



A Prototype System for Chemical Hydrogen Generation and Storage for Operating ITS Devices

Final Report

Prepared by:

Steven P. Sternberg
A. Rashid Hasan

Department of Chemical Engineering

Venkatram R. Mereddy

Department of Chemistry and Biochemistry

**Northland Advanced Transportation Systems Research Laboratories
University of Minnesota Duluth**

CTS 13-11

Technical Report Documentation Page

1. Report No. CTS 13-11	2.	3. Recipients Accession No.	
4. Title and Subtitle A Prototype System for Chemical Hydrogen Generation and Storage for Operating ITS Devices		5. Report Date April 2013	
		6.	
7. Author(s) Steven P. Sternberg, A. Rashid Hasan, and Venkatram R. Mereddy		8. Performing Organization Report No.	
9. Performing Organization Name and Address Department of Chemical Engineering University of Minnesota Duluth 1303 Ordean Court Duluth, MN 55812		10. Project/Task/Work Unit No. CTS Project #2012018	
		11. Contract (C) or Grant (G) No.	
12. Sponsoring Organization Name and Address Intelligent Transportation Systems Institute Center for Transportation Studies University of Minnesota 200 Transportation and Safety Building 511 Washington Ave. SE Minneapolis, Minnesota 55455		13. Type of Report and Period Covered Final Report	
		14. Sponsoring Agency Code	
15. Supplementary Notes http://www.its.umn.edu/Publications/ResearchReports/			
16. Abstract (Limit: 250 words) <p>This research project sought to develop a prototype hydrogen-based fuel cell system for ITS devices. The project investigated hydrogen storage capacities of the various candidate chemical hydride analogs; selected the most efficient of the candidates for energy storage based on volume, mass, and cost; developed a prototype system; and estimated the capital and operating cost for such a system.</p> <p>A hydrogen fuel cell combines hydrogen and oxygen to produce electricity, providing a clean, high-efficiency energy source that circumvents the problems associated with conventional batteries. A major drawback that limits its utility, however, is the use of heavy and bulky compressed metal cylinders as the source of hydrogen. The chemical-based hydrogen generation used in this project can provide a compact, atmospheric-pressure storage option for the controlled release of hydrogen. Many ITS-based applications can be envisaged with hydrogen-based fuel cells, such as alternating-traffic signs, directional signals, speed-limit signs, blinkers in series, warning blinkers, and backup power sources at traffic signals during power outages. This system is particularly attractive because many remote traffic signals on northern Minnesota roads lack access to a power grid, requiring the use of batteries that must be changed often, thus incurring maintenance costs.</p>			
17. Document Analysis/Descriptors Off-grid power, Fuel cells, Hydrogen power, Hydrides, Hydride chemistry		18. Availability Statement No restrictions. Document available from: National Technical Information Services, Alexandria, Virginia 22312	
19. Security Class (this report) Unclassified	20. Security Class (this page) Unclassified	21. No. of Pages 44	22. Price

A Prototype System for Chemical Hydrogen Generation and Storage for Operating ITS Devices

Final Report

Prepared by:

Steven P. Sternberg
A. Rashid Hasan

Department of Chemical Engineering

Venkatram R. Merreddy

Department of Chemistry and Biochemistry

Northland Advanced Transportation Systems Research Laboratories
University of Minnesota Duluth

April 2013

Published by:

Intelligent Transportation Systems Institute
Center for Transportation Studies
University of Minnesota
200 Transportation and Safety Building
511 Washington Ave. S.E.
Minneapolis, Minnesota 55455

The contents of this report reflect the views of the authors, who are responsible for the facts and the accuracy of the information presented herein. This document is disseminated under the sponsorship of the Department of Transportation University Transportation Centers Program, in the interest of information exchange. The U.S. Government assumes no liability for the contents or use thereof. This report does not necessarily reflect the official views or policies of the University of Minnesota.

The authors, the University of Minnesota, and the U.S. Government do not endorse products or manufacturers. Any trade or manufacturers' names that may appear herein do so solely because they are considered essential to this report.

Acknowledgments

The authors wish to acknowledge those who made this research possible. The study was funded by the Intelligent Transportation Systems (ITS) Institute, a program of the University of Minnesota's Center for Transportation Studies (CTS). Financial support was provided by the United States Department of Transportation's Research and Innovative Technologies Administration (RITA).

The project was also supported by the Northland Advanced Transportation Systems Research Laboratories (NATSRL), a cooperative research program of the Minnesota Department of Transportation, the ITS Institute, and the University of Minnesota Duluth College of Science and Engineering, departments of Chemistry and Chemical Engineering.

Table of Contents

Chapter 1. Introduction.....	1
Chapter 2. Background	3
Battery Pack	3
Diesel and Biofuel Generators	4
Solar Panels.....	4
Wind Turbines	5
Fuel Cells	6
Chapter 3. Hydrogen Storage	9
Ambient Gas	9
Compressed Gas.....	9
Liquid Hydrogen.....	9
Metal Hydrides.....	9
Chapter 4. Hydrogen Fuel.....	11
Generation.....	11
Fuel Cell Operation.....	14
Chapter 5. Prototype Design	21
Reactor	22
Liquid Storage.....	23
Liquid Dispenser.....	23
Air Inlet Heat Exchanger	24
Fuel Cell.....	24
Battery.....	24
Control System.....	24
Safety Equipment.....	25
Chapter 6. Cost.....	29
Capital.....	29
Operation and Maintenance	29

Chapter 7. Additional Work	31
Chapter 8. Conclusions.....	33
References	35

List of Tables

Table 1: Rechargeable battery characteristics.....	4
Table 2: Amount of hydrogen in several metal hydrides.....	10
Table 3: Yield of hydrogen at different temperature conditions.....	12
Table 4: Reaction of SBH with various solvents under non-accelerated conditions.....	13
Table 5: Reaction of SBH with ethylene glycol/water mixture using acetic acid accelerant.....	13
Table 6: Efficiency of fuel cell at different temperatures and resistance.....	15
Table 7: Results of 0.75 grams of NaBH ₄	18
Table 8: List of prototype subsystems.....	21
Table 9: Design assumptions.....	21

List of Figures

Figure 1: Schematic of a Fuel Cell [(Wikicommons, 2007)].....	6
Figure 2: Experimental equipment schematic for determining hydrogen generation rates.....	12
Figure 3: Rate of hydrogen production from SBH and mixture of ethylene-glycol and water at different temperatures.....	14
Figure 4: Fuel cell operation at room temperature.....	16
Figure 5: Fuel cell operation at 0.1 °C.....	16
Figure 6: Fuel cell operation at (-9 <T<-20)°C.....	17
Figure 7: Power generation during experiment described in table 7.....	19
Figure 8: Temperature evolution during experiment described in table 7.....	19
Figure 9: Prototype schematic for the generation of hydrogen for use in a fuel cell.....	27

Executive Summary

This project explores the development of a power source that is independent of the power-grid, does not need frequent recharging, can work in cold weather, and is dependable. In particular, the project explores the use of a hydrogen powered fuel cell for constant, local charging of a battery pack. The battery pack would be much smaller than a battery-only system since the power storage medium is hydrogen and the waste heat from the fuel cell can be used to keep the system warm. This project proposed research to develop a reliable H₂-based portable power system that can be used to operate various traffic systems including DSRC-based wireless applications, variable message signs, traffic sensors, and intersection traffic signals. The primary goals of this project are to: (1) investigate the hydrogen storage capacities and operational safety of the various candidate chemical hydrides, (2) further develop a short listing of an appropriate candidate chemical hydride, (3) develop a prototype system, and (4) estimate the capital and operating cost for such a system.

Results for this project include:

1) Several hydrogen generating materials were investigated. The most promising consisted of the alkali-hydrides and -borohydrides. An ammonia borohydride was also explored.

2) The selection of a hydrogen generating reaction system was based on the ability to control the reaction such that it produced hydrogen at approximately the rate at which it would be consumed by the fuel cell, that the reaction would work between temperatures of -40 °C to 30 °C, that the reactants would be inherently safe to humans and the environment, and be inexpensive. The system chosen uses sodium borohydride combined with a 50/50 mixture of ethylene glycol and water. A small amount of acetic acid can be added to accelerate the reaction at colder temperatures. In a late addition to the project, tartaric acid was explored as an alternative to acetic acid. This acid provided better control of the reaction at higher temperatures (above 0°C).

Results of our work show that we were able to successfully produce hydrogen at temperatures as low as -50°C. However, the production rate was significantly slowed at temperatures lower than -40°C. The yield of hydrogen was observed to be >90% for temperatures between 25°C to -20°C, and at -40°C, the yield was observed to be ~80%.

3) A prototype reactor was designed and constructed. This system provides a 20 watt, 12 volt load with electricity for one week using 2.5 pounds of sodium borohydride and one gallon of the liquid mixture. Potential problems not addressed in this report include water / ice buildup within the equipment enclosure, hydrogen release during refueling, and unintended buildup of hydrogen within the equipment enclosure due to unknown leakages.

4) The cost of the prototype system was approximately \$7,500. Costs of fuel materials for operation will be approximately \$35 /week or about \$2,000 / year.

Chapter 1. Introduction

Intelligent Transportation System (ITS) technologies advance transportation safety and mobility and enhance American productivity by integrating advanced communications technologies into transportation infrastructure and into vehicles. ITS devices encompass a broad range of wireless and traditional communications-based information and electronic technologies. They are used to measure, collect, analyze, and inform users of transportation services. For roadway transportation this may mean monitoring traffic and speed, warning drivers of changes in traffic conditions, and collecting information needed to enhance use of or re-design of existing infrastructure. The monitors, sensors, and communication equipment needed to do this require electricity. In urban areas this rarely presents a problem as grid power sources are generally widely available or easy to bring to a site. In rural areas it may be miles between power grid locations, limiting the use and deployment of ITS devices. These off-grid locations could be used if there was a reliable, inexpensive, all-weather alternative power source. Typical off-grid power sources include battery packs or diesel generators. However, these sources require constant maintenance to recharge/ replace batteries or to refuel generators. The frequency of such trips can be daily. If a site is far from a maintenance area, the trip may require multiple hours for the maintenance crew. An additional issue in Northern Minnesota is the winter weather (snow, ice) and cold temperatures (-30 to -40 °F at night) both of which can greatly reduce the efficiency and up-time of these power sources.

This project explores the development of a power source that is independent of the power-grid, does not need frequent recharging, can work in cold weather, and is dependable. In particular, the project explores the use of a hydrogen powered fuel cell for constant, local charging of a battery pack. The battery pack would be much smaller than a battery-only system since the power storage medium is hydrogen and the waste heat from the fuel cell can be used to keep the system warm. This project proposed research to develop a reliable hydrogen (H₂)-based portable power system that can be used to operate various traffic systems including

(DSRC)-based wireless applications, variable message signs, traffic sensors, and intersection traffic signals. The primary goals of this project are to: (1) investigate the hydrogen storage capacities and operational safety of the various candidate chemical hydrides, (2) further short listing of an appropriate candidate chemical hydride, (3) develop a prototype system, and (4) estimate the capital and operating cost for such a system.

Results for this project include the selection of a reactor system for generating hydrogen at temperatures between -40 °C to 30 °C: sodium borohydride combined with a 50/50 mixture of ethylene glycol/ water with a small amount of acetic acid to accelerate the reaction at colder temperatures. Also, a prototype reactor was designed and constructed. This system will provide a 20 watt, 12 volt load with electricity for one week using 5 pounds of sodium borohydride and one gallon of the liquid mixture. Potential problems not addressed in this report include water / ice buildup within the equipment enclosure, hydrogen release during refueling, and unintended buildup of hydrogen within the equipment enclosure due to unknown leakages. The cost of the prototype system is approximately \$7,500. Costs of materials for operation are approximately \$35 /week or about \$2,000 / year.

Chapter 2. Background

There are several electric power choices for off-grid applications. The main considerations for this project are portability, cold weather suitability, and safety. This project requires the power source to be easily transported for deployments of a few days to several months and that it not endanger maintenance workers or the public. The main commercially available choices for this equipment are battery packs and diesel engines. Alternative equipment includes solar power, wind turbines, and fuel cells. These alternatives are just beginning to be commercialized and offer several potential advantages over battery packs or combustion engines. In this chapter we will briefly discuss each of these technologies and look at their utility for off-grid power supplies for Intelligent Transportation Systems (ITS) devices.

Battery Pack

A battery pack is a set of any number of (preferably) identical batteries or individual battery cells. They may be configured in a series, parallel or a mixture of both to deliver the desired voltage, capacity, and power density. The components of a battery pack include the individual batteries or cells and the interconnects which provide electrical conductivity between them. Rechargeable battery packs usually contain a temperature sensor, which the battery charger uses to detect the end of charging. Interconnects are used to connect each cell in either a series or parallel connection. Battery regulators are used to keep the peak voltage of each individual battery or cell below its maximum value so as to allow weaker batteries to be fully charged, bringing the whole pack back into balance. A well-balanced pack lasts longer and delivers better performance, (Engineering.com, 2013).

The main advantages of battery packs are that they are portable, so they can be swapped into and out of any device. This allows the pack to be charged at a central location, while a replacement pack is used to power the device. Battery packs can be added together to obtain higher power or to last longer. A small device (sensor, communication) may be able to be run for a week from a battery pack, whereas a larger, more energy intensive device (lighting) may need to have the batteries replaced daily. A user would need approximately twice as many battery packs as devices so that one set is charging while the other pack is being used.

The main disadvantages of battery packs are their cycle life and their reduced efficiency in cold weather. Batteries have a cycle life, which could also be described as the number of times it may be recharged. The typical range is 200 – 1000 cycles, depending on usage environment and maintenance level of the battery equipment. Batteries have a working temperature range of -20 °F to 60 °F. The temperature will also control the charging and discharge rate. Batteries need more frequent recharging in colder weather (or need to be that much larger). Batteries cannot be charged if they are cold (<20 °F), but will recover if they are heated. Indeed, some battery pack systems include a battery warming circuit which uses electricity from the battery in a heating resistor.

The performance of all battery chemistries drops drastically at low temperatures. At -20°C (-4°F) most nickel-, lead- and lithium-based batteries stop functioning. Specially built Li-ion brings the operating temperature down to -40°C, but only on discharge and at a reduced

discharge. Lead acid batteries have the danger of the electrolyte freezing, which can crack the battery casing. Cold temperature also increases the internal resistance and diminishes the capacity. Batteries that would provide 100 percent capacity at 27°C (80°F) will typically deliver only 50 percent at -18°C (0°F). The capacity decrease is linear with temperature. Batteries achieve optimum service life if used at temperatures of 20°C (68°F) or slightly below.

Table 1: Rechargeable battery characteristics.

Battery Type	Whr/kg	Joules/g	Whr/liter	\$/Whr
Lead-acid	41	146	100	0.17
Alkaline long-life	110	400	320	0.19
Carbon-Zinc	36	130	92	0.31
NiMH	95	340	300	0.99
Ni-Cd	39	140	140	1.50
Lithium-ion	128	460	230	0.47

Diesel and Biofuel Generators

Diesel engines are a well-developed technology. A quality unit starts at around \$10,000 and is capable of running full time. The limitations are need for constant refueling, fuel efficiency, and equipment maintenance. Fuel tanks start at 20 gallons and can be considerably larger. The engine and generator can produce electricity at levels starting at 10,000 watts. Equipment is about 3' x 3' x 2' and larger if given a weather resistant enclosure. Fuel usage is typically 0.5 to 1.0 gallons per hour, so they require daily refueling (including holidays and weekends). Basic maintenance requires oil and filter changes every 500 hours (every three weeks). Typically these maintenance activities are done in a central shop, so the unit must be transported to and from the shop to work site. This is a great choice for short term applications that require 1000+ Watts, such as lighting. Winter weather tends to decrease efficiency and increase maintenance requirements. Weight starts at 500 – 1000 lbs, which requires the engine be mounted on a trailer. Typical cost of fuel is 0.0004\$/Wh. This does not include cost of routine maintenance and replacement of oil and air filters, which can double or triple the cost depending on distance it must be transported for the maintenance. For small electric loads this choice is not economical due to the large size and initial cost of the equipment, (Wikipedia, Diesel Engine, 2013).

Solar Panels

A solar panel is a packaged assembly of solar cells, electricity inverter, a battery, perhaps solar tracking hardware, and a mounting system. The solar cells directly convert sunlight into electricity. The inverter is used to correct the voltage to a single value. It is needed because the voltage output (and power) will vary with solar intensity and time of day. Time of day effects can be partially offset by solar tracking hardware. Solar tracking allows the panel to always be perpendicular to the sun's rays. The mounting system holds the panels in place and is used to locate the panels above surrounding buildings and vegetation, (Wikipedia, Solar Panel, 2013).

Solar panels work when light, in the form of photons, hits the solar cell. If the photon has sufficient energy it can energize a single electron. This creates an electron-hole pair within the cell. The electron is prevented from rejoining the hole due to the inherent electric field in the

solar cell. These electrons can be collected on one side of the solar cell and then routed through a load and back to the solar cell's other side where the electron holes have collected. The electron flow provides current, and the cell's electric field causes a voltage. With both current and voltage, power is created, which is the product of the two. The actual voltage output of the panel changes as lighting, temperature and load conditions change, so there is never one specific voltage at which the panel operates. The panel is sized by its nominal voltage. Nominal voltage refers to the voltage of the battery that the package is best suited to charge, and it is a semi-empirical quantity.

Obviously solar panels only work during the daytime. These systems require a charged battery to work at night. The panel must be sized large enough to provide for the power requirements of the device plus enough to charge the battery to provide power until the next day. This size would need to be 3 - 4 times the daytime size to account for the reduced daylight available in winter. Batteries may return 70% of the incoming energy as electricity; the rest is unavoidably expended as heat due to thermodynamic constraints. Most batteries cannot be fully recharged if the temperature is below 20°F. Cold weather applications must provide for heating of the battery, which in turn uses more of the stored energy which requires larger solar panels and a larger battery pack to store the charge.

While this system is similar to the battery packs described above, the battery pack is smaller or can be swapped out less frequently. The system can even send out a signal to warn that its batteries are getting too low in reserve power and may need to be serviced. This would happen during periods with overcast skies, when the solar panels are dirty or get covered in snow or ice. Also in the winter there is less light, and the cold temperatures will cause the batteries to have slower recharge and quicker drain. Any of these conditions will require maintenance personal to visit the site more frequently.

The cost of solar panels is decreasing because they are becoming more efficient and less expensive to manufacture. The battery is typically the main capital expense, and these systems may soon become less expensive than the battery-only system, if only because of fewer maintenance visits to recharge the batteries. The solar panel system works well in summer time in Minnesota, but performs poorly in winter.

Wind Turbines

Another potential method for generating off-grid power is the wind turbine. These systems consist of a turbine, a battery pack for low wind time periods, inverter to correct voltage to a single value, and a tower upon which the turbine is mounted. The turbine converts wind motion into mechanical motion (rotating fan blades) which is then converted into electricity. This system, like the solar panels, will require a battery pack. The system needs energy storage for when wind speeds are too low to generate electricity (< 8 mph), although the required battery would be smaller in size than the battery-only option. A typical installation would require a 50 to 100 foot tower with a rotor diameter of about 5 to 20 feet. The size of the equipment, especially the tower, and the previously mentioned battery recharge in cold temperature issues make this system unadvisable for cold weather, portable, ITS applications (Wikipedia, Wind Turbine, 2013).

Fuel Cells

A fuel cell is a device that converts chemical energy into electricity. The fuel cell uses a chemical reaction that typically involves a hydrocarbon fuel and oxygen. Hydrogen gas is the most common fuel, although natural gas or methanol can also be used. Fuel cells work almost the same as a battery, except the fuel cell requires the addition of external reactants (fuel and oxygen) rather than storing them completely within the battery. Indeed, fuel cells have been called gas batteries. They may also produce electricity for much longer time periods – as long as the reactants are provided in sufficient quantity (Wikipedia, 2012), (Barbir, 2005).

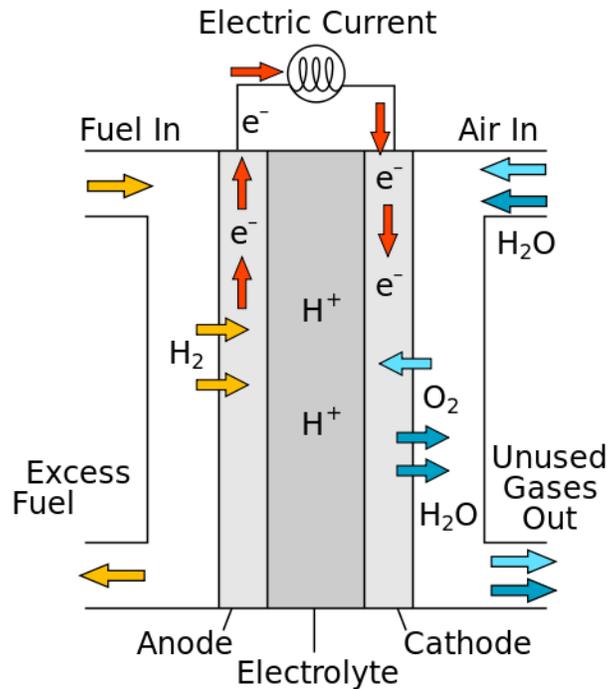


Figure 1: Schematic of a Fuel Cell [(Wikicommons, 2007)].

There are several types of fuel cells. All types consist of an anode, a cathode, and an electrolyte which allows charges to move between the electrodes (Larminie, et al., 2003). Electrons are drawn from the anode to the cathode through the external circuit as direct current (DC) electricity. The main difference between types of fuel cells is the electrolyte. Fuel cells are capable of converting approximately half of the chemical energy into electricity, with the remaining energy converted to heat. Fuel cells also produce standard combustion products for the fuel that is used – typically water and carbon dioxide.

A hydrogen fuel cell uses a catalyst (platinum) at the anode to convert the hydrogen atom into a hydrogen ion (bare proton) and an electron. The electrolyte which connects the anode to the cathode allows the positively charged proton to pass and it prevents the electron from moving through it. If an external circuit is provided, the electron may pass through it to travel to the cathode. A second catalyst (nickel) is used at the cathode to combine the electron, proton and oxygen to create water and heat, which drives the mass transfer potential by converting and removing the protons. The most widely used fuel cell for portable applications uses hydrogen at

ambient conditions in a proton exchange membrane (PEM). The membrane is a polymer material that does not conduct electricity but allows protons to diffuse through it.

Major concerns with PEM fuel cells are water/ air management and temperature management. The fuel cell requires that the electrolytic membrane be sufficiently hydrated. Too little water will reduce the proton mobility, increasing resistance and reducing efficiency. Too much water will flood the cell and prevent the mass transfer of oxygen to the cathode which also reduces / stops the cell from functioning. Temperature management must be used to maintain the same temperature throughout the cell in order to prevent destruction of the cell through thermal loading. This is particularly challenging as the hydrogen combustion reaction is highly exothermic, so a large quantity of heat is generated within the fuel cell. Both concerns are addressed by having a controlled fan on the cathode side to draw off water and heat. The fan uses the fuel cell as its power source and uses a calibrated power curve and temperature measurement to determine when the fan should be run.

Fuel cells are not as efficient as batteries, but do have the potential to augment batteries by reducing the need to exchange/ replace batteries. They also supply heat which can keep the battery operating at a high efficiency even in cold weather. Professor Jeremy P. Meyers, (Meyers, 2008) wrote, "While fuel cells are efficient relative to combustion engines, they are not as efficient as batteries, due primarily to the inefficiency of the oxygen reduction reaction (and ... the oxygen evolution reaction, should the hydrogen be formed by electrolysis of water). ... [T]hey make the most sense for operation disconnected from the grid, or when fuel can be provided continuously. For applications that require frequent and relatively rapid start-ups ... where zero emissions are a requirement, as in enclosed spaces such as warehouses, and where hydrogen is considered an acceptable reactant, a [PEM fuel cell] is becoming an increasingly attractive choice [if exchanging batteries is inconvenient]".

Fuel cell advantages include their efficiency, size, and safe operation. A PEM fuel cell can convert approximately 30-50% of the fuel chemical energy into electricity, with the remainder forming heat. The electricity can be used to charge a battery, which is used to power any electrical load requiring DC power (or AC power if a power inverter is used). The heat generation can be used to keep the battery and auxiliary equipment warm. The incoming air will also need to be heated to prevent temperature changes from damaging the fuel cell. The size of a fuel cell is quite small, a 100 W system is the size of a brick, and a 1 kW system is about the size of a small laptop computer. The system size will depend on what other equipment is needed: battery pack, power inverter, measurement and control hardware, air pre-conditioning (a heat exchanger for controlling air temperature and an adsorption column to remove contaminants), and a hydrogen source. The battery pack is used to smooth the power supply and to cover peak loads. Fuel cells are quick to adapt to power changes, but are not instantaneous devices - requiring several seconds to respond to power changes. The power inverter is used to supply the proper type of electricity to the load (voltage, AC or DC). Measurement and control hardware are used to keep the system operating at high efficiencies. These include temperature and moisture levels in the fuel cell which are used to control the fuel cell fan, pressure device to monitor and control fuel input to the fuel cell, and hydrogen sensor to monitor for safety within the system. Air pre-conditioning is used to maintain a steady air inlet temperature to prevent thermal stresses within the fuel cell. This is especially important for winter conditions. Also, certain contaminants in the air could damage the fuel cell: particulate matter, carbon monoxide,

nitrogen oxides, and sulfur oxides could all cause problems. Each of these is associated with road traffic so some sort of filter may be needed to remove /reduce these contaminants from the inlet air stream. The hydrogen source is the main variable consideration for this project, see next chapter on hydrogen fuel.

Fuel cell disadvantages mainly center on the fact that it is a new technology: slow start-up times, low power output, sluggish response on power demand, poor loading capabilities, narrow power bandwidth, short service life and high cost. Similar to batteries, the performance of all fuel cells degrades with age, and the stack gradually loses efficiency. The relatively high internal resistance of full cells also poses a challenge. Each cell of a stack produces about one volt when in open-circuit condition, and a heavy load causes a notable voltage drop. Fuel cells operate best at a 30 percent load factor; higher loads reduce efficiency. A load factor approaching 100 percent, as is common with a battery, is not practical with the fuel cell. In addition, the fuel cell has poor response characteristics and takes a few seconds to react to power demands. This requires that the fuel cell provides a support function to a master battery, whereby the fuel cell provides the charge duty. This relationship enables both parts to deliver continuous service.

Chapter 3. Hydrogen Storage

Hydrogen is very abundant on earth, however very little hydrogen exists as the gas H_2 . Instead hydrogen is chemically bound in other molecules. Hydrogen exists in water (H_2O), natural gas (CH_4) or other hydrocarbons (oil and coal), and many minerals. In order to use the hydrogen as fuel it must be chemically converted to generate the gas form (H_2). Once the hydrogen has been generated it may be used, stored for later use, or transported to the fuel using device.

There are many ways in which hydrogen can be stored for use in a fuel cell: ambient gas, compressed gas, liquefied gas, or a hydrogen compound, [(Puru, 2011), (Mandal, 2009), (Klebanoff, 2010), (V. Pe' rez-Herranz, 2010)]. This last form requires the compound to be transformed into hydrogen before use within the fuel cell device.

Ambient Gas

This is the easiest to use form, but it is also the least dense, containing only 1 mol in 22.5 liter, or 0.09 g/liter. This is equivalent to 1.5 Whr/liter. This form is not practical for long term storage, but is acceptable for generation at the source, where the low density is not an issue.

Compressed Gas

Hydrogen can be compressed to 150 - 350 bar (2000 - 5,000 psi) or with specialty storage materials up to 700 bar. This increased pressure changes the gas density to about 14 mols/liter. The energy storage density increases to an equivalent heating value of 450 Whr/liter. However, compressed hydrogen requires a storage vessel that can contain these pressures and creates a safety risk if a leak occurs due to corrosion or accident. Such containers are by necessity quite heavy even for small amount of hydrogen. A standard compressed gas cylinder (26 x 140 cm outside dimensions) can store about 50 L at 2500 psi (7 mol/liter) or 350 mol of hydrogen but it weighs nearly 70 kg (165 lbs). This amount will provide nearly 3 weeks of hydrogen for the prototype case described later in this report, compared to the 1 week time for the chemical storage as a metal hydride. However the metal hydride and reactor will weigh considerable less, and have greater safety.

Liquid Hydrogen

Hydrogen liquid has a high storage capacity (35 mol/liter or 71 g/liter), but requires a tremendous amount of energy to convert to the liquid form, and also requires continuous energy inputs to remain liquid. This is because hydrogen liquid boils at $-252.882\text{ }^\circ\text{C}$ or $-423.188\text{ }^\circ\text{F}$. This is not an appropriate technology for small scale off grid electricity generation.

Metal Hydrides

Hydrogen can also be chemically stored as a metal hydride. The hydrogen can be generated from the hydride on an as needed basis (Soloveichik, 2002), (Gervasio, et al., 2005), (Breault, et al., 1999). This storage medium has the benefit of good energy density by volume, and low reactivity in the atmosphere. The low reactivity means they are safe to handle during maintenance or during and after an accident. Some of the more well-known mineral forms

include lithium hydride (LiH), lithium borohydride (LiBH₄), sodium borohydride (NaBH₄), lithium aluminum hydride (LiAlH₄), and sodium aluminum hydride (NaAlH₄), (McClaine, et al., 2000). The overall reactions for each mineral with water are as follows. Note that intermediary reactions are not included, even though each reaction proceeds through several steps. Also, the exact form of the products may differ depending on other characteristics such as pH. These reactions are all normalized to the same product form for the comparison presented in table 2.

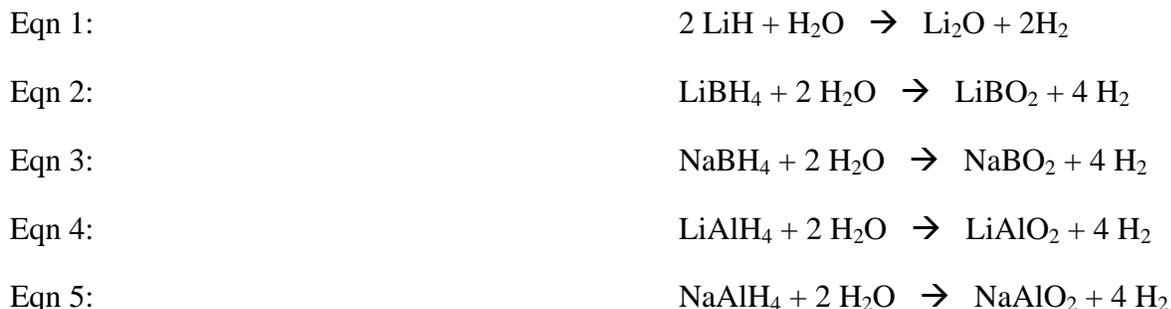


Table 2 lists the hydrogen weight fraction for each of these compounds and the overall weight ratio of hydrogen generated as a fraction of all the reactants.

Table 2: Amount of hydrogen in several metal hydrides.

Compound	wt% H	wt% H reactants
LiBH ₄	18.4	13.8
LiH	14.4	11.6
NaBH ₄	10.6	10.8
LiAlH ₄	10.5	10.8
NaAlH ₄	7.4	8.9

Some alternative hydride complexes can be made from ammonia, aluminum, and borohydrides (Staubitz, et al., 2010). These materials have a hydrogen yield of 9% by weight or even less. Several of these compounds have been studied including some that contain only B, N, and H (both positive and negative ions), such as; amine boranes, boron hydride ammoniates, hydrazine-borane complexes, and ammonium octahydrotriborates or tetrahydroborates. Of these, the amine boranes have been investigated as hydrogen carriers the longest (during the 1970s and 1980s by the U.S. Army and Navy). Their chief benefit was that they contained no metal ions, otherwise they performed similarly to the metal hydrides.

This project explores the use of the metal hydride compounds for storing hydrogen. This choice is due to the lower overall weight, the high energy density, and the safety considerations for on-site storage.

Chapter 4. Hydrogen Fuel

Generation

The technologies involving hydrogen storage have only recently been under investigation and they are not well understood. They are also economically non-viable for routine and commercial applications. The most widely understood hydrides for hydrogen storage are sodium borohydride (NaBH₄ or SBH) and ammonia-borane (NH₃BH₃ or AB) (Demirci, et al., 2009). These compounds are safe, compact, and readily provide large quantities of hydrogen on demand. Sodium borohydride especially is nontoxic, nonflammable and is available in large supplies; in fact, the United States has the world's largest reserves of borax, an ore from which sodium borohydride is readily prepared.

The reaction of sodium borohydride with water leads to the slow release of hydrogen gas along with sodium borate as shown below. Sodium borohydride has been previously studied as a hydrogen storage material. The other reactants most studied are water and methanol.



These reactions represent the reaction mechanism for sodium borohydride with water and methanol respectively. The reaction is exothermic with the heat of reaction of (-210) kJ/mol. Both these reactants provide excellent reaction kinetics, but both are limited by temperature, and the reaction almost ceases at temperature below 0 °C. To enhance the rate of reaction at cold temperatures various metal catalysts have been used such as copper, aluminum, zinc, silica gel, ruthenium, nickel, or platinum (Amendola, et al., 2000). The application of catalyst enhances the rate of reaction but at the same time increase the cost of operations. One of the project goals was to develop a chemical reaction system that could operate at cold temperatures, and be economical.

One project parameter was set by the cold climate in Minnesota where, during the winter, an evening low may approach -40°C (-40°F). At this low temperature, both water and methanol will freeze solid. We explored several substances that could depress the freezing point of water. We eventually found a simple mixture of ethylene glycol (found in anti-freeze in car cooling systems) mixed with water kept the solution from freezing (Wikipedia, 2012). When a suitable accelerant is also added, the reaction can use the glycol as well as the water for hydrogen generation. We were able to successfully produce hydrogen at temperatures as low as -50°C without freezing. However the production rate was significantly slowed at temperatures lower than -40°C. The low temperature experiments required the use of an accelerant (protic or Lewis acids). The yield of hydrogen was observed to be >90% for the temperature range between 25°C to -20°C and at -40°C the yield was observed to be ~80%.

The data was gathered for the reaction between 2 mmol NaBH₄ and 5 ml of solvent using the laboratory setup as shown below in figure 2. Lower temperatures were attained using dry ice

around the round bottom reaction flask. The gas dryer was used to remove any moisture from the product gases. The moisture could occur during evaporation of the water reactant due to the heat generated from the reaction. The clear bulb was for observation of the gas (hydrogen is colorless). The gas burette was used to measure the quantity of gas generated by the reaction. The water reservoir was used to refill the burette between experiments. Each experiment reacted approximately 0.08 g of SBH with an excess of the glycol / water mixture. This amount was chosen to develop approximately 200 ml of hydrogen, which could be easily measured in the 250 ml gas burette. Actual amounts varied for each run, see table 3 for more detail.

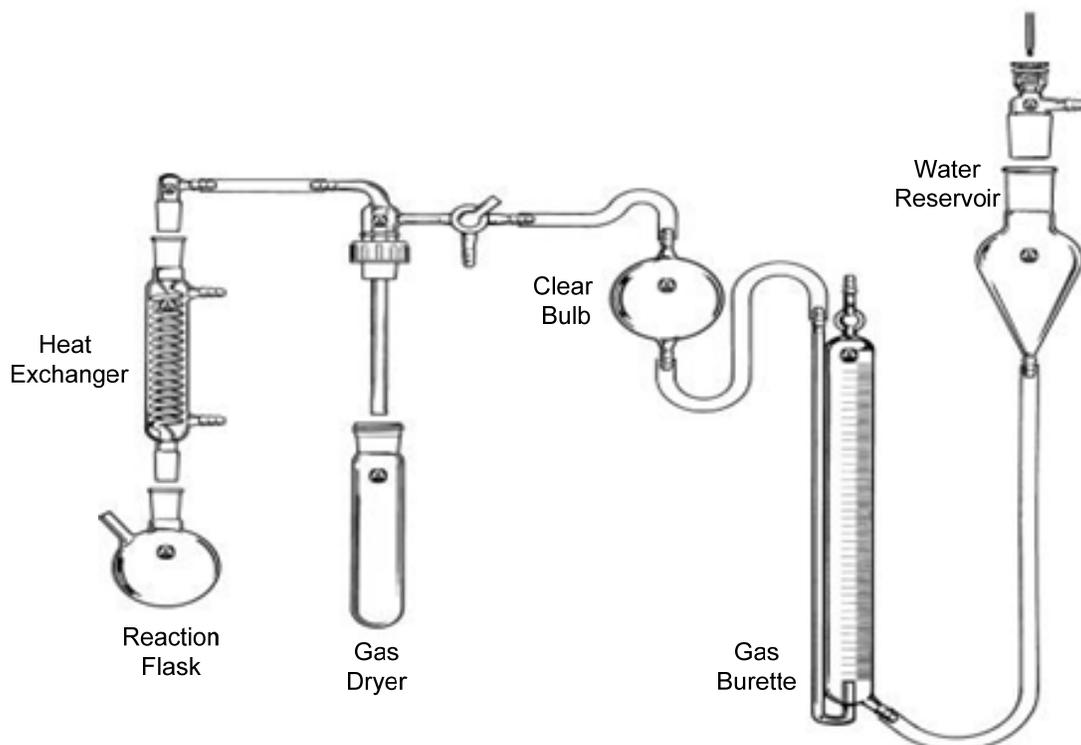


Figure 2: Experimental equipment schematic for determining hydrogen generation rates.

Table 3: Yield of hydrogen at different temperature conditions.

Experiment	Temperature °C	Mass of NaBH ₄ /g	Theoretical H ₂ volume/ml	Experimental H ₂ volume/ml	Yield %
1	22	0.0763	180.72	164	90.75
2	0	0.0733	173.61	160	92.16
3	-10	0.088	208.43	207	99.31
4	-20	0.0965	228.56	223	97.57
5	-40	0.0837	198.24	160	80.8

This table shows an increase in efficiency of hydrogen generation as temperature decreases until -20°C. The reaction is exothermic, so this trend is expected.

The detailed temperature dependent hydrogen evolution studies using sodium borohydride (SBH) and ethylene glycol without (table 4) and with (table 5) the presence of acetic acid (vinegar) as the protic acid are reported in the following tables. Acetic acid was added to the solvent to create a slightly acidic mixture (pH=5.5)

Table 4: Reaction of SBH with various solvents under non-accelerated conditions.

Solvent	Temperature [°C]	Reaction Time	Reaction Completion [% of maximum hydrogen evolved]
Water	25	24 hours	~50%
Methanol	25	15 minutes	>95%
Ethanol	25	30 minutes	>95%
2-Methyl-2-propanol	25	24 hours	Trace
Ethylene glycol	25	15 minutes	>95%
Propylene glycol	25	15 minutes	>95%

Table 5: Reaction of SBH with ethylene glycol/water mixture using acetic acid accelerant.

Temperature °C	Time minute	Actual Hydrogen Produced ml	Theoretical Hydrogen ml	Yield %
25	3	164	180	91
0	5	183	200	92
-10	6	207	210	99
-20	7	215	220	98
-40	9	160	200	80

These results show that a 50/50 mixture of water and antifreeze, with a small addition of acetic acid, is suitable for generating hydrogen from the SBH at temperatures as low as (-40) °C. As the reaction in equation 7 shows, one mole SBH requires 2 moles of the ethylene glycol / water mixture and releases 4 moles of H₂. The yield of hydrogen is found to be greater than 90% at temperatures as low as (-20) °C and 80% at (-40) °C. The time to reaction completion was approximately 5 - 10 minutes.

Figure 3 presents the kinetic results for the yield of hydrogen from SBH in the ethylene glycol/water mixture with acetic acid accelerant for different temperatures. The graph provides the volume of hydrogen collected in the equipment (see figure 2). It must be noted that only the reactor itself was kept at the reaction temperature conditions, and the remainder of the equipment was at room conditions. The results are corrected to standard conditions for presentation in this figure.

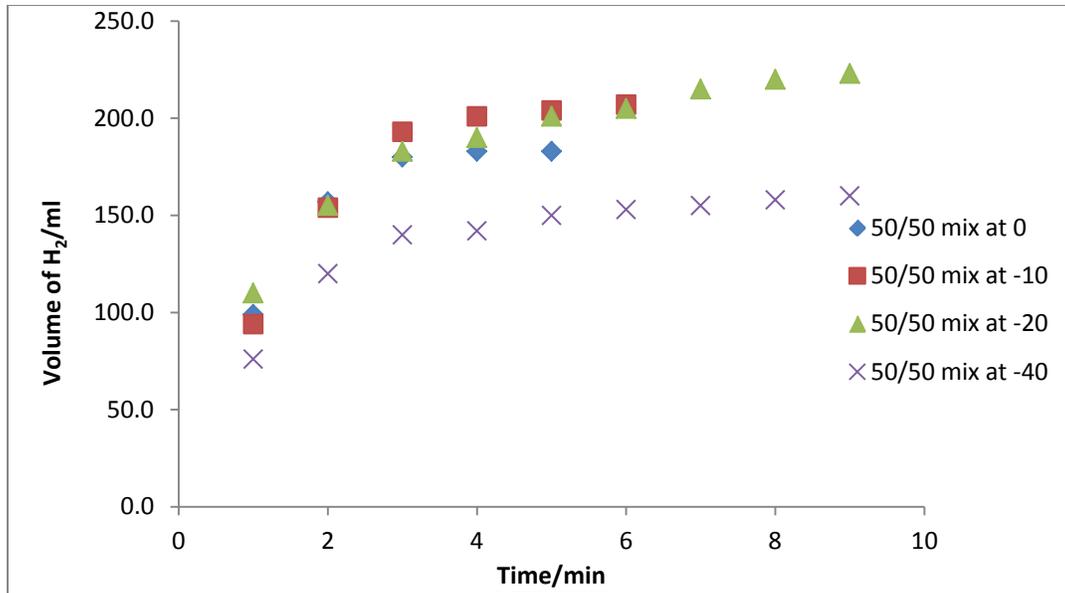


Figure 3: Rate of hydrogen production from SBH and mixture of ethylene-glycol and water at different temperatures.

Fuel Cell Operation

During the second phase of the project, a 20Watt fuel cell was used to generate electricity using the hydrogen generated as discussed above. Voltage and current were measured from the fuel cell using a multi-meter and stopwatch. The power was calculated using the following equation:

Eqn 9:
$$P = VI$$

Where:

V is for voltage potential (Volt), and
 I is the current (Amp).

The efficiency of the fuel cell was calculated using the following equation:

Eqn 10:
$$\eta = \frac{IVt}{H_{H_2} V_{H_2}}$$

Where:

t is time (sec),
 η denotes the energy efficiency,
 H_{H_2} is the heating value of hydrogen, which is a constant $10.8 \text{ (J cm}^{-3}\text{)}$, and
 V_{H_2} is the volume of hydrogen (cm^3) supplied to the fuel cell.

The efficiency of the fuel cell was measured as a function of temperature and loads (the resistance). The data are shown in table 6. These results show that both efficiency and maximum

power output of the fuel cell are higher at higher temperatures. This observation is in agreement to other reports on fuel cells. It suggests that the best operation will occur if the fuel cell is kept warm (above freezing as the minimum operating temperature). The data presented in Table 6 used approximately 2 mmols (0.08 g) of NaBH_4 , which was able to run the fuel cell for approximately 2.5 minutes

Table 6: Efficiency of fuel cell at different temperatures and resistance.

Trial	Reactor Temperature [°C]	Temperature of the fuel cell [°C]	Resistance [Ω]	Max Voltage [V]	Max Current [A]	Max power [W]	η [%]
1	21	18	6	9.26	1.543	14.291	76
2	21	18	20	10.23	0.5115	5.233	29
3	21	17	13	9.26	0.723	6.797	78
4	21	19	120	9.3	0.0775	0.7208	4.6
5	21	18	10000	9.25	0.00092	0.0086	-
6	0.1	18	6	9.96	1.66	16.534	94
7	0.1	18	13	9.77	0.7515	7.343	42
8	0.1	17	20	9.32	0.466	4.341	25
9	-9	-5	6	8.01	1.335	10.693	50
10	-17	-15	13	7.23	0.5562	4.021	-
11	-10	-6	20	9.63	0.4815	4.64	18

Figures 4, 5, and 6 show how the fuel cell operated once an experiment was begun. These plots show the effects of load (resistance) and temperature. Each of the results shows a quick increase to a steady value. This suggests that there is short start-up time. This is probably due to the reactor being initially filled with air which is displaced by the hydrogen from the reaction. The 40 ml volume suggested by these figures is approximately 2 times the gas space in the reactor. This observation is noted and any operating procedures must include a warning to operators that they must account for this start-up each time the hydrogen generation reaction is started.

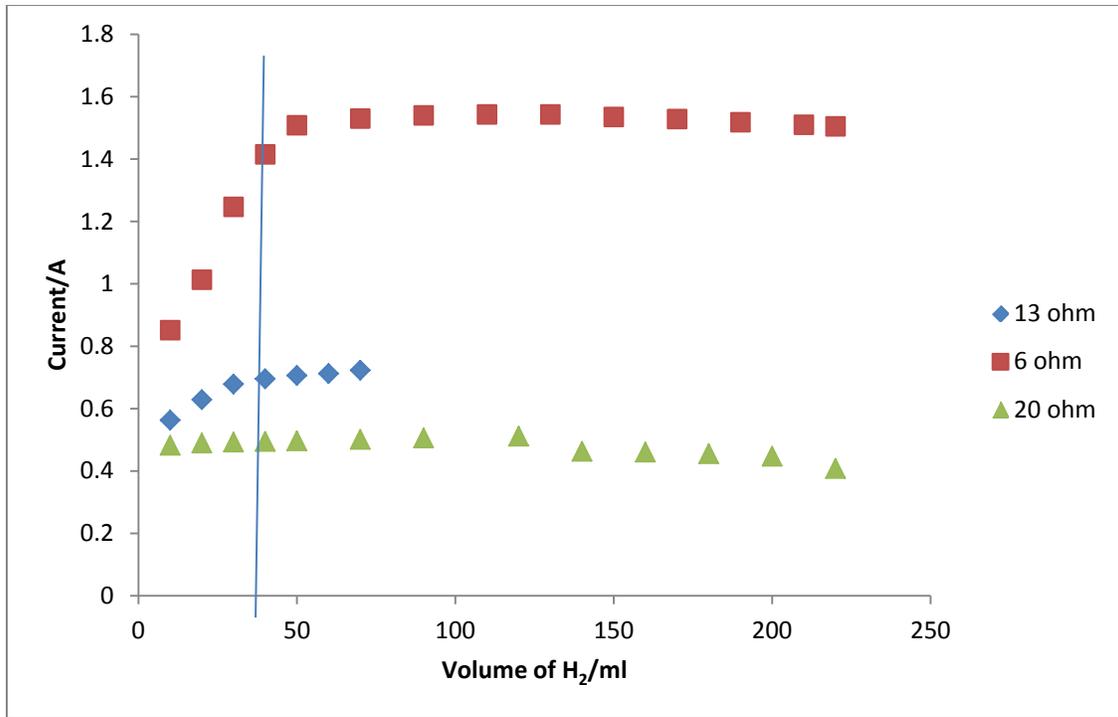


Figure 4: Fuel cell operation at room temperature.

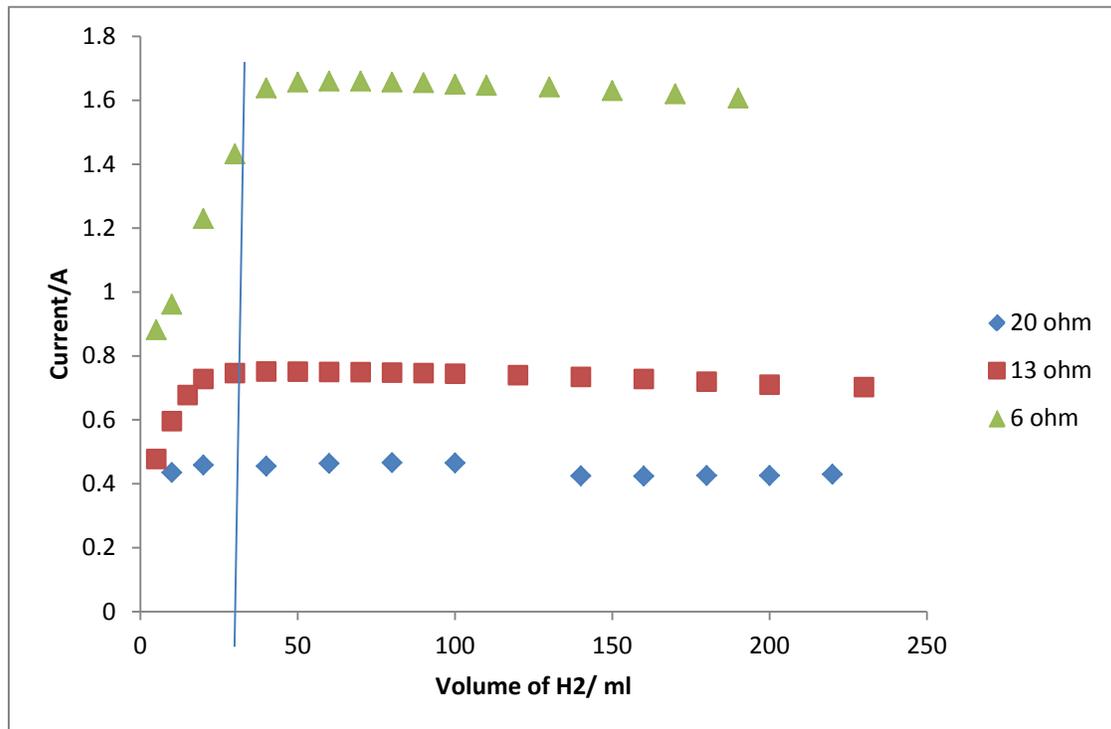


Figure 5: Fuel cell operation at 0.1 °C.

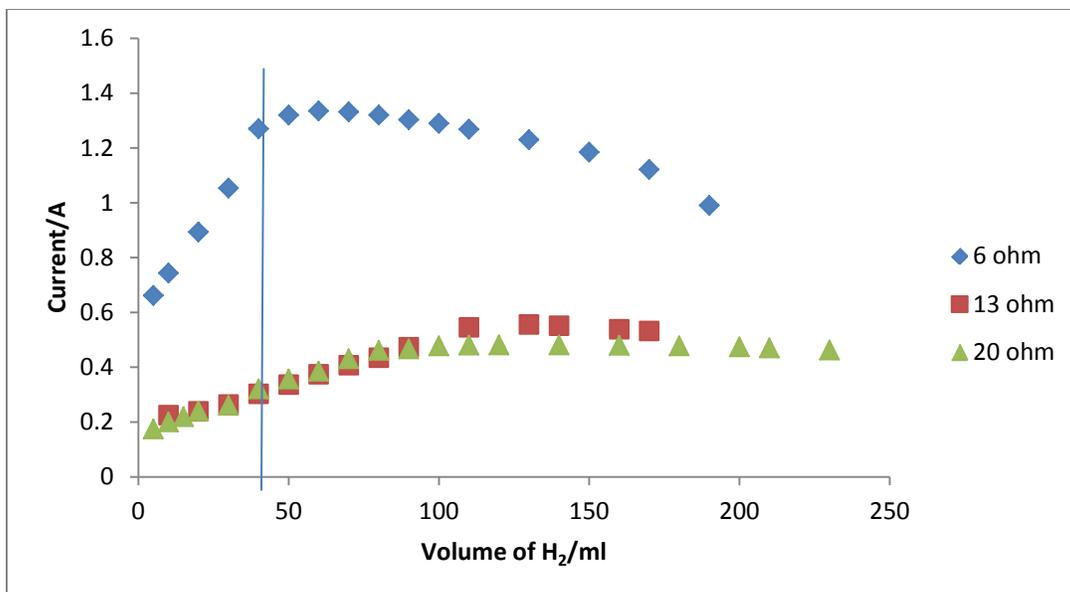


Figure 6: Fuel cell operation at (-9 <math><T</math><math><-20</math>)$^{\circ}$C.

To observe the performance of the fuel cell over an extended period of time, approximately 0.75 g of NaBH₄ was reacted at room conditions to supply H₂ to the fuel cell. The results are provided below in Table 7.

Table 7: Results of 0.75 grams of NaBH₄.

Time [min]	Voltage [Volt]	Reactor Temperature °C [°C]	Injection volume mL	Current [Amp]	Power [Watt]
1	8.9	18.6	2	0.68	6.09
2	9.0	18.7	3	0.69	6.16
3	9.0	18.9	4	0.69	6.16
4	9.0	19.3	5	0.69	6.22
5	9.0	19.6	6	0.70	6.29
6	9.1	20.0	6	0.70	6.33
7	9.1	20.3	6	0.70	6.37
8	7.3	20.6	6	0.56	4.10
9	9.2	20.7	8	0.71	6.47
10	9.2	20.7	8	0.71	6.48
11	9.2	20.7	8	0.71	6.50
12	9.2	20.6	10	0.71	6.54
13	9.2	20.6	10	0.71	6.57
14	9.1	20.6	10	0.70	6.40
15	9.3	20.7	11	0.71	6.64
16	7.3	20.8	11	0.56	4.11
17	9.0	20.8	12	0.70	6.29
18	9.3	20.8	14	0.71	6.61
19	7.1	20.8	15	0.54	3.86
20	4.4	20.8	15	0.34	1.47
21	3.0	20.8	15	0.23	0.71
22	3.0	20.8	17	0.23	0.70
23	3.0	20.7	17	0.23	0.67
24	2.7	20.7	18	0.21	0.55
25	1.2	20.6	20	0.09	0.11

This experiment was run with a 13 ohm resistor at room temperature. The temperature of the gas space of the reactor was recorded at each time interval. The glycol/water mixture was added slowly by injecting some solution every minute. The fourth column reports the cumulative amount of the liquid mixture added. The final two columns report the measured current in the resistive load, and the calculated power from the fuel cell.

The maximum power attained during this experiment was 6.638 watts, and the temperature inside the reactor increased 2.2 degrees after 16 minutes. At 19 minutes into reaction, the reaction rate decreased, and further injection of the solvent did not prolong or increase the rate of reaction. Figures 7 and 8 graphically present the fuel cell performance. Figure 7 shows the power output during the experiment, showing a small increase during the first 18 minutes, then a quick

decrease as the hydrogen supply was exhausted. Figure 8 shows the temperature profile of the reaction, again demonstrating the exothermic nature of the reaction.

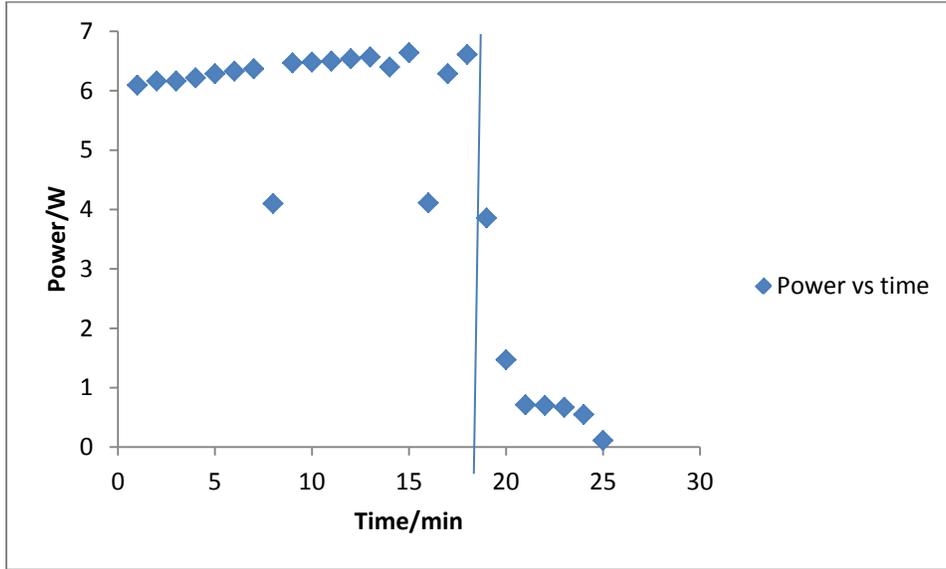


Figure 7: Power generation during experiment described in table 7.

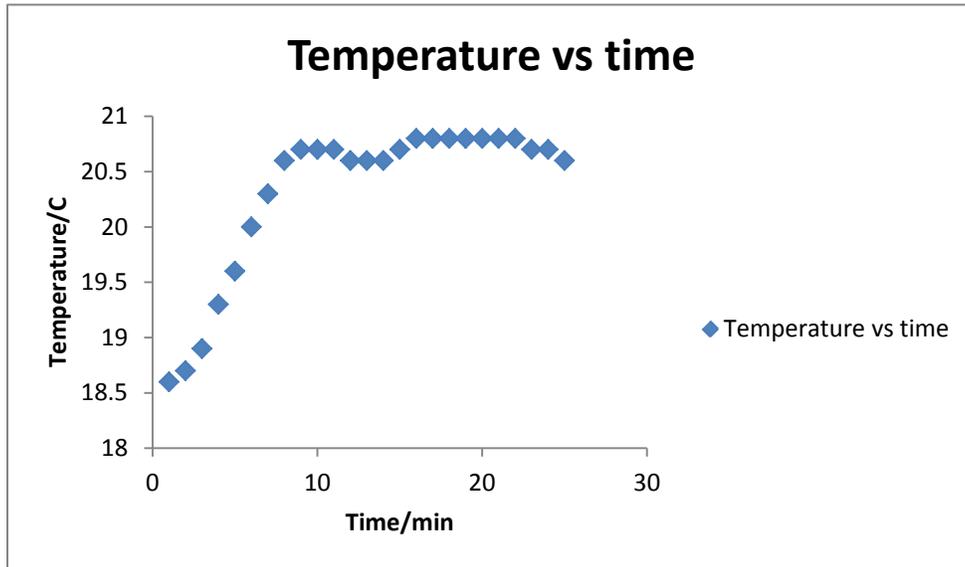


Figure 8: Temperature evolution during experiment described in table 7.

The fuel cell was able to use almost 47% of the hydrogen produced to generate electricity. The typical limit is 50%, with the remaining energy producing heat. Other sources of waste include fuel cell bypass, other losses within the system, or waste during startup and shutdown.

Chapter 5. Prototype Design

This chapter will describe the preliminary design considerations for the prototype off-grid power supply system. Figure 9 shows a simplified system schematic highlighting the major components of the prototype system. This section will describe each subsystem, as listed in table 8.

Table 8: List of prototype subsystems.

Reactor
 Liquid Storage
 Liquid Dispenser
 Air Inlet Heat Exchanger
 Fuel Cell
 Power Production
 Water
 Heat
 Battery
 Control System
 Safety Equipment

The basic design assumptions are listed in the table 9. Several discussions with intelligent transportation system (ITS) users helped us decide on the various design parameter values. One of the first ideas from users was to supply power for emergency lighting. This task is currently powered by batteries or diesel generators (which can supply 10,000 Watts of power). This is an ideal long range goal, but is not realistic for our proto-type system. Another use would provide constant low-level power to measurement, recording, and transmission systems. This type of system requires approximately 10 – 100 watts of power and is currently supplied by battery systems. While the larger power supply would be very useful, it was decided that a smaller prototype system would be built for testing and development, and for creating the process control logic. It would also allow unforeseen problems to be addressed in a more safe and inexpensive system.

Table 9: Design assumptions.

Power requirements:	20 W maximum
Voltage requirements:	12 V.
Operation time:	1 week constant power (24/7).
Load variability:	Minimal variation (+/- 20% during week), and always on.

The total power generation required between weekly resupply is 3,360 W-hr/week (20 Watts * 24 hours * 7 days/week). The amount of SBH needed to provide this is:

$$Xg_{SBH} = 3.36 \text{ kW-hr} \times \frac{859.8 \text{ kcal}}{\text{kW-hr}} \times \frac{1 \text{ mol } H_2}{57.7 \text{ kcal}} \times \frac{1 \text{ eff}}{0.45} \times \frac{\text{mol } NaBH_4}{(0.9)4 \text{ mol } H_2} \times \frac{37.9 \text{ g } NaBH_4}{\text{mol } NaBH_4} = 1,171 \text{ g}$$

Where:

$\frac{57.7\text{kcal}}{1\text{molH}_2}$ is the energy produced in the fuel cell per mol of hydrogen consumed,

0.45 efficiency is the rate at which the energy produced can be converted into electricity,

0.9 efficiency is the conversion rate obtained in the reactor for producing hydrogen, and

1 molH₂/mol NaBH₄ is the stoichiometric limit of the reaction (equation 7).

The efficiencies listed above are the lower values obtained in our experiments. The energy production efficiency may be closer to 50%, and the reaction efficiency may approach 98.5%. However, operation in the field is likely to be worse than in the lab, so the lower values were chosen for design purposes.

The amount of water/glycol solution required is:

$$Xl_{\text{solution}} = 3.36 \text{ kW-hr} \times \frac{859.8\text{kcal}}{\text{kW-hr}} \times \frac{1\text{mol}_{\text{H}_2}}{57.7\text{kcal}} \times \frac{1 \text{ eff}}{0.45} \times \frac{4\text{mol}_{\text{solution}}}{(0.9)4\text{mol}_{\text{H}_2}} \times \frac{40\text{g}}{\text{mol}_{\text{solution}}} \times \frac{\text{liter}}{1200\text{g}} = 4.12\text{liter}_{\text{solution}}$$

Where:

4 mol H₂ are produced for 4 mol of solution (H₂O and Glycol),

The average molecular weight of the solution is 40 g/mol, and

The density of the solution is 1200 g/liter.

The results in the US system of units are roughly 2.5 lbs of SBH and one gallon of solution (50% water and 50% ethylene glycol) for one week of power.

Each sub-system was designed with the whole in mind. The following section provides discussion for each unit.

Reactor

The reactor is sized to minimize volume, but also to allow for the solid-liquid reactants to form the solid and gas phase products. Since one of the products is a gas (H₂) the system must be designed to accommodate changes in pressure. These changes will be periodic, with the greatest pressure just after addition of the liquid reactants, and pressure will be lowest just before their addition. The chosen equipment is capable of adding 0.5 ml of solution each time the supply valve is opened. This valve could be open longer, but that would create larger spikes in pressure. Further, we will assume the entire amount added reacts within one minute or less.

$$X\text{ml}_{\text{H}_2} = 0.5\text{ml}_{\text{solution}} \times \frac{1200\text{g}}{1000\text{ml}_{\text{solution}}} \times \frac{1\text{mol}_{\text{solution}}}{40\text{g}} \times \frac{(0.9)4\text{mol}_{\text{H}_2}}{4\text{mol}_{\text{solution}}} \times \frac{22,400\text{ml}_{\text{STP}}}{1\text{mol}_{\text{H}_2}} = 302\text{ml}_{\text{H}_2}$$

Where:

STP is standard conditions (P = 1 atm, T = 273 K)

The allowable pressure change in the reactor will be less than 2% (2 kPa, or 0.3 psi). The added gas (302 mlH₂) is the equivalent of (302/22400) = 0.0135 mol of H₂. Assuming ideal gas conditions allows us to calculate the volume of gas space required in the reactor:

Let P = .02 atm
T = 273 K
n = 0.0135 mol
R = 0.0821 atm/ mol K

$$V = \frac{nRT}{P} = \frac{(0.0135 \text{ mol}) \left(0.082 \frac{\text{l} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (273 \text{ K})}{0.02 \text{ atm}} = 15.1 \text{ liter} = 4 \text{ gallons}$$

This is the volume needed for just the additional gas in the reactor such that it does not change the pressure by more than 2%. There must also be volume for the reactants and left over solid products. We are adding one gallon of liquid, but most of that will be consumed in the reaction. The SBH has a density similar to water (1.04 g/cm³) and the product solid has a density of 1.73 g/cm³. This suggests that the volume of solids will decrease as the reaction progresses; however the reaction will not go to completion, so some residual liquid will remain within the reactor. The required volume for the SBH is about 1,125 cm³ or 1.1 liters. The volume of products and unreacted solution is expected to be about 1,100 cm³ or 1.1 liters. Hence the required reactor volume to hold all the solid reactant and product, the unreacted liquid, and the hydrogen gas (at a no more than 2% pressure increase) is 16.2 liters, or 4.3 gallons. A low cost reactor capable of holding this pressure and volume is available in a 5 gallon size.

Liquid Storage

The liquid solution of water and ethylene glycol requires a storage volume of 4.1 liters (1.1 gallons). This container will also collect the water produced from the fuel cell, so it could be somewhat smaller if the recycled water is accounted for. The amount of liquid water that will drain back to this container is not well known at this time, so no allowance is made for reducing the total needed volume. Preliminary results showed some water produced, but not at a consistent rate. Also experiments were run for less than one hour, so steady state conditions were not observed. Therefore the liquid storage container was sized to be one and a half gallons.

Liquid Dispenser

Liquid solution will be dispensed to the reactor through a gravity feed controlled by an actuated valve. The smallest repeatable time the device could be open (to allow flow) was 0.5 seconds. This allowed 0.2 to 0.5 ml of solution to flow, depending on the liquid head in the storage container. This size aliquot was chosen as the design constraint for the reactor volume sizing.

Air Inlet Heat Exchanger

The fuel cell requires the operating conditions to be above 0°C. Colder temperatures will cause the water, which forms at the cathode, to freeze. Below freezing temperatures will stop the fuel cell reaction and could damage the fuel cell. The hydrogen feed will be generated within the reactor (described above) in an exothermic reaction. The air will be drawn in from outside where it may be as cold as -40°C. This air must be heated to above 0°C before entering the fuel cell. The excess heat in the reactor can be used to preheat the inlet air. The hydrogen will be generated at the reactor temperature and will not require any heating. We do not have any experimental data yet on the required level of heat exchange. The current design uses the heat within the environmental chamber to preheat the air. If this proves insufficient, the air will be ducted through the reactor. The reactor would need to be larger to account for the volume loss to this ducting.

Fuel Cell

The fuel cell chosen for this application is a 100W unit with built in control module. The module controls the flow of hydrogen to the fuel cell, and operates a fan to prevent water buildup on the cathode side, as well as to maintain a constant temperature within the cell. The fuel cell will produce water as part of the reaction to generate electricity. This water must be removed from the fuel cell, or it will flood the cathode. If the cathode is flooded it will prevent oxygen from reaching it, and it will stop the reaction. Conversely, if the proton exchange membrane is too dry, it will reduce the flow of protons across it, also slowing/ stopping the reaction.

The 100 W model was chosen because fuel cells are known to have much lower efficiencies at their rated power output. Typically it is most efficient to operate at 20 – 30 % of the rated value. This also allows for the system to occasionally supply greater bursts of power should the need arise. Finally, the cost difference between a 100W fuel cell and a 50W fuel cell is quite small, possibly because the 100 W cell is produced in larger volumes.

Battery

The fuel cell will be used to maintain the charge (and temperature) of a battery, which will be connected to the power load. The battery is the main power supply and the fuel cell is the secondary (or slave) power supply. This system allows the load to have a constant and steady power supply that is unaffected by the delays in the fuel cell due to load shifting. The battery will be much smaller than the battery packs required for typical off-grid supplies because it has the fuel cell to recharge it and to keep it warm. The warm temperature allows the battery to operate at its most efficient.

Control System

Controls for the system include:

- Temperature measurements of the fuel cell, of the air and hydrogen inlets, and of the interior of the environmental chamber.
- Pressure measurements inside the reactor

- Voltage and current measurement from the fuel cell to battery, and for the actual load.
- Hydrogen concentration within the environmental chamber.

Temperatures of the feeds to the fuel cell must be above freezing. The cell can withstand temperatures as high as 40 °C. The temperature of the inlet air and environmental chamber will be used to estimate the amount of air that can be preheated. The hydrogen temperature sensor will serve to monitor the reactor temperature.

Pressure is used to measure the efficiency of the reaction and to signal when an additional aliquot of liquid solution should be added to the reactor.

Hydrogen concentration is measured to prevent the interior of the environmental chamber from reaching the lower explosive limit for hydrogen. The box will not be air-tight, so a slowdown of the reaction should allow the interior to vent and remain at a safe condition.

Safety Equipment

The system is designed for safety. The possible hazards include:

- High temperatures
- Low temperatures
- Water buildup
- Hydrogen gas buildup within the environmental chamber
- Pressure buildup in the reactor
- Hydrogen buildup during handling (charging and replacement)
- Unintended damage from other factors

Heat is generated from the reaction to generate the hydrogen and from the reaction to generate electricity in the fuel cell. This heat must be removed from the unit. However, the heat will also be used to maintain the interior of the unit above freezing. The heat can be removed as excess air is returned outside, and as heat loss from the box to the surroundings. The box is insulated to minimize its heat loss (and to maintain above freezing temperatures within it).

Low temperatures would result from very cold air in the air inlet. This could cause freezing of the fuel cell, or freezing of the moisture released from the fuel cell. It is expected the heat from the two reactions will be able to keep the entire environmental chamber above the freezing point.

Water buildup will result from the water product of the fuel cell being vented into the environmental chamber and condensing or freezing onto the other components. It is anticipated that the heat from the reactions will prevent freezing and that the air vent to the outside will remove most moisture. However, in the event of water buildup (a maximum of two gallons in the worst case scenario) all equipment within the environmental chamber will be elevated and a drain will be provided in the bottom of the box.

Hydrogen gas buildup within the environmental chamber will be monitored. If the level reaches 25% of the lower explosive value, the reaction will be stopped until the excess hydrogen is

vented from the environmental chamber. The chamber will not be air-tight, so any buildup should be removed within minutes.

Pressure buildup in the reactor would happen if too much solution is added and the fuel cell is not operating. The pressure buildup will be reduced by the operating fuel cell. If the pressure buildup is too high, an internal pressure relieve valve will open and vent the reactor into the environmental chamber. This condition will also halt the addition of the liquid mixture into the reactor, to prevent the formation of additional hydrogen until the excess is used or vented.

There is some concern that there will be some residual SBH and solvent in the reactor at the end of the week. The concern is that these materials may suddenly react when the operator disconnects the reactor during recharging. The concern arises from observations that the residual materials after an experiment release hydrogen during cleanup. The sudden generation of unwanted hydrogen may create an unsafe condition for the operator. A safe operating procedure must be developed for use during handling of the equipment and materials during replacement. One possible suggestion is to have the operator inject a small volume of caustic solution to kill the reaction, rendering any residual materials unable to generate hydrogen. This concern and operating procedure have not been fully developed at this time.

Unintended damage from other factors includes problems from insect or rodents, accidental damage from roadside incidents, and mishandling during recharging. Insects and rodents could move into the environmental chamber because it will be warm. All inlets and outlets must be screened to prevent their entering. Accidental damage may result from a roadside incident such as the system being struck by a moving vehicle. Such accidents are not avoidable, so the system needs to fail in a safe way. Fortunately the reaction only generates small amounts of hydrogen, and hydrogen, once released into the air will quickly dissipate before reaching a dangerous concentration. The reactant and product materials are non-toxic and are in small quantities, so they should pose no environmental problems. Mishandling of the unit would most likely result in the unit not working. This may cause the equipment to freeze and be damaged. The operator must be trained with a standard operating procedure to make sure the system is working after recharging. This may involve installing a small LED light showing the unit is functioning as intended. This aspect of the prototype system has not yet been developed.

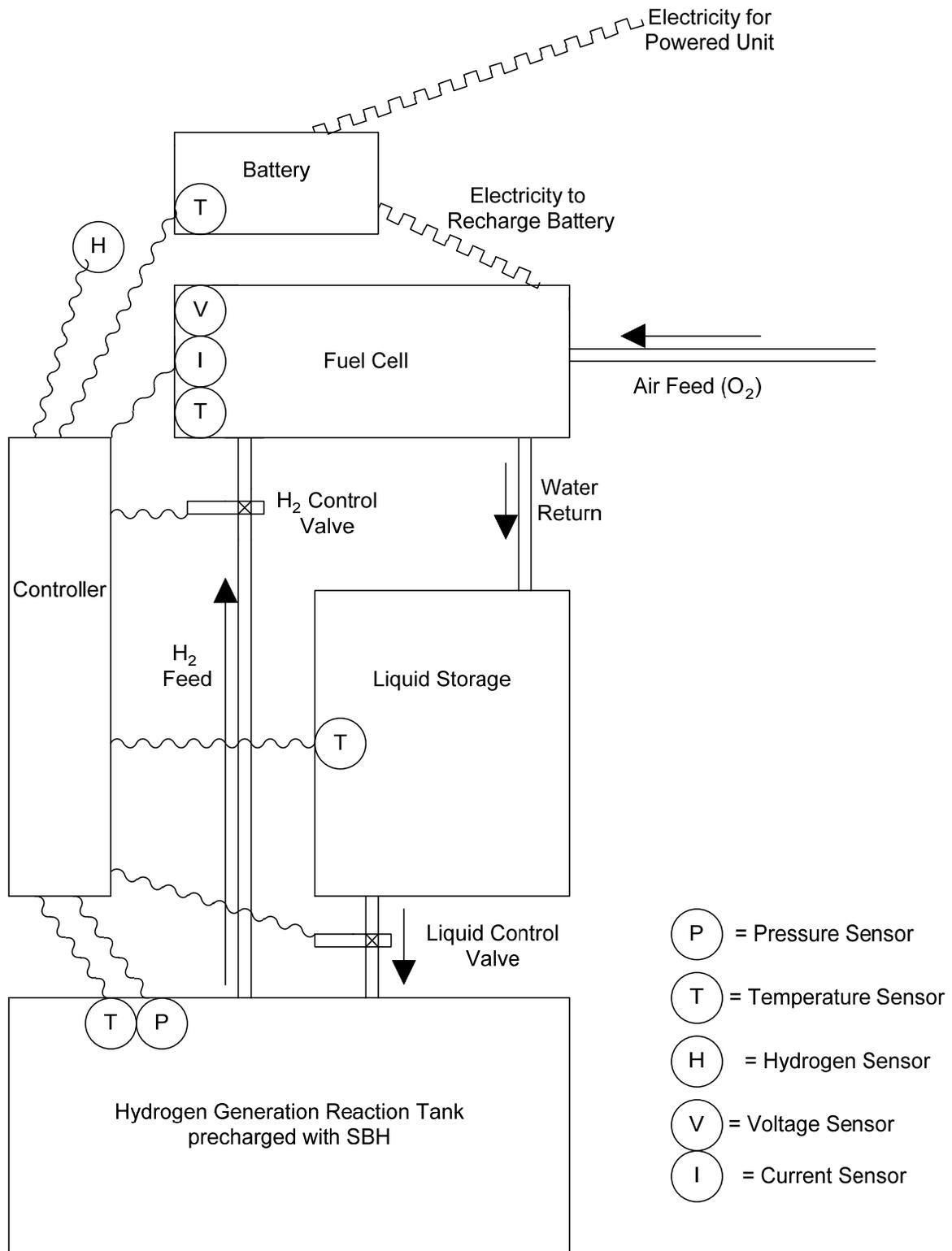


Figure 9: Prototype schematic for the generation of hydrogen for use in a fuel cell.

Chapter 6. Cost

Capital

A prototype system was constructed for collecting hydrogen generation / fuel cell operation data for cold conditions. The cost of this system was approximately \$7,500. The system parts, as shown in figure 9, and cost estimates are listed below:

- 100 W Fuel Cell with hydrogen control module (\$1500),
- Reaction vessel, storage tanks, tubing and wiring (\$500),
- Insulated environmental chamber (\$500),
- Process control (\$5000)
 - Actuated valves (2)
 - Pressure sensor (1)
 - Temperature sensors (4)
 - Hydrogen concentration sensor (1)
 - Pressure relieve valves (1)
 - Logic circuit to collect sensor information and control unit (1).

Operation and Maintenance

Cost of the glycol/water, acid. and SBH would be approximately \$35 / week per device.

Chapter 7. Additional Work

Near this project's conclusion some additional work was performed to explore an additional reaction for the generation of hydrogen. While this reaction is expected to have higher costs, it may also be easier to control over a greater range of temperatures.

This system used sodium borohydride (NaBH_4) also written as SBH, reacting with a mixture of water and tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$). The tartaric acid acts as an accelerant when at high concentrations and as a catalyst at low concentrations. The implication is that the reaction is accelerated when the tartaric acid solution is initially added, but becomes catalyzed at lower concentrations.

The reaction is slower than the ethylene glycol/water reaction with SBH, which can be useful at higher temperatures (above 0°C). This reaction is not recommended for sub-zero conditions, but it is much more stable above 20°C .

Testing for this reaction was performed on small batches of SBH, similar to initial work with the ethylene glycol / water system. In each experiment enough material was added to generate approximately 200 ml of H_2 gas upon completion. The experiments were analyzed to obtain the needed kinetic model equations, which would be used in designing the chemical reactor.

The experiments showed the accelerated reaction to have a rate equation of:

Eqn 11:
$$\text{rate} = 1.38 \times 10^{-3} \frac{\text{g} - \text{mol}}{\text{liter} \cdot \text{sec}} \exp \left[-\frac{735}{T[\text{K}]} \right]$$

The experiments showed the catalyst reaction to have a rate equation of:

Eqn 12:
$$\text{rate} = 1.26 \frac{\text{g} - \text{mol}}{\text{liter} \cdot \text{sec}} \exp \left[-\frac{3,220}{T[\text{K}]} \right]$$

Both of these rate equations are valid for temperature between 0°C and 32°C .

These results provide for greater flexibility in choice of materials for the reaction when higher temperatures are expected.

Chapter 8. Conclusions

The goals of this project were to choose a chemical reaction system for safe storage and generation of hydrogen; develop a prototype fuel cell powered by hydrogen that can be used in cold weather applications; and to estimate the cost of such a system. This power system is to be used to power Intelligent Transportation System (ITS) application for use in Northern Minnesota, especially during wintertime when nighttime temperature conditions can range to -30 to -40 °C. Other desirable traits for the system are that it is; independent of the power-grid, small, portable, does not need frequent recharging, can work in cold weather, is dependable, and does not create a hazard for operators or the environment.

The reaction system selected for this project was sodium borohydride combined with a 50/50 mixture of ethylene glycol/ water with a small amount of acetic acid to accelerate the reaction at the coldest temperatures.

A prototype reactor was designed and constructed, see figure 9. This system will provide a 20 watt, 12 volt load with electricity for one week using 5 pounds of sodium borohydride and one gallon of the liquid mixture. Potential problems not addressed in this report include water / ice buildup within the equipment enclosure, hydrogen release during refueling, and unintended buildup of hydrogen within the equipment enclosure due to unknown leakages.

The cost of the prototype system is approximately \$7,500, where the majority of the cost is due to the process control equipment needed for safe and reliable operation. Costs of materials for operation are approximately \$35 /week or about \$2,000 / year.

References

- Amendola, S. C., Sharp-Goldman, S. I., Saleem-Janjua, M., Spencer, N. C., Kelly, M. T., & Petillo, P. J. (2000). "A safe portable hydrogen gas generator using aqueous borohydride solution and Ru Catalyst." *Int. J. Hydrogen Energy*, pp. 969-975.
- Barbir, F. (2005). *PEM Fuel Cells-Theory and Practice*. New York, NY: Elsevier Academic Press.
- Breault, R. W., Larson, C., & Rolfe, J. (1999). *Hydrogen for a PEM Fuel Cell Using a Chemical Hydride Slurry*. Washington DC: U.S DOE, Hydrogen Program Review.
- Demirci, U. B., & Miele, P. (2009). "Sodium borohydride versus ammonia borane, in hydrogen storage and direct fuel cell applications." *Energy & Environmental Science*, pp. 627-637.
- Engineering.com. (2013). *Battery Packs*. Retrieved January 25, 2013, from Product Showcase: <http://www.engineering.com/ProductShowcase/BatteryPacks.aspx>.
- Gervasio, D., Tasic, S., & Zenhausern, F. (2005). "Room temperature micro-hydrogen-generator." *J. Power Sources*, pp. 15-21.
- Klebanoff, L. (2010). Five-Year Review of Metal Hydride Center of Excellence, Annual Progress Report, IV Hydrogen Storage. Washington, DC: U.S. Department of Energy.
- Larminie, J., & Dicks, A. (2003). *Fuel Cell Systems Explained, 2nd Edition*. New York, NY: John Wiley and Sons.
- Mandal, T. K. (2009). "Hydrogen storage materials: present scenarios and future directions." *Annual Reports on the Progress of Chemistry, Section A: Inorganic Chemistry, 105*, pp. 21-54.
- McClaine, A. W., Breault, R. W., Larsen, C., Konduri, R., Rolfe, J., Becker, F., et al. (2000). *Hydrogen Transmission/Storage with Metal Hydride-Organic Slurry and Advanced Chemical Hydride/Hydrogen for PEMFC Vehicles*. Washington DC: US DOE Hydrogen Program Review.
- Meyers, J. P. (2008). "Getting Back Into Gear: Fuel Cell Development After the Hype." *The Electrochemical Society Interface*, pp. 36-39.
- Puru, J. (2011). "Materials for Hydrogen Storage: Past, Present, and Future." *Journal of Physical Chemistry Letters*, pp. 206-211.
- Soloveichik, G. L. (2002). "Metal Borohydrides as Hydrogen Storage Materials." *Material Matters, 11*.
- Staubitz, A., Robertson, A. P., & Manners, I. (2010). "Ammonia-Borane and Related Compounds as Dihydrogen Sources." *Chemical Reviews*, pp. 4079-4124.

V. Pe´rez-Herranz, M. P.-P. (2010). "Monitoring and control of a hydrogen production and storage system consisting of water electrolysis and metal hydride." *International J Hydrogen Energy*, pp. 912-919.

Wikicommons. (2007). *Fuel Cell*. (Wikipedia) Retrieved November 11, 2012, from http://en.wikipedia.org/wiki/File:Solid_oxide_fuel_cell.svg.

Wikipedia. (2012, November 7). *Ethylene glycol, Coolant and heat transfer agent*. Retrieved November 11, 2012, from Wikipedia: http://en.wikipedia.org/wiki/Ethylene_glycol.

Wikipedia. (2012, November 9). *Fuel cell*. Retrieved November 11, 2012, from http://en.wikipedia.org/wiki/Fuel_cell.

Wikipedia. (2013). *Diesel Engine*. Retrieved January 26, 2013, from http://en.wikipedia.org/wiki/Diesel_engine.

Wikipedia. (2013). *Solar Panel*. Retrieved January 25, 2013, from http://en.wikipedia.org/wiki/Solar_panels.

Wikipedia. (2013, January 18). *Wind Turbine*. Retrieved January 25, 2013, from http://en.wikipedia.org/wiki/Wind_turbine.