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Catalysts for Portable, Solid State Hydrogen Generation Systems

Jason Robert Gabl
Purdue University

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For the degree of Master of Science in Aeronautics and Astronautics

Is approved by the final examining committee:

Timothée Pourpoint

Stephen D. Heister

William Anderson

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Approved by Major Professor(s): _____

Approved by: Weinong Chen

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Head of the Department Graduate Program

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CATALYSTS FOR PORTABLE, SOLID STATE HYDROGEN GENERATION
SYSTEMS

A Thesis

Submitted to the Faculty

of

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by

Jason Robert Gabl

In Partial Fulfillment of the

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To my parents, for your support and encouragement.

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LIST OF SYMBOLS

General:

Pt	Elemental Platinum
C	Elemental Carbon
pKa	Acid Dissociation Constant
r	Molar reaction Rate (mol/s)
k	Reaction Rate Constant (-)
T	Temperature (K)
A	Pre-Exponential Constant (1/s)
E _a	Activation Energy (kJ/mol)
R	Universal Gas Constant (J/K-mol)

Subscripts:

Sys	System
-----	--------

Abbreviations:

PEM	Proton Exchange Membrane
QFD	Quality Function Deployment
DoE	Department of Energy
AB	Ammonia Borane
SBH	Sodium Borohydride
ppm	Parts per million
abs	Absolute
GC	Gas Chromatograph
RSD	Relative Standard Deviation
FTIR	Fourier Transform Infrared Spectrometer
EDS	Energy Dispersive Spectrometry
SEM	Scanning Electron Microscope
SCS	Solution Combustion Synthesis

ABSTRACT

Gabl, Jason Robert. M.S.A.A., Purdue University, August 2014. Catalysts for Portable, Solid State Hydrogen Generation Systems. Major Professor: Timothée L. Pourpoint.

Hydrogen and air powered proton exchange membrane fuel cells are a potential alternative to batteries. In portable power systems, the design requirements often focus on cost efficiency, energy density, storability, as well as safety. Ammonia borane (AB), a chemical hydride containing 19.6 wt. % hydrogen, has a high hydrogen capacity and is a stable and non-toxic candidate for storing hydrogen in portable systems.

Throughout this work, Department of Energy guidelines for low power portable hydrogen power systems were used as a baseline and comparison with commercially available systems. In order to make this comparison, the system parameters of a system using AB hydrolysis were estimated by developing capacity and cost correlations from the commercial systems and applying them to this work.

Supporting experiments were designed to evaluate a system that would use a premixed solid storage bed of AB and a catalyst. This configuration would only require a user input of water in order to initiate the hydrogen production. Using ammonia borane hydrolysis, the hydrogen yield is ~9 wt. %, when all reactants are considered. In addition to the simplicity of initiating the reaction, hydrolysis of AB has the advantage of

suppressing the production of some toxic borazines that are present when AB is thermally decomposed. However, ammonia gas will be formed and this problem must be addressed, as ammonia is damaging to PEM fuel cells. The catalyst focused on throughout this work was Amberlyst – 15; an ion exchange resin with an acid capacity of 4.7 eq/kg and ammonia adsorbent. At less than \$0.30/g, this is a cost effective alternative to precious metal catalysts. The testing with this catalyst was compared to a traditional catalyst in literature, 20% platinum in carbon, costing more than \$40/g. The Amberlyst catalyst was found to reduce the formation of ammonia in the gas products from ~3.71 wt. % with the Pt/C catalyst to <0.01 wt. %. Since Amberlyst adsorbs ammonia, it acts as a “consumable” catalyst, requiring a minimum loading for complete reaction. A mass ratio of a least ~10:1 Amberlyst to AB is needed for a complete reaction. Conversely, the Pt/C is a reusable catalyst and only used at 5 wt. % loading throughout testing. The activation energy of the Amberlyst catalyzed reaction were measured to be 11.6 kJ/mol, which improves upon the activation energy measured with the Pt/C catalyst of 49.3 kJ/mol, making it a more effective catalyst. However, from the results of an aging study, the proposed system configuration of storing the AB and Amberlyst together will need further development, as the theoretical hydrogen yield dropped from > 90 % to < 30 % over a 70 day aging study. This results implies the need for a systems scale solution, such as mechanical separation, or a material scale solution, such as coating the Amberlyst or AB in a water soluble coating.

It was found that ammonia borane catalyzed hydrolysis, using Amberlyst – 15 as a catalyst, has potential to be a cost effective, energy dense, and safe option for generating hydrogen for a portable fuel cell system.

CHAPTER 1. INTRODUCTION

As technology progresses, portable devices are getting smaller, and their power requirements are growing. The pursuit of meeting this need is an area that has been the drive for much of today's research. Historically, rechargeable battery power systems have been the most universally studied, however, portable fuel cell power systems have been shown to be successful in achieving the energy density a modern portable system requires. More specifically, research has been conducted using various chemical hydrides to provide hydrogen for air breathing fuel cell power systems. The focus of this work is to create a hydrogen generation system that will be useful in such an air breathing portable power system application.

1.1 Need for portable power

In recent history, there has been a demand for portable power systems for various applications. Primary requirements for portable applications include having a low cost, energy dense, storable, and safe system. Applications vary from general consumer systems, such as portable phones or emergency radios [1], to medical use, for example, a need for extremely reliable emergency defibrillators [2], as well as military applications concerning communication equipment. Additionally, applications in sea, land, and air-based drones are becoming increasingly important. One such example of this type of system is the power systems soldiers carry with them in the field. The BA 5590 battery is

used by military personnel in the United States armed forces; however, at 2.25 pounds each, it is apparent that carrying multiple batteries can become cumbersome. General Atomics designed a system using solid state hydrogen storage in order to improve on the traditional battery system for portable power. With their system, a fuel cell and seven specially designed hydrogen cartridges generate 500 W-hr of total energy, replacing 21 of the BA 5590 batteries, reducing the total weight by 78% and the total volume by 43% [3]. While each system is unique, the motivation of using a hydrogen fuel cell system in each is the same: there is a need for high energy density and efficient portable power systems with long shelf life. As seen in Figure 1, the interest in fuel cell systems for portable power has risen over the past two decades, showing others have recognized the importance of developing this technology.

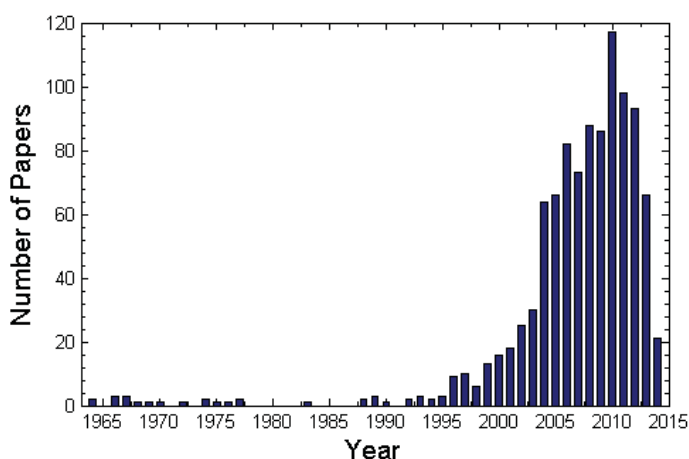


Figure 1: Trend in papers written with the keywords “portable fuel cell systems” [4]

1.2 Hydrogen Fuel Cell Power Systems

As discussed previously, the focus of this work is with portable power systems; however, some research contributions from other hydrogen fuel cell applications are applicable to a

portable system. Other applications include mobile land/sea and stationary power systems. With mobile systems, the energy density is a primary design criterion, whereas with a stationary application, it is efficiency. Even though the applications are different, the information learned from stationary systems is useful in portable systems. With portable systems, energy density and efficiency both have heavy influences on design considerations. It will be valuable to use methodology and materials learned in other applications to maximize these parameters. Part of the goal of this work is to bridge the gap between these applications and determine what information is useful in both sets of applications.

1.3 Thesis Objectives and Outline

This work focuses on evaluating portable hydrogen storage configurations for use in portable fuel cell power systems. The goal is to find and test a safe, energy dense, storable, and cost effective method of storing and releasing hydrogen. Ammonia borane, a media used in solid state hydrogen storage, was used as the source of hydrogen, and the hydrolysis of it was studied using a variety of methods and catalyst materials. In order for ammonia borane hydrolysis to be a valid storage and generation method, the evaluation performed herein tested all aspects desirable for a portable application.

CHAPTER 1 defines needs and sets the groundwork for why portable power systems are worth pursuing in a research setting. CHAPTER 2 discusses why a hydrogen fuel cell system is a valid alternative to batteries. Hydrogen storage, as a whole, is discussed in order to understand the various storage methods and their advantages and disadvantages as they are used for a portable application. This chapter also details current fuel cell

systems and how they compare to batteries and where there is room for improvement. In the next chapter, CHAPTER 3, the experimental methods are described. This consists of introducing the materials used, how they were processed, the specific methods and procedures used in conducting tests, and how results were obtained from these tests. CHAPTER 4 contains the results from the tests described in CHAPTER 3 as well as a discussion interpreting the results and translating them to system level design considerations. The system level design considerations go a step further and compare the theoretical characteristics of a system using the materials tested in this work to the current systems on the market already described in CHAPTER 2. Finally, CHAPTER 5 concludes the findings herein and discusses the implications in a portable hydrogen fuel cell power system. The chapter also provides directional suggestion for continuation of this work.

CHAPTER 2. BACKGROUND

Portable hydrogen fuel cell power system systems are a potential alternative to batteries. They consist of a hydrogen storage system connected to a fuel cell. This chapter discusses the hydrogen storage methods available and how they apply to a portable system, as well as the most applicable type of fuel cell to this application.

2.1 Air breathing proton exchange membrane fuel cells

The enabling technology that allows hydrogen to be used as a source of electrical power is a fuel cell. A fuel cell converts the internal energy of hydrogen directly into electrical energy. In a proton exchange membrane (PEM) or polymer electrolyte membrane fuel cell, the chemical energy in hydrogen is directly converted to electrical energy that can be used in everyday devices. During normal operation, hydrogen enters the anode side of the cell, and splits into protons and electrons via an immobilized catalyst. The protons pass through an ionomer membrane to combine with oxygen to form water, and the free electrons drive a voltage potential across the membrane. In an air breathing system, the oxygen is supplied to the cathode side of the cell from the ambient air. This is advantageous in a portable system since it allows for the only required input to the fuel cell to be the hydrogen. Other advantages of air breathing PEM fuel cells are their relatively manageable operating conditions. A typical PEM fuel cell using hydrogen and

air operates at pressures between ambient and 400 kPa, and temperatures from 50 to 80°C [5], making it ideal for a portable system where the user may be in close proximity or interacting with the device. One issue with PEM fuel cells is their sensitivity to contaminants. Contaminants, their effects on fuel cell operations and the steps taken to prevent their formation will continue to be discussed throughout this chapter.

2.2 Hydrogen storage methods

The next component of a hydrogen fueled portable power generator is the hydrogen. Typically, the methods of storing hydrogen are broken up into four categories: compressed gas, cryogenic liquid, metal hydride, and chemical hydride. Each method of storing hydrogen as it pertains to this particular application has its advantages and disadvantages. Safety, shelf life, cost, environment impacts, and energy density all hold heavy weights on deciding on a storage method for a portable system. In order to translate the qualitative design objective to quantitative parameters, a decision making process called quality function deployment, or QFD, was employed. This method allows for a quantitative definition of importance to be applied to specific objectives, and then a qualitative definition of the ability for a design or method to meet that objective is applied. At the end of the study, the results show the weighted score, or how well a particular design or method satisfies the objectives as a whole. The results are shown in Table 1.

Table 1: QFD for hydrogen storage methods

List of Objectives	Weights (%)	Compressed Gas	Cryogenic Liquid	Metal Hydride	Chemical Hydride
Energy Dense	0.25	-1	1	3	9
Safe Operation	0.25	-3	-3	3	3
Ease of Use	0.15	9	-1	3	3
Cost Effective	0.05	3	-3	9	9
Storage Life	0.20	1	-9	9	9
Environmental Impact	0.05	9	9	3	3
Reusability	0.05	9	3	9	-3
Totals:		27	-3	39	33
Weighted totals:		1.6	-2	4.8	5.7

Legend

9	Strong positive toward objective
3	Positive toward objective
1	Weak positive toward objective
-1	Weak negative toward objective
-3	Negative toward objective
-9	Strong negative toward objective

2.2.1 Advantages and drawbacks of hydrogen storage methods

For the desired application of portable systems, compressed gas would not be a good choice due to a couple of factors. The inherent safety in a system using high pressure hydrogen gas is low. In order to have a system that operates safely with a compressed gas, the support system must include fail safes and backup systems [6]. These additional support systems add to the cost and weight of the system, making it unreasonable to use

when compared to alternative storage methods at the scale of interest. Similar issues arise when looking at cryogenic liquid storage. At such a small scale, liquid is not an ideal storage method either. Typically, liquid hydrogen is only used in bulk supplies when the relative energy needed to maintain the cryogenic temperatures is much lower than the potential energy stored in the hydrogen.

Chemically bound hydrogen is a more general name for the last two categories: metal hydrides and chemical hydrides. Both of these systems have distinct advantages for portable applications over the previous two methods. Depending on the specific material being used, both metal and chemical hydrides can store hydrogen stably and safely at ambient or near ambient temperature and pressure, with little to no sensitivity to variations in these conditions. Again, depending on the specific hydride, both metal and chemical hydrides are able to release their hydrogen with little to no user input. For a metal hydride, this could mean the addition of heat, or opening a valve on a metal hydride tank to relieve the pressure and allow the material to dehydride, whereas for a chemical hydride, this could mean adding heat or water to initiate a reaction.

2.2.2 Chemical and Metal Hydrides

In order to choose between these two types of hydrides, their specific differences must be evaluated. Since there are such a wide variety of possible candidates to compare for both metal and chemical hydrides, the following discussion will be a generalization. Like with other forms of hydrogen storage, safety is a key issue to consider when choosing a hydride for a system. For example, metal hydrides can be pyrophoric, due to their rapid and exothermic oxidation reaction with air. In terms of a final system design, ensuring that the hydride bed is isolated from ambient conditions must be considered; however,

not all metal hydrides are pyrophoric. Chemical hydrides, in general, do not have the stability issues that metal hydrides have at atmospheric conditions.

Another point of difference between the two is the dehydriding procedure. With a metal hydride, it is possible to release the bound hydrogen simply by lowering the pressure in the hydride bed. For example, a typical AB_5 metal hydride, where A is a rare earth metal or mixture of rare earth metals, and B is usually nickel, cobalt, or aluminum, store hydrogen at just over ambient pressure. Therefore, if the pressure in an AB_5 hydride tank were to be relieved, the bound hydrogen would be released until equilibrium pressure was reached in the tank. Other types of metal hydrides, such as magnesium hydride, rely on heat to release hydrogen. In a portable system with the solitary purpose of generating hydrogen for a fuel cell, this particular type of metal hydride is impractical. When catalyzed, the temperature magnesium hydride desorbs has been shown to reach as low as 250°C [7], requiring more thermal energy input than would be generated in electrical energy output.

Chemical hydrides can be decomposed using thermolysis, pyrolysis, or hydrolysis.

Typically, the thermal decomposition of chemical hydrides via thermolysis or pyrolysis requires less heat than with low pressure metal hydrides, making chemical hydrides more practical for application in portable systems. Hydrolysis often requires a catalyst to increase the reaction kinetics and allow for decomposition reactions to happen more readily.

Chemical and metal hydrides also differ in their gravimetric capacity of hydrogen. In general, a metal hydride that would be suitable for use in a portable system would contain about 1.5 wt. % hydrogen [6]. Some chemical hydrides can contain almost 20 wt. %

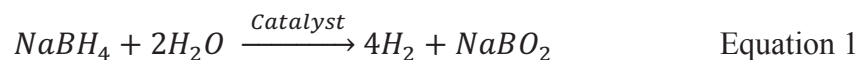
hydrogen. This is a significant difference; however, it comes at a price. In general, metal hydrides are more reusable than chemical hydrides. Metal hydrides can be hydrided with a gaseous source of pressurized hydrogen. Chemical hydrides are decomposed into a series of chemical compounds, and in order to use them again, they have to undergo an energy intensive chemical regeneration. This regeneration process makes chemical hydrides less attractive in terms of a reusable hydrogen source, however, in some portable applications, regenerating the material may not be a requirement.

2.3 Boron based chemical hydride choices

For the purposes of creating a safe, energy dense system for a portable application, a chemical hydride is a logical candidate. In previous and ongoing research with hydrogen generation, boron based hydrides are common. This is due to the high hydrogen capacity they possess. In particular, sodium borohydride (SBH) and ammonia borane (AB) contain 10.6 and 19.6 wt. % hydrogen, respectively.

2.3.1 Sodium Borohydride (NaBH₄)

Sodium borohydride has been a focus of research for many fuel cell applications. Other than its relatively high hydrogen content, the hydrolysis reaction of SBH has been proven as a reliable and consistent method of producing hydrogen. The reaction is shown in Equation 1.



From this equation it is realized that the recoverable hydrogen makes up 10.9 wt. % of the reactants. This has been the motivation for work in implementation of sodium borohydride use in a portable fuel cell system.

One challenge in using sodium borohydride is its stability. SBH is hydrophilic and readily decomposes with water; therefore, it will decompose in humid air. The challenge of storing SBH has been approached two ways. One way is to store it in a water solution and stabilize it with sodium hydroxide. At a high pH of 14, SBH was shown to have a half-life of 426.2 days [8]. This is a valid approach to hydrogen storage; however, it starts to become impractical when considering a portable system. It is not practical to have a solution with a pH of such high magnitude in a portable system as this would pose design problems when considering safety and materials.

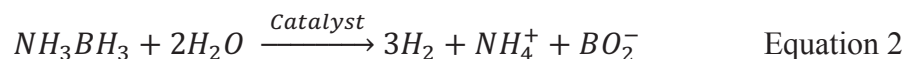
The alternative is dry storage, or in other words, keeping the SBH isolated from the environment until ready to use. This method is better suited for a portable application in that the SBH is in a stable and safe form and can be stored for an extended period of time without decomposing. In Pfeil et. al.[34], it was shown that SBH and a cobalt based catalyst could be stored in a dry environment, and when hydrogen production was desired, water would be introduced to the system, and after a short induction time, starting from room temperature, a steady flow of hydrogen was observed.

Based on previous work, SBH is a viable option for hydrogen storage in portable systems; however, while the hydrolysis reaction is exothermic, at starting temperatures of room temperature or below, the reaction kinetics would be prohibitively low and would lead to long induction times of greater than 45 seconds.

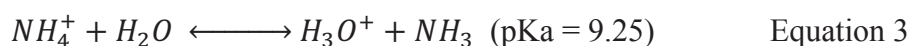
2.3.2 Ammonia Borane (NH_3BH_3)

An alternative boron based hydride is ammonia borane. It is nontoxic and stable, making it an ideal candidate for a portable system. Studies have been carried out for the thermal decomposition, as well as for the hydrolysis of this particular hydride. Since the thermal

decomposition of AB is exothermic, and self-sustaining at ambient conditions, a more controlled and favorable method of decomposing AB for a portable application is through hydrolysis, as shown in Equation 2.



From this equation, it is realized that the recoverable hydrogen makes up 9 wt. % of the reactants. Many catalysts for this reaction have been studied, primarily transition metal catalysts. For example, Chandra [9] performed a study to evaluate different metal catalysts and their effectiveness in AB hydrolysis. A mix of 20 wt. % Pt and 80 wt. % C was most effective at fully decomposing the AB as well as increasing the reaction rate the most of all the metal based catalyst candidates that were evaluated. In previous work, by Liu et. al. [11], it was shown that with transition metal catalysts, ammonia is formed and measured in the produced gas. Ammonia is produced when ammonium is in a basic solution and is shown by Equation 3.



This is a critical problem for PEM fuel cells. In Uribe [12], it was shown that exposure to ammonia in concentrations as low as 30 ppm could permanently damage a PEM fuel cell. This result suggests that the conventional hydrolysis method of AB will have to be modified if it is to be used in a fuel cell system. Suggestions have been made to use ammonia filtering methods previously developed, such as using silica gel [12] or simply using a water trap. When considering a portable system, any filtering method may, however, become bulky and difficult to design a small system around.

2.3.3 Improvements to AB

Work by Hwang [14] showed that, by using an acid catalyst, it is possible to reduce the amount of ammonia formation by lowering the pH of the reactants. Hwang [14] recorded a drop in ammonia concentration from 3500 ppm to 10-20 ppm when boric acid was added to the reactants at a 1:1 mass ratio to AB. If Equation 3 is looked at and the pKa of ammonium is considered, it is logical that a reduction in pH will lead to a reduction in ammonia formation. However, for this reduction in pH to be sufficient as to completely suppress the formation of ammonia, the reacting solution would have to have a prohibitively low pH of less than one.

The previous work in this area, along with the need for an energy dense portable fuel cell system, provides the motivation to investigate alternative catalysts for use with AB in a portable fuel cell system. The specific catalyst being used will be an ion exchange resin called Amberlyst – 15 ($C_{10}H_{10}.C_8H_8O_3S$)_x. This material acts like a polymer when dry and like an acid when wet. The molecular structure is made up of sulfonic acid groups with a polystyrene backbone. The acid sites and backbone together form a negatively charged matrix, with exchangeable positively charged ions at the surface [15]. A SEM image of the Amberlyst – 15, in addition to a visual representation of its structure is shown in Figure 2.

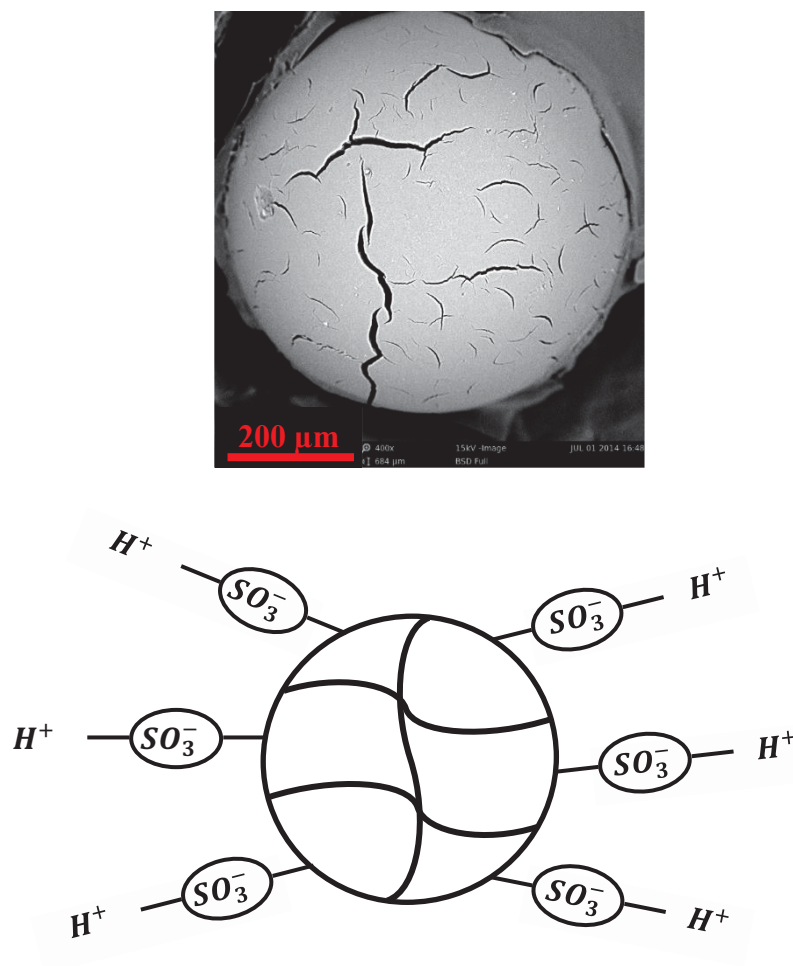


Figure 2: SEM Image of Amberlyst – 15 (Top) and Schematic of Amberlyst - 15 [15] (bottom)

2.4 Advantages of AB as compared to battery systems

A hydrogen fuel cell system possesses numerous advantages over battery powered systems. These advantages include, but are not limited to, storage life, cost, environmental impact, and energy density. All of the factors listed in Table 1 are also heavily influenced by the method of storing the hydrogen. Unless stated otherwise, lithium batteries will be used as a baseline for comparison throughout this section.

2.4.1 Storage life

In a typical air breathing fuel cell system configuration, there is a storage container for the hydrogen and a fuel cell. This means there are two major system components that are subject to aging and deterioration.

A modern PEM fuel cell is very durable and can be stored without degradation for many years [5]. The main components responsible for any possible loss in performance include the membrane, anode and cathode catalyst layers, and seals. In each of these components, the primary performance loss is caused by contaminants in the gas streams. It should be noted that for these contaminants to affect the performance the fuel cell must be in use.

In other words, if the fuel cell is not being used, it can be stored safely, without concerns of deterioration [5]. The second half of the system that is subject to aging is the hydrogen storage material. Since AB is a stable compound at room temperature and pressure [16], when it is compared to batteries, that have a storage life of 10 years [17], the advantage of ammonia borane and using a fuel cell system for a long term energy storage media is clear.

2.4.2 Raw Material Cost

In order for a fuel cell system to be a valid approach to portable power from an economic viewpoint, the materials for generating power must be reasonably priced. Based on today's pricing of commercially available AB at \$116.50 per 10 g [18], and neglecting the cost of the catalyst material, the cost of generating power from an average fuel cell system (50% efficiency [5]) would be approximately \$3.43 per watt-hour of energy produced. It should be noted that there are methods currently being developed to mass produce AB by Ramachandran [19] in high purity for a fraction of the cost that is

available today. A modern lithium battery capable of the same output would cost \$2.21 per watt-hour (based on lithium battery outputs and costs [17]). It is apparent that fuel cell technology is gaining momentum. As the field grows and the materials used in such systems grow in demand, new methods will be developed to manufacture them, and prices will decrease.

2.4.3 Energy Capacity

Based on the estimates for average fuel cell system efficiencies [5], using AB as a hydrogen storage media, without taking into account the system weight (material only), the estimated energy capacity is approximately 2.3 Wh/g. Conversely, a modern lithium battery capable of the same output has an approximate energy capacity of 0.31 Wh/g [17]. A comparison of energy densities is shown for many materials, including some batteries and forms of hydrogen, in Figure 3.

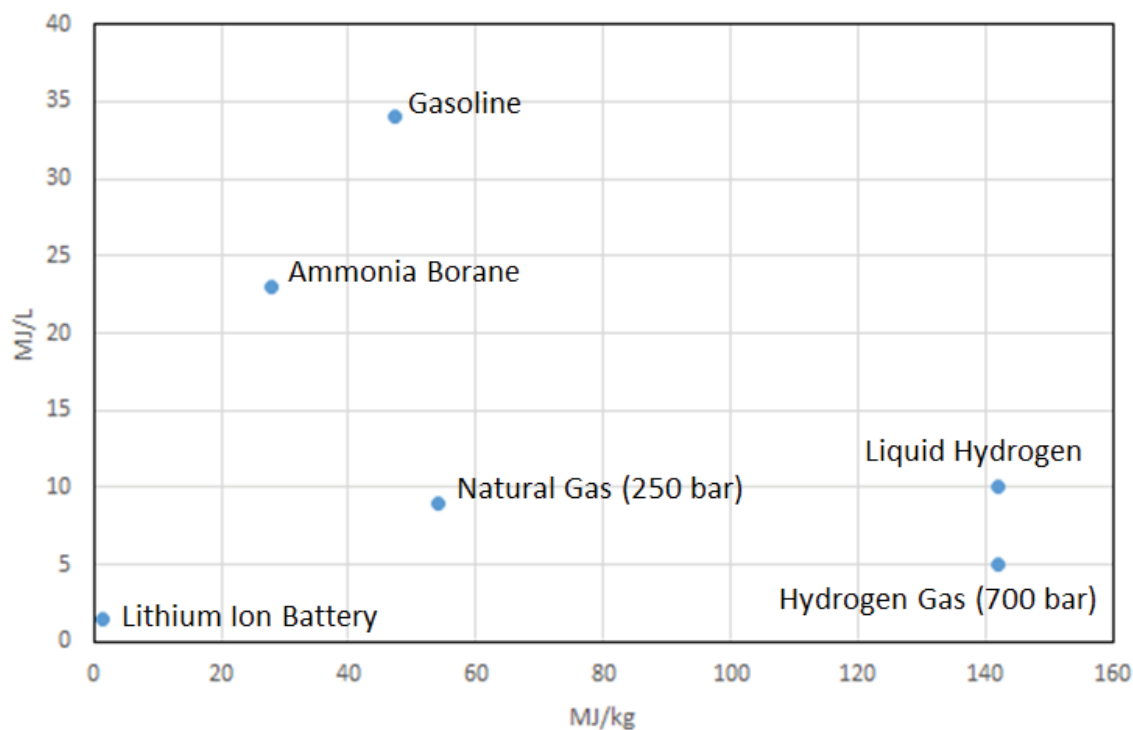


Figure 3: Energy Density Comparison for Selected Systems [20]

2.4.4 Safety and Environmental Impact

The need for a portable power system that is safe has to be considered, as the system in question will be in close proximity to the user and will require direct interaction. In terms of safety, there is always a concern when dealing with a flammable gas like hydrogen, however, when stored in the form of a chemical hydride, the amount of actual gas present in the system at any given time is limited. Additionally, PEM fuel cells operate at low pressures and temperatures, further reducing safety concerns. Ammonia borane itself is benign, non-toxic, and stable, therefore, the safety concerns in a portable fuel cell system, specifically one that uses AB hydrolysis, are minimized. The hydrolysis of AB also suppresses the formation of borazines, toxic vapors formed in

thermolysis [21]. On the other hand, current portable power systems using lithium batteries have safety issues associated with the materials used, such as the lithium itself. There are many dangerous failure mechanisms associated with lithium batteries including: uncontrolled hydrogen production and ignition, electrical shorting, thermal runaway, and oxidation of organic solvents [22]. These issues all produce effects harmful to anyone and anything in the immediate area. There are, however, many safety systems in place to handle these hazards, both on the system level and cell level, such as current interrupt monitors for current flow if the charge/discharge rate becomes too great, similar current interrupt monitors for temperature, and system infrastructure that would vent an over-pressurized cell as well as contain the vented material. Even with safety management systems in place, a far more attractive alternative is to do away with the risks all together. For both materials, recycling can be a complicated process, however, work is being done to resolve this issue, and the experimental results show >95% yield in the regeneration of ammonia borane [19] and >90% material recovery from lithium-ion batteries [23], that can be applied to lithium batteries as well. This recycling process is especially crucial to the success of lithium batteries since it has been shown to be a limited resource. Using the automotive industry as an example, the amount of equivalent lithium available for electric cars is less than the amount of the petroleum it is being pushed to replace [24].

2.5 Operational Parameters for Portable Hydrogen Fuel Cell Systems

The DoE goals for portable fuel cell power systems were used as a goal [1] in order to set guidelines for this work. One challenge that fuel cell systems face is impurities causing contamination in the fuel cell and leading to decreases in performance.

2.5.1 PEM-FC Contaminants

Contaminants that affect a fuel cell membrane must be introduced through either the anode or cathode side to affect the performance. This means that gas must carry said contaminants into the system. The primary gasses that are damaging to a fuel cell are carbon monoxide, hydrogen sulfide, ammonia, and sulfur oxides [5]. In air-breathing fuel cell configurations, the primary concern for contaminants comes from impurities in the hydrogen generation. Depending on the materials used in generating hydrogen, some of these impurities are more probable than others. For example, when reforming natural gas, there can be low levels of hydrogen sulfide. In the case of AB hydrolysis, the most likely and primary concern is the formation of ammonia, and managing that formation was a priority consideration throughout this work.

2.5.2 DoE Goals for portable equipment

The focus of this work is based on improving the current methods of generating portable power on the market today in order to better satisfy the DoE guidelines for such systems. As previously stated, the focus of this work is driven by the demand for a low cost, energy dense, storable, and safe portable power system. The DoE guidelines serve to quantify these metrics. In addition to the four main demands, DoE also expresses guidelines for operational practicality. This is inherent within the guidelines for start time, as well as the operating temperatures. The DoE targets tables, showing guidelines for both low power and medium power systems, last updated in 2012, are shown in Table 2 through Table 4.

Table 2: DoE goals for low power portable hydrogen generators [1]

**Hydrogen Storage Systems for Low Power
($\leq 2.5\text{W}$) Portable Equipment**

Storage Parameter	Units	2015		2020	
		Single-Use	Rechargeable	Single-Use	Rechargeable
Hydrogen Capacity	g H ₂	≤ 1			
System Gravimetric Capacity	kWh/kg (kg H ₂ /kg _{sys})	0.7 (0.02)	0.5 (0.015)	1.3 (0.04)	1.0 (0.03)
System Volumetric Capacity	kWh/L (kg H ₂ /L _{sys})	1.0 (0.03)	0.7 (0.02)	1.7 (0.05)	1.3 (0.04)
Storage System Cost	\$/Wh _{net} (\$/g H ₂ _{stored})	0.09 (3.0)	0.75 (25)	0.03 (1.0)	0.4 (13)

Table 3: DoE goals for medium power portable hydrogen generators [1]

**Hydrogen Storage Systems for Medium Power
($> 2.5\text{W}-150\text{W}$) Portable Equipment**

Storage Parameter	Units	2015		2020	
		Single-Use	Rechargeable	Single-Use	Rechargeable
Hydrogen Capacity	g H ₂	$> 1 - 50$			
System Gravimetric Capacity	kWh/kg (kg H ₂ /kg _{sys})	0.7 (0.02)	0.5 (0.015)	1.3 (0.04)	1.0 (0.03)
System Volumetric Capacity	kWh/L (kg H ₂ /L _{sys})	1.0 (0.03)	0.7 (0.02)	1.7 (0.05)	1.3 (0.04)
Storage System Cost	\$/Wh _{net} (\$/g H ₂ _{stored})	0.2 (6.7)	1.0 (33)	0.1 (3.3)	0.5 (17)

Table 4: DoE goals for durability and operation of portable hydrogen generators [1]

Portable Power Durability & Operational Targets ^a

Storage Parameter	Units	2015	2020
		Single-Use & Rechargeable	Single-Use & Rechargeable
Durability/Operability			
External operating temperature range	°C	-40/60	-40/60
Min/max delivery temperature	°C	10/85	10/85
Min delivery pressure from storage system	bar (abs)	1.5	1.5
Max delivery pressure from storage system	bar (abs)	3	3
External temperature	°C	≤40	≤40
Discharging Rates			
Minimum full flow rate	(g/s)/kW	0.02	0.02
Start time to full flow (20 °C)	s	5	5
Start time to full flow (-20 °C)	s	10	10
Transient response 10%-90% and 90%-0%	s	5	2
Fuel Purity (H₂ from storage)	% H ₂	Meets applicable standards	
Environmental Health & Safety			
Safety	Meets ISO-16111:2008; IEC 62282 Part 6; or other applicable standards as appropriate or required for the application and targeted usage		
Toxicity			
Safety			
Loss of usable H₂			

2.6 System Comparison

Part of this work is to determine the feasibility and advantages that an ammonia borane hydrolysis system has in today's market. This consisted of finding comparable portable power systems. This was done by first comparing an AB system directly to other hydrogen systems based on running a fuel cell for power, and then, comparing an AB system to modern portable rechargeable batteries.

The specific systems that were targeted for this study were “portable” systems. As shown previously in Table 2 and Table 3, the DoE has two definitions of portable systems. There is a low power system that contains less than 1 g hydrogen intended for systems with power requirements less than 2.5 Watts, and a medium power system that contains 1 – 50 g hydrogen intended for systems with power requirements of 2.5 – 150 Watts.

For the purposes of this study, portable is defined as being a device under approximately one pound that could reasonably be carried on a belt loop or in a small backpack. The General Atomics system mentioned in section 1.1 is meant for a portable application, but for comparison sake, only systems that are smaller and lighter will be used as comparisons. Five commercially available or near commercial systems, four being unique, were found to meet the weight requirement defined herein.

The systems in this study are all similar in that they are portable and generate hydrogen to power a fuel cell. However, their means of doing so and operation procedures are different.

The MiniPak [25], made by Horizon Fuel Cell Technologies, and the Hydrogen Reactor, made by Brunton [26], are examples that use a metal hydride for their method of hydrogen generation. They both make use of an AB_5 metal hydride that liberates its hydrogen once pressure in the hydride drops below the equilibrium temperature for that specific hydride. They both use refillable and replaceable metal hydride canisters that can be swapped out of the device itself. From a system standpoint, this is a very straightforward design, with little to no moving parts. However, a typical AB_5 metal hydride contains only 1.5 wt. % hydrogen, and to refill them, a specially designed filling

station must be used that is costly and requires a 120V power source to operate. The two devices are shown in Figure 4 along with a metal hydride canister used in the MiniPak.



Figure 4: Brunton Hydrogen Reactor [26] and Horizon MiniPak [25]

The PowerTrek, made by myFC [27], uses a replaceable, single use “powerpukk” comprised of sodium silicate and sodium borohydride. Once water is added to the system, it reacts with the sodium silicate to form heat and hydrogen, and also decomposes the sodium borohydride into sodium metaborate to form more hydrogen. Once one “powerpukk” is completely reacted, the aluminum canister can be recycled. An exploded view of the PowerTrek and “powerpukk” are shown in Figure 5.



Figure 5: myFC PowerTrek [27]

Another type of system in this study is the 24-7 Power Pack [28], made by Medis. This device uses sodium borohydride, a catalyst, and internally stored water. It is similar to the PowerTrek except for the on board water storage and possibly the type of catalyst. When ready to use, the user breaks the internal water storage vessel, and the sodium borohydride decomposes into sodium metaborate and hydrogen. This device is shown in Figure 6.



Figure 6: Medis 24-7 Power Pack [28]

The Nectar, made by Lilliputian Systems [29], uses a metal hydride as with the devices made by Horizon and Brunton, however, the hydrogen is used to power a solid oxide fuel cell rather than a PEM fuel cell. Solid oxide fuel cells are more efficient in terms of energy conversion, but have longer start-up times and require a high operating temperature. Very little is known about the operation of the Nectar because it has not actually been publically released for sale. The Nectar is shown in Figure 7.



Figure 7: Lilliputian Nectar [29]

For the purpose of predicting the overall system storage capacity for this work, a relationship was formed between the estimated hydrogen capacity of the commercial systems and their respective masses and volumes. When using the systems that did not list a specific mass of hydrogen, the totals were back-calculated from the specific device's power capacity. This back-calculation was done using a fuel cell efficiency of 40% (typical air breathing PEM fuel cells have efficiencies of 40-60% [5]) and hydrogen specific energy of 142 kJ/g [6] as shown in Equation 4.

$$H_2 \text{ Capacity} = \text{Device Power capacity} / 142 \frac{\text{kJ}}{\text{g}} * 40\% \quad \text{Equation 4}$$

In other words, if the power capacity is known and the minimum typical PEM fuel cell efficiency is used, the estimated hydrogen in the system will be maximized, making the estimates of potential hydrogen production conservatively high. Since the system mass and dimensions are known, the gravimetric capacity and volumetric capacity of the system can be estimated by dividing the hydrogen capacity by the system masses and volumes, respectively. The cost per gram hydrogen is calculated by the total system cost divided by the previously estimated hydrogen content. The estimated hydrogen capacities and relative costs are shown in Table 5.

Table 5: Maximum estimated hydrogen capacity

Device	H ₂ Capacity (g)	Gravimetric Capacity (gH ₂ /g _{sys})	Volumetric Capacity (gH ₂ /mL)	System Cost (\$/gH ₂)
MiniPak [25]	0.888	0.004	0.004	134
Brunton [26]	1.005	0.004	0.003	179
PowerTrek [27]	0.179	0.001	0.001	840
Nectar [29]	2.455	0.012	0.016	n/a
Medis [28]	0.893	0.003	0.001	39

Using the estimated hydrogen capacity, system mass, and system volume data collected from the systems listed in Table 5, a relationship was developed to relate the mass of hydrogen stored and the mass of the overall system in order to estimate the system parameters of this work. The result of this comparison is shown below in Table 6.

Table 6: Hydrogen storage and to total system mass, volume, and cost.

Device	H ₂ Storage / System Mass (g)	H ₂ Storage / System Volume (mL)	H ₂ Storage / System Cost (\$)
MiniPak [25]	105 / 210	34 / 214	29 / 119
Brunton [26]	96 / 242	53 / 335	19 / 169
PowerTrek [27]	173 / 240	93 / 307	5 / 100
Nectar [29]	35 / 200	55 / 150	n/a
Medis [28]	349 / 363	239 / 1224	20 / 40

A linear regression of the data shown in Table 6 was established with SAS 9.3 [30] in order to develop a relationship between the hydrogen storage container mass and volume and the total system mass and volume. This relationship was then used to estimate the system mass and volume of this work. All of the estimates to follow are based on a system that produces 1 g of hydrogen. The resulting SAS output plots are found in Figure 8, and the parameter estimates are found below in Table 7.

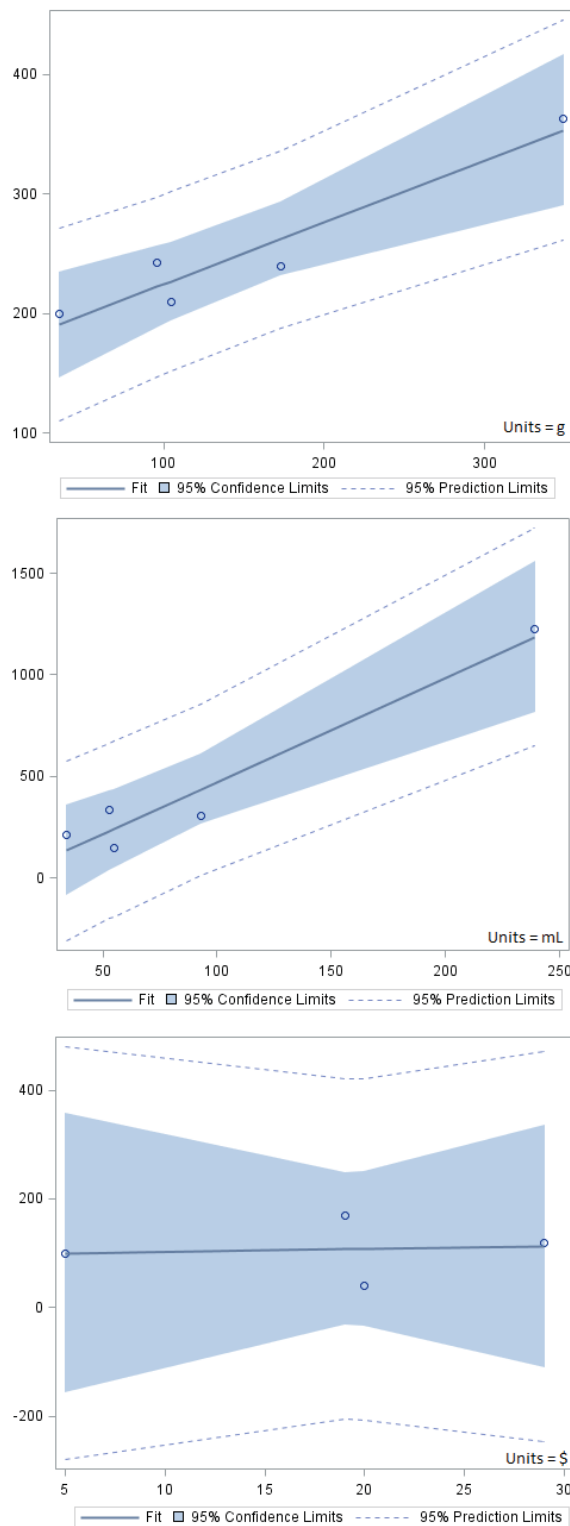


Figure 8: SAS output of Gravimetric Capacity, Volumetric Capacity, and Cost (top to bottom) showing the confidence interval

Table 7: Total system parameter estimates for this work

Parameter	Estimate Equation	R ²	Total System Estimates	95% Confidence Interval
Mass (g)	Total = 0.52*H ₂ Storage(g) + 172	0.921	197	[118 277]
Volume (mL)	Total = 5.14*H ₂ Storage(g) - 42	0.944	113	[-334 560]
Cost (\$)	Total = 0.51*H ₂ Storage(g) + 98	0.009	139	[-914 1192]

As seen from the estimates made and the sum of squared residuals (R^2), there seems to be a reasonable fit for mass and volume. The large variance in volume data resulted in low confidence level for volume, causing the confidence interval to span a significant range. The R^2 value and the confidence level for cost are low. This is due to both the large variation in these parameters among devices, as well as the lack of a price with the Nectar model.

It is important to understand the category that each of these devices fall into. The DoE has separate guidelines for rechargeable and single-use systems. It depends strictly on what defines a rechargeable system in this case. The Brunton, Horizon, and Nectar devices all use refillable hydrogen generating cartridges that plug into the base system while the myFC and Medis devices both use a hydrogen generating cell that is recycled and completely replaced once used. The overall system in the latter two devices is reusable, but the gas generator is not.

Other important parameters that can be compared to the DoE guidelines can be found in Table 8.

Table 8: Operational parameters and corresponding DOE guidelines

Device	Min/Max Operating Temp. (°C)	Min/Max H ₂ Temp. (°C)	Delivery Pressure (bar)	External Temp. (°C)	Induction Time at -20 / 20°C (seconds)
MiniPak	0 / 35	0 / 55	< 30	0 - 55	na / 0
Brunton	Similar to the MiniPak				na / 0
PowerTrekk	5 / 35	>10 / 80**		5 / 85	na / 60
Medis	0 / 40	>10 / 80**		> 50	na / 30
Nectar	0 / 80	700 / 900	2* - 4*	0 - 60	na / 600
DoE 2015	-40 / 60	10 / 85	1.5 - 3	≤40	10 / 5
DoE 2020	-40 / 60	10 / 85	1.5 - 3	≤40	10 / 5

* Based on typical solid oxide fuel cell performance [30]

** Based on typical PEM fuel cell performance [5]

Legend:

Guidelines	Meets or exceeds guidelines	Unknown	Does not meet guidelines
------------	-----------------------------	---------	--------------------------

In order to compare fuel cell systems to comparable battery systems, the relevant system parameters of all systems are shown in Table 9. The three rechargeable battery systems depicted have three different power outputs and were chosen from a list of the most popular devices of their kind in 2013 [32].

Table 9: Power capacities compared to comparable battery systems and DoE guidelines

	Device	Power Capacity (W-h)	Power Volume Density (W-h/mL)	Power Mass Density (W-h/g)
Fuel Cells	MiniPak	14	0.065	0.067
	Brunton	22.5	0.067	0.093
	PowerTrek	4	0.013	0.017
	Medis	20	0.016	0.055
	Nectar	55	0.367	0.275
Batteries	Anker Astro Mini	15	0.319	0.195
	Jackery Bar Premium	28	0.277	0.183
	Trent iCarrier	60	0.085	0.155
DoE Guidelines	DoE 2015 (rechargeable)	-	0.7	0.5
	DoE 2015 (single use)	-	1	0.7
	DoE 2020 (rechargeable)	-	1.3	1
	DoE 2020 (single use)	-	1.7	1.3

* Based on a 40-60% fuel cell efficiency

As seen in Table 9, the power capacities of the batteries are very similar to that of the fuel cell systems. Even though their power densities are similar, there are advantages and disadvantages in both types of devices.

In order to improve upon, and learn from the focus and concentration of past work, these commercial systems provided valuable insight. From a standpoint of materials, either a

metal hydride or a chemical hydride was used, validating the assumption that a gas or liquid system is too impractical for portable application. From a system standpoint, the devices simply had to have enough casing to protect and support the systems within, and by estimating the amount of additional material needed per gram of hydrogen, a relationship could be made to estimate the total system's parameters in this work. There is not a lot of information available on the hydrogen purity in these systems, however the selected hydrides are known to produce pure hydrogen. Operating temperature seemed to be important in all systems, due to the use of PEM fuel cells in most systems, with the exception of the Nectar, which has a substantial amount of insulation to protect the user. Finally, in each system, recycling is addressed. In the metal hydride systems, the cartridges can be refilled and reused, and with the chemical hydride systems, the spent materials are contained in a recyclable container that gets replaced completely after every use.

CHAPTER 3. TESTING THEORY AND DESIGN

Several catalysts suitable for the decomposition of ammonia borane via hydrolysis were evaluated for use in portable fuel cell systems. This performance evaluation consisted of multiple tests in order to assess several aspects of a chemical hydride based system as they relate to guidelines set by the DoE. The discussion to follow describes the specific experimental instruments and procedures implemented. The experiments performed herein allowed for each element of what makes up a desirable portable fuel cell system, as described by the DoE guidelines, to be tested. These tests also include factors not specifically covered in the DoE guidelines.

3.1 Material Sourcing and Preparation

All the material handling and preparation during this work was performed in an MBraun Labmaster 130 Glovebox unless otherwise stated. The glovebox, shown in Figure 9, maintains a high purity argon environment that contains <0.1 ppm moisture and <0.1 ppm oxygen. This was done to ensure that the materials used were not contaminated by outside sources. Typically, the sample material to be tested would be prepared inside this environment and, once sealed, brought out of the glovebox to test with.



Figure 9: MBraun Labmaster 130 Glovebox installed at the Hydrogen Systems Laboratory

3.1.1 Grinding AB and Ball Milling Catalysts

Ammonia borane ($\geq 98\%$, as prepared by Dr. Ramachandran [19]) was pulverized to particle sizes less than $50\ \mu\text{m}$ using a blade mill as well as a mortar and pestle to prevent overheating of the hydride. Platinum Black (Sigma Aldrich, black, powder, $\leq 20\ \mu\text{m}$, $\geq 99.97\%$ trace metals basis, CAS Number 7440-06-4), and Activated Carbon (Sigma Aldrich, untreated, granular, 8-20 mesh, CAS Number 7440-44-0) were mixed at a mass ratio of 1:4 platinum to carbon. In order to achieve a homogeneous mixture of platinum and carbon, similar particle sizes were desired. The mixing was performed by ball milling the two together. While the platinum has an average particle size less than $20\ \mu\text{m}$, the average particle size of the activated carbon was between 0.8 and 2.4 mm, before milling. The ball milling process served to thoroughly mix the two powders, as well as to

reduce the particle size of the carbon. This was done in an IKA ULTRA TURRAX Tube Drive mixer with stainless steel balls, using a ball to powder mass ratio of ~10:1. A ratio of one 12 mm to five 4 mm balls was used when milling. Each batch of the mixture was milled for a total of 15 minutes in cycles of 5 minutes on and 2 minutes off.

Amberlyst – 15 (Sigma Aldrich, hydrogen form, dry, CAS Number 39389-20-3), an ion exchange resin, was used to catalyze the hydrolysis of AB and was also ball milled separately with the same procedure as described for the mixture of platinum and carbon. The purpose in the case of the Amberlyst was to reduce the particle size from ~750 μm to <100 μm . All other catalysts in the study were used as received from their respective suppliers. The mixer, along with a sample holder is shown in Figure 10.



Figure 10: IKA ULTRA TURRAX Tube Drive

A Phenom Pro-X scanning electron microscope was used to confirm the Pt/C material was well mixed and to confirm the particle size of both the Pt/C material and the Amberlyst material. The microscope used is shown in Figure 11.

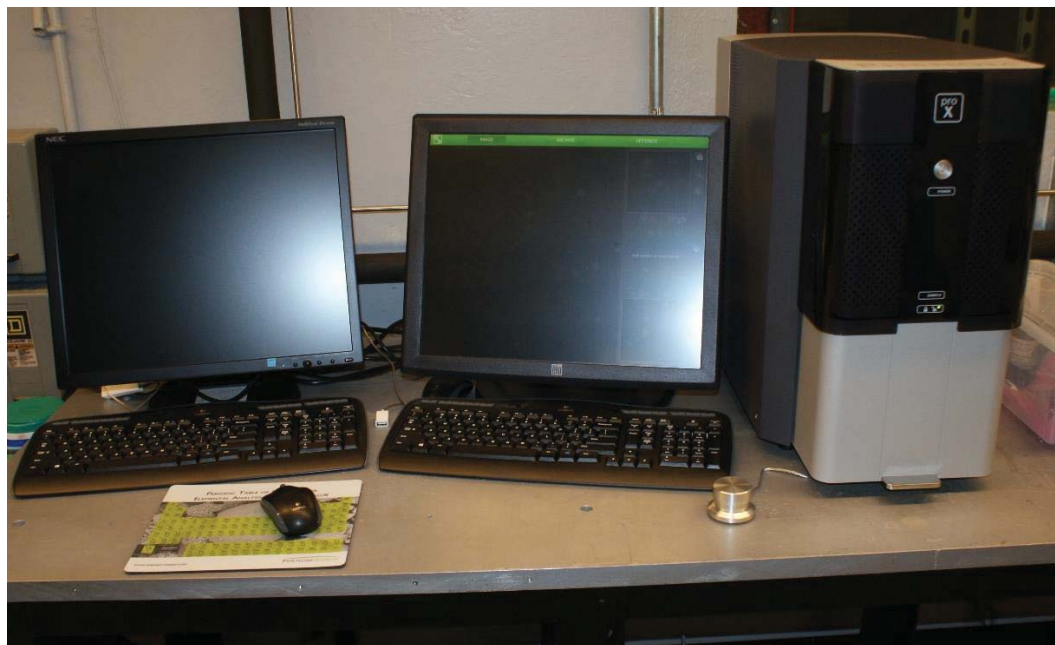


Figure 11: Phenom Pro-X SEM installed at the Hydrogen Systems Laboratory

3.1.2 Catalyst and AB mixing

Unless otherwise noted, the mixing of the AB and the catalyst material was done immediately prior to the experiment being performed to mitigate any degradation caused by the interaction of the two dry materials. Mixing of these materials consisted of combining them in a common vessel and stirring and shaking the two, by hand, until the materials were visually well-mixed.

3.2 Hydrolysis Experiments

3.2.1 Burette setup

A robust experimental setup was developed by Sumit Basu [21] and adapted for this work to test the aspects of the decomposition reaction that contribute to the operation of a portable fuel cell system. The adaption included additional diagnostic hardware, as well as an alternative water delivery system. A typical hydrolysis experiment was performed

in a 50 mL three-neck flask that could be partially submerged into a temperature controlled oil bath. One inlet of the flask was for purging the system or as an inlet for the pH probe, another inlet was for the injection of water as well as a thermocouple probe, and the third port was used as an outlet for the hydrogen produced that fed into the various diagnostic tools described in this chapter. The test material would be added to the flask in the glovebox, the flask would then be brought to a fume hood and placed on a ring stand. Once the connections on the flask were secure and the flask was thoroughly purged with high purity hydrogen gas (Indiana Oxygen), water would be injected into the system via a peristaltic pump (APT SP100.006) controlled via LabVIEW® or a manual syringe. The injection of water would initiate the reaction and hydrogen was then released. Depending on the test configuration, the pH probe would be secured or the purge gas would be turned off, and the outlet would be directed to the appropriate test equipment. For all experiments, the hydrogen flow was always terminated at a 250 mL inverted glass burette. The burette allowed for accurate measurement of the total gas produced as well as a leak checking aid in setting the experiment up. A schematic of the base setup is shown in Figure 12.

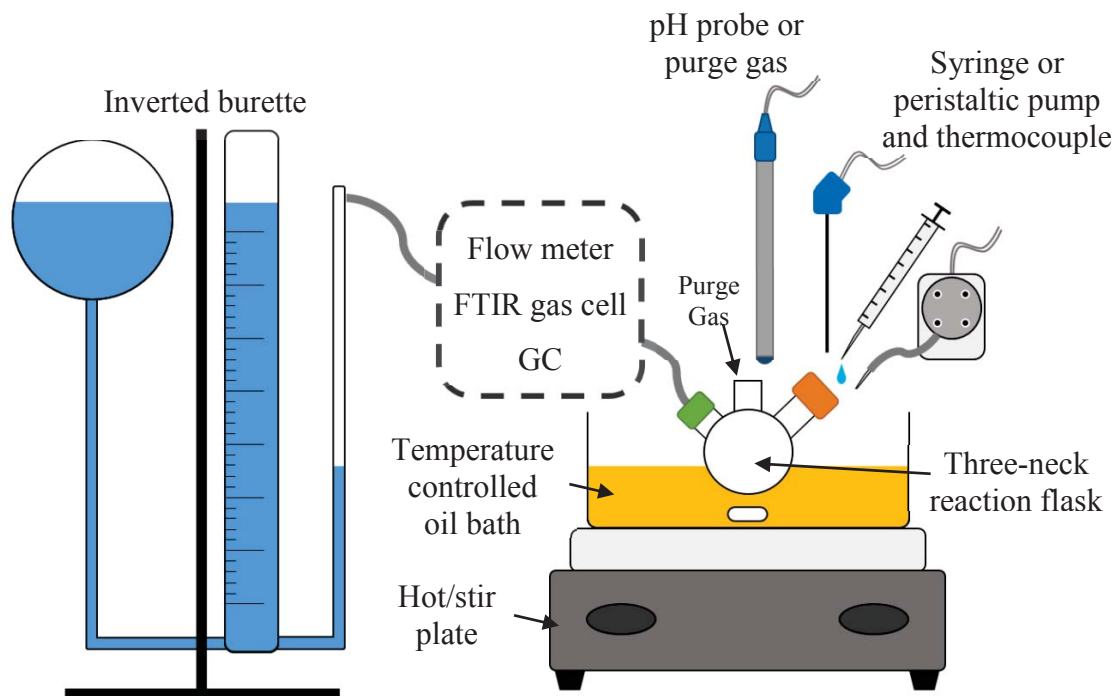


Figure 12: Hydrolysis Schematic with Hardware Placement

Using LabVIEW®, this system was capable of recording reaction temperature, induction time, conversion efficiency, and other general reaction behavior. The addition of a flow meter (Alicat M 5SLPM) allowed for the rate of hydrogen production to be recorded easily as well. A pH probe (Omega ALpHA® Series Rugged Gel-Filled Electrode, PHE - 1311) was also used for a subset of these experiments in order to better understand the transient behavior of the ion exchange resin catalyst and the effect loading would have on the completeness of reaction.

3.2.2 Gas Purity Analysis

The main advantage the Amberlyst catalyst possesses is hypothesized to be the ability to “capture and contain” the ammonia from the gas products, reducing contaminants to the

fuel cell. Since this is a key difference between the Amberlyst and traditional metal catalysts, multiple methods to confirm or deny this hypothesis were employed.

The first method used in determining the purity of the hydrogen the system produced was using a gas chromatograph (Agilent 3000 Micro GC). This GC is capable of measuring hydrogen concentrations with an uncertainty of 0.36% RSD. The GC used is shown in Figure 13.



Figure 13: Agilent Micro 3000 GC

Another tool used to determine if there were contaminants present in the gas generated from the hydrolysis reaction was a Cary 680 Fourier transform infrared spectrometer (FT-IR). Since hydrogen is a diatomic molecule and the stretching vibrational mode produces no net dipole shift, the FTIR will not detect it. With these tests however, the objective was to identify any impurities produced in hydrolysis experiments. This piece of equipment was fitted with a 100 mm short-path flow through gas cell from PIKE Technologies, in order to have the capability to sample gas produced from the hydrolysis

experiments. The gas cell was fitted with calcium fluoride windows to resist moisture, while preserving the largest spectral range possible. The calcium fluoride windows provide a spectral range from 896 cm^{-1} to 79500 cm^{-1} . While error associated with quantifying species concentrations in gas phase mixtures is great, even refined techniques for some gases can give an absolute error of as much as 1-3 wt. % [33], therefore, in this work, the FTIR was used primarily to determine the type, if any, of foreign species in the gas generated. The FTIR used, as well as the gas cell are shown in Figure 14.



Figure 14: Cary 680 FTIR and Short-path gas cell from PIKE Technologies

In order to quantify the contamination results and quantify the ammonia being produced, since it is the most detrimental to a fuel cell, the generated gas was bubbled through a room temperature sodium hydroxide solution, dissolving any ammonia in the water. Titrations of this solution were then completed in order to determine the quantity of ammonia gas that was released by the reaction. This was done using back titration. When in solution, ammonia will form ammonium, a weak acid, shown by Equation 3 in the previous chapter. Since a known amount of sodium hydroxide was added to the water,

the decrease in the hydroxide concentration can be measured. This decrease represents the amount that reacted with the ammonium ions. The reaction of sodium hydroxide and ammonium forms ammonia gas and water. This is shown in Equation 5.



The solution was boiled to drive off any ammonia gas that was formed in the solution to leave behind a sodium hydroxide solution. This process is known as Le Chatelier's principle. The sodium hydroxide solution was then titrated with hydrochloric acid, and the difference between the amount of sodium hydroxide added to the original test solution and the amount measured with the titration can be determined. This difference represents the amount of ammonium that reacted with the sodium hydroxide, and, in turn, the amount of ammonia produced by the experiment can be calculated.

3.2.3 Activation Energy

In order to quantify the effectiveness of the catalysts, the activation energy of ammonia borane hydrolysis was calculated with data gathered from a series of hydrolysis tests at controlled temperatures. Tests were run at 20, 30, and 40°C in order to develop a relationship between reaction rate and temperature. In these tests, reaction temperature was varied with the temperature controlled oil bath; the water used for the hydrolysis was also brought to temperature. The reaction rate of ammonia borane was measured indirectly by metering the hydrogen produced. Since it is known that the hydrolysis reaction of ammonia borane hydrolysis yields three equivalent moles of hydrogen by Equation 2, the molar reaction rate of hydrogen was measured and divided by three. The reaction rate was taken as an average rate during the middle 80% of hydrogen generation;

the first and last 10% was not used, as they represented the startup and tail-off rates, respectively. Once the molar reaction rate was measured at each temperature, defined by Equation 6, the activation energy can be solved for using the relationship between reaction rate and temperature. The steps for solving for activation energy are shown below, in Equation 7, Equation 8, and Equation 9.

$$r = k(T) * [A]^m * [B]^n \quad \text{Equation 6}$$

$$r = Ae^{\frac{-E_a}{RT}} [A]^m [B]^n \quad \text{Equation 7}$$

$$\ln(r) = \ln(A + [A]^m + [B]^n) + \frac{-E_a}{RT} \quad \text{Equation 8}$$

$$E_a = -R \frac{\ln(\Delta r)}{\Delta \frac{1}{T}} \quad \text{Equation 9}$$

In Equation 8, it can be seen that the natural logarithm of reaction rate and the inverse of temperature can be related by the activation energy. In order to experimentally determine the activation energy, a plot of the natural logarithm of reaction rate as a function of inverse temperature was made in which the slope was the negative of the activation energy divided by the universal gas constant.

3.2.4 Aging study

An additional parameter tested in determining the feasibility of an AB hydrolysis system for fuel cell power involved an aging study. In order to address concerns with storing both the ammonia borane and the catalyst together, a three month aging study was done by mixing the prepared materials into numerous vials and letting them age in the

glovebox, periodically testing the overall loss in hydrogen capacity as a metric for the success or failure of a particular catalyst. The vials were left cracked open to prevent pressure buildup in the case that there was hydrogen release. Additionally, vials were filled and balloons were attached to visually monitor any gas production.

CHAPTER 4. RESULTS AND DISCUSSION

The efficiency and reaction characteristics of catalyzed hydrolysis of ammonia borane were evaluated using the processes and tools described in the previous chapter. The purpose was to create a dry storage system using benign chemicals that would produce hydrogen upon the addition of water. The experimental results from this work show the operational efficiency and feasibility of such a system.

4.1 Preliminary Results / Past Work

While the primary focus of this work was ammonia borane hydrolysis, tests were performed with a different known chemical hydride/catalyst combination. The purpose of these brief tests was to determine, quantifiably, the influence catalyst morphology has on the reaction kinetics of a chemical hydride. For this study, NaBH_4 was decomposed via hydrolysis using 5 wt. % Co_3O_4 as a catalyst. Two different samples were chosen for comparison due to the vastly different production methods of the Co_3O_4 . The first Co_3O_4 production method was developed and tested in Pfeil [34], and the second procedure is explained in Pol [35]. Data from Pfeil was used and compared to tests performed using the material developed in Pol. The parameters of interest are compared in Table 10.

Table 10: Comparison of Co_3O_4 Performance with varying production methods

Parameter	SCS – Co_3O_4	V. Pol – Co_3O_4 (2 tests)
Induction Time (s)	5	52, 67
Average Active HGR (LPM)	0.25	0.04, 0.04
Conversion (%)	97 ± 2	71 ± 2 , 73 ± 2

As shown from this data, it is apparent that the production method of the catalyst material has a profound effect on the overall performance. In order to examine this further, SEM images were taken to compare the surface morphology of the two catalyst samples and can be seen in Figure 15.

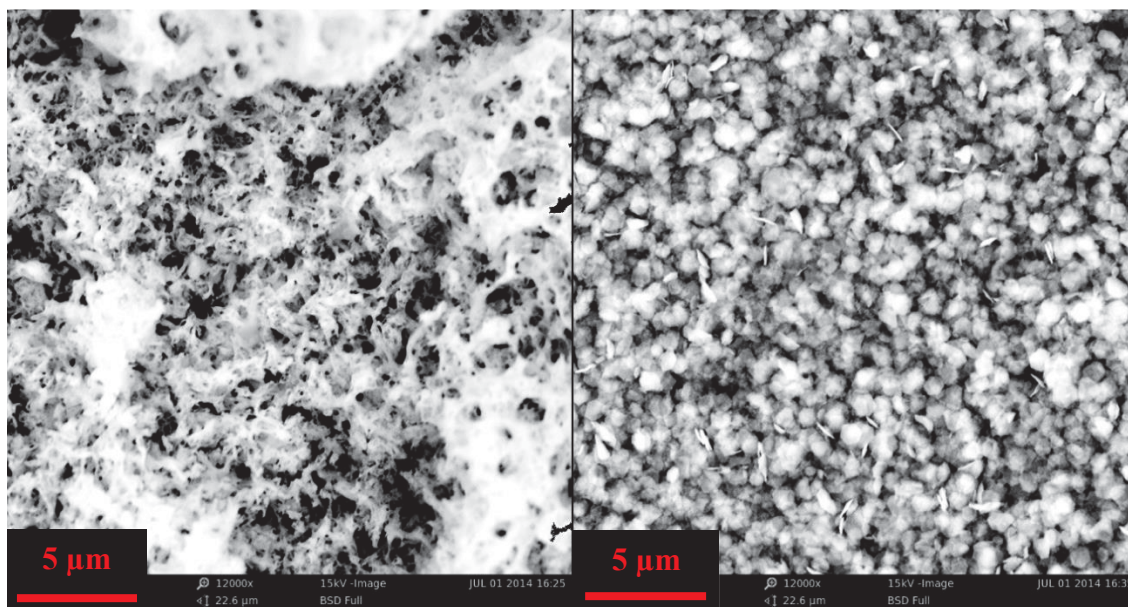


Figure 15: Comparison of Co_3O_4 Morphology: Pfeil (left), Pol (right)

From these images, it is clear that the morphology is significantly different. The material prepared by methods described in Pfeil [34] appears to have a high surface area, porous structure, whereas the material prepared by Pol [35] has a very uniform, spherical particle

size. This spherical shape lends itself to having a significantly smaller surface area, making it a less effective catalyst, by weight.

In addition to SEM imaging, energy dispersive spectroscopy (EDS) was done on the two samples in order to confirm their composition and purity. The results of this analysis are shown in Table 11.

Table 11: Molar concentrations in Co_3O_4 Catalysts

Element	Pfeil Co_3O_4 Molar concentration %	Pol Co_3O_4 Molar concentration %
Co	39.8	50.6
O	60.2	49.4

From the EDS analysis, cobalt and oxygen were the only elements present. For both samples, the molar ratio is within reason to confirm that they are both similar compositions of cobalt oxide.

It is clear that the reaction kinetics vary significantly with morphology differences alone. Based on these findings, the morphology of any catalysts used will be documented to ensure the repeatability of any results herein.

4.2 AB Catalyst Selection

The following results will discuss the methods and tools used in selecting and justifying a catalyst to evaluate.

4.2.1 NASA CEA code

The preliminary tool used in determining the feasibility of any catalyst considered was NASA CEA, chemical equilibrium software [36]. While not providing any information

on reaction kinetics, CEA is able to provide a prediction of products, given known reactants and reaction conditions. This was used to identify products in the gas produced that might be hazardous or harmful to fuel cells. In order to accommodate all the species that might be formed or used as reactants, the NASA CEA library files needed to be modified by adding previously unavailable species to the database.

From previous work by Hwang [14], it was shown that by decomposing ammonia borane in an acidic environment, the ammonia production can be greatly reduced. CEA was used to evaluate this claim. The amounts of primary reactants, being water and ammonia borane, used were held constant and added as a stoichiometric mixture in accordance with Equation 2. The amount of acid catalyst was varied by changing the concentration of H^+ ions from 2 mol. % to as much as 20 mol. % of reactants, and the resulting ammonia production was recorded. It was found that the weight percentage of ammonia formed in the products was reduced from ~25 wt. % to ~10 wt. % when the acid concentration was increased as described above. These results were verified for nitric acid, hydrochloric acid, phosphoric acid, and sulfuric acid. It should also be noted that this is the case with no excess water, therefore any ammonia formed would be released into the gas products rather than dissolved in the leftover water.

4.2.2 Acid-Based Catalyst

Using this result, acid catalysts were chosen to be potential test candidates based on the fact that they can reduce ammonia formation by increasing the acidity. In order to maintain a low pH throughout the duration of the reaction as well as in the waste products, phosphoric acid (Sigma Aldrich, crystalline, $\geq 99.999\%$ trace metals basis, CAS Number 7664-38-2), a strong acid, was used in an attempt to reduce the pH to a point where no

ammonia would be formed. However, while mixing the solid acid with the ammonia borane, the ammonia borane started to decompose immediately. From this result, it was likely that any other “dry” acid, strong enough to eliminate the ammonia formation, would also decompose the ammonia borane in a dry and inert atmosphere.

Amberlyst – 15 is a unique type of material, in that it acts like an acid when wet, but when dry, it behaves like an ordinary polymer. As discussed previously, the structure of the Amberlyst - 15 is what allows for it to act in this manner. SEM images of the Amberlyst - 15 material are shown in Figure 16 before and after ball-milling.

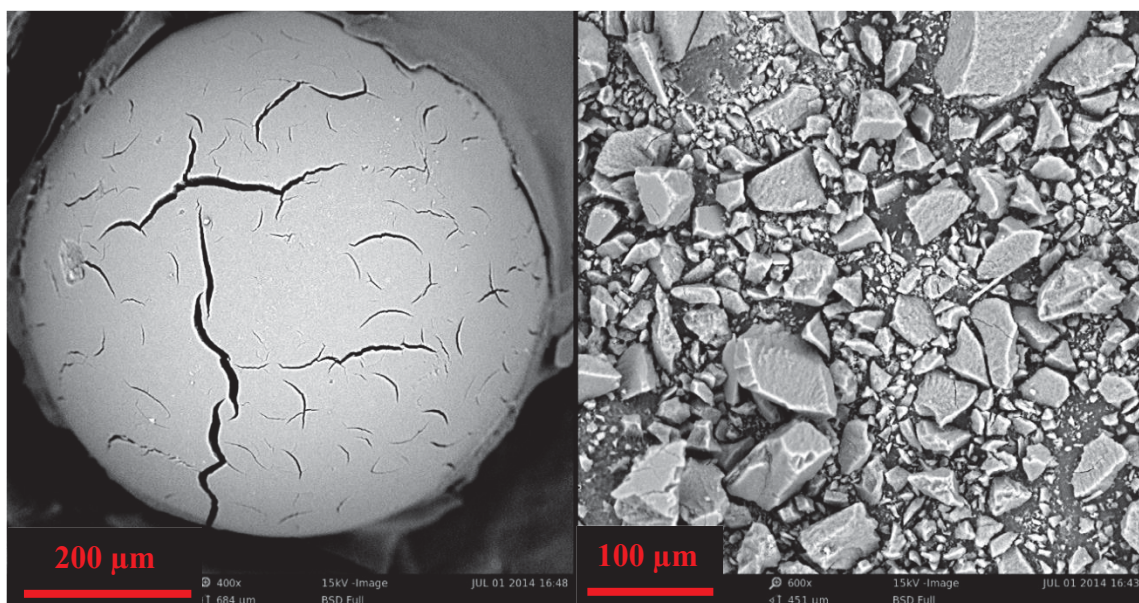


Figure 16: Amberlyst – 15 Morphology imaged at 15 kV before (Left) and after (Right) ball milling.

The particle sizing software available on the SEM was run to determine the average size of the particles. From the image on the right, in Figure 16, the average particle diameter measured 7.6 μm with a median of 5.6 μm. The discrepancy of the two values indicates the presence of outliers on the large particle end of the spectrum. Since the goal in

milling this material was to decrease the particle size down to a similar order as the platinum carbon catalyst it was being compared to, the amount of milling was adequate for the purposes of comparison.

Given the structure and lack of moisture in Amberlyst – 15 (≤ 1.6 wt. %), it should not react with ammonia borane in a dry state, and does not upon immediate observation. In the proceeding sections, tests will be conducted using ball-milled Amberlyst – 15, unless otherwise stated. All tests were also run using a 20 wt. % platinum in carbon catalyst, as described earlier, as a baseline for performance comparison.

4.3 Gas generated compatibility with PEM fuel cells

Previously discussed was the importance of gas compatibility with a PEM fuel cell. In order to be useful in a PEM fuel cell, the hydrogen produced must be pure and free of any contaminants that are particularly harmful to fuel cells. The tests conducted in this section were performed in order to determine if the purity and contaminants, if any, were present in the produced gas stream.

4.3.1 Hydrogen purity

The concentration of hydrogen produced during a hydrolysis experiment was measured via gas chromatography. The GC used was calibrated for hydrogen using a linear relationship between concentration and sensor peak area ($\mu\text{V/s}$). Since the expected concentration of hydrogen was high, this was a valid assumption. The 3-neck reaction flask containing the ammonia borane and catalyst, as described previously, was purged with high purity hydrogen (Indiana Oxygen) prior to the addition of water and thus the initiation of the reaction. Once the reaction was initiated, the product gases would flow up to the GC inlet and excess would flow out through a bypass line and to the burette.

This acted as a constant purge cycle with gases generated from the hydrolysis experiment. While the reactant gases were passing through the lines, the GC would take a sample, ensuring that the sample taken with the GC would be a true representation of the produced hydrogen. The results from this test are shown in Table 12.

Table 12: GC results for hydrogen concentration (std. dev. = 0.3% concentration)

Test	Baseline H ₂ Area ($\mu\text{V}^*\text{s}$)	Measured H ₂ Area ($\mu\text{V}^*\text{s}$)	Concentration %H ₂
Pt/C Run 1	325632	311040	95.5
Pt/C Run 2		311820	95.8
Amberlyst – 15 Run 1	328530	326460	99.4
Amberlyst – 15 Run 2		325700	99.1

4.3.2 Gas Impurities

From the GC results show that the gas produced, while mostly hydrogen, contains some impurities. In order to determine what these species are, the same gas that was run through the GC for the previous results was also collected in a short path gas cell for FTIR analysis. By using the FTIR in conjunction with the GC, the species that make up the remaining gas concentration can be identified. Since the gas cell was not heated, a small amount of water was able to condense on its windows. This produced both an absorption profile of condensed phase water as well as a shifted baseline at wavenumbers $>4000\text{ cm}^{-1}$ most likely due to light diffraction through the condensed phase water. In order to clearly see the gas phase products, spectral data for condensed phase water taken

at Purdue, with the same machine, was subtracted from the original spectrograph taken of the sample gas. Since the expected species are all in a wavenumber range $<4000\text{ cm}^{-1}$, the graph was simply cut off there. The results of this analysis are shown in Figure 17.

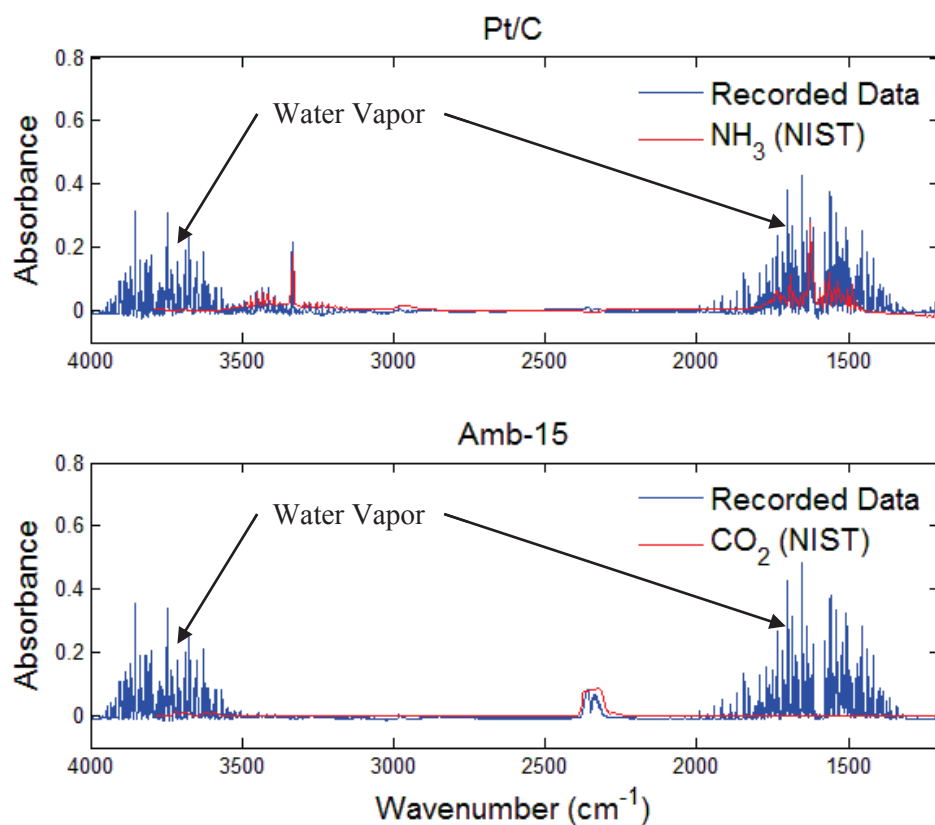


Figure 17: FTIR spectrograph of gas evolved from hydrolysis experiments with Pt/C (Top) and Amberlyst – 15 (Bottom)

Comparing the spectrograph to spectral data of known species [37], it can be seen that with both materials, there is water vapor (symmetrical stretching, 3657 cm^{-1} , and bending, 1595 cm^{-1} , vibrational modes visible), with the platinum/carbon catalyst there is ammonia (asymmetrical, 3444 cm^{-1} , and symmetrical stretching, 3337 cm^{-1} , vibrational modes visible), and with the test using the Amberlyst – 15 catalyst, the ammonia disappears and carbon dioxide (asymmetrical stretching, 2351 cm^{-1} , vibrational mode visible) is seen.

In terms of compatibility with PEM fuel cells, the Amberlyst – 15 catalyst appears to suppress the ammonia release by adsorbing it, as previously discussed. In order to quantify the ammonia production using the baseline catalyst and confirm that there is no ammonia released while using the Amberlyst catalyst, the product gases of the hydrolysis experiments were bubbled through a weak sodium hydroxide solution, and a back titration was performed with hydrochloric acid.

By performing this titration, the concentration of ammonia can be determined. The concentration data resulting from the titration is shown in Table 13.

Table 13: Concentration of NH₃ as determined by titration

Test Catalyst Material	Wt. % NH ₃ in products (Two tests)	Error Wt. %
Platinum / Carbon	3.64, 3.86	± 0.11
Amberlyst – 15	0.01, -0.02	

This data clearly shows a substantial, greater than 36000 ppm, ammonia formation when using the Pt/C catalyst and a much reduced, less than 100 ppm, amount of ammonia formation when using the Amberlyst – 15 catalyst. In addition, the amount of ammonia measured with the platinum/carbon catalyst is compatible with the GC results. That is to say, the weight percent concentration of ammonia added to the weight percent of hydrogen measured with the GC does not exceed 100%.

4.4 pH testing

At this point, the data supports the claim that ammonia released as part of the hydrolysis reaction of ammonia borane is adsorbed onto the Amberlyst – 15 catalyst. This process makes the catalyst a consumable catalyst, meaning there is a minimum amount of catalyst

required in order for the reaction to reach completion. A set of experiments was done to verify this. In the first set of these experiments, ammonia borane and the Amberlyst catalyst were added to the three neck flask fitted with a pH probe to measure the transient pH of the reactants as water was added. The next set of experiments was similar, however, the reaction flask contained a catalyst solution, and a solution of ammonia borane was added. Varying amounts of catalysts were used in order to show how the catalyst is consumed. The goal was to show that even with leftover AB, the reaction will stop after the catalyst is consumed. Since the reaction theoretically produces one mole of ammonia per mole of ammonia borane, stoichiometric was defined as the amount of catalyst needed to adsorb all of the ammonia produced. In the case of Amberlyst – 15, there is one mole of acid sites per mole of catalyst, therefore, the stoichiometric amount of Amberlyst was one mole, making the molar ratio of Amberlyst to AB 1:1 and the mass ratio ~10:1. The results of these two sets of experiments are shown in Figure 18 and Figure 19.

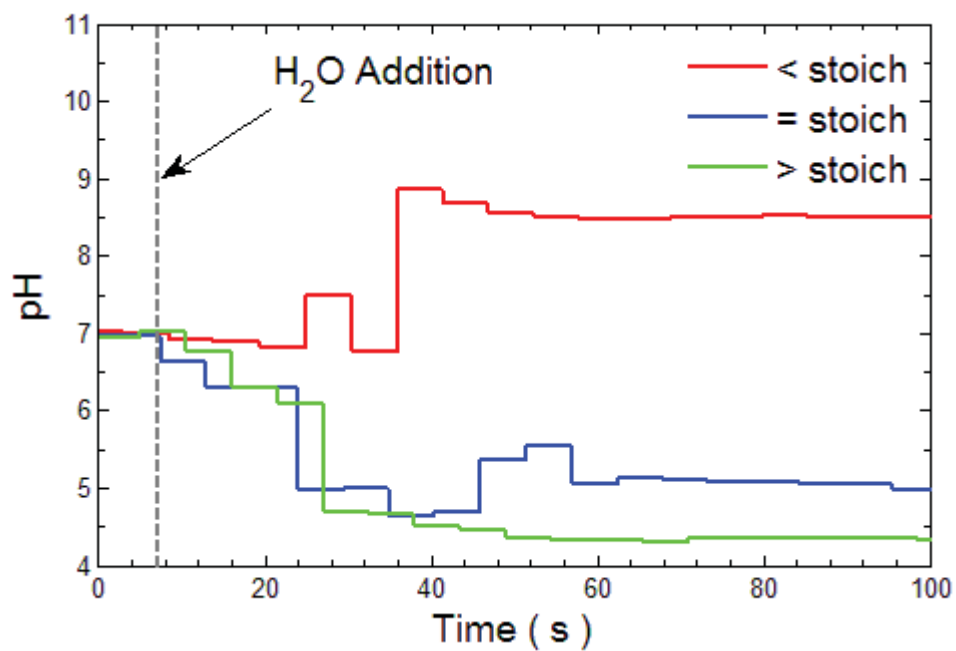


Figure 18: Transient pH testing of reactants (adding water to AB and Amberlyst)

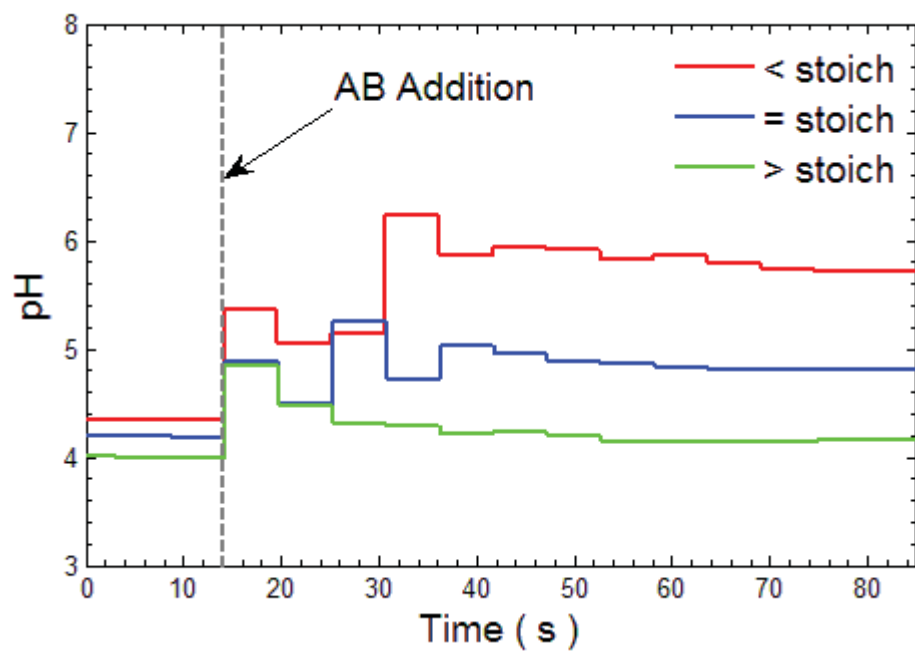


Figure 19: Transient pH testing of reactants (adding AB solution to Amberlyst solution)

The transient behavior of pH observed is as expected. With greater than or equal amounts of catalyst, there is either an excess or equal concentration of H^+ (shown as pH) than was initially in the reactants. Gas generation in these experiments was also measured. In experiments with less than stoichiometric amounts of catalyst, it was determined that the reaction stopped once the catalyst was consumed. This was based on the reduction in catalyst directly affecting the amount of gas generated. For example, if the theoretical hydrogen yield was 100 mL and 50% of stoichiometric catalyst was used, ~50 mL of hydrogen was produced.

4.5 Kinetics

The activation energies using both catalysts were experimentally determined to quantify the kinetics of the reaction and allow for direct comparison of the effectiveness of each catalyst. This was done using the three neck flask in a temperature controlled oil bath. Since the reaction temperature is known and controlled, and the reaction rate can be measured, activation energy can be determined by examining the relationship between this temperature and molar reaction rate. Tests were run at 20, 30, and 40°C. An Arrhenius plot was constructed from the results and is shown in Figure 20 and the corresponding activation energies calculated can be found in Table 14.

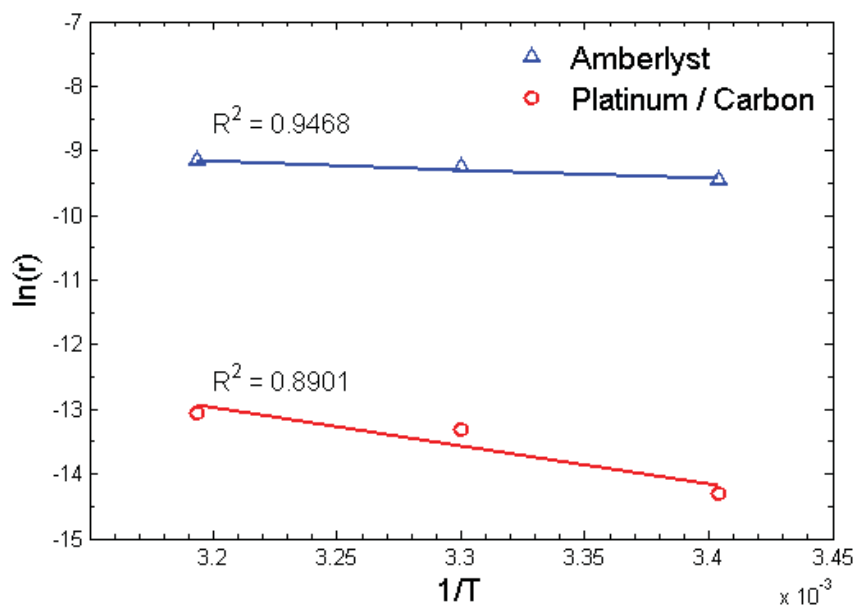


Figure 20: Arrhenius Plot to determine activation energies with Pt/C (red circles) and Amberlyst – 15 (blue triangles)

Table 14: Experimentally determined activation energy

Catalyst Material	Activation Energy (kJ/mol)
Amberlyst – 15	11.6
20 wt. % Pt/C	49.3
Uncatalyzed	129 – 184 [38]

The Pt/C catalyst was found to have a similar activation energy to the metal based catalysts shown in Jiang [39], where the activation energies ranged from 21 – 87 kJ/mol, proving the validity of the testing method. The calculated activation energy using the Amberlyst – 15 catalyst is reduced to 11.6 kJ/mol, lower than any metal based catalyst found in the literature, illustrating the effectiveness of this particular material as a catalyst in the hydrolysis of AB.

4.6 Aging Study

From a system level design, one aspect of interest is the storability of the ammonia borane and its catalysts. Since both catalysts investigated in this study (Pt/C and Amberlyst – 15) and the ammonia borane alone are known to be stable, an aging study was performed with ammonia borane and each respective catalyst stored together. Samples from the same batch of ammonia borane and catalyst were prepared in vials, mixed by hand, and left to age in the glovebox with the screw cap of the vials on loose to prevent over pressurization in the case of a gas release. In order to evaluate the viability of this storage method, the theoretical hydrogen produced in a hydrolysis experiment was used as the test metric. The results of the study are shown in Figure 21.

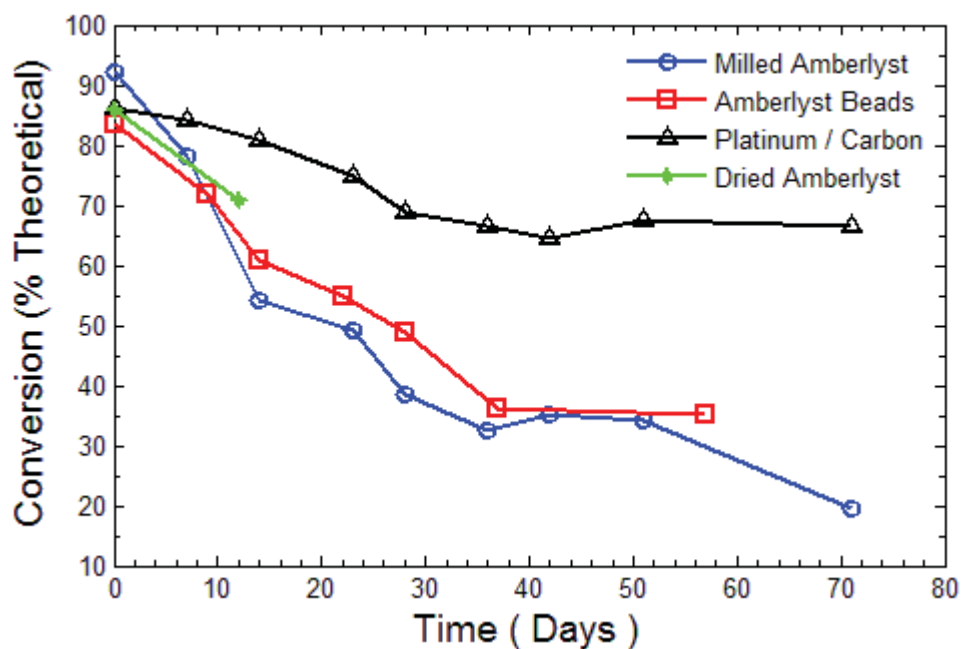


Figure 21: Aging study results with Pt/C (black triangles), as-received Amberlyst – 15 beads (red squares), ball-milled Amberlyst – 15 (blue circles), and dried Amberlyst – 15 beads (green stars)

From these results, it is clear that there is some decomposition of the ammonia borane when stored with either catalyst. One possible explanation for the decrease in conversion efficiency with the Amberlyst – 15 is its moisture content, which may be enough to slowly react with the AB. In order to isolate this possibility, Amberlyst beads were dried under vacuum at 50°C for 80 hours and then tested with a short one week aging study. The mass before and after drying was measured, and it was found that the reduction in weight was ~1.6 wt. %. The datasheet from the manufacturer states that the moisture content is ≤ 1.6 wt. % [40], therefore, it is reasonable to assume that the weight loss can be attributed to water. SEM images were taken before and after to determine visually if there were any morphology changes to the catalyst. These images are shown in Figure 22.

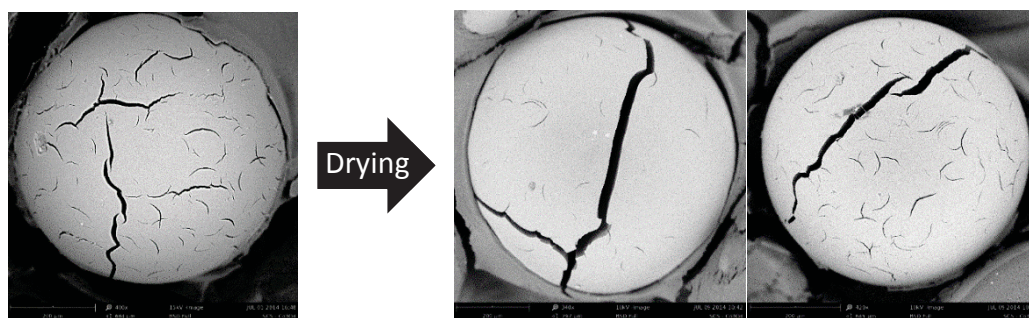


Figure 22: Before and after drying images of Amberlyst – 15 catalyst beads

It can be seen that the only change in morphology is an expansion of the cracks on the surface of the Amberlyst. This change in surface area is not expected to have a significant effect on the aging study results as ball-milled Amberlyst exhibited similar performance to the as-received material. The control test produced 86% theoretical hydrogen, and after one week of aging, the amount of theoretical hydrogen produced dropped to 71%. This data shows that the moisture content in the Amberlyst alone, is not the reason for the aging. The storability issue would need to be addressed in a system

scale design with possible solutions including coating the catalyst or ammonia borane in a water soluble material or mechanically separating the AB from the catalyst for long term storage.

4.7 System Scaling and DoE Guideline Comparison

Using the results above for ammonia borane hydrolysis, catalyzed by as received or ball-milled Amberlyst – 15 as the catalyst for AB, along with the system parameter estimates defined in Table 7, estimates can be applied to a full scale system design. Using these estimates, a direct comparison can be made to the commercially available portable fuel cell power systems, as well as to the DoE guidelines for these types of systems. The comparison of gravimetric capacity vs. volumetric capacity is shown in Figure 23.

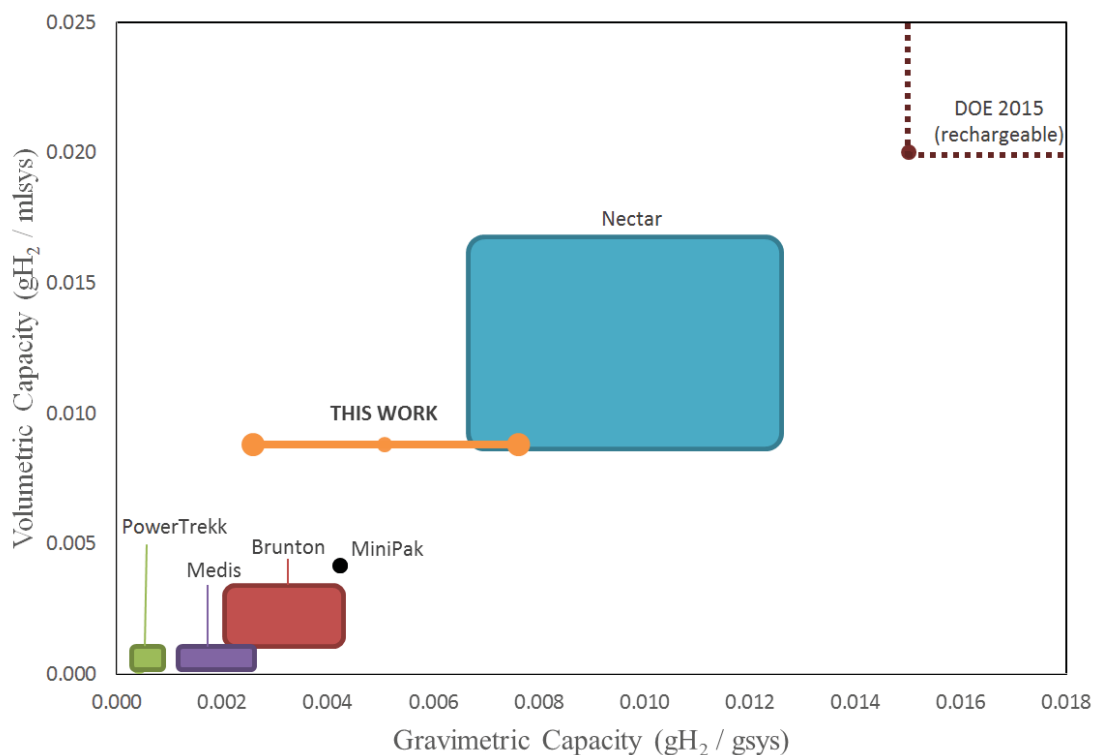


Figure 23: System capacity in grams of hydrogen per gram of system mass

The uncertainties in estimates are depicted as a range, with the center of the range being the parameter estimate. Since the volumetric capacity estimates for this work fall outside the bounds of the graph, they were not included. As seen from the graphic, the system estimates for this work exceeds other comparable systems, with the exception of the Nectar. All, however, fall short of the most modest of the DoE guidelines. The system estimates for this work are very conservative given the method of estimation. When the nature of operation of the system in this work is considered, it is reasonable to say that the system weight will not be as high as the estimate suggests, but without detailed design, it is the closest estimate of the resulting full system. In addition to volumetric and gravimetric capacity, DoE has guidelines for operation. The estimates of this work, assuming as-received, or ball-milled Amberlyst – 15 as the catalyst for AB, are compared to the commercially available systems in Table 15.

Table 15: Operational parameters and corresponding DoE guidelines

Device	Min/Max Operating Temp. (°C)	Min/Max H ₂ Temp. (°C)	Delivery Pressure (bar)	External Temp. (°C)	Induction Time at -20 / 20°C (seconds)
MiniPak	0 / 35	0 / 55	< 30	0 - 55	na / 0
Brunton	Similar to the MiniPak				na / 0
PowerTrek	5 / 35	>10 / 80**		5 / 85	na / 60
Medis	0 / 40	>10 / 80**		> 50	na / 30
Nectar	0 / 80	700 / 900	2* - 4*	0 - 60	na / 600
THIS WORK	? / 50	>10 / 50	Can control	≤40	na / 0
DoE 2015	-40 / 60	10 / 85	1.5 - 3	≤40	10 / 5
DoE 2020	-40 / 60	10 / 85	1.5 - 3	≤40	10 / 5

*Based on typical solid oxide fuel cell performance [30]

** Based on typical PEM fuel cell performance [5]

Legend:

Guidelines	Meets or exceeds guidelines	Unknown	Does not meet guidelines
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The estimates above clearly show the advantage of a system using the materials in this work. The main disadvantage of it is the operating temperature limit, which comes from the material properties of AB itself. At temperatures near 50°C, ammonia borane starts to thermally decompose [21]. In addition to capacity and operational guidelines, there are power guidelines. Since the guidelines are stated as power per system mass, the system estimates from this work are compared to similar rechargeable battery systems [32], in addition to the commercially available hydrogen fueled systems. This comparison is shown in Table 16 and Figure 24.

Table 16: Power capacities compared to comparable battery systems and DoE guidelines

	Device	Power Capacity (W-h)	Power Volume Density (W-h/mL)	Power Mass Density (W-h/g)
Fuel Cells	MiniPak	14	0.065	0.067
	Brunton	22.5	0.067	0.093
	PowerTrek	4	0.013	0.017
	Medis	20	0.016	0.055
	Nectar	55	0.367	0.275
	THIS WORK*	[27 40]	[0.235 0.352]	[0.135 0.202]
Batteries	Anker Astro Mini	15	0.319	0.195
	Jackery Bar Premium	28	0.277	0.183
	Trent iCarrier	60	0.085	0.155
DoE Guidelines	DoE 2015 (rechargeable)	-	0.7	0.5
	DoE 2015 (single use)	-	1	0.7
	DoE 2020 (rechargeable)	-	1.3	1
	DoE 2020 (single use)	-	1.7	1.3

*Based on a 40-60% fuel cell efficiency

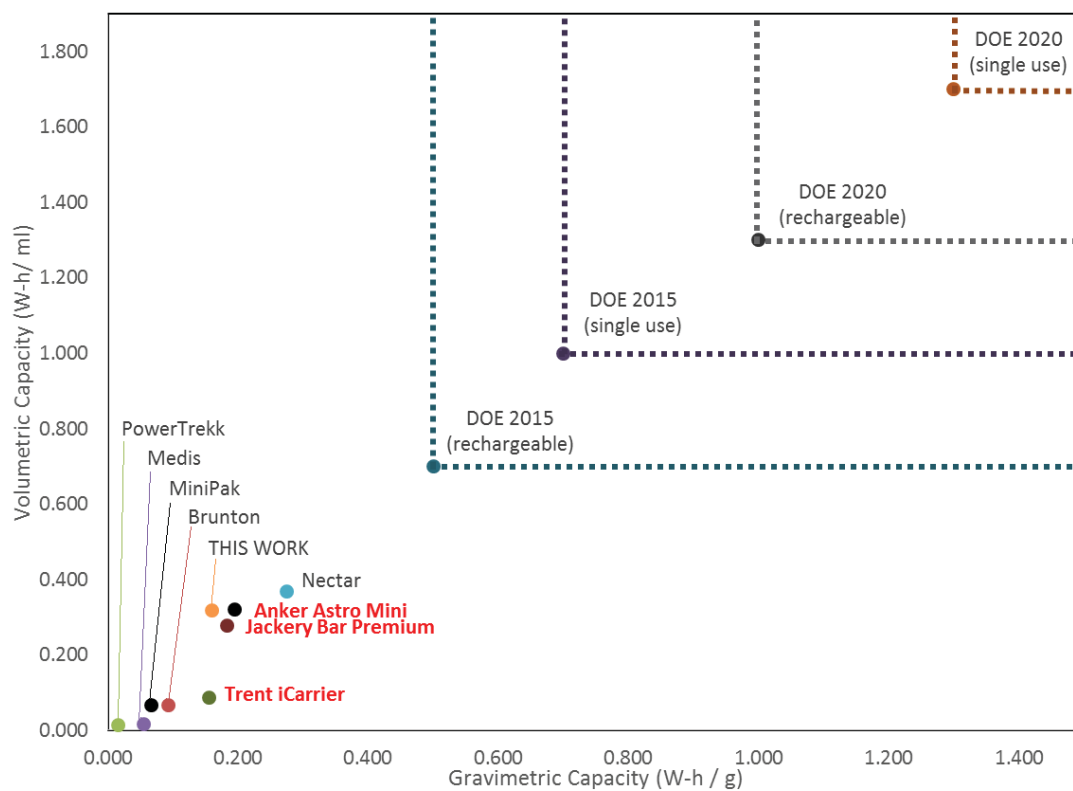


Figure 24: System capacity in W-h of total power stored (battery systems in red font)

Observing the results, it is noted that the power capacity of the system in this work would closely compare to similar, modern rechargeable battery systems. Considering the other benefits, including the safety and lifetime, it is clear that a portable fuel cell system using ammonia borane hydrolysis would have advantages, and it should be considered for system design.

CHAPTER 5. CONCLUSION

This work has tested the validity, and shown that ammonia borane hydrolysis has potential for use in portable hydrogen fuel cell power systems. The results show that not only will it be functional, but it is likely to surpass comparable systems in terms of capacity and performance. The unique catalyst used for ammonia borane, a consumable, ammonia adsorbent material, is the reason that high purity is possible using ammonia borane hydrolysis. Previous attempts at using this hydride resulted in detrimental amounts of ammonia formation in the product gases, proven to degrade PEM fuel cell membranes. Steps in the past have been taken to correct this problem, and some success was achieved by reducing the ammonia content, but it was never shown to do away with ammonia completely without a secondary filtering or ammonia scavenging material. The Amberlyst – 15 catalyst can be used to make ammonia borane hydrolysis a potential choice for portable fuel cell applications.

5.1 Summary

While traditional metal based catalysts used with ammonia borane produce ammonia in the gas stream, Amberlyst – 15 adsorbs ammonium, preventing the formation of potential ammonia gas. This material combination has the advantage of producing pure (>99%) hydrogen quickly. The kinetics of the reaction are faster than any other catalyst tested in literature. The configuration tested for this work consisted of small scale (1:10)

hydrolysis experiments where the water addition could be controlled and the gas production was observed, measured and diagnostic equipment was used to measure purity as well as test for contaminants. It was found that the gas produced using the Amberlyst – 15 catalyst prevented the measurable formation of ammonia. The gas production rate, as well as the capacity when all materials are considered, was compared to similar portable power systems. Even though this configuration outperformed most comparable fuel cell systems and batteries, it still fell short of the DoE guidelines. The DoE guidelines for volume and mass capacity may be unrealistically high for portable fuel cell systems at the current level of technology. PEM fuel cells are typically 40-60% efficient, once that rises, the DoE guidelines will be more attainable in similar systems to this work.

The main issues with the system described in this work are the aging characteristic as well as the recycling of the material. First, the aging shows, without question, that the ammonia borane and Amberlyst – 15 will react and degrade over time when stored together, even when the moisture was removed from the Amberlyst – 15. This issue could be the focus of future work. The next problem with using ammonia borane is the recycling. The waste products of AB hydrolysis are not harmful, but in order to restore them to their original composition, it takes a process that uses more energy than potentially stored in the ammonia borane initially. Work is being done to improve this process, but there is room to further that effort. In order for Amberlyst – 15 to be effective as a catalyst, there has to be enough present in the reaction, since it is “consumed” by ammonium adsorption during the reaction. Once fully covered in

ammonium, it can no longer be used. It has the feature of being economical, but it would also have to be replaced along with the ammonia borane.

5.2 Recommendations

Future work in this area could include focus on additional contaminants testing, system level design, and methods to fix the aging issue discovered in this work.

One aspect of contaminants testing that was not performed in this work was with water contaminants. This would be useful data in order to confirm that there is little to no difference in reaction behavior with water contaminants present. For example, water with high ammonia content, such as urea, would require higher catalyst loading since the ammonia would adsorb to the catalyst, consuming it before the reaction even begins.

System level design work should continue to optimize a configuration that would be most efficient and reliable. Hydride and catalyst storage bed geometry, and the water delivery optimization would contribute greatly to a full scale system. Design work with powder, or packed, bed configurations using Amberlyst – 15 beads or powder, as they did not show much difference in performance, would be extremely beneficial. Finally, methods to fix the aging problem can be improved. Possible solutions include mechanically separating the two reactants until the user is ready to use it, or coating the Amberlyst or AB in a water soluble coating. In summary, ammonia borane hydrolysis aided by the Amberlyst catalyst, has potential to be a cost effective, energy dense, storable, and safe hydrogen generation systems for portable fuel cell power.

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