# A New Method of Generating and Storing Hydrogen for Fuel Cell Applications

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**Abstract**

Current hydrogen technology relies on natural gas to generate the hydrogen and high pressure gas tanks to store the hydrogen. The new process illustrated here eliminates the negative aspects associated with these processes. Sodium borohydride, or any other metal hydride, is stored in solid form, thereby creating the most energy dense scenario as well as allowing for the use of current infrastructure. However, instead of using a precious metal catalyst, a cheap solid acid such as citric acid, is added to the metal hydride to regulate hydrogen production. With this method, a solid metal hydride/acid powder can be stored under low pressures until hydrogen is needed. At that point, water created from the fuel cells can be added in controlled amounts to the metal hydride/acid powder creating a controllable, humidified hydrogen flow perfect for fuel cell applications.

Keywords: Sodium Borohydride, Fuel Cell, Hydrogen, Hydrogen Economy

## 1. Introduction

There has been a considerable effort over the past several years to bring hydrogen fuel cell technology to the masses. Through both public and private initiative, fuel cell research and development has yielded vast improvements over fuel cell stacks of previous years. Although several different types of fuel cells exist, classified by the type of fuel they require and the means by which they utilize this fuel, the proton exchange membrane fuel cell (PEM) has become the standard when talking of small scale power generation (<250kW). The PEM utilizes direct hydrogen and oxygen gas to create power by way of a proton conducting membrane. Such a membrane isolates the protons from the hydrogen, allowing them to flow through the thickness of the membrane. The electrons, also from the hydrogen, are then forced through wires creating electrical power. The protons, electrons, and oxygen from a separate gas, typically air, are then combined to complete the reaction and create pure water. As noted, the only byproducts from this method of generating power are heat and water.

The PEM has been slotted for use in vehicle and portable applications for a variety of reasons. The PEM is typically considered to have the highest energy density of any fuel cell[1]. This fact, along with its fast start up time (<1 sec) and relatively low operating temperature has led many to believe that this is the future of portable power generation[1]. However, a single PEM fuel cell, by itself, does not create the necessary voltage or power for use in any meaningful application. For this reason, it is necessary to stack several individual cells together in order to obtain the necessary voltages and power[2].

### *1.1 Challenges Remain*

While the future for PEM technology appears bright, several key issues must be resolved before widespread adoption of this technology can take place, not the least of which is the production and distribution of the hydrogen fuel. Current thought revolves around natural gas reformation and other methods to generate the hydrogen and then compressed gas cylinders to store it. This is a proven technology, but it is not an ideal candidate for PEM fuel cells. For the greatest efficiency, the hydrogen needs to be humidified before entering the fuel cell. When using compressed hydrogen, this feat is accomplished using external humidifiers which add to the cost, power requirements, and complexity of the system. Furthermore, the use of high pressure (up to 10,000psi) hydrogen stored on vehicles leads to questions about the safety of such a technology. As 95% of the hydrogen currently produced in the US comes from steam-methane reformation (SMR) it will eventually be necessary to find a more ecologically friendly method of production[3]. The lack of a single technology for all applications (transportation, portable, etc.) creates a fragmented technology system where each different application requires a different technology. This leads to a higher priced system and a steeper learning curve for any potential customers.

*1.2 The Complex Hydride*

An emerging school of thought centers on a form of hydrogen storage known as complex hydrides, wherein hydrogen is stored in the bonds within the chemical and is released during a chemical reaction. One such complex hydride receiving a great deal of attention is sodium borohydride ($NaBH_4$). This chemical is relatively inexpensive and has the capability to be mass produced as a derivative of borax. When added to water sodium borohydride reacts to produce hydrogen gas and an environmentally friendly sodium metaborate ($NaBO_2$) as seen in the following reaction[4]:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$$

As illustrated, borohydrides in general benefit by deriving two hydrogen molecules from the borohydride itself and two additional molecules from the water it reacts with. This creates a theoretical hydrogen density of almost 11% when the sodium borohydride and a corresponding amount of water are reacted[4]. However, conventional wisdom had been to store the sodium borohydride within a caustic solution of sodium hydroxide (NaOH) and water. The caustic additive worked to slow the reaction between the water and the borohydride; allowing for a safer and longer lasting product. When hydrogen was needed, a platinum or other precious metal catalyst was brought into contact with the solution and hydrogen was released[5]. This approach successfully utilized the sodium borohydride reaction, but the full potential of the chemical as a hydrogen storage medium was not achieved. Expensive precious metal catalyst, low hydrogen content per volume due to large percentages of caustic additives, as well as limited solubility of the sodium borohydride all create problematic issues when this technique is employed in a consumer friendly way.

## 2. Procedure

A new procedure that may lead to a workable hydrogen economy employs sodium borohydride in solid form, as opposed to a caustic solution. Normally, when sodium borohydride is added to water, hydrogen is produced. However, this rate of production of hydrogen is insufficient to power a fuel cell of reasonable size. For that reason this technique utilizes a solid acid as a reaction controlling agent. Previous techniques have used a caustic ingredient to retard the reaction. This technology, however, allows an inexpensive solid acid, such as citric acid, or a metal salt, such as nickel chloride, to be used to accelerate the reaction to levels adequate for fuel cell use[6]. Typically, the solid sodium borohydride and reaction controlling agent would be placed together in a low humidity container until needed. This is possible as there is no reaction between the powders until water is added. When hydrogen is needed, water may be added in controlled amounts until the desired quantity of hydrogen is produced. This allows the hydrogen to maintain a solid form as long as possible, requiring no high pressures or high temperatures. Furthermore, the hydrogen is able to stay in the densest form until needed in order to conserve space.

Initial results to determine the amount and rate of hydrogen produced were carried out by collecting the hydrogen over water. The solid fuel is reacted with excess water. The created hydrogen is then led through plastic tubing to a graduated container inverted in a bath of water. The hydrogen gas displaces the water in the container, and from periodic measurements, the rate of hydrogen production can be calculated. Such experiments were performed using different combinations and concentrations of solid acids and borohydride at or close to standard temperature and pressure. The sodium borohydride was procured from MP Biomedicals, LLC while the acids were purchased from Spectrum Chemicals & Laboratory Products. The results were then plotted verse time to show the rate of hydrogen production and compared to hydrogen generation rates without the acid controller.

It was also necessary to determine the humidity and composition of the hydrogen gas. This was necessary in order to determine the viability of using the borohydride/acid fuel for hydrogen fuel cells. The TSI Model 7565 Q-Trak from Argus-HAZCO was used to determine the relative humidity of the produced gas as well as to determine any extraneous carbon gases created from the reaction[7]. The Q-Trak was utilized to measure different quantities in the gas created from different fuel concentrations. While the CO sensor was not able to be utilized due to its cross-sensitivity to hydrogen gas, the $CO_2$ showed no increase in concentrations over the base line. The lack of $CO_2$ supported the assumption of a lack of CO emissions.

## 3. Results and Discussion

This technique of adding a solid acid does more than just increase the reaction rate. Previous attempts to use solid borohydrides have resulted in a situation known as caking.

Caking occurs when a layer of the reaction product, sodium metaborate, forms on top of the unreacted sodium borohydride, effectively cutting off any reaction. By increasing the reaction kinematics, the citric acid effectively eliminates all caking issues by churning and bubbling, thereby mixing the metaborate into the powder. The hydrogen produced by this reaction is ideal for fuel cell applications. The reaction rate can be controlled by using different acids at different concentrations and, as the reaction environment remains acidic for longer, a greater percentage of the theoretical hydrogen can be liberated. This relationship between hydrogen production with and without an acid control agent can be seen in Figure 1. Figure 1 shows the hydrogen liberation rate for the reaction between sodium borohydride and excess water (Blue) and sodium borohydride with 50% citric acid by weight and excess water (Red). With most fuel cell systems, an external humidifier is necessary to humidify the hydrogen gas before it enters the fuel cell.

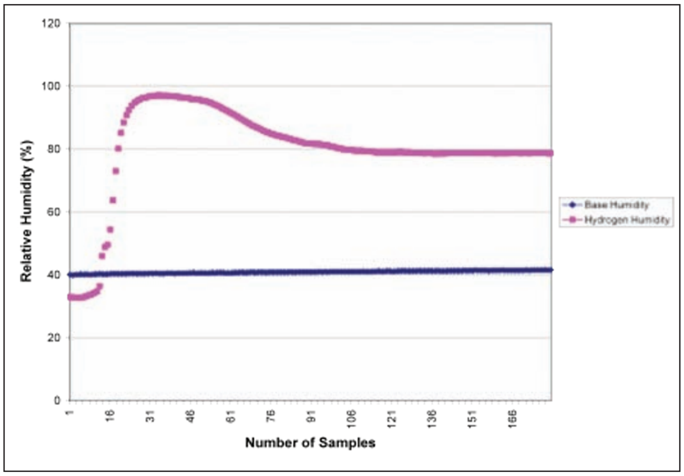


**Figure 1.** Hydrogen liberation comparison of $NaBH_4$ with and without acid agent and hence reduced nonlinearity.

This humidity helps increase the efficiency and lifetime of the PEM membranes. However, it has been found that the addition of an acid eliminates the need for such equipment. The hydrogen produced from the reaction between the sodium borohydride, acid, and water produces pre-humidified hydrogen void of any gases that may poison the fuel cell such as CO. This pre-humidified hydrogen is also able to achieve relative humidity greater than that of most electrical humidifiers, almost 100% relative humidity. Figure 2 illustrates a comparison of relative humidity between hydrogen produced with 50% acid and gas produced without the agent.

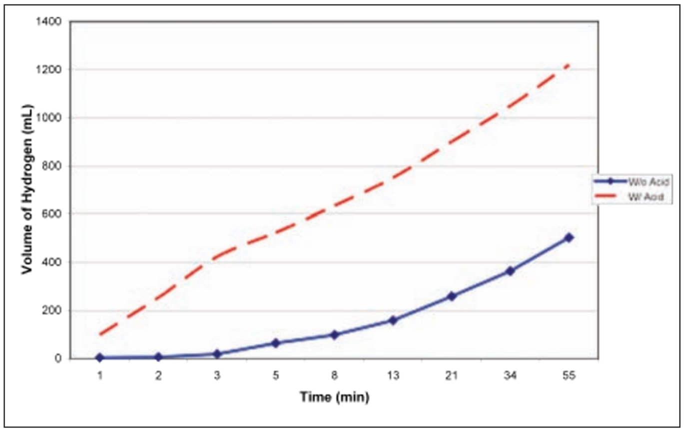


**Figure 2.** The relative humidity of a hydrogen sample taken at STP. The hydrogen was produced using a 50% acid by weight sodium borohydride/citric acid fuel with excess water.

Both of these figures illustrate the benefits to the hydrogen gas with an addition of 50% acid. It is important to note that the same benefits have been observed in concentrations of as little as 5% acid by weight. This allows for a wide variety of applications to be met with a single technology. The acid concentrations, and therefore, the rate of hydrogen production can be customized to meet the needs of the fuel cell or application.

A low power fuel cell stack may only require a 5% acid concentration. This low acid concentration would allow hydrogen to be created at a slower rate as needed for the stack. The hydrogen is maintained as a solid to provide the greatest energy density. The higher acid percentages would be used for a higher load system. An automobile would require a higher, more dynamic fuel system. Water may be added to this fuel in differing amounts depending on the requirements of the stack.

## 4. Conclusions

The addition of a solid acid to borohydrides, sodium borohydride in particular, opens the door to its use in future fuel cell applications. Keeping the fuel in solid form allows for easy distribution and transportation and maintains the safety factor of low pressures. Also, the precious metal catalyst is replaced by an inexpensive and readily available solid acid such as citric acid. Furthermore, the hydrogen produced by these reactions has been shown not to contain any gases that may poison the fuel cell membrane, and it offers relative humidity near that of 100%. This fuel combination can be scaled as needed to allow this single technology to be used for applications ranging from micro and portable electronics all the way to automotive applications.

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## About the Author

Ian M. Fuller is a senior at Wright State University where he is majoring in Engineering Physics. He has spent his college career doing research and development on hydrogen fuel cells and their accompanying equipment as an intern at Nanotek Instruments in Dayton, Ohio. He has received numerous awards for his work from the Ohio Fuel Cell Coalition, Dayton Engineering Sciences Symposium, and also has filed for US Patents. Outside of school and work, Ian is very active in local soccer leagues where he has coached and trained younger players, as well as played on local adult leagues.