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Short communication

An analysis of hydrogen production from ammonia hydride hydrogen generators for use in military fuel cell environments

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Abstract

In an effort to simultaneously improve upon existing power storage and generation devices while supplying America's war fighters with state-of-the-art equipment, the US military has focused on fuel cell technology for several military applications. These applications include soldier and sensor power (0–100 W) and auxiliary power units (500–3000 W). Over the past few years, the fuel cell industry has realized remarkable decreases in the size and weight of proton exchange membrane (PEM) fuel cell systems. However, a safe and affordable means of storing and generating hydrogen does not yet exist to justify their transition into the field. In order to assess the hydrogen storage capacity and hydrogen generation rates of ammonia (NH_3) based systems, the US Army Communications-Electronics Research, Development, and Engineering Center (CERDEC), tested several ammonia hydride hydrogen generator systems built by Hydrogen Components Inc. (HCI).

Experimental results and analysis illustrate that while there are developments necessary at the sub-system level, the hydrogen generators are ideal energy storage devices for low power (5 W) operations over wide temperature ranges. The results show that the hydrogen generators are capable of operating autonomously for over 50+ h of operation (at a 5 W load) and producing hydrogen delivery system energy densities of 480 Wh/kg.

Keywords: PEM fuel cells; Hydrogen production; Ammonia

1. Introduction

Major force structure systems such as objective force warrior (OFW) and future combat systems (FCS) are focusing on transitioning the military into a rapidly deployable, tactically superior and sustainable force that can provide quick reaction capabilities anywhere in the world. These forces will heavily rely on innovative technology solutions in order to achieve the overall goals.

Under these new force structures, traditional battery chemistries, which have energy densities of 100–200 Wh/kg, cannot meet the aggressive energy density and weight requirements for the soldier's power demands. Therefore, programs such as OFW and FCS will require novel, high-energy dense power systems such as fuel cells that are capable of delivering at least a 20 W continuous load.

Unattended ground sensors are another key FCS application that will require novel power generation technology. The FCS force will incorporate and exploit information obtained by networks of these sensors in order to assess and manage the battlefield. Ideally, these networks will be deployed and operated for long durations of time without maintenance or fuel resupply. Average power consumption for an individual sensor is in the 2–10 W range. Test profiles were designed to replicate an average power profile for unattended ground sensor applications, where long mission duration and reliable performance under various weather conditions is essential.

Over the past few years, the fuel cell industry has realized remarkable decreases in the size and weight of proton exchange membrane (PEM) fuel cell systems. However, a safe and affordable means of storing or generating hydrogen for these systems does not yet exist to justify their transitions into the field. Therefore, the military has recently shifted its focus from the 'cell' to the 'fuel' in order to develop high energy dense hydrogen storage and generation devices.

Several fuels are currently used to store hydrogen for fuel cell consumption. One such fuel is ammonia (NH_3). Ammo-

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nia stores 17.6 wt.% hydrogen, which is greater than 'neat' methanol (CH_3OH) at 12.5 wt.%. In order to capitalize on the high hydrogen wt.% of ammonia, Hydrogen Components Inc. (HCI) has developed a system that reacts ammonia vapor with solid lithium aluminum hydride ($LiAlH_4$) to produce high purity hydrogen gas. The reactor is called the ammonia hydride hydrogen generator (AHHG).

To better assess the hydrogen storage capacity and hydrogen generation rates of HCI's ammonia hydride hydrogen generators, the US Army Communications-Electronics Research, Development, and Engineering Center (CERDEC) tested several reactors under low to mid power ranges (0–50 W).

1.1. Operating principles

The AHHG is composed of three main components: a rechargeable ammonia canister, a $LiAlH_4$ reactor bed, and an ammonia getter. The AHHG operates on a simple check valve system. A first check valve is located between the reactor bed and the ammonia canister, and the second is at the reactor outlet connection to the ammonia getter. Once the ammonia reservoir is connected to the reactor bed, ammonia vapor flashes through the connection to react with the $LiAlH_4$. When the reactor reaches steady state pressure, dependant on the vapor pressure of ammonia at ambient conditions, the ammonia check valve closes.

As hydrogen is consumed by the fuel cell, the pressure in the reactor drops and causes the ammonia check valve to open, allowing more ammonia into the reactor. Thus, hydrogen is generated only on-demand as it is consumed by the PEM fuel cell. The hydrogen gas exiting the reactor is passed through the ammonia getter to remove trace amounts of ammonia and other compounds before being fed to the fuel cell system.

The ammonia tank can be refilled to produce additional amounts of hydrogen. However, once the $LiAlH_4$ supply is depleted, the system will cease to produce hydrogen.

There are both a 400 and 267 Wh configuration of the AHHG (depending on size of reactor bed). Fig. 1 illustrates an AHHG system and Table 1 provides an analysis of theoretical energy densities and weight breakdowns for a sample 400 Wh system.

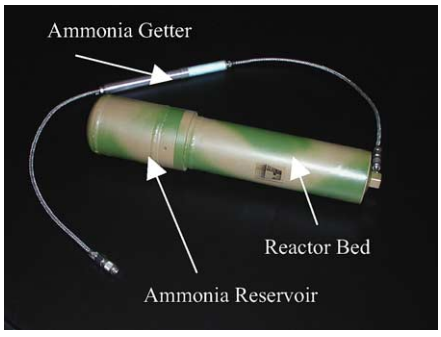

Fig. 1. The ammonia hydride hydrogen generator.

Table 1
Specifications for a 400 Wh system

400 Wh system specifications	
NH_3 mass (g)	145.0
NH_3 tank mass (empty) (g)	96.8
NH_3 tank mass (full) (g)	241.8
Ammonia getter (g)	60.00
$LiAlH_4$ mass (g)	324.00
Reactor mass (empty) (g)	205.09
Reactor mass (full) (g)	589.09
Total system (g)	830.86
System energy density (Wh/kg)	481
Hydrogen weight (%)	3.1

1.2. Ammonia: high energy dense fuel

Ammonia is primarily produced through synthesis processes such as the Haber–Bosch–Mittasch process. Historically, ammonia has been widely used in the industrial sector as a fertilizer, cleansing agent, and explosive. With the rapid development of fuel cell technology, coupled with the ever-growing need to supply a safe, hydrogen dense fuel, ammonia has recently received attention as a candidate source for atomic hydrogen storage.

Ammonia stores 17.6% hydrogen on a mass basis and has a lower heating value of 5.2 kWh/kg, which is less than that of methanol (5.5 kWh/kg). However, methanol and other hydrocarbon fuels typically must be diluted to be suitable with current steam reforming technology. When the additional water for steam reforming is accounted for, ammonia has a greater relative energy density than hydrocarbon fuels such as methanol. In addition, ammonia does not contain carbon atoms that can cause coking or carbon monoxide poisoning, two common drawbacks to hydrocarbon fuel reforming systems. However, ammonia can foul the catalyst and electrolyte materials typically used in fuel cell systems. Concentrations as low as 10–20 ppm can cause significant performance degradation to PEM fuel cells [1]. Therefore, all ammonia-based systems must incorporate a means for polishing the hydrogen-rich product gas in order to reduce ammonia concentrations to as low as possible.

Ammonia production prices have fluctuated over the past several years. In 2002, (anhydrous) ammonia prices were around US$ 250/t. Current ammonia prices are approximately US$ 360/t [2]. This production price equates to approximately US$ 0.13/kWh of exploitable hydrogen fuel (at 0.7 V per cell). Comparatively, hydrogen stored in methanol costs US$ 0.11/kWh H_2 [3].

In terms of chemical safety, ammonia poses a low risk of ignition in the presence of sparks or open flames. However, exposure to high concentrations of ammonia may cause severe bodily burns or injuries. In extreme cases, exposure to high concentration levels may also cause blindness, lung damage, heart attack, or death [1]. Safety considerations must be taken into account in the design, testing, and use of all ammonia-based hydrogen generators.

Despite the safety and poisoning concerns, ammonia's favorable thermodynamic properties and low production costs help establish a solid case for ammonia as an economically feasible, high energy dense fuel for fuel cell applications.

2. Army test and evaluation

2.1. Procedure

The ammonia hydride hydrogen generator systems were tested under several existing and future power profiles typically encountered within the military.

A 50 W trial was designed to simulate both modern and projected power requirements for communications devices and soldier system applications. A 5 W trial replicates an average power draw for a remote sensor.

A Ball Aerospace PPS-50 W fuel cell system was used for each AHHG trial. The PPS-50 W system requires 0.1–8.0 psi hydrogen feed at 0.5–1.0 slpm. All purged hydrogen volumes were measured and included in overall hydrogen production and energy density calculations. At a minimum, the following measurements were taken for each trial: external temperature of reactor bed, pressure and flow rate of hydrogen exiting the reactor, weight of AHHG system and individual component pieces before and after trial, volume of hydrogen purged from fuel cell. The key goal in the test and evaluation of the AHHG systems was to obtain experimental system energy densities (Wh/kg) and total hydrogen production capabilities (H_2 (mol)/NH_3 (mol)) for each AHHG.

3. Results and discussion

3.1. Experimental results

Table 2 shows a summary report for four trials.

3.2. 50 W load profile

Fig. 2 depicts the AHHG's performance at 50 W and high temperature (46 °C). Under both ambient and high temperature conditions, the AHHG systems could not provide the required hydrogen flow rate (0.5–1.0 slpm) for a 50 W load. The loads were continuously reduced in order to allow the AHHG and fuel cell systems to reach steady state operation. While the AHHG reactors were able to support a 40 and a 25 W load for short durations, they could not operate in a continuous fashion utilizing all available ammonia fuel. This resulted in reduced reactor bed utilization (60–70%) and a decreased system energy density.

Table 2
Summary of US Army CERDEC test results for ammonia hydride hydrogen generators

Power profile	5 W	5 W	25–50 W	25–50 W
Hydrogen production from reactor beds				
Temperature (°C)	2	23	23	47
Ammonia consumed (mole)	10.7	12.9	3.2	5.9
Hydrogen produced (mole)	30.3	30.5	9	24.4
Hydrogen (mol)/ammonia (mol)	2.8	2.4	2.8	4.1
Net electrical energy (Wh)/theoretical	354/400	379/400	161/268	280/400
Energy density (Wh/kg)	483	442	247	326
Reactor bed utilization (%)	89	95	60*	70*

* Ammonia getter failed/consumed. Not all ammonia consumed.

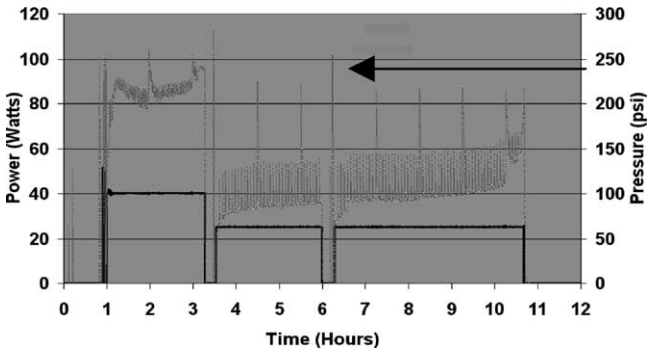

Fig. 2. 50 W trial at 46 °C. Note 250 psi pressure gradient.

The probable mechanism for the AHHGs poor performance at these higher loads is the ammonia getter. During all of these tests, large pressure drops were experienced across the getter. Fig. 2 shows that at 40 W, a pressure drop as large as 250 psi occurred. Poor hydrogen flow through the getter often resulted in vacuum pressure to the hydrogen inlet to the fuel cell. This was especially apparent during controlled fuel cell purge cycles. This pressure gradient was increased over time (as seen in Fig. 2) as the ammonia getter reached its ammonia saturation limit at 10.5 h into the trial.

The getter also restricted hydrogen flow due to increasing levels of ammonia in the hydrogen-rich gas. Higher power levels equate to higher fuel demand. For the AHHG system, this increased hydrogen demand causes a larger flow rate through the reactor bed, which results in a reduced residence time for the ammonia gas in the reactor bed. A reduced residence time translates to larger concentrations of unreacted ammonia passing through the reactor bed and into the ammonia getter. The ammonia getter compound expands as it adsorbs ammonia gas, thereby restricting the overall flow of hydrogen through the getter compound. Thus, elevated concentrations of unreacted ammonia decreases both the overall lifetime of the non-regenerable ammonia getter and the utilization of the ammonia fuel and $LiAlH_4$ reactor bed. Future testing of the AHHG system should focus on gas diffusion through the getter and residence times in the reactor bed at higher flow rates.

The 50 W trial at 46 °C resulted in the highest H_2 (mol)/NH_3 (mol) production ratio (4.1 H_2 (mol)/NH_3 (mol)) and highest reactor bed temperature (~85 °C external) for all trials. The reaction below shows the most stable

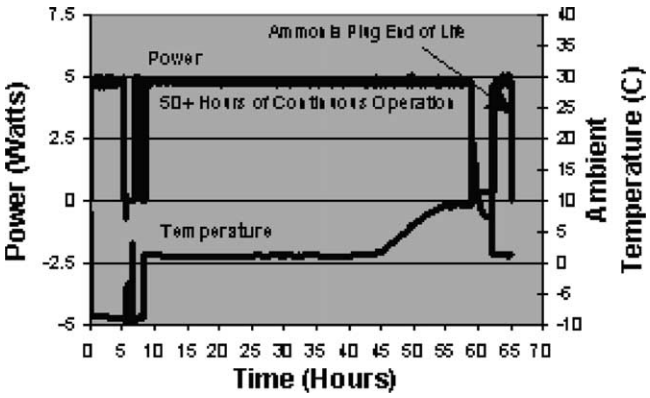

Fig. 3. 5 W load at 2 °C ambient conditions.

AHHG reaction.

$$3LiAlH_4 + 4NH_3 \rightarrow 3AlN + Li_3N + 12H_2$$

This reaction occurs around 30–50 °C and results in a H_2/NH_3 molar ratio of approximately 3.0. The increased ratio for the 46 °C trial suggests that a secondary reaction was occurring. A study of $LiAlH_4$ reaction chemistry shows that the $LiAlH_4$ reactor bed may have undergone thermal decomposition, which typically occurs at temperatures near and above 100 °C [4-6]. During thermal decomposition, the $LiAlH_4$ reacts with heat to evolve hydrogen gas and solid byproducts, thus producing more hydrogen fuel for the fuel cell [4,5].

3.3. 5 W sensor profile

Fig. 3 shows the results of the low temperature trial. Under both ambient and low temperature conditions, test results show that the AHHG systems can run continuously and autonomously for over 50 h while utilizing up to 95% of the rated reactor bed.

The high pressure gradient across the ammonia getter that occurred during the 50 W trials did not occur for the 5 W trials. This lower power level resulted in a diminished demand for hydrogen, which consequently led to a reduced gas flow through the reactor. This led to a higher residence time for the ammonia gas, higher fuel and reactor bed utilizations, and increased ammonia getter lifetime. All of these factors contributed to producing the highest experimental system energy densities (of 483 Wh/kg, see Table 2) for CERDEC trials.

4. Conclusions

Initial testing indicates that the AHHG hydrogen generator systems may be suitable for low power, long duration missions where improved system energy density and independent operation is vital. Under low power profiles, the AHHG systems can provide up to 483 Wh/kg and operate autonomously for over 50 h at both ambient and near freezing conditions.

At higher loads (40–50 W) the AHHG systems are not technologically mature enough to produce the required flow rate/pressure of hydrogen gas. The primary limitations are associated with the ammonia getter sub-system. The ammonia getters must go through further design and testing to assure adequate hydrogen diffusion through the 'getter' compound at increased hydrogen flow rates while maintaining suitable purity levels of hydrogen for fuel cell consumption.

The AHHG system compares favorably to current military batteries due to its higher energy density of 480 Wh/kg. However, for a complete soldier power system, the weight of the fuel cell and its balance of plant must also be taken into account for an entire fuel cell system energy density. Once these additional weights are taken into account, batteries typically remain as the most energy dense power system for short-term missions (<24 h). For longer missions, fuel cell systems become attractive because the soldier only needs to carry and replace fuel cartridges. Thus, the AHHG may not be appropriate for short duration missions because the overall fuel cell system does not offer any weight advantages over current battery systems. However, the AHHG is a suitable energy storage device for long term, remote sensor operation in various climates.

Further research and development efforts should focus on new ammonia scrubbers that eliminate fuel cell contamination as well as innovative nitrogen-based systems that evolve hydrogen from solid products and byproducts. These types of systems may resolve some issues with ammonia scrubbing and chemical safety.

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