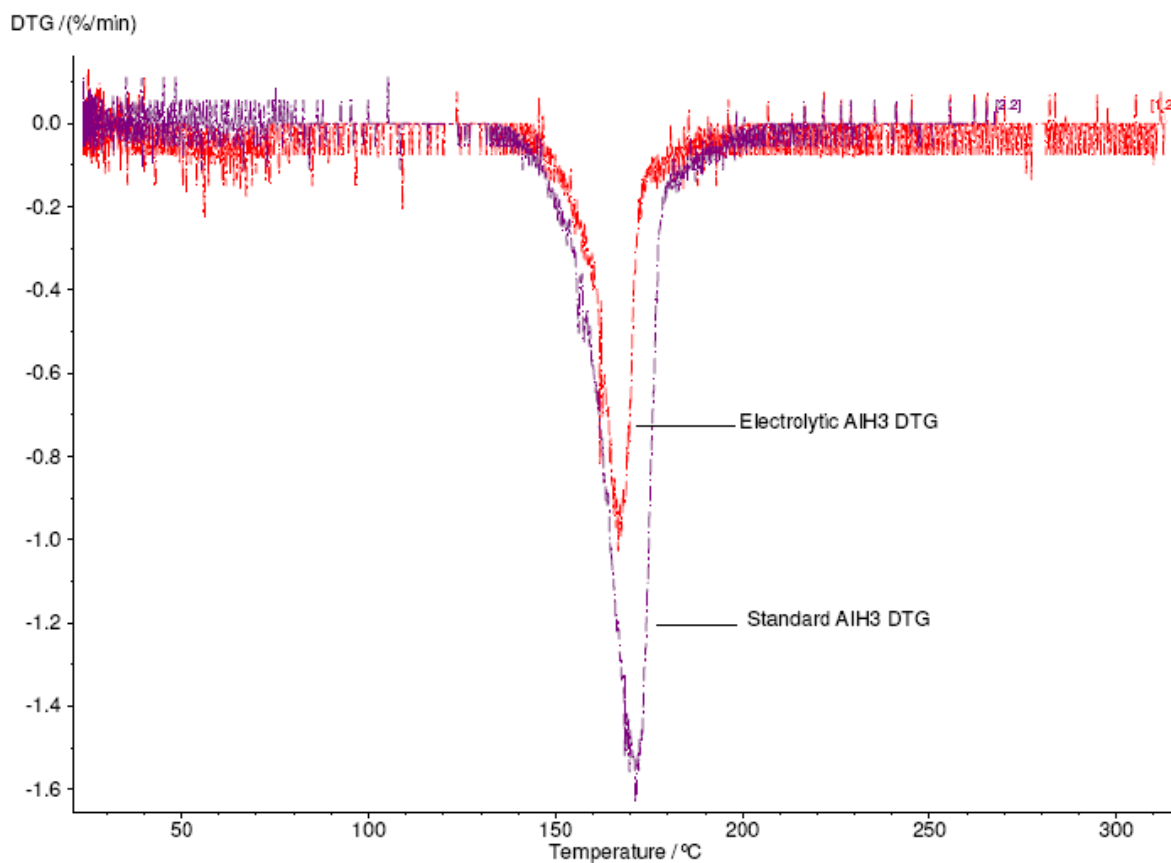


Figure 6. Differential weight loss of alane synthesized electrochemically and a commercial sample procured from Dow. The onset temperature of the electrochemically prepared alane is identical to that of the Dow product.

**Table 1. Reaction equilibrium potentials for NaAlH<sub>4</sub>, Al, and H<sub>2</sub> in an aprotic solution.**

<b>Reaction Letter</b>	<b>Reaction</b>	<b>E<sup>0</sup> (V) vs. SHE</b>
A	$Na^+ + e^- \leftrightarrow Na$	-2.71
B	$\frac{1}{2}H_2 + Na^+ + e^- \leftrightarrow NaH$	-2.37
C	$Al + 2H_2 + Na^+ + e^- \leftrightarrow NaAlH_4$	-2.28
D	$AlH_3 + \frac{1}{2}H_2 + Na^+ + e^- \leftrightarrow NaAlH_4$	-1.73
E	$4AlH_3 + Na^+ + 3e^- \leftrightarrow 3NaAlH_4 + Al$	-1.57