Recent Achievements with Alane (Aluminum Hydride, AlH_3) and Fuel Cell Power Systems

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Abstract: *Fuel cells have many advantages compared to conventional power sources including high efficiency and solid-state operation. Until now, a key shortcoming of fuel cell technology has been the fuel itself, as conventional methods for storing hydrogen were unsafe or impractical for portable use. This paper discusses a lightweight, energy-dense, non-toxic, recyclable, stable, and easy to transport solution for hydrogen storage. It is a material known as Alane that exists as powder and, when heated to the proper temperature, controllably releases hydrogen gas. Alane has near ideal attributes in terms of reactivity, stability, and safety - making it an excellent choice for several applications in need of a portable hydrogen supply. However, it has historically been difficult to produce efficiently. Through partnerships with leading industry experts in the government and private sector, Ardica Technologies has advanced the state of the art of Alane production. Ardica has developed a small-scale process which has been proven to yield high quality Alane that meets or exceeds the characteristics of the generally accepted gold standard reference material.*

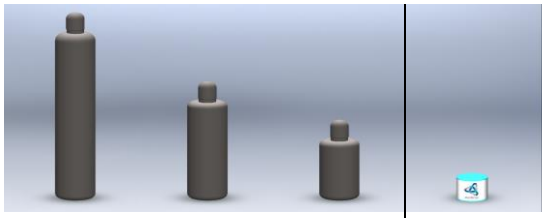
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Introduction

Fuel cell technology has the potential to provide an unmatched capability for supplying portable power and energy over incumbent solutions such as batteries and internal combustion engines. Fuel cells are silent and solid state, like batteries, yet can run continuously and nearly indefinitely off a chemical fuel, like internal combustion engines do. However, until now, a key limitation of fuel cell technology was the fuel itself. Traditional methods for storing hydrogen are heavy, bulky, and often dangerous due to the high pressures involved. Alane, or Aluminum Hydride (AlH_3), offers an alternative solution for storing hydrogen and is widely recognized as one of the world's most promising energy compounds [1].

Alane is a stable, non-toxic, lightweight powder that can be stored for decades at ambient temperature with no appreciable loss of hydrogen. The mechanism for releasing hydrogen from Alane is a simple, single-step decomposition reaction that easily starts, stops, and proceeds to nearly 100% completion [2]. When Alane is paired with a fuel cell to produce power, the only by-products are a minute amount of water vapor and pure aluminum powder, making it an exceptionally environmentally friendly choice. Alane-based power systems are also almost totally silent.

Without the need for heavy storage tanks, Alane allows for truly superior energy density of fuel cell power systems. The chart in Figure 1 shows a comparison of conventional hydrogen storage options versus Alane.



	Industrial Compressed Gas	Composite Tank Compressed Gas	Metal Hydride	Alane
Weight	136 lb	33 lb	43 lb	15 lb
Volume	50 L	37 L	19L	6 L
Pressure	2400 psi	4351 psi	1450 psi	0 psi
Wt % H2	1.1%	4.5%	3.4%	9.8%
Total H2	670 g	670 g	670 g	670 g
Notes	Heavy, Pressurized, Bulky, Flammable	Highest Pressure, Flammable	Small but Heavy for its size	No Pressure, Lightweight, Compact, Safe

Figure 1: Conventional hydrogen storage methods vs Alane storage. Alane safely stores hydrogen chemically bound to aluminum powder at a fraction of the weight and volume of other solutions. By storing hydrogen as a solid, Alane avoids the inherent danger of high pressure gas storage.

Alane Powered Systems

The ability to store a significant quantity of hydrogen at ambient pressure and release it in a controlled fashion lends itself to many applications. Since 2008, Ardica has worked with Army CERDEC to develop Alane powered fuel cell systems, the most notable being a soldier wearable power system known as the Ardica Wearable Power System (WPS). The WPS is a lightweight power generator that produces 20 watts of continuous electricity at 12 – 16.8V

DC. It has a flat, flexible form factor which allows the WPS to be worn either against a SAPI armor plate in the soldier's vest or elsewhere on their body. For a mission time of 72 hours at 20 W, the WPS has an energy density of 463 Wh/kg and 528 Wh/L, which is a 55% savings compared to standard batteries [3]. The WPS is a hybrid system which contains an internal battery to allow for instant power on and continuous power even when changing the fuel cartridges (i.e. "hot swap" capability). In addition, the solid-state nature of the fuel cell enables near silent operation in a wide range of environmental conditions.



Figure 2: Ardica Wearable Power System (WPS).
A 20-watt, solider wearable, portable power generator.

Alongside individual soldier wearable power systems, the Army has also shown interest in higher power generators [4] [5]. These systems would serve as portable battery chargers for groups of soldiers, from the squad level up to platoon level, for example. In Spring 2017, Ardica modeled two potential systems for meeting this Army need, a 1000-watt generator (AFC-1000) and a 500-watt generator (AFC-500). The AFC-1000 system weighs 14.3 lb and has a system volume of 732 cubic inches. The smaller AFC-500 system is slightly more than half the weight and volume of the AFC-1000 system, however two of them are still well below the incumbent solution which weighs over 30 pounds. In addition, the AFC-500s represent a more modular solution that is easier for an individual to carry. Figure 3 shows mock-up systems of both the AFC-500 and AFC-1000 compared to a generator comparable in size and weight to the current Army 1000-watt generators.



Figure 3: 500-watt AFC-500 and 1000-watt AFC-1000 compared to a typical off-the-shelf 1000-watt generator that is comparable to state-of-the-art Army generators.

In June 2017, Ardica began work with Army TARDEC on an Alane based fuel cell system for an all-terrain transport vehicle (FCATT). This vehicle will make use of a 15-kW fuel cell to give it a range of 100 to 300 miles. A traditional compressed hydrogen storage tank to carry the fuel would be too large and remote filling stations pose a challenge. An Alane solution would offer the required hydrogen without these drawbacks.

There has recently also been huge growth in unmanned aerial vehicles (UAVs). Smaller UAVs are typically powered by batteries, most often lithium-ion batteries. These solutions have short runtimes, which limit their usefulness. Larger UAVs are sometimes powered by diesel or gasoline engines, which have an acoustic and thermal signature in addition to producing carbon emissions and other pollution. Using Alane to supply hydrogen to a fuel cell in a UAV would allow for significantly higher energy storage, and thus extended runtime for the same weight. When compared to a typical lithium ion battery, a 375% increase in runtime could be achieved by switching to an Alane powered system of equivalent weight, while still maintaining the advantages of electric propulsion including low noise, low temperature, and only water vapor as an emission. In addition, simple cartridge swaps enable fast refueling, resulting in more uptime and increased productivity. Spent cartridges can be safely and easily stored until they are recycled.

Unmanned underwater vehicles (UUVs) provide another opportunity for enhanced performance with an Alane powered solution. Ardica has worked since 2015 with the Naval Undersea Warfare Center (NUWC) on concepts for Alane powered Navy systems. The Remus 600, shown in Figure 4, was identified as a platform with which to explore the performance metrics of an Alane powered fuel cell-based power system. The Remus 600 is a 12.75" diameter UUV which requires 250 watts of power. An Alane based system would provide a 1.8-2.4x improvement in runtime over the current design, which is an increase of 44 to 60 hours [6].



Figure 4: An Alane powered Remus 600 UUV would have approximately twice the runtime as the current technology

Alane Production

While Alane offers obvious tremendous performance benefits over other hydrogen storage solutions, its biggest shortcoming is that it is not readily available and has only been made by a handful of groups in the past. The Former Soviet Union (FSU), Dow Chemical, and the Office of

Naval Research (ONR) with a contractor have all made Alane before, but the fuel they produced was generally too expensive for commercial applications.

The traditional method to make Alane utilizes costly feedstocks and very dilute solutions in ether and toluene solvents. This drives up the cost in terms of safety, labor, and materials. This method is generally referred to as the "Dow Process" due to their pioneering work in this field during the 1960's [7].

Over the past several years, Ardica has partnered with SRI International and Savannah River National Lab (SRNL) to leapfrog the Dow Process to reduce costs, increase batch sizes, and improve the safety of the manufacturing steps. The result is a small-scale process which advances the state of the art in terms of production and has been proven to yield high quality Alane [8].

In general, Alane produced by the Former Soviet Union (FSU) is considered the "gold standard" to which all newly generated Alane material is compared. Ardica has conducted analytical tests for safety, performance, and thermal stability on both Ardica Alane and FSU Alane to compare and benchmark our progress. We ran several characterization tests including:

- X-Ray Diffraction (XRD)
- Thermogravimetric Analysis (TGA) / Differential Scanning Calorimetry (DSC)
- Thermal desorption-gas chromatography mass spectrometry (TD GC-MS)
- Modified bureau-of-mines (MBOM) impact
- Alleghany Ballistic Laboratory (ABL) friction
- ABL electrostatic discharge (ESD)
- Thermal stability

In third party testing, Ardica Alane compared favorably with FSU Alane in terms of performance and safety, and in certain cases, described below, exceeded the stability of the FSU Alane. The Threshold Initiation Level (TIL) approach was utilized for the impact, friction, and ESD sensitivity tests because it provides a simple and direct comparison of materials for easy ranking. In general, the TIL characterizes the minimum amount of energy required to react a sample.

XRD testing was conducted at an independent 3rd party lab, Balazs Nanoanalysis (Balazs), Fremont, CA. Three samples were tested, one of FSU Alane and two of Ardica Alane. The Ardica samples demonstrated greater than 98% content alpha Alane, which is slightly better than the FSU Alane baseline.

Balazs also conducted the TGA/DSC testing. The TGA test was conducted in a nitrogen atmosphere at a ramp of 10 °C per minute. The Ardica samples were comparable to the FSU Alane sample as both demonstrated less than 0.5% weight loss by 120 °C and between 9% and 10.5% weight loss by 210 °C.

With respect to the DSC, in contrast to the FSU result, the Ardica Alane showed two closely spaced endothermic peaks, which is characteristic of the bimodal distribution in particle size that Ardica has informally observed during production runs. This is a minor distinction and has not presented any challenges with downstream use of the material. The DSC for both the FSU and the Ardica samples was mildly endothermic as expected.

The TD GC-MS organic outgassing testing was also conducted by Balazs. Three samples were tested, one of FSU Alane and two of Ardica Alane. A sum of the organic contaminants in parts per million by weight (ppmw) was used as the critical assessment criteria. Both samples of the Ardica Alane were found to have lower total organic ppmw than the FSU baseline as shown in Table 1.

Table 1: Total Organic Outgassing measured in parts per million by weight. Both Ardica Alane samples show less total contaminants than the FSU baseline sample.

Component	FSU	Ardica1	Ardica2	Units
Low boilers C7 - C10	110.5	77.7	87.2	ppmw
Medium boilers >C10 – C20	10	16.5	31.6	ppmw
High boilers >C20	0.1	0.2	0.4	ppmw
Sum >- C7	**120.6**	**94.4**	**119.2**	**ppmw**

An MBOM impact test was conducted at an independent 3rd party lab, Safety Management Services (SMS), West Jordan, UT. Both the FSU baseline and the Ardica Alane samples did not react even at the highest setting of the MBOM impact machine. This leads us to conclude that the samples' behavior is equivalent, to the best of our measurement capabilities, and that they are both relatively insensitive to impact.

ABL friction testing was also conducted by SMS. The TIL for the Ardica Alane sample was tested to be over 30% higher than the TIL for the FSU baseline (as shown in Table 1), indicating that the Ardica material is less sensitive to friction than the FSU Alane.

Table 2: ABL friction test results. The Ardica Alane exhibited less sensitivity to friction than the FSU sample.

Material	TIL
FSU sample	56 lbf at 4 ft/s
Ardica sample	75 lbf at 4 ft/s

SMS also conducted ABL ESD testing. ESD testing is used to determine the response of an energetic material when subjected to various levels of electrostatic discharge energy. The TIL for both the FSU baseline and the Ardica Alane sample were relatively low, indicating that they are both ESD sensitive materials. In contrast to the FSU sample, the TIL for the Ardica Alane sample was below the machine's detection limit, so we have not yet been able to quantify its sensitivity. Through prior work, however,

Ardica has found that ESD sensitivity can be modified and improved through doping with a low weight fraction of conductive materials to meet requirements.

The most notable finding for users interested in Alane's shelf-life is the thermal stability test. For this test, a sample of known mass is placed into a sealed glass vessel. The vessel is then evacuated to a vacuum level less than 1 torr. The temperature of the vessel and sample is then regulated, measured, and maintained based on the test protocol. The pressure inside the vessel is continuously recorded to monitor the reaction of the sample over time. An independent 3rd party lab, Safety Management Services (SMS), West Jordan, UT, tested one sample of Ardica Alane and one sample of FSU Alane at temperatures ranging from 80 °C to 140 °C. At each temperature, the Ardica material was found to be more thermally stable than the FSU baseline. In fact, at 80 °C, the test results indicate that the Ardica material exhibits over two times the onset time to reaction compared to the FSU baseline.

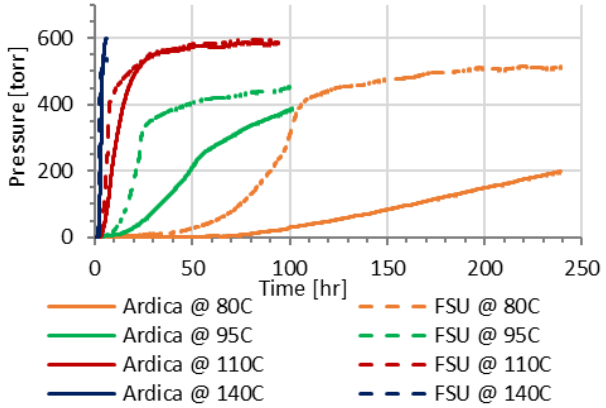


Figure 5: Thermal stability test results. The FSU Alane reacts faster than the Ardica Alane, indicating that the Ardica material is more thermally stable.

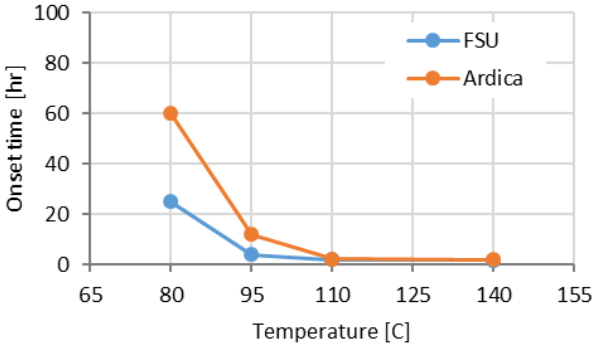


Figure 6: The onset time to reaction is extrapolated from the chart above and plotted here for reference. The onset time to reaction is longer for the Ardica Alane sample than for the FSU Alane sample, providing exceptionally superior stability at more moderate temperatures.

For longer time scales, Alane has been found to be stable for decades at room temperature. Ardica has been in possession of FSU Alane that is over 15 years old, which has generally been stored at ambient temperature. This Alane currently has a hydrogen content in the 9.5-10% range and is regularly used safely in Ardica fuel cartridges. Enough time has not yet passed to have an equivalent measurement for the freshly produced Ardica Alane, but the testing to date leads us to expect a similar result.

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