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Development and demonstration of a deployable apparatus for generating hydrogen from the hydrolysis of aluminum via sodium hydroxide

David W. Hurtubise ^a, Donald A. Klosterman ^{a,b,*}, Alexander B. Morgan ^{a,**}^a University of Dayton Research Institute, 300 College Park, Dayton, OH 45469, USA^b Chemical & Materials Engineering Dept., University of Dayton, 300 College Park, Dayton, OH 45469, USA

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ABSTRACT

Emergency and backup power is often enabled through the use of petrochemical based fuels and combustion-based generator systems, and while reliable, these backup power systems fail when petrochemical supplies are disrupted due to refinery, oil outages, or transportation delays. Fuel cells in some cases can serve as a backup to these traditional generators, but they also are fuel-limited to supplies of available energy sources. Recent work conducted in our laboratories focused on the development of a “backup” emergency hydrogen generation system that could be employed when existing energy stockpiles have failed or depleted. Specifically, aluminum metal can be used to generate hydrogen for fuel cells via hydrolysis with sodium hydroxide. In this paper, we summarize the engineering work to produce a deployable aluminum to hydrogen generator which is capable of producing 3.75 kg of hydrogen per day from scrap aluminum feedstocks. The generator was built upon an aircraft deployable pallet, allowing for hydrogen to be generated remotely in cases of power and fuel outages.

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Introduction

Electrical power is an essential infrastructure component for modern society, and that infrastructure can be disrupted by both natural events (storms, earthquakes) and man-made events (power station failure, fuel outage, mechanical failure, geopolitical event). In such cases, for critical systems which need electricity to run, backup power generation systems are put in place. Most common are internal combustion engine based generators that run off of hydrocarbon fuels (gasoline, kerosene, diesel, propane, natural gas, etc.), but

battery packs that charge from renewable energy sources also exist. Another backup power supply can be fuel cells, but as the name implies, fuel is needed to run the fuel cell so that it can generate power. Both methanol, hydrogen, and hydrocarbon-based fuel cells exist, with hydrogen fuel cells being more commonly known. Still, the same disruption events which interrupt electrical supply can interrupt fuel supply for generators and fuel cells, as one can only stockpile so much fuel for generators or fuel cells in a safe manner. Specifically, such a stockpile can present a significant fire hazard depending upon what type of fuel is stored and the quantity stored. More importantly, in cases of major natural

* Corresponding author. University of Dayton Research Institute, USA.

** Corresponding author.

E-mail addresses: dklosterman1@udayton.edu (D.A. Klosterman), Alexander.Morgan@udri.udayton.edu (A.B. Morgan).

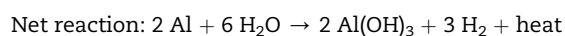
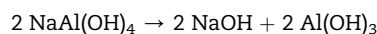
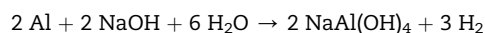
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disasters or even major man-made events where both power and fuel supply infrastructure can take weeks to restore, the ability to generate fuel to run the generators or fuel cells may be needed as a “backup to the backup”. Returning to the concept of fire safety for a fuel precursor stockpile, depending upon the fuel precursor chemistry, even stockpiling the fuel precursor can present safety issues. With these considerations in mind, our laboratory was tasked with developing a hydrogen generation system that did not rely upon wind or solar power, and could tap into other precursors to generate hydrogen as needed for emergency purposes. The purpose of this system was to provide hydrogen (~5 kg/day) to run fuel cells for emergency power in remote locations where bringing in more hydrogen or fuel for generators was not an option. Other requirements of the hydrogen generation system included:

- Ability to be airlifted from one location to another.
- Easy to operate and would consume minimal energy on its own to generate and compress hydrogen for fuel cell use.
- Would use a non-flammable and readily available fuel precursor to generate hydrogen.
- Would not use potable water as a fuel precursor to generate hydrogen.
- Would produce nominally recyclable waste.

With the above design requirements in mind, there were limited choices available. Electrolysis of water was eliminated, as was reformation of hydrocarbons. Waste-To-Energy to generate syngas ($\text{CO} + \text{H}_2$) was an option, but that technology effectively requires a stockpile of flammable waste (hence its ability to generate syngas via pyrolysis). The last option to consider was hydrolysis of aluminum metal via an aqueous solution of sodium hydroxide, via the following chemical reactions:



Aluminum is catalytic in splitting water into hydrogen gas, which can be collected and used elsewhere, and hydroxyl ions which combine with aluminum to yield a friable solid powder called alumina trihydrate/aluminum hydroxide (ATH). Aluminum metal is for all practical purposes a material that can be stockpiled without resulting in new fire hazards, and furthermore, scrap aluminum metal from cans, foil, or machine shops could be used as well. The ATH byproduct is stable and non-toxic. The amount of heat generated by the system is significantly large, and its removal has proven to be the rate-limiting factor for this process.

This reaction has been studied for several decades, with two seminal publications appearing in 1970–72 [1,2]. More recently, Huang et al. [3] compiled an excellent review article on the feasibility of using the reaction between water and aluminum to generate hydrogen for fuel cells. A key to enabling this reaction is the removal of the naturally occurring oxide layer on the surface of aluminum, also referred to

as “activating” the surface. Surface activation can be accomplished through several options, including alkaline solutions (such as NaOH and KOH), oxide additives (such as baeyerite and boehmite), carbon materials (graphite, SiC), amalgam, water soluble inorganic salts, and others, as summarized in Ref. [3]. Since 2013, several additional articles have been published. These include topics such as the combination of carbon nanotubes with aluminum powder in a spark plasma sintering process [4]; study of the mechanism of how metal oxides affect the passive oxide film on aluminum, thereby promoting the aluminum-water reaction without using NaOH [5]; reaction of water with molten aluminum and aluminum-lithium alloys [6]; investigation of milling techniques to reduce waste aluminum cans to a powder, as well as various additives including NaCl, Ni, Bi, and low concentration NaOH (0.25 M) [7]; production of hydrogen from aluminum foils with Bi and NaCl mixtures in low alkaline solution *without* prior ball milling [8]; use of a glow discharge hydrogen gas plasma process to modify the surface oxide layer of aluminum powder [9]; characterization of the microstructure of aluminum-Ga-In alloys activated with planetary ball milling [10]; and refinement of the previously developed and widely known “shrinking core model” which describes the fundamental reaction kinetics [11]. The goal of the majority of these studies was to develop alternatives to using highly concentrated caustic (or acidic) solutions to remove the oxide layer. All these studies were conducted on the laboratory scale (<1 kg), vs. our methodology, which was focused on larger scale hydrogen production.

With the selection of aluminum metal as the fuel precursor, our group designed a portable batch reactor for implementing this reaction. The system is referred to as Deployable Aluminum-to-Hydrogen Generator (DAHG) system. The following design requirements were considered and implemented during the design of this system:

- How to load/feed in aluminum metal;
- How to transfer, purify, contain, compress and store hydrogen as it is generated;
- How to remove heat from the system, and if possible, consider it for energy recovery;
- How to address the solid byproducts of the reaction;
- Be able to operate with non-potable water; and
- Be able to build the system on a standard aircraft pallet.

In this paper, we outline our successful approach toward the design and operation of the DAHG, and how it performed considering the 5 kg H_2 per day target. We elected to use concentrated solutions of NaOH and shredded waste beverage cans (without paint removal) in order to have access to large and readily available quantities of the reactants (10–30 kg batches). This allowed us to focus on the scale-up issues such as reactor design, material loading, heat transfer, reaction rate phenomena, waste removal, etc.

There are only a few systems of similar scale mentioned in the literature. Two U.S patents [12,13] outline plans for scaled up apparatuses, but it is not clear whether the equipment was ever produced and tested (the data in those patents, while fairly detailed, was collected on laboratory scale equipment). Vlaskin et al. [14] developed a pilot scale continuous process

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