Investigation of the Rechargeability of a Liquid Metal-Air Battery

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Abstract

Increasing energy demand has created a new global market for renewable energy. Renewable energy, however, is intermittent and improved electrical energy storage is necessary. This project investigates the feasibility of a rechargeable liquid metal-air battery by testing different liquid metal anodes and electrolytes. The longest discharge time was obtained with a 92% gallium-8% tin alloy anode with 6M KOH and 0.17M gallium oxide electrolyte. It was found that a liquid gallium metal anode with tetrabutylammonium hydroxide electrolyte showed evidence of rechargeability. However, gallium leaking through the electrolyte separator was observed so different separators should be investigated. Adaptation into a flow battery configuration would improve the energy density of the battery.
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# Table of Contents

Abstract ................................................................................................................................. i

Acknowledgements................................................................................................................. ii

Table of Figures ......................................................................................................................... v

Table of Tables vii

Chapter 1: Introduction ........................................................................................................... 1

Chapter 2: Literature Review .................................................................................................... 4

2.1 Energy Usage ..................................................................................................................... 4

2.2 Batteries as Energy Storage ............................................................................................... 7

2.3 Rechargeable Lithium-Ion Battery .................................................................................... 11

2.4 Metal-Air Batteries ............................................................................................................ 13

2.4.1 Rechargeable Zinc Air Batteries .................................................................................. 18

2.5 Liquid Metal Battery ......................................................................................................... 21

2.6 Redox Flow Batteries ....................................................................................................... 23

2.7 Liquid Metal-Air Battery .................................................................................................. 27

2.8 Liquid Metal Anode .......................................................................................................... 28

2.8.1 Gallium .......................................................................................................................... 28

2.8.2 Gallium Tin Alloy ......................................................................................................... 29

2.9 Electrolyte ........................................................................................................................ 29

2.9.1 Potassium Hydroxide Electrolyte ................................................................................ 29

2.9.2 Gallium Oxide and Gallium Nitrate Electrolyte Additives ........................................... 30

2.9.3 Ionic Liquid .................................................................................................................. 31

2.10 Electrochemical Reaction of a Metal-Air Battery ............................................................. 32

2.10.1: Gallium ..................................................................................................................... 32

Chapter 3: Methods .................................................................................................................. 35

3.1 Battery Design ................................................................................................................... 35

3.2 Materials ............................................................................................................................ 35

3.2.1 Structural Assembly ...................................................................................................... 35

3.2.2 Anode .......................................................................................................................... 36

3.2.3 Cathode ........................................................................................................................ 36

3.2.4 Electrolyte ..................................................................................................................... 37

3.2.5 Electrolyte Separator .................................................................................................... 38

3.3 Electrochemical Cell Setup and Testing .......................................................................... 38
Table of Figures

Figure 1: World energy usage from 1990-2040 (U.S. Energy Information Administration, 2016 (a)) .......................................................... 5
Figure 2: Net Load (Megawatts) over the Course of a Day for 2012 and projected through 2020 (California, 2016) .......................................................... 6
Figure 3: Basic battery set up (Hiroyuki, n.d.) .......................................................................................................................... 8
Figure 4: A comparison of different types of batteries. (Dunn, 2011) ................................................................. 10
Figure 5: An internal schematic of a lithium ion battery (Johnson Matthey Battery Systems, 2014) ........................................ 12
Figure 6: The structure of a metal-air battery .......................................................................................................................... 14
Figure 7: Chemical Reaction within a Metal Air Flow Battery (Na9234, 2011) ................................................................. 15
Figure 8: Structure of a Zinc-Air Button Battery (Duracell, 2004) ................................................................. 18
Figure 9: Diagram of a liquid metal battery (Stauffer, 2016) ................................................................................................. 21
Figure 10: Structure of a Redox Flow Battery (Flow, n.d.) ................................................................................................. 24
Figure 11: Reaction of a Zi-Air Battery affected by Adding Manganese Ions into the Electrolyte (Pan, et al., 2016) ................................................................................................. 30
Figure 12: Expanded conceptual view of previous baseline ................................................................................................. 35
Figure 13: Baseline result established for this project using the baseline conditions detailed in Table 2 ........ 43
Figure 14: The x-ray diffraction results for the product of the gallium-air battery ................................................................. 44
Figure 15: Alloy battery with 6M KOH Electrolyte discharge ................................................................................................. 46
Figure 16: Alloy battery with 6M KOH electrolyte no discharge ................................................................................................. 46
Figure 17: Alloy battery with 0.25M gallium oxide and 6M KOH electrolyte ................................................................................................. 47
Figure 18: Concentration profile of liquid metal-air battery using a 92% Gallium-8% tin alloy anode at 60°C ................................................................................................. 48
Figure 19: Temperature profile of liquid metal-air battery using a 92% gallium-8% Tin Alloy Anode and 6M KOH electrolyte mixed with 0.17M Ga2O3 ................................................................................................. 49
Figure 20: Comparison of the gallium and alloy batteries discharged at optimal operating conditions .... 50
Figure 21: Polarization curves for the gallium and alloy batteries and optimum conditions ................................................................. 50
Figure 22: Gallium battery with a gallium nitrate electrolyte ................................................................................................. 52
Figure 23: Gallium with gallium oxide electrolyte .......................................................................................................................... 53
Figure 24: Alloy battery with gallium oxide electrolyte ................................................................................................. 53
Figure 25: Gallium Battery with gallium oxide and KOH electrolyte ................................................................................................. 54
Figure 26: Gallium battery with tetrabutylammonium chloride electrolyte ................................................................................................. 55
Figure 27: Voltage over time of a gallium anode with two zirconia cloths soaked in tetrabutylammonium hydroxide discharged at 0.5mA ................................................................................................. 56
Figure 28: Zirconia separators and catalyst following discharge with an ionic liquid electrolyte ........... 57
Figure 29: Discharge at 0.5mA of a tetrabutylammonium hydroxide and gallium oxide electrolyte with a pure gallium anode ................................................................................................. 58
Figure 30: Visual Representation of the Discharge Time of Different Separators tested with the tetrabutylammonium hydroxide electrolyte and pure gallium anode with 0.5mA discharge ................................................................. 59
Figure 31: Charging the gallium battery at 55C with 6M KOH electrolyte ................................................................................................. 61
Figure 32: Result of charging a gallium nitrate and KOH ................................................................................................. 62
Figure 33: Charging the alloy battery with 6M KOH and 0.17M Gallium Oxide ................................................................................................. 63
Figure 34: Charging the gallium battery with an ionic liquid electrolyte ................................................................................................. 65
Figure 35: A sample flow battery configuration for the liquid gallium-air battery ................................................................................................. 67
Figure 36: Heating the gallium (left); Soaking the 1.1 cm diameter zirconia cloth separators in 6M KOH (right) ................................................................. 75
Figure 37: The anode components (left) and final assembly (right) ......................................................... 76
Figure 38: Anode assemble (left) added to the anode/cathode connector (right) ........................................... 76
Figure 39: Cathode assembly .................................................................................................................. 77
Figure 40: Gallium weighing process; ~1.2g of gallium ........................................................................ 77
Figure 41: Crucible assembly (left); Teflon gasket with an outer diameter of 1.4cm and an inner diameter of 0.9cm (right) .................................................................................. 78
Figure 42: 2 zirconia cloth layers with diameters of 1.1cm ..................................................................... 78
Figure 43: Platinum catalyzed gas diffusion layer with a diameter of 1.1cm .............................................. 79
Figure 44: The completed cell (left); Inverted battery with the anode (top) and cathode (bottom) wires attached (left) ................................................................................................. 79
Figure 45: Start page of the BA500WIN program with a real time plot, temperature, voltage, time, and current measurements ................................................................. 80
Figure 46: Programs drop down menu opened. Tests can be made with the program editor. Once saved, these programs can be run by first loading them, then clicking run program ...................................... 80
Figure 47: The program editor window .................................................................................................. 81
Figure 48: Under the function tab, select the appropriate step for the battery program ........................... 81
Figure 49: The third tab consists of the parameters for that step ............................................................. 82
Figure 50: By selecting Options under the Analyzer tab, the data recording settings can be changed ..... 83
Figure 51: The program can automatically pause after charge or discharge if desired .......................... 83
Table of Tables

Table 1: Common Metal-Air Battery Characteristics (Zhang, X, 2016) ....................................16
Table 2: Open circuit voltage for gallium hydroxide product ..................................................33
Table 3: Open circuit voltage for gallium oxide product ..........................................................34
Table 4: Baseline Conditions Established in the 2016 Project .................................................42
Table 5: Restrictions for Recharging ......................................................................................45
Table 6: Separator Tests ........................................................................................................60
Chapter 1: Introduction

Energy consumption in the past 25 years has increased from approximately 350 billion quads to over 550 billion quads (U.S. Energy Information Administration, 2016 (a)). This energy is mainly produced from fossil fuels, which produce carbon emissions when burned (U.S. Energy Information Agency, 2016 (b)). Hazardous to the environment, integration and research of renewable energy sources, which don’t produce carbon emissions, is a growing field. Renewable energy sources include solar, wind, and geothermal energy which currently provide only 7% of the energy consumed by the United States (U.S. Energy Information Agency, 2016 (b)). One of the most prevalent issues associated with the use of renewable energy is intermittence. While the sun and wind can produce a lot of energy, the sun is not always shining and wind is not constantly blowing past turbines. Electrical energy storage is very limited, so during periods of renewable energy intermittency, especially at night, fossil fuels are needed to provide power.

To rely on renewable energy as a main source of power, electrical energy storage is necessary to combat its intermittence. Currently, the one of the main sources of energy storage is pumped hydroelectric, where water is pumped to higher elevations using excess energy and passed downhill through turbines when energy is in demand (Parkinson, 2013). However, pumped hydroelectric is geographically specific and cannot be placed wherever energy storage is needed. Another, more portable, option for energy storage is a battery. While batteries are not developed enough to store and provide mass amounts of energy, there are four high-density battery configurations currently being widely used to store small amounts of energy.

Metal-air batteries have the highest theoretical energy density of all batteries, because of the abundance of $O_2$ in the air. This battery has a metal anode, which reacts with an unlimited
supply of O₂ from the air (Cao et al., 2012). These batteries are small and light, an excellent option for powering electric vehicles. One downfall of metal-air batteries is their inability to recharge.

Liquid metal batteries have a metal cathode, metal anode, and an electrolyte all in the liquid phase, separated based on density. Since these batteries are all liquid, the reaction occurs with faster kinetics than if one of the metals were solid. One major problem with a liquid metal battery is that they are very sensitive to movement (Kim, et al., 2009).

Redox flow batteries function by constantly flowing two different electrolytes through the battery and back into holding tanks. They are able to store large amounts of energy because of the large size of the storage tanks (Weber et al., 2011). Unfortunately, their technology has so far not advanced to a point of having been implemented into the power grid.

Lithium Ion Batteries are a common household energy storage source. They are widely used in cell phones, laptops, remote controls, and other hand held, rechargeable devices. These batteries use a lithium compound, such as LiMnO₂ or LiCoO₂, as the cathode and carbon graphite as the anode. They are rechargeable, withstanding hundreds of charge-discharge cycles before failure (Brian, 2015). However, due to degradation of internal components, these batteries do fail after just a few years, regardless of use, and are highly sensitive to temperature.

A liquid metal-air battery is a combination of a liquid metal and a metal-air battery. This battery, theoretically, has all of the positives and none of the negatives of a liquid metal and a metal-air battery. Liquid metal-air batteries can easily be scaled up to a flow battery configuration, and gain all the positives of a flow battery configuration. Currently, not much research has been performed to understand and develop a liquid metal-air battery.

Previously, two Major Qualifying Projects (MQPs) at Worcester Polytechnic Institute analyzed how to improve the efficiency, discharge time, rechargeability of a liquid gallium-air
battery. Gallium is a non-toxic metal that melts when heated just above room temperature. It has electrical conductivity, making it a great option for use as a metal anode, despite how little literature research there is about gallium electrochemical reaction.

In this project, we will look to improve the efficiency, discharge time, and rechargeability of the liquid gallium-air battery. Two major areas of research will be performed. First, an investigation of different electrolytes will be performed. Both water-based hydroxides and ionic liquids will be tested. Previous research on this project has led us to believe that the water in the alkali electrolyte in the battery is significantly limiting the rechargeability of the battery. Second, the feasibility of changing the battery will be examined with different electrolytes and liquid metal anodes. By removing water from the electrolyte and hence its electrolysis, recharging may be possible. Additionally, by changing from pure gallium metal to a gallium-tin alloy, the electrochemical reactions vary, providing stability for the battery and a lower melting point.

The following report summarizes the work done on this project. Chapter 2 provides a literature review and background information relevant to this project, including the need for improved batteries and an analysis of currently available batteries. Chapter 3 describes the methodology involved in charging and discharging the battery, along with the chosen anodes and electrolytes, and conditions under which the battery was run. Chapter 4 details the results of tests performed, both to replicate previous projects and new findings. Finally, Chapter 5 provides conclusions and recommendations regarding what areas of this research should be continued and the most feasible next steps.
Chapter 2: Literature Review

2.1 Energy Usage

Energy, by definition, is power derived from the utilization of physical or chemical resources, especially to provide light, heat, or to work machines. It has become an integral part of our lives, the results of which can be seen almost everywhere you look. Since the industrial revolution, machines and technology have become a necessity for life, integrating energy into everyday tasks. This becomes critical when studying sources of energy and the increasing energy demand seen around the world.

Population and economic development are key influencers on the amount of energy a country or community consumes. As a country begins to prosper economically, personal technology becomes more common and widely available. This increases the number of people utilizing objects such as computers, cell phones, and televisions. All of these objects have one major characteristic in common: a reliance on an energy supply to function. As more people gain access to these materials, the demand for energy increases. Another factor in energy demand is the population size. With more people, more appliances will be used, more lights will be turned on, and energy consumption will rise. This is particularly important when looking at population trends around the world. According to the United Nations Population Fund, the world population as of 2016 is 7.4 billion and is expected to rise to nine billion by the year 2040 (United, 2015). As a result, energy consumption is expected to increase from 549 quadrillion BTUs in 2012 to 815 quadrillion Btus in 2040 (U.S. Energy Information Administration, 2016 (a)). Figure 1 shows the increase in energy consumption since 1990, projected through the year 2040.
To meet an ever-increasing energy demand, more energy must be produced. As of 2015, the United States produced 33% of its electricity from coal, and an additional 33% from natural gas. These sources are fossil fuels and they produce carbon emissions, such as carbon dioxide, which contribute to climate change (U.S. Energy Information Agency, 2016 (b)). These emissions cause air and water pollution, land degradation, rising sea levels, and a degrading ozone layer that results in severe weather. As a result, at the United Nations Climate Change Conference in Paris in 2015, 60 countries agreed to make changes to their regulations and energy production to reduce carbon emissions globally (Davenport, 2016). For many, including the United States, this means increasing reliance on renewable energy in order to reduce the use of coal, natural gas, and other fossil fuels.

Renewable energy sources include solar, wind, hydroelectric power, and newer options, such as geothermal and ocean wave energy, which are still in the research and development stage. The main issue with these renewable sources is that they are intermittent. From day to day, the
wind varies speeds inconsistently, and the sun is only out for a certain number of hours per day, and even that depends on the weather and cloud coverage. Additionally, the highest energy demand is in the evening when people return home from work, turn on lights, cook dinner, and wash laundry. This usually occurs after the sun has set, eliminating the option of utilizing solar energy.

This problem is highlighted in the figure below. Thus, Figure 2 shows the actual energy demand on the grid in California over the course of one day in 2012, and shows predicted energy demands for 2013 through 2020. During the middle of the day, solar panels, increasing in popularity in California, offset a significant portion of the energy consumed by citizens. However, by 6 pm, approximately when the sunsets solar panels no longer provide energy, requiring energy to be drawn from the grid. So, despite efforts being made to be independent of fossil fuels, renewable energy is too intermittent, and fossil fuels are still needed during the night. In order to combat intermittent renewable energy, more advanced energy storage options which can reserve excess renewable energy produced during the day need to be developed.

![Figure 2: Net Load (Megawatts) over the Course of a Day for 2012 and projected through 2020 (California, 2016).](image-url)
One common type of grid scale energy storage is pumped hydroelectric. This is when excess energy is used to pump water to higher potential energy, as in moving it uphill or into tall storage tanks. When energy is needed later, the water can flow down, through a turbine to generate this energy (Parkinson, 2013). However, since pumped hydroelectric energy storage either adapts existing ponds, or fabricates new ones, it has a negative effect on the environment, and can be detrimental to the surrounding ecosystems.

Another option for energy storage is a battery, which is able to store and dispense energy while being small and portable. Batteries, however, do not currently have the ability to maintain charge-recharge cycles on a scale large enough to sustain the energy grid. This fuels the need for further research into battery energy storage.

2.2 Batteries as Energy Storage

While there are a variety of different types of batteries, all batteries have the same general setup. All batteries have an anode, a cathode, and an electrolyte layer in between the anode and cathode (MIT, 2012). Typically, the anode and cathode are metals, however air can also be used as a cathode depending on the battery configuration. The electrolyte layer has two main functions. First, it creates separation between the anode and cathode, without which the battery would short-circuit. Second, the electrolyte keeps the battery at a neutral charge by facilitating the movement of ions (Li, Y. et al., 2014; MIT, 2012). The electrolyte should have high ionic conductivity and a low viscosity, so that ions can readily move throughout the electrolyte. In many cases, an electrochemically inactive, yet porous, electrolyte separator soaked in a liquid electrolyte is used. The separator keeps the liquid electrolyte in place and creates further separation between the anode and the cathode (Li, Y. et al., 2014).
A battery's energy comes from chemical reactions, which occur within the battery cell (MIT, 2012). These chemical reactions produce electrons, which can be directed through a wire to create a current (MIT, 2012). When a battery is discharging, the metal anode is oxidized and can release electrons and metal ions. Both the ions and the electrons react with the cathodic material, however their means to reach the cathodic material are different. The ions travel into, and across, the electrolyte, while the electrons can be captured and run through an exterior wire before interacting with the cathodic material. The ions and electrons react with the cathodic material, reducing the cathode (Cao et al., 2012). When the battery is charging, the reverse reaction occurs: metal ions move across the electrolyte from the cathode to the anode, where the anodic material is reduced while the cathodic material is oxidized (Cao et al., 2012). This process is illustrated in Figure 3. In some configurations, however, the anion formed at the cathode is the diffusing ion.

Batteries are broken up into two groups: primary and secondary. Primary batteries are not rechargeable, while secondary batteries can be used for multiple charge-discharge cycles. Primary batteries would not be sufficient for large scale energy grid storage, since they can only be discharged once. Secondary batteries, however, could handle fluctuation of energy supply and demand that the energy grid has. For this reason, secondary batteries are a growing research field as scientists look to develop higher capacity, longer lasting, and cheaper secondary batteries.
To further analyze batteries, a variety of terminology is used. The electric potential of a battery, or voltage, allows for analysis of how much energy can be supplied from the battery. The voltage of a battery is determined based on the battery’s size and the thermodynamics of the reactions that occurs. When discharging, if enough of the anode is reacted into electrons and ions, the battery loses electric potential, which is reflected in a decrease of the battery voltage. The open circuit voltage (OCV) of a battery is the electric potential of a battery without any current flowing through. This value is usually somewhat higher than the discharging voltage of a battery. Batteries are further defined by different parameters:

1. Storage Capacity: the amount of energy stored in the battery as a result of the chemical reaction that occurs and size of the battery
2. Energy Availability: the amount of energy that can be discharged from the battery, given as a percentage of the storage capacity
3. Energy Density: the storage capacity of the battery normalized by weight
4. Discharge Time: the length of time a battery discharges
5. Lifespan: how long a battery can sit on a shelf without losing potential energy
6. Durability: the number of stable charge-discharge cycles a battery can survive

The specific energy of a battery is the amount of energy in a battery, based on the reaction the occurs within the battery. The specific power of the battery of the rate at which energy is dispelled from the battery, in the form of a current. To be able to function on a grid system, a battery should ideally have a high amount of energy, to be able to store large amounts of energy, and a high rate of discharge, to be able to meet energy demands. Currently, lithium ion batteries have the highest specific power and specific energy, while Vanadium flow batteries have the
lowest. The specific power and specific energy of various types of batteries, based on the weight of the battery, are shown in Figure 4.

![Figure 4: A comparison of different types of batteries. (Dunn, 2011)](image)

Often, all battery configurations face the same problems. One problem that limits the lifespan of a battery is dendrite formation, which can occur on the interface between the electrolyte and the metal anode (Cao et al., 2012; Li, P. et al., 2014). Dendrite formation is the formation of branched, solidified metals which form from a reaction of the metal anode and the electrolyte (Steiger, 2015). This corrodes the surface of the metal anode, and causes the battery to short circuit, significantly decreasing the lifespan and voltage of the battery (Cheng, et al., 2011). A variation of dendrite formation, called dendrite fingering, can occur when branched metal penetrates the electrolyte. One way to overcome dendrite formation is to form the metal anode into a porous, nano-scale scaffold, which will prevent dendrites from forming (Hamilton, 2009). A simpler way to overcome dendrite formation is by creating a flow battery, where the electrolyte and metal are constantly circulated so the reaction does not have time to occur. This battery configuration will be discussed more in detail in Section 2.6.
Water electrolysis is another problem for batteries, specifically for those with aqueous electrolytes. Under typical charging potentials needed to charge the battery, water can break down into hydrogen gas and oxygen gas, which is known as water electrolysis (U.S. Department, n.d.). If water is present in an electrolyte, and the battery is charged and reaches a voltage at, or above, 1.2V, water hydrolysis could occur. If hydrogen gas is produced in a battery, it can react with, and corrode, metal, which can cause the battery to die. If the produced gas is not allowed to escape from the battery, this could cause an explosion.

There are many different battery configurations, which all have their own benefits and limitations. Since so many configurations exist, the storage and lifespan of a battery can be chosen and modified for different situations. In the next few sections, some of the more promising rechargeable battery configurations will be discussed. This includes a rechargeable lithium-ion battery (Section 2.3), a metal-air battery (Section 2.4), a liquid metal battery (Section 2.5), a redox flow battery (Section 2.6) and a liquid metal-air battery (Section 2.7).

2.3 Rechargeable Lithium-Ion Battery

Rechargeable lithium-ion (Li-Ion) batteries, first developed in the 1970s, are common in everyday devices, such as laptops, cell phones, and I-Pods. Lithium-ion batteries are lightweight and easy to transport, while having a higher energy density that most batteries, as Figure 4 (Section 2.2) illustrates. Additionally, these batteries are rechargeable and capable of hundreds of charging cycles before loss of stability, and failure.

Typically, the cathode is a lithium compound, such as LiMnO₂ or LiCoO₂, the electrolyte is a lithium salt in an organic solvent, such as LiBF₄ in ethylene carbonate, and the anode is carbon graphite. During charging, the cathode is oxidized and Li⁺ ions pass through the electrolyte to the anode. During discharging, Li⁺ ions move back through the electrolyte to the cathode, while
electrons pass from the anode to cathode through an outside circuit. The standard electrochemical potential of a Li-Ion battery is around 3V, based on which materials are being used. The charge and discharge process for a Li-Ion battery is shown in Figure 5.

Figure 5: An internal schematic of a lithium ion battery (Johnson Matthey Battery Systems, 2014).

One major benefit of these batteries is that they have no memory effect. This means that the battery does not need to be fully discharged before being recharged. This makes Li-Ion batteries a great fit for both portable electronic devices and the grid system. In regard to portable electronic devices, most people do not wait for their cell phone or laptop battery to fully die before plugging the electronic device in to charge. On a grid system, solar and wind energy, and the energy demand, is never constant. Being able to rapidly and readily adjust to the change energy supply and demand without having to wait for a fully discharge of the battery, is necessary. This reduces the amount of energy lost due to storage restraints, and increases energy storage (Brian, 2015).

There are some drawbacks to Li-Ion batteries which make them unfit for use on the energy grid. First, after a few years, a Li-Ion battery will begin to degrade and the components of the battery will begin to break down. This slowly decreases the storage capacity of the battery, until it is unusable. For optimal grid storage, a battery needs a long shelf life. Additionally, Li-Ion batteries are very sensitive to high temperatures, which limit the environments in which the battery
can be effectively used. Another major drawback to Li-Ion batteries is that these batteries have been designed to operate with computer controls. A complex electronic system would be needed for efficient operation of Li-Ion batteries on a grid scale, which would be both expensive to manufacture and operate (Physics Central, 2009). Lastly, high production cost of Li-Ion batteries are cause many people to turn away from Li-Ion batteries, and push the research and development of cheaper, smaller, rechargeable metal-air batteries (Li, Y. et al., 2014).

2.4 Metal-Air Batteries

Metal-air batteries, found in everything from hearing aids to electric vehicles, are environmentally friendly, lightweight, and cost effective. This type of battery has achieved such widespread success because it has the highest theoretical energy density of all batteries, which can be up to 5 times that of a typical alkaline battery, commonly known as a AA battery (Cao et al., 2012). The high theoretical density is a result of using oxygen as the cathode, which has a near unlimited source in the atmosphere (Duracell, 2004). With the theoretically highest energy density, these batteries would be able to power portable electronics and electric vehicles longer, and cheaper, than any other type of battery (Cao et al., 2012). Recent material advances have led to an increase in research to further advance metal-air batteries (Li, et al., 2016).

Structurally, metal air batteries have a solid metal anode, a catalyst to accept $O_2$ from the air, and a liquid alkaline electrolyte in between the metal and the catalyst. Oxygen is the cathodic material, but it does not need to be structurally contained in the battery as it is readily obtained from the atmosphere. This allows metal-air batteries to be constructed smaller and lighter than most batteries. In most cases, a platinum or manganese oxide catalyst is used. In metal-air batteries, the electrolyte needs a high oxygen diffusion coefficient, so that oxygen readily moves into the
electrolyte and the battery’s electrochemical reaction can occur. The basic structure of a metal-air battery can be seen in Figure 6.

![Figure 6: The structure of a metal-air battery.](image)

When the battery is discharging, an oxygen reduction reaction occurs. The metal anode is oxidized and releases electrons and metal ions. The metal ions travel into the electrolyte, while the electrons can be captured and run through a wire to create a constant current. The metal ions then travel across the electrolyte where they meet oxygen at the electrolyte-catalyst interface. A chemical reaction occurs, producing metal oxides from oxygen and the metal ions (Cao et al., 2012). When the battery is charging, the reverse reaction occurs: metal ions move across the electrolyte towards the metal anode and are reduced into pure metal while oxygen is produced and released from the battery cell (Cao et al., 2012). One major benefit of metal-air batteries is that they can quickly switch from charging to discharging. This would allow these batteries to easily adapt to an ever-changing energy demand when storing renewable energy in the power grid (Cao et al., 2012). The charging and discharging processes of a metal-air battery are illustrated in Figure 7.
The catalyst is a major part of a metal-air battery, as it has a direct impact on the battery power, efficiency, and lifespan of the battery (Li Y. et al., 2014). In metal-air batteries, the cathodic reaction that occurs is an oxygen reduction reaction:

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \]

This reaction involves numerous intermediate components and various steps, which makes the reaction very slow (Stephens et al., 2012). Using a catalyst rapidly speeds up the reaction, allowing a metal-air battery to quickly draw in more \( \text{O}_2 \) from the air (Li, P. et al., 2014). Additionally, the reaction occurring is a triple-phase reaction; gaseous \( \text{O}_2 \) is reduced by a solid catalyst and a liquid electrolyte (Toussaint et al., 2010). A catalyst can greatly help facilitate the multi-phase reaction that needs to occur. Platinum catalysts, despite their high cost, are one of the most widely used catalyst in batteries and fuel cells because of their high stability and activity (Li, P. et al., 2014; Stephens et al., 2012). Research is currently being performed to examine if Pt-alloys or Pt-based nanoparticles are a suitable and cheaper replacement for pure Pt catalysts (Stephens et al., 2012). Metal-based catalysts, such as Co-based, non-noble metal oxides, such as \( \text{Co}_3\text{O}_4 \), metal free materials, such as heteroatom-doped carbon nanotubes, and composite materials, such as \( \text{MnO}_2 \)-graphene, have all been found to be cost-effective catalyst alternatives (Li, P. et al., 2016).
The metal anode of a metal-air battery can be composed of many different pure metals and metal alloys. Two of the more promising metals used are lithium and zinc. Li-air batteries have the highest theoretical energy density of all metal-air batteries. However, they are potentially deadly if swallowed (Energizer, 2016). Zn-air batteries are a cheaper and safer alternative than Li-air batteries (Lee, 2010; Cao et al., 2012). Zn-air batteries have a 3-year storage life and little chance of explosion (Duracell, 2004). Because of their low cost, efficiency, and safety, zinc-air batteries are, so far, the only metal-air battery to be commercialized (Li, et al., 2016). Two other types of metal-air batteries are commonly used by the military, Al-air and Mg-air (Hu, et al., 2016). Since Al and Mg are easily found in nature, both metals are cheap and likely to be commercialized in the future (Hu, et al., 2016). Some common metal-air batteries and their voltages, theoretical energy densities, and overall reactions are shown in Table 1.

<table>
<thead>
<tr>
<th>Battery</th>
<th>Voltage (V)</th>
<th>Theoretical specific capacity (Ah/kg)</th>
<th>Theoretical energy density (Wh kg⁻¹)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–air</td>
<td>2.71</td>
<td>1030</td>
<td>2791</td>
<td>4Al + 3O₂ + 6H₂O ↔ 4Al(OH)₃</td>
</tr>
<tr>
<td>Mg–air</td>
<td>3.09</td>
<td>920</td>
<td>2843</td>
<td>Mg + ½ O₂ + H₂O ↔ Mg(OH)₂</td>
</tr>
<tr>
<td>Zn–air</td>
<td>1.65</td>
<td>658</td>
<td>1085</td>
<td>Zn + ½ O₂ ↔ ZnO</td>
</tr>
<tr>
<td>Li–air</td>
<td>2.96</td>
<td>1170</td>
<td>3463</td>
<td>2Li + O₂ ↔ Li₂O₂</td>
</tr>
<tr>
<td>Na–air</td>
<td>2.27</td>
<td>487</td>
<td>1105</td>
<td>Na + O₂ ↔ NaO₂</td>
</tr>
<tr>
<td></td>
<td>2.33</td>
<td>687</td>
<td>1600</td>
<td>2Na + O₂ ↔ Na₂O₂</td>
</tr>
<tr>
<td>K–air</td>
<td>2.48</td>
<td>377</td>
<td>935</td>
<td>K + O₂ ↔ KO₂</td>
</tr>
</tbody>
</table>

Table 1: Common Metal-Air Battery Characteristics (Zhang, X, 2016)

Theoretically, metal-air batteries have the highest energy density of all batteries, but several problems prevent experimental and commercial metal air batteries from achieving perfect efficiency. One problem is the common use of alkali electrolyte, which is prone to evaporation and
carbonation. The battery cell has to be open to the environment to allow oxygen to enter, but this also allows the electrolyte to evaporate. As water evaporates from the electrolyte, the chance of the metal-air battery being able to recharge decreases. Additionally, carbon dioxide in the air can enter the battery cell and react with the electrolyte, called carbonation, which will consume the electrolyte. For example, the commonly used hydroxide electrolyte, potassium hydroxide (KOH), reacts with carbon dioxide in the following way (Appell, et al., 2013):

\[ \text{CO}_2 + 2\text{KOH} \rightleftharpoons \text{K}_2\text{CO}_3 + \text{H}_2 \]

This reaction consumes the electrolyte, forming a solid carbonate compound in its place (Park et al., 2015). As more of the electrolyte is consumed, the discharge time and efficiency of the battery decreases.

To improve long-term stability of the electrolyte and the energy density and efficiency of the battery, the equilibrium of the carbonation reaction could be offset to decrease the amount of carbonation occurring. This could be done by keeping the electrolyte as basic as possible or adding \(\text{K}_2\text{CO}_3\) into the electrolyte (Schröder et al., 2015; Sumboja, et al., 2016). Additionally, the inlet air feed could be bubbled through KOH before reaching the battery (Toussaint et al., 2010). This would carbonate the outside source of KOH and significantly decrease the amount of carbon dioxide available to react with the battery (Toussaint et al., 2010).

Carbon dioxide can also react with water in the catalyst to produce carbonic acid over time. Although this is a relatively slow reaction, with long-term battery discharge, recharging cycles, and an infinite amount of carbon dioxide in the air, carbonic acid can build up in the electrolyte and reduce the efficiency of the battery (Knoche, 1980). The aqueous nature of the electrolyte facilitates both carbon dioxide reactions, indicating the potential benefits of a non-water based electrolyte.
Although most metal-air batteries are not generally rechargeable, advances are being made to create rechargeable metal-air batteries. The major hindrance to rechargeability is that when the metal-air battery discharges an irreversible compound can form, such as ZnO forming in a Zn-air battery. This prevents the reverse reactions from being able to occur and prevents rechargeability (Park, et al., 2015). To recharge the battery, both the metal and electrolyte would need to be replaced (Cheng, et al., 2011). Much of the research to advance metal-air battery rechargeability is being performed using zinc-air batteries, the most common and commercialized type of metal-air battery.

2.4.1 Rechargeable Zinc Air Batteries

Zinc-air batteries, powering everything from hearing aids to small-scale power grids, can provide consistent, constant voltage over a long period of time, with high discharge currents (Crompton, 1996, Zhang, 2015). The major application of Zn-air batteries are button batteries, named so because of their small size and cylindrical shape, which can power a hearing aid for months (Zhang, 2015).

In a zinc-air button battery, oxygen enters the battery cell through small holes on the bottom of the battery where it reacts with a catalyst (Park, et al., 2015). A hydrophobic later within the battery prevents water, such as humidity in the atmosphere, from entering the battery cell and disrupting the zinc anode (Duracell, 2004). Inside the battery cell is a zinc anode, which is often a slurry of zinc ions suspended in a hydroxide gel (Park, et al., 2015).

Figure 8: Structure of a Zinc-Air Button Battery (Duracell, 2004).
Looking closer at the reactions that occur during discharging, oxygen that enters the battery cell interacts with a catalyst and a cathodic reduction reaction occurs, which produces hydroxide ions. In the zinc anode, an oxidation reaction occurs, oxidizing zinc metal into zinc hydroxide and releasing electrons. The zinc hydroxide produced in the oxidation reaction further reacts to form zinc oxide (ZnO), an irreversible product (Park, et al., 2015). The Zn-air battery reactions are shown below.

\[
\text{Cathodic Reduction: } O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \\
\text{Anodic Oxidation: } Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^- \\
\text{Zinc Oxide Formation: } Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^- \\
\text{Overall Reaction: } 2Zn + O_2 \rightarrow 2ZnO
\]

The overall reaction has an electric potential of 1.65V and open circuit voltage of 1.4V (Park, et al., 2015). The battery typically discharges between 1.0V and 1.25V, with most of the cell capacity used by the time the battery voltage drops to 0.9V (Duracell, 2004). During recharging, in principle the reverse reactions occur: pure zinc would be produced from zinc oxide as oxygen is produced and dispelled from the battery cell.

A significant amount of research over the past two decades has been done to develop a rechargeable Zn-air battery. Three major limits to rechargeability were found: dendrite formation on the zinc anode, instability of the catalyst, and evaporation of the electrolyte (Li, Y. et al., 2014; Toussaint et al., 2010). In addition, water electrolysis can occur during recharging.

There were two ways to overcome dendrite formation in a zinc-air battery: modifying the atomic structure of the zinc anode, and modifying the reaction equilibrium in the electrolyte. By creating a greater nano-structure in the zinc anode, there will be less disorder between the zinc metal and the electrolyte, and less dendrites will grow into the zinc anode (Toussaint et al., 2010).
Additionally, the electrolyte could be modified to prevent dendrite growth. Various studies found that adding an oxide, such as gallium oxide, into the electrolyte created a nano-scopic electronic network within the electrolyte. In addition to enhancing conductivity, the network promoted the deposit of zinc into the electrolyte, which prevented the formation of zinc dendrites in the anode (Li, Y. et al., 2014).

To overcome the instability of the catalyst, a bifunctional catalyst needs to be used. Since oxygen is produced during recharging, the catalyst needs to both capture oxygen when the battery is discharging, but also allow oxygen to be released from the battery cell when recharging. A bifunctional catalyst has the ability to both capture and release oxygen, as compared to a unifunctional catalyst, which only has the ability to capture oxygen (Li Y. et al., 2014). Functionally, pure platinum catalysts are unifunctional and not suited for rechargeable batteries. By modifying the catalyst, rechargeability can be achieved (Toussaint et al., 2010).

To overcome electrolyte evaporation, an ionic liquid could be used in place of an aqueous electrolyte. Many benefits were shown to occur when an ionic liquid electrolyte is used in a zinc-air battery. First, because water is removed from the electrolyte, the growth of dendrites and minor corrosion of the zinc anode is prevented. Additionally, carbonation and evaporation of the electrolyte no longer occurs (Li, Y. et al., 2014). The one problem with using an ionic liquid electrolyte is that metal-air batteries are designed to function with an aqueous electrolyte, which pairs with the cathodic oxygen reduction reaction that occurs. Tetrabutylammonium salts have been shown to function comparably to aqueous electrolytes by encouraging the reversible reduction of oxygen, as compared to other ionic salts, which encourage an irreversible reduction of oxygen. However, the voltage of a zinc-air battery with a tetrabutylammonium salt electrolyte is only around 0.8V, while a zinc-air battery with an aqueous electrolyte discharges around 1.2V.
Overall, not much research focusing on rechargeable, ionic liquid electrolyte, metal-air batteries has yet been performed, so a lot is still unknown (Li, Y. et al., 2014).

2.5 Liquid Metal Battery

Liquid metal batteries, first studied in the cold war era, have rapidly developed over the last ten years. The unique aspect of these batteries is that all three main components, the anode, cathode, and electrolyte, are in the liquid phase. Typically, the battery has two different liquid metals for the anode and cathode, with a molten salt electrolyte in between the metals. No separation layers are used in this battery, instead the liquid phase components are naturally separated based on density. The anodic metal is the least dense, the cathodic metal is the densest, and the molten salt electrolyte has a density somewhere in the middle. The configuration is shown in Figure 9.

![Diagram of a liquid metal battery](Stauffer, 2016)
When designing a liquid-metal battery, characteristics of the materials must be considered. First, when choosing the anodic metal and cathodic metal, a strong electron donor must be paired with a strong electron acceptor. This will aid in the electron transfer process, increasing the energy density of the battery and increases the efficiency of the battery. Another key characteristic is that all three main components must have reasonable melting points. If the melting points are too high, the heat needed to maintain the battery would offset some of the energy produced by the battery. Lastly, the metals chosen should be naturally stable and abundant in order to increase safety and lower cost (Stauffer, 2016).

A liquid metal battery currently being studied at Massachusetts Institute of Technology is composed of a lead-bismuth alloy, sodium metal, and a hydroxide halide electrolyte. This battery is able to operate at only 270°C, which is an attainable and sustainable temperature for the system. The lead-bismuth alloy serves as the cathode, while the sodium metal is the anode (Stauffer, 2016). Another possible metal for the cathode is a lithium-antimony-lead alloy.

One of the main benefits of using liquid phases is that they allow for faster reactions and lower overpotentials. In general, liquid phase reaction kinetics are faster than solid-state reaction kinetics. Studies have shown that because of the liquid phase of the components, liquid metal batteries have high storage capabilities and can deliver that energy quickly (Kim, et al., 2013). Since renewable energy fluctuates, the ability of this battery configuration to dispense large amounts of energy quickly would allow it to adapt to sudden changes in the renewable energy supply, without causing outages for consumers.

Another benefit of this battery is that is has been shown to achieve thousands of charge-discharge cycles without significant declines in the amount of energy stored or efficiency. Since no separation layers are used, degradation of components is less common, which results in an
increased lifespan of the battery. Only the main shell of the battery is of concern for degradation and corrosion (Wang, et al., 2014). However, because the battery layer structure is based on density differences, these batteries are very unstable and sensitive to small movements, which is not ideal for use within a large-scale energy grid, or for powering electric vehicles.

2.6 Redox Flow Batteries

Redox flow batteries, first developed by NASA in the 1970s, are able to cheaply store large amounts of energy (Weber et al., 2011). As research and development keep pushing technology forward, the redox flow battery has a long lifespan, high efficiency, and a quick response time. It can quickly change from charging to discharging in seconds (Weber et al., 2011; Skyllas-Kazacos et al., 2011). These characteristics make the redox flow battery an excellent option for large-scale grid energy storage. Additionally, a redox flow battery is not geographically specific and can be constructed wherever there is a demand to store power (Weber et al., 2011).

A redox flow battery operates by using two flowing liquid electrolytes, an anolyte and a catholyte, to store electrical energy as chemical energy (Skyllas-Kazacos et al., 2011). The anolyte is a positive electrolyte, which is involved in an oxidation redox reaction, while the catholyte is a negative electrolyte involved in a reduction redox reaction. The two electrolytes flow through a battery cell stack, where they are separated by a membrane and can react, before flowing back into holding tanks, as shown in Figure 10 (Weber et al., 2011). Electrons move from the catholyte to the negative electrode, through wires, and then to the positive cathode where the electrons enter the anolyte (Alotto et al., 2014). The membrane separating the flowing electrolytes allows ions to pass through to keep the battery cell at a neutral charge. In most redox flow batteries, an ionically conducting membrane is used to encourage the movement of ions (Weber et al., 2011).
One benefit of a redox flow battery is that the electrolytes are liquid. Reactions occur with liquid-phase kinetics, significantly faster than if the battery were solid metals (Hu, et al., 2016). The reactions that occur in the battery are reversible, and the battery can easily be recharged simply by switching the flow of the current (Skyllas-Kazacos et al., 2011). Redox flow batteries can quickly change from charging to discharging which makes it excellent at adapting to changes in the power grid system (Alotto et al., 2014). There is currently 70-85% efficiency when recharging the battery, and improvements in technology keep pushing that closer and closer to 100% (Skyllas-Kazacos et al., 2011). The battery can be charged and discharged up to 20,000 cycles without great performance or efficiency loss, and they have a 20-year life span (Knight, 2014).

One unique feature of a flow battery is its ability to separate power and energy. Energy is stored in the electrolytes and depends on the size of the storage tanks used to hold the electrolytes (Redox, n.d.). The number of flow battery cells stacked together determines power capacity (Redox, n.d.). Multiple battery cells can be connected in cell stacks to increase power capacity.
The greater the area for the oxidation and reduction reactions to occur, the greater the power of the battery.

The ability to separate power and energy allows many different types of flow battery designs to be created and optimized for each specific situation based on energy storage and power demands (Weber et al., 2011). The electrolyte storage tank can be increased in size depending on how much energy needs to be stored and the cell stacks can be increased depending on how much power load is needed (Redox, n.d.). Redox flow batteries are great for a grid system, since the storage tanks simply need to be scaled up to increase their energy storage capacity (Service, 2015).

Specifically, redox flow batteries can efficiently store energy on a micro-grid scale from solar panels. Solar power is collected in large quantities at a low power voltage (Knight, 2014). If power and storage were not independent, the battery would have a limited amount of storage to account for the lower power output of a solar panel.

Since redox flow batteries require large storage tanks, and flowing liquids, development of flow batteries can often be difficult and time consuming. Other battery configurations can be used to model and test the chemical reactions involved in a flow battery, before a full flow battery configuration is created. The benefit of a flow battery is larger energy capacity and the ability to separate power and energy. Neither of these benefits pose major restriction to developing the chemistry of the battery using a smaller, cheaper, configuration. A metal-air battery, for example, could be a model for a flow battery. Once the chemical reaction within the model battery is perfected, the correct electrolyte separator is found, and rechargeability is achieved, the battery could be easily converted into a rechargeable flow battery.

One downfall to redox flow batteries is that the electrolytes could mix through the membrane via crossover. To address this problem, the vanadium redox flow battery uses the same
compound for the anolyte and catholyte. Thus, if there were to be mixing across the ionic separating membrane, there would not be any unwanted side reactions, and the battery would not short circuit. In this battery, 1.7M vanadium dissolved in 5M sulfuric acid is used for both the catholyte and anolyte (Knight, 2014). The anolyte is $V^{2+}/V^{3+}$, while the catholyte is $V^{4+}/V^{5+}$ (Alotto et al., 2014). One limitation of vanadium redox flow batteries is that they must be composed of corrosion resistant materials, otherwise the sulfuric acid the vanadium is dissolved in will dissolve the battery cell (Alotto et al., 2014).

Three major problems limit widespread use of redox flow batteries: a maximum cell stacking, the battery’s large size, and high capital cost (Redox, n.d.; Weber et al., 2011). Through battery cells can be stacked together, there is a maximum cell stacking, and thus a maximum power capacity, that can be attained (Redox, n.d.). This greatly limits the grid-scale application of a redox flow battery if the battery can only reach a certain power output. Secondly, the large size of a redox flow battery geographically limits its widespread usage. Structurally, redox flow batteries need two large storage tanks to hold the electrolytes (Service, 2015). As a result, these batteries have a massive size and need to be places in areas with enough space to hold the battery. Because of their size, these batteries are not suitable for small electronic appliances (Alotto et al., 2014). Lastly, despite the cost effectiveness of a redox flow battery, these batteries have a high initial capital cost (Weber et al., 2011). The US Department of Energy is encouraging technological development of redox flow batteries to decrease the cost of the battery from $250/kWh to $100/kWh by 2030 (Weber et al., 2011). Until that is reached the initial capital investment greatly limits widespread usage of redox flow batteries.
2.7 Liquid Metal-Air Battery

A liquid metal-air battery combines a metal-air and a liquid metal battery in the hopes of achieving all the positives of both battery types, while removing the disadvantages of each battery configuration. Liquid metal-air batteries have high energy densities, estimated to be able to store 11 times more energy than a Li-Ion battery, and long life spans (Foley et al., n.d.).

Very little research has been focused on liquid metal-air batteries, and this battery configuration is still very much considered a new technology. One of the major downfalls of this battery type is that it must been kept at temperatures higher than room temperature to ensure the metal anode stays in the liquid state. This limits widespread, commercial use of this battery type. Two previous Major Qualifying Projects (MQPs) completed at Worcester Polytechnic Institute investigated the optimization of a liquid metal-air battery with gallium as the metal anode.

The first project, completed in April 2015, was titled “A New Liquid Metal-Air Battery” (Howard et al., 2015). This team designed a Swagelok cell adaptation to test a gallium-air battery. The battery was composed of liquid gallium metal, a Teflon gasket, a zirconia cloth electrolyte separator soaked in 6M KOH electrolyte and a platinum catalyst. Repeated testing at approximately 50°C with a discharge current of 0.5 mA (~ 1 mA/cm²) indicated a 12.6 hour discharge cycle at 1V, a promising result.

The following year, another project, “Liquid Metal-Air Battery for Energy Storage” (Hu et al., 2016), built off the original team’s progress. This project studied variations in temperatures, electrolyte concentrations, re-soaking the electrolyte, and adding an additional separator. They concluded that increasing the amount of the electrolyte in the battery by adding a second separator soaked in the 6M KOH electrolyte greatly improved the battery. A discharge time of approximately 24 hours at 1V was achieved with a discharge current of 0.5 mA (~ 1 mA/cm²).
This project, a continuation of those two Major Qualifying Projects, will investigate the effect of changing material components of the liquid gallium-air battery to improve rechargeability. Both gallium and a gallium-tin alloy will be studied as the anode, while various solutions and compounds will be studied as the electrolyte.

2.8 Liquid Metal Anode

The metal for a battery anode can be composed of either a pure metal, or a metal alloy. When working with a gallium air battery, pure gallium metal, or a gallium based alloy can be used as the anode.

2.8.1 Gallium

One promising metal for the anode of a liquid metal-air battery is gallium. Gallium, a silvery, metallic metal, has a very low melting point (29.7 °C). This is beneficial, as the battery could be operated using a simple heat lamp to keep the metal in a liquid state. Non-toxic and safe to work with, gallium is widely used in the electronic industry in semiconductors and LEDs because of its ability to convert electricity to light and high boiling point (2,400°C). Although gallium has the potential to be an efficient electrode for a battery, there has not been extensive research done regarding its electrochemical properties. While there are a few other metals that melt at low temperatures, such as mercury, phosphorus, and potassium, with better known reaction chemistry, these metals do not have the chemical stability and low toxicity that gallium has. Another advantage is that gallium has a low activation energy barrier, so it reacts easily. However, this also allows gallium to easily react with oxygen in the air, forming a film of gallium oxide on the surface of the metal (Hu, et al., 2016). It is not known how reversible the reaction is.
2.8.2 Gallium Tin Alloy

An alternative to using a pure metal anode is to use an alloy, to obtain desired characteristics of each individual metal. Testing of Li-Ion and sodium-ion batteries showed that a tin alloy anode is more stable discharge than a pure metal anode. Cycling capabilities, storage capacity, and the lifespan of the battery were also improved. As little as 2% tin by weight in the alloy was able to yield better results. A viable gallium-tin alloy, 92% Ga-8% Sn. The benefit of tin is that this metal has been studied electrochemically in batteries, as both an anode and as an electrolyte. A tin anode has been shown to store 2.5 times as much energy as graphite. Gallium has a low melting point, and despite tin’s melting point of 232 °C, a 92% Ga-8% Sn alloy has a melting point of only 25°C. The most common uses for a gallium-tin alloy are in medical thermometers, and as refrigerants to cool computer chips. Both tin and gallium readily react with oxygen, which is ideal for a metal-air battery reaction.

2.9 Electrolyte

When choosing an electrolyte, there are many characteristics that should be taken into consideration, including the type of ion, i.e., anion or cation. Since one of the functions of the electrolyte is to facilitate the movement of electrons and ions, the electrolyte should have high ionic conductivity, so that ions are not repelled by the electrolyte, and a low viscosity, so that ions and electrons can readily move throughout the electrolyte. The electrolyte-separator layer should also be able to serve as a good barrier to keep the anode and the cathode materials from mixing.

2.9.1 Potassium Hydroxide Electrolyte

One of the most widely used anionic electrolytes in batteries is potassium hydroxide (KOH) solution. Aqueous KOH has high ionic conductivity, a high oxygen diffusion coefficient, and low viscosity, which all make KOH an ideal electrolyte (Sumboja, et al., 2016). Sodium hydroxide
(NaOH) is very similar to KOH, however KOH has better ionic conductivity than NaOH (Sumboja, et al., 2016). Two previous MQPs have shown that 6M KOH is a viable electrolyte for a liquid gallium-air battery (Howard et al., 2015; Hu et al., 2016).

2.9.2 Gallium Oxide and Gallium Nitrate Electrolyte Additives

The two major downfalls to using KOH as the electrolyte are carbonation and evaporation, discussed in Section 2.4. Recent research using a zinc-manganese oxide battery found that changing the electrolyte equilibrium influenced the rechargeability of the battery (Pan, et al., 2016). Figure 11 below shows the reactions that occur within this battery. By adding Zn$^{2+}$ ions into the electrolyte, the electrolyte was saturated with Zn$^{2+}$, causing a shift in the reaction equilibrium. The formation of solid zinc oxide was discouraged, allowing the reverse, recharging reaction to occur while favoring the formation of zinc hydroxide. The reactions are shown in Figure 11.

![Figure 11: Reaction of a Zi-Air Battery affected by Adding Manganese Ions into the Electrolyte (Pan, et al., 2016).](image)

In a gallium-air battery, gallium reacts to form gallium hydroxide (Ga(OH)$_3$) which can further react to form gallium oxide (Ga$_2$O$_3$), a precipitate:

\[
\text{Ga} + 3\text{OH}^- \rightarrow \text{Ga(OH)}_3 + \text{OH}^-
\]

\[
\text{Ga(OH)}_3 \rightarrow \text{Ga}_2\text{O}_3 + 3\text{H}_2\text{O}
\]

Precipitated gallium oxide would not be able to react reversibly, preventing recharge of the battery. By modifying the electrolyte equilibrium to decrease formation of gallium oxide and favor the
stability of gallium hydroxide, the potential of rechargeability increases. Utilizing gallium compounds in the electrolyte could enhance the reverse reaction and increase the potential to charge the battery by increasing the presence of Ga$^{3+}$ ions in the electrolyte. Both gallium oxide and gallium nitrate would be suitable additives.

Gallium oxide, a white odorless powder with a melting point greater than 1,760°C, has a low solubility in water and is highly reactive to acids. It is commonly used as a catalyst in addition to semiconductor applications and has been studied in high voltage power devices. As mentioned in Section 2.4.1, using an oxide compound could increase stability and rechargeability of a metal-air battery. Gallium oxide does, however, have a low thermal conductivity compared to other semiconductors (Stepanov, et al., 2015).

Gallium nitrate is most commonly used medically to treat hypercalcemia, which is an abundance of calcium ion in the blood. It inhibits osteoclast activity and prevents the breakdown of bones as the body tries to lower the amount of calcium in the blood. Gallium nitrate compound decomposes at 110°C and is highly soluble in water (National, n.d.).

2.9.3 Ionic Liquid

Evaporation and electrolysis of an aqueous electrolyte, as discussed in Section 2.4 and Section 2.2, respectively, limit rechargeability of a metal-air battery. A gelled 6M KOH electrolyte using polyvinyl alcohol polymer gel was previously tested in a liquid gallium-air battery, and yielded insignificant effect (Hu et al., 2016). An ionic liquid, an ionic salt that is liquid at, or around, room temperature, is not volatile, and wouldn’t be subject to evaporation (Hamilton, 2009). Ionic liquids are conductive and have previously been studied as electrolytes in metal-air batteries. It is theorized that batteries with ionic liquid can have up to 11 times the energy density of a battery with an aqueous electrolyte (Hamilton, 2009). The major downfall to using ionic
liquids is cost. However, despite a high initial cost, ionic liquids could be more cost effective than an aqueous electrolyte as a result of the issues of carbonation and evaporation when compared to a battery with an aqueous electrolyte (Hamilton, 2009).

Compared to water, which decomposes into gases above 1.2V, ionic liquids have a larger electrochemical window and are stable up to, and even above, 5V. Batteries with ionic liquid would be able to be charged at higher voltages without the risk of electrolysis. Additionally, water is immiscible in most ionic liquids, which prevents water from dissolving through the catalyst and into the electrolyte, where it could react with the metal anode and limit the battery’s lifespan (Lee, J., 2010).

Ionic liquid usage in batteries is a developing field of study, and there is not yet a consensus among researchers about how ionic liquid best work when used as battery electrolytes. It depends greatly on the battery configuration and the reactions involved. One study found that adding sodium ions into the ionic liquid electrolyte of a sodium metal battery increased the number of charge and discharge cycles of the battery (Forsyth et al., 2016). Another study found that in a Li-Ion battery, using hydrophobic ionic liquid was more ideal than hydrophilic liquid (Kuboki et al., 2005).

2.10 Electrochemical Reaction of a Metal-Air Battery

2.10.1: Gallium

In a liquid gallium-air battery, gallium is oxidized into gallium cations and electrons are released. These electrons flow to the cathode, where they reduce O₂ into hydroxide. These hydroxide ions then flow into the electrolyte to join the other potassium hydroxide ions (Hu, et al., 2016).
When the hydroxide ions reach the anode, gallium oxide or gallium hydroxide can form. Gallium oxide creates a problem at the surface between the electrolyte and gallium, where a thin layer of solid gallium oxide precipitates and prevents an electrochemical reaction from occurring. Gallium hydroxide, on the other hand, decreases the efficiency of the electrolyte, also affecting the battery’s lifespan. It is currently unknown which reaction, gallium oxide or gallium hydroxide, dominates the battery cell. The two reactions have similar electrochemical potentials, and very little research has been performed on the liquid gallium-air battery to determine what compounds are present in the battery (Hu, et al., 2016).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Reaction</th>
<th>Potential (V)</th>
<th>$\Delta G^0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>$Ga + 4OH^- \rightleftharpoons Ga(OH)_4^- + 3e^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anode</td>
<td>$Ga(OH)_4^- \rightleftharpoons Ga(OH)_3 + OH^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overall Anode</td>
<td>$Ga + 3OH^- \rightleftharpoons Ga(OH)_3 + 3e^-$</td>
<td>$V_A^0 = -1.242$</td>
<td>$-360$</td>
</tr>
<tr>
<td>Cathode</td>
<td>$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$</td>
<td>$V_C^0 = +0.401$</td>
<td>$-155$</td>
</tr>
<tr>
<td>Overall</td>
<td>$Ga + \frac{3}{4}O_2 + \frac{3}{2}H_2O \rightleftharpoons Ga(OH)_3$</td>
<td>$V^0 = V_C^0 - V_A^0$</td>
<td>$-476$</td>
</tr>
</tbody>
</table>

*Table 2: Open circuit voltage for gallium hydroxide product.*
<table>
<thead>
<tr>
<th>Electrode</th>
<th>Reaction</th>
<th>Potential</th>
<th>ΔG° (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Ga + 4OH⁻ ⇌ Ga(OH)₄⁻ + 3e⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anode</td>
<td>Ga(OH)₄⁻ ⇌ Ga(OH)₃ + OH⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anode</td>
<td>Ga(OH)₃ ⇌ Ga₂O₃ + 3H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overall Anode</td>
<td>Ga + 3OH⁻ ⇌ ( \frac{1}{2} ) Ga₂O₃ + ( \frac{3}{2} ) H₂O + 3e⁻</td>
<td>( V_a^0 = -1.323 )</td>
<td>-383</td>
</tr>
<tr>
<td>Cathode</td>
<td>O₂ + 2H₂O + 4e⁻ ⇌ 4OH⁻</td>
<td>( V_c^0 = +0.401 )</td>
<td>-155</td>
</tr>
<tr>
<td>Overall</td>
<td>Ga + ( \frac{3}{4} ) O₂ ⇌ ( \frac{1}{2} ) Ga₂O₃</td>
<td>( V^0 = V_c^0 - V_a^0 )</td>
<td>( V^0 = 1.724 \text{ V} )</td>
</tr>
</tbody>
</table>

*Table 3: Open circuit voltage for gallium oxide product.*
Chapter 3: Methods

3.1 Battery Design

The setup used in the lab to test a gallium-air battery was developed by Howard, et al. (2015) and further modified by Hu, et al. (2016). The battery is a modified Li-air Swagelok cell, with the general assembly shown in Figure 12. Appendix A has a detailed procedure for assembling the battery.

![Battery Assembly Diagram](image)

*Figure 12: Expanded view of battery assembly.*

3.2 Materials

The four main parts of the battery are the structural assembly, anode, cathode, and electrolyte. Further details on the specific materials and setup for each part are detailed below.

3.2.1 Structural Assembly

The structural parts for the battery were set forth by a previous Major Qualifying Project by Howard, et al. (2015). All testing was performed using this setup. The structural parts include two current collectors and a plastic Swagelok shell to contain the battery. The technical specifications are:

- Two stainless steel node current collectors, manufactured by Target Machine
• Stainless steel crucible, machined by WPI Unit Operations Lab
• McCaster Carr 302 Stainless Steel Precision Compression Spring (0.750 in. long, 0.36 in. O.D., 0.026 in. thick wire)
• PTFE Swagelok Tube Fitting with Ferrules, Union, 0.5 in. Tube O.D.

3.2.2 Anode

As set forth by a previous MQP (Howard, et al., 2015), 99.999% gallium purchased from Alfa Aesar was used as the metal anode. Using a heat lamp, this was kept as a liquid through all battery runs. Gallium has ideal properties for a liquid metal-air battery, as it is non-toxic, conductive, and has a low melting point of 29.77°C (Howard, et al., 2015).

In addition to 99.999% gallium, a 92 wt% gallium and 8% tin alloy was tested from Alfa Aesar. Similar to pure gallium, this alloy has a low melting point, approximately 25°C, and will melt when placed under a heat lamp (Alfa Aesar, n.d.). This alloy is stable for use in a liquid metal-air battery. The alloy has minor corrosive and hazardous properties, but so long as gloves are used when working with this alloy, the risks are minimized.

3.2.3 Cathode

In a metal-air battery, the cathodic material is oxygen in the air. The reduction reaction of oxygen is very slow, so a catalyzed gas diffusion layer (GDL) was used. As used in a previous MQP (Howard et al., 2015), a platinum-catalyzed carbon paper coated in Teflon from the Fuel Cell Lab was used for the GDL. The GDL used was LT40EW Low Temperature ELAT GDE microporous layer including 5g/m² Pt electrode on woven web made by Pemeas Fuel Cell Technologies. All tests were completed using this GDL.
3.2.4 Electrolyte

Five different electrolytes were tested in the battery throughout this project. The electrolyte separators were soaked in the electrolyte before assembling the battery. The five electrolytes are potassium hydroxide, gallium nitrate, gallium oxide, tetrabutylammonium chloride hydrate, and tetrabutylammonium ammonia hydroxide.

Last year’s research found a 6 molar solution of potassium hydroxide (KOH) to be the most efficient molarity of potassium hydroxide electrolyte for a liquid gallium-air battery. For runs, 2 zirconia cloth electrolyte separators were soaked in a 5 mL solution of 6M KOH for 20 minutes. This solution was made in the Fuel Cell Lab using solid KOH and deionized water.

The second electrolyte material tested was a gallium nitrate (Ga(NO$_3$)$_3$) solution. This powder was dissolved in deionized water to make 0.25M Ga(NO$_3$)$_3$ and 0.5M Ga(NO$_3$)$_3$ solutions. A 0.25M Ga(NO$_3$)$_3$ and 6M KOH solution was also created in the Fuel Cell Lab using solid KOH, deionized water, and gallium nitrate powder. Two zirconia cloth electrolyte separators were soaked for 20 minutes in the electrolyte solution before assembling the battery.

Gallium oxide, Ga$_2$O$_3$, purchased from Aldrich Chemical, was used in a similar manner as gallium nitrate. A solution of 0.5M Ga$_2$O$_3$ in deionized water surpassed the chemicals solubility limit, so a solution of 0.25M Ga$_2$O$_3$ in deionized water was used in testing. Additionally, a 6M KOH solutions with 0.05M to 0.35M Ga$_2$O$_3$ was tested. Electrolyte separators were soaked for 20 minutes in the electrolyte solution before assembling the battery.

Ionic liquids were tested as electrolytes for this battery. Both tetrabutylammonium chloride hydrate and tetrabutylammonium hydroxide were studied. Both ionic liquids have melting points below 45°C, so they are liquids at the battery’s typical operating temperature of 55°C. Under a heat lamp, electrolyte separators were soaked in the ionic liquid before being assembled into the battery for testing.
3.2.5 Electrolyte Separator

The electrolyte separator used in this gallium-air battery is ZYK-15 zirconia cloth from Zircar Zirconia Inc. It is a knit cloth with a thickness of 0.012 inches. The cloth can withstand temperatures over 2,000°C, allowing it to easily function within the temperature range of the gallium-air battery. Chemically, zirconia cloth can withstand a wide variety of electrolytes, allowing flexibility in experimentation (Zircar Zirconia, n.d.). The zirconia cloth was cut to fit the interior diameter of the battery, before being soaked in the desired electrolyte solution.

3.3 Electrochemical Cell Setup and Testing

Testing of the gallium-air battery was performed in the Fuel Cell Lab in Goddard Hall at Worcester Polytechnic Institute. Depending on which electrolyte was used, different testing set up procedures were followed, detailed below. The metals used were either gallium or a gallium-tin alloy.

Once assembled, the battery was inverted and placed in a clamp on a ring stand under the heat lamp. The battery is inverted to increase contact between the liquid gallium, and the electrolyte soaked membranes. A temperature probe was used to record the temperature, which was kept around 55°C. This was found to be the optimal temperature in a previous MQP (Hu et al., 2016). Appendix A contains a detailed procedure for setup.

3.3.1 Aqueous Electrolyte

To begin, about 1.2 grams of liquid metal was weighed into the stainless-steel crucible, with care taken to ensure the metal stayed liquid. The Teflon gasket, two zirconia cloths, and the GDL were then punched to size, as detailed in Appendix A. The two zirconia cloths were soaked in 5 mL of the electrolyte solution for 20 minutes, to ensure uptake of the electrolyte. After 20
minutes, the battery was assembled, as shown above in Figure 12. The electrolyte solutions created and tested included:

- 6M KOH in deionized water
- 0.25M Ga(NO$_3$)$_3$ in deionized water
- 0.5M Ga(NO$_3$)$_3$ in deionized water
- 0.25M Ga$_2$O$_3$ in deionized water
- 0.25M Ga(NO$_3$)$_3$ and 6M KOH
- 6M KOH solutions with variable amounts of Ga$_2$O$_3$ (0.05M to 0.35M Ga$_2$O$_3$)

3.3.2 Ionic Liquid Electrolyte

To assemble the battery, about 1.2 grams of metal was weighed into the stainless steel crucible, with care taken to ensure the metal stayed liquid. The Teflon gasket, two zirconia cloths, and the GDL were then punched to size, as detailed in Appendix A. Drops of the ionic liquid were dropped onto electrolyte separator until it was thoroughly soaked with the ionic liquid. Only two ionic liquids were tested: tetrabutylammonium chloride hydrate and tetrabutylammonium hydroxide. After soaking the electrolyte separators, the battery was assembled as shown above, in Figure 12.

3.4 Battery Metric Tester

Once the battery is fully assembled, a BA500WIN Battery Metric was used to test the battery. The battery metric is able to control and measure the current, voltage and time, through a script running via software on a computer in the lab. The software program used is BA500WIN Ver 1.38. The battery metric model used is a modified MC2020 that is able to measure low voltages and discharge currents. This was used to test batteries in two previous MQPs (Howard, et al., 2015; Hu et al., 2016).
To set up the BA500WIN script, numerous settings were imputed. The “Battery Type” chosen depending on the test being run. If the battery was just being discharged, Primary (Non-rechargeable) was chosen. If the battery was being charged, a Nickel-Cadmium battery was chosen. For either situation, there is only 1 battery cell, and it is rated up to 1,000 mAh capacity. This was taken from the previous report, Howard et al., (2015).

The base case run was a 20 minute pause, followed by a galvanostaircase polarization curve, 15 minute pause, 0.5mA discharge, and concluded with a 20 minute pause. This script was run continuously, with a discharge cutoff voltage of 0.1V. The 20 minute pause allowed for an open-circuit voltage hold. The galvanostaircase polarization curve measures the voltage of the battery as the current increased from 0 mA to 7.5 mA in 0.1mA increments every 20 second. Once the current reached 7.5 mA, 0.5 mA increments occurred every 20 seconds, until a current of 15 mA was reached. After the galvanostaircase polarization curve, a 15 minute pause allowed the battery to recover from the polarization curve. After the short pause, a current discharged the battery. In the base case, a current of 0.5 mA was used, however the battery could be discharged anywhere from 0.5 mA to 3mA. After the battery voltage dropped below 0.1V, a 20 minute pause allowed the battery to stabilize so an ending open-circuit voltage could be determined. Appendix A further details how to setup the BA500WIN script.

One problem that arose was overheating of the Battery Metric MC2020. Approximately 10 hours into every run, the voltage of the battery would suddenly drop from 1.2V to 0.5V. It would continue to read a voltage of 0.5V until the end of the run. After examining the Battery Metric, and with the help from the Goddard Machine Shop, it was concluded that the fan on the Battery Metric was not functioning properly. The electrical circuitry was overheating, which was affecting
the voltage reading. After adding a small, exterior fan to the battery setup to cool the battery metric box, proper replication of the previous MQP results was able to occur.

3.5 X-Ray Diffraction

X-Ray diffraction was used to determine the products formed by the chemical reaction in the battery cell. Over the past year, the product of the reaction, a solid film covering the surface of the liquid anode, was collected in a glass vial. To test via x-ray diffraction, the solid product was crushed into a powder and placed on a glass slide. The x-ray diffraction machine in Goddard Hall at WPI was used to complete the testing and analysis of the chemical product. The glass slide, with the powder sample was placed into the x-ray diffraction instrument. X-Rays are sent towards the sample, and diffracted based on the anatomic composition and organization of the material (Science, 2016). The angle and density of the diffracted rays can be measured and analyzed to determine the chemical composition of the sample. By comparing the results plot of an unknown chemical substance to standardized plots of known chemicals, a chemical can be identified (Science, 2016). Testing was done with the help of Douglas White from the WPI Department of Chemical Engineering.
Chapter 4: Results and Discussion

4.1 Objectives

For this project, 5 main objectives were determined with the overall intention of improving a liquid gallium-air battery.

1. Replicate previous results to ensure reproducibility of results
2. Identify the product of the gallium-air battery reaction
3. Identify restrictions and mitigation strategies for recharging
4. Modify the gallium-air battery to improve discharge time and rechargeability
5. Establish optimal operating conditions

4.2 Reproducibility of Previous Results

This project continues two previous MQP studies (Howard, et al., 2015, Hu, et al., 2016). To ensure the equipment was functioning properly and to ensure accuracy of the methodology, reproducibility of results was performed using baseline conditions established in the 2016 project.

<table>
<thead>
<tr>
<th>Electrolyte:</th>
<th>33.6 wt. % KOH (6M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separator Material:</td>
<td>2 Zirconia Cloth</td>
</tr>
<tr>
<td>Metal Anode:</td>
<td>1.2g pure liquid gallium</td>
</tr>
<tr>
<td>Heat Source:</td>
<td>Heating Lamp</td>
</tr>
<tr>
<td>Discharge Current:</td>
<td>0.5 mA</td>
</tr>
<tr>
<td>Cell Orientation:</td>
<td>Inverted (Cathode facing down)</td>
</tr>
<tr>
<td>Ambient Temperature:</td>
<td>55°C</td>
</tr>
</tbody>
</table>

*Table 4: Baseline Conditions Established in the 2016 Project.*

The baseline run established in 2016 ran for approximately 24 hours, with some variations in time due to inconsistent assembly and inconsistent environmental conditions, such as temperature and humidity (Hu, et al., 2016). Although there was some fluctuation in voltage,
especially at the beginning of the test when the battery was reaching thermal equilibrium under the heat lamp, the voltage was overall relatively constant between 1.0-1.2V for the duration of the 24 hours test. A sharp drop in voltage occurred when the battery died. Figure 13 shows the reproduced baseline result, which ran for 17 hours, illustrating reproducibility and accuracy of this project’s results.

One problem, which had to be overcome before reproducibility could be achieved, was overheating of the battery metric box. This box controls the program, which tests the battery. Around 6 hours into every run, the box would overheat and show inaccurate voltage readings. By adding an additional fan to cool the battery metric box, reproducibility of results could be achieved.

4.3 Identification of Electrochemical Products

Since the overall chemistry of the battery was unresolved, there were two possible products being formed by the reaction occurring to discharge the battery. It was possible for the battery to form gallium oxide (Ga₂O₃) or gallium hydroxide (Ga(OH)₃). Knowing the products formed is
critical because this allows for a deeper understanding of the recharging reaction, and what restrictions to recharging are.

As tests were run, the product formed on the surface of the anode was collected. Once a sufficient amount was collected, the product was tested by x-ray diffraction with the help of Doug White from the WPI Goddard Hall Machine Shop. By measuring the diffraction of the sample, it was determined that the overall product of the reaction is indeed gallium oxide. The results of the XRD can be seen below in Figure 14, with the collected sample as the top graph and the standardized gallium oxide graph below it.

Figure 14: The x-ray diffraction results for the gallium oxide product of the gallium-air battery.
4.4 Recharging Restrictions

Through literature review, three main recharging restrictions and their mitigation strategies were identified. There restrictions mainly apply to metal-air batteries, and how the problems were resolved for that battery configuration. Electrolysis of water is a restriction that applies to all battery configurations. Further details on the recharging restrictions and how these were mitigated are detailed in Chapter 2. Table 5 summarizes the recharging restrictions and mitigation strategies.

<table>
<thead>
<tr>
<th>Recharging Restriction</th>
<th>Restriction Mitigation Strategies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonation</td>
<td>Offset reaction equilibrium by changing the metal anode</td>
</tr>
<tr>
<td></td>
<td>Offset reaction equilibrium by modifying the electrolyte</td>
</tr>
<tr>
<td>Electrolyte drying out</td>
<td>Use a non-volatile ionic liquid electrolyte</td>
</tr>
<tr>
<td>Electrolysis of water</td>
<td>Use an ionic liquid electrolyte</td>
</tr>
</tbody>
</table>

Table 5: Restrictions for Recharging.

4.5 Modification of the Alloy

Research showed that using an alloy as the anode can have a variety of different benefits for the battery, as Section 2.7 details. These benefits include both stabilizing the chemical reaction and changing the chemical reaction equilibrium. For this project, an alloy of 92% gallium and 8% tin was studied as the anode. The gallium-tin alloy has a lower melting point than gallium, indicating it could require less energy to keep it warm and thus cost less to maintain.

The first tests run with the alloy simply used it as a replacement in the gallium-air battery that has been established by the prior MQP teams. It used approximately 1.2g of alloy with 2 zirconia cloth layers soaked for 20 minutes in 6M KOH. When discharging, the battery did not have a stable voltage, or a consistent discharge time. Sometimes the gallium alloy-air battery with
a 6M KOH electrolyte discharged for 4½ hours, shown in Figure 15, while other times the battery discharged for less than an hour, shown in Figure 16. The difference in discharge time could be due to the differences in the reactivity of gallium and tin, as tin is more electronegative and will react more. However, gallium composes the majority of the alloy, and is the main chemical reaction taking place.

**Figure 15:** Alloy battery with 6M KOH Electrolyte discharge.

**Figure 16:** Alloy battery with 6M KOH electrolyte no discharge.
Previous studies have shown that adding an oxide into the electrolyte can stabilize the discharge and rechargability of a battery (Section 2.4.1). Since the battery is gallium based, and a run was performed with the alloy to see if gallium oxide additive in the electrolyte would respond better than just KOH. After creating a few gallium oxide and KOH mixtures, it was found that the solubility limit of gallium oxide in 6M KOH was around 0.35M gallium oxide. A 0.25M gallium oxide with 6M KOH solution was chosen to be tested as the electrolyte, so that the electrolyte would not be over saturated.

This proved to be successful, and the battery initially discharging for 13 hours at 1.2V with a 0.25M gallium oxide and 6M KOH electrolyte solution, as seen in Figure 17. The presence of the gallium oxide in the electrolyte clearly benefitted the liquid gallium alloy-air battery, although the mechanism for this is yet unclear.

![Figure 17: Alloy battery with 0.25M gallium oxide and 6M KOH electrolyte](image)

Based on the success of 0.25M gallium oxide, a concentration profile was completed. This compared discharge times to the concentration of gallium oxide in the electrolyte. Concentrations varied from 0.05M to 0.35M gallium oxide. Figure 18 shows the completed concentration profile.
The 0.05M gallium oxide solution electrolyte likely did not have enough gallium oxide to make a significant impact on the reaction, leading to a discharge of less than 7 hours. Similarly, the 0.35M gallium oxide solution electrolyte was oversaturated with gallium oxide, overpowering the presence of KOH as the main electrolyte. The 0.17M gallium oxide with 6M KOH electrolyte solution proved to have the longest discharge time, about 18 hours. From this point on, further tests with the alloy were performed with a 0.17M gallium oxide in 6M KOH electrolyte.

It has previously been determined that the best temperature to operate the gallium-air battery was at 50℃, which resulted in the longest discharge times. A temperature study was completed for the alloy with a 0.17M gallium oxide and 6M KOH electrolyte. The temperature range tested was from 40℃ to 75℃. The temperature range was restricted at the lower end by the melting point of the alloy. The maximum temperature tested was restricted by the maximum temperature that could be achieved from the heat lamp in the Fuel Cell Lab. Figure 19 shows the results of the temperature profile.
At 40°C, the voltage did not stabilize, indicating that the alloy may not have been completely melted inside the crucible. The temperature of the system is measured from just outside the cell, so it is possible that the interior did not actually reach 40°C. On the other end of the spectrum, at 75°C, the battery had a voltage drop part way through from 1.2V to 0.5V, and never achieved a stable voltage. This could be due to the elevated temperatures and the electrolytes reliance on water. The higher temperatures would increase the evaporation of the water in the electrolyte, causing it to dry out and become ineffective. The zirconia cloth layers were dry upon disassembly, supporting this theory. This study found that 60°C is the optimum operating temperature for the alloy battery.

When comparing the optimal operating conditions of the alloy battery to the standard gallium battery, the alloy battery performed better. Figure 20 shows that the alloy battery discharged longer the gallium battery and had a more stable discharge voltage. Additionally, polarization curves were created for the two optimal conditions by running a galvanostaircase program. A polarization curve shows the battery’s ability to handle different currents and provide...
a good voltage even at high currents. Ideally, the polarization curve should be as stable as possible. Visually, the alloy at optimal conditions had a more stable polarization curve than pure gallium at optimal conditions. Figure 21 shows the polarization curves.

![Figure 20: Comparison of the gallium and alloy batteries discharged at optimal operating conditions.](image1)

![Figure 21: Polarization curves for the gallium and alloy batteries and optimum conditions.](image2)
4.6 Modifications of Electrolytes

After investigated the effect of modifying the metal anode of the battery, an investigation of different electrolytes was performed. This was done using pure gallium as the anode, in order to conserve the limited amount of gallium-tin alloy available in the Fuel Cell Lab. If an electrolyte was found to be beneficial with the pure gallium anode, it could then be tested with the gallium-tin alloy.

4.6.1 Gallium Nitrate and Gallium Oxide

Gallium nitrate was tested as the electrolyte with the hopes of shifting the equilibrium. Gallium nitrate should ionize into \(\text{NO}_3^-\) and \(\text{Ga}^{3+}\) ions, which matches the gallium ion in the reaction of the gallium-air battery. 1M, 2M, and 4M solutions of gallium nitrate in water were tested at the electrolyte.

Overall, this setup had an open circuit voltage (OCV) of approximately 0.8V, but each test failed to stabilize during the initial pause period of the runs. The 1M run even died during the initiation 20 minute pause, yet managed to chemically react and come back alive. However, no discharge was ever achieved with any amount of gallium nitrate in water. The voltage continuously fluctuated, and clear results could not be obtained. Figure 22 shows the results of the 1M gallium nitrate in water electrolyte run. Gallium nitrate in water is not a viable electrolyte for a gallium-air battery.
Gallium oxide in water was also tested as an electrolyte. Gallium oxide is the product of the reaction and was readily available in the lab. A 0.5M solution of gallium oxide in water was tested with the goal of offsetting the equilibrium of the reaction enough to achieve rechargeability of the battery. In order for the battery to charge, the reverse reaction of the system needs to occur. By using gallium oxide as the electrolyte, Le Chatelier’s principle indicates that the reverse reaction is more likely to occur.

Tests with pure gallium as the anode and a 0.5M gallium oxide in water electrolyte were able to produce an OCV of up to 0.8V, but the battery died as soon as a current was applied. Not only was this electrolyte not alkaline, gallium oxide has low solubility in water, which minimized the concentration of ions formed in solution, which hinders the steady flow of electrons. Figure 23 shows the result of this test.
Since gallium oxide mixed with KOH was a viable electrolyte for the alloy, gallium oxide in water was also tested as the electrolyte with the alloy. Overall, the battery did not stabilize and the OCV continued to rise over time. Upon applying a 0.5mA current, the battery failed to discharge, and died immediately.

Adapting the electrolyte from the gallium-air to the gallium alloy-air battery did not prove successful; the optimal gallium alloy-air electrolyte was adapted to the gallium-air battery. The
first electrolyte additive tested with the alloy was 0.25M gallium oxide in 6M KOH, which showed the viability of this electrolyte solution. This same electrolyte solution was mixed in the Fuel Cell Lab and tested with the liquid gallium-air battery.

The battery did discharge for 18 hours, which is comparable to the gallium-air battery with a simple 6M KOH electrolyte. However, after 8 hours there was a voltage drop. The last 10 hours of the run were very unstable. Though this tests shows that this electrolyte could be a viable option for the gallium-air battery, it was not further investigated because of its instability. The results for this run are shown in Figure 25.

![Gallium Battery with gallium oxide and KOH electrolyte](image.png)

*Figure 25: Gallium Battery with gallium oxide and KOH electrolyte.*

4.6.2 Tetrabutylammonium Chloride Ionic Liquid

One factor that limits the discharge period and the charging ability of the battery is electrolyte drying out, which was explained in Section 2.4.1. As Section 4.3 details, one-way to mitigate this issue is to use a non-volatile ionic liquid as the electrolyte. Tetrabutylammonium chloride, an ionic liquid available in the Fuel Cell Lab, was tested as the electrolyte in a gallium-air battery.
Following multiple tests at temperatures between 50°C and 60°C, it was concluded that tetrabutylammonium chloride was not a viable electrolyte, as the battery failed to discharge for longer than 5 minutes, despite having an OCV between 0.85V and 0.6V. A key problem with these tests is that the voltage did not stabilize throughout the runs. As seen in Figure 26, the OCV was recorded for 15 minutes prior to discharging at 0.5mA. During this time, the voltage steadily dropped from 0.85V to 0.65V. After a very short discharge, where the battery died almost immediately, the OCV was measured for another 5 minutes. During this time, the voltage continued to drop.

![Figure 26: Gallium battery with tetrabutylammonium chloride electrolyte.](image)

Tetrabutylammonium chloride ionic liquid was tested because it was the only available in the Fuel Cell Lab with a low melting point. One reason this ionic liquid did not work could have been because the gallium-air battery is an alkaline battery, while the ionic liquid chosen had chloride as the free ion, not hydroxide. This could hinder the ion transfer and the established reactions taking place in the battery. Attempts were made to replace the chloride ion with hydroxide ions, but the high water solubility of the tetrabutylammonium chloride prevented the
exchange. Tetrabutylammonium chloride ionic liquid is not a viable electrolyte for a gallium-air battery.

4.6.3 Tetrabutylammonium Hydroxide Ionic Liquid

One of the first objectives for this project was to establish the reaction occurring in the gallium-air battery. It was found that the gallium reaction is known to involve hydroxide ions. It was speculated that using an ionic liquid with a free ion that matches the gallium reaction would improve performance of the battery by allowing the reaction to proceed smoothly at the interfaces between the anode and the electrolyte. An ionic liquid with a hydroxide free ion, tetrabutylammonium hydroxide, was purchased and tested in the gallium-air battery.

At 50°C ambient temperature, pure gallium anode was tested with two zirconia cloths soaked in tetrabutylammonium hydroxide. An inverted set-up (cathode facing down) was used, and the battery was discharged at 0.5mA. The test results are shown in Figure 27.

The battery discharged for 29 hours, which shows promising results. However, after two and a half hours, the battery voltage dropped from 1.1 V to around 0.5V. After disassembling the
battery, it was discovered that gallium had leaked through the membrane and beaded in between the catalyst and electrolyte separator, seen below in Figure 28. This caused minor short-circuiting of the battery, which resulted in the voltage dropping to approximately half.

![Figure 28: Zirconia separators and catalyst following discharge with an ionic liquid electrolyte.](image)

After replicating this test, a modification of the electrolyte was also tested. Adding gallium oxide to the electrolyte for the gallium-tin alloy anode improved the gallium-tin alloy battery performance and stability. This idea was adapted to the gallium and ionic liquid battery to see if modifying the electrolyte could improve stability of the battery. An electrolyte mixture of 1.08g of tetrabutylammonium hydroxide was mixed with 0.16g of gallium oxide. Two zirconia cloths were soaked in the electrolyte mixture and the pure gallium anode battery was discharged at 0.5mA. Shown in Figure 29, after 2.5 hours the battery experienced a voltage drop, but continued to run for a total of just over 30 hours.
Since modification of the electrolyte did not improve battery performance, an investigation of different electrolyte separators was performed to see if a different separator would result in a stable ionic liquid discharge. Gallium is immiscible in water, but has a higher affinity for the ionic liquid electrolyte. For this reason, the same electrolyte separator does not work for the ionic liquid as it did for the 6M KOH electrolyte.

One speculation for the leakage of the gallium through the zirconia cloth separators could be the configuration. Since the battery is inverted, gallium would be pulled through the membrane purely because of gravity. To investigate this issue, a battery was set up as usual with two tetrabutylammonium hydroxide soaked zirconia cloths and inverted. The battery was left there for 8 hours, while the open circuit voltage was measured. After 8 hours, there was small decrease in voltage. After disassembling the battery, it was observed that gallium has soaked into the zirconia cloth membranes, but not as much as if the battery has been discharging at a 0.5mA current. Both gravity and the gallium electrochemical reaction are factors that cause a drop in the voltage of a tetrabutylammonium hydroxide and gallium anode battery.
Different battery configurations were attempted to mitigate the issues and increase stability of the battery. The 2016 project found that alumina cloth had the same results as zirconia cloth when tested with 6M KOH and pure gallium, so alumina cloth was tested as a possible separator for the ionic liquid and pure gallium battery. It was speculated that the pore size of the zirconia cloth was too large, allowing gallium to easily leak through. Using a mixture of 2.5g of zirconium oxide-yttria stabilized powder and water, different tests were done to attempt to decrease the pore size of the zirconia cloth. Different separators, number of separators, and battery configurations were also tested to see if a stable ionic liquid battery discharge could be achieved.

Using the same set-up conditions, different separators were tested with the ionic liquid and pure gallium. The battery was discharged at 0.5mA in an ambient temperature of 55°C. The different separators tested and the results are detailed in Table 6, with times rounded to the nearest half hour. Figure 30 shows the discharge times visually.

![Figure 30: Visual Representation of the Discharge Time of Different Separators tested with the tetrabutylammonium hydroxide electrolyte and pure gallium anode with 0.5mA discharge](image)
<table>
<thead>
<tr>
<th>Separator Tested</th>
<th>Results</th>
<th>Total Time</th>
<th>Time to Voltage Drop</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 zirconia cloth</td>
<td>Gallium leaked through separator</td>
<td>9.5 hours</td>
<td>1 hour</td>
</tr>
<tr>
<td>2 zirconia cloth</td>
<td>Gallium leaked through separator</td>
<td>29 hours</td>
<td>3 hours</td>
</tr>
<tr>
<td>3 zirconia cloth</td>
<td>Gallium leaked through separator</td>
<td>41 hours</td>
<td>7 hours</td>
</tr>
<tr>
<td>2 alumina cloth</td>
<td>Gallium leaked through separator</td>
<td>6.5 hours</td>
<td>2.5 hours</td>
</tr>
<tr>
<td>2 zirconia cloth Non-inverted configuration</td>
<td>Gallium leaked through separator</td>
<td>7.5 hours</td>
<td>2 hours</td>
</tr>
<tr>
<td>Slurry of 1.2g gallium and ionic liquid to fill the crucible</td>
<td>No voltage ever detected</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Slurry of 1.2g gallium and ionic liquid to fill the crucible with non-inverted configuration</td>
<td>No voltage ever detected</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>2 zirconia cloths rinsed with a solution of 2.5g zirconium oxide powder and 10 mL of water and left to fully dry</td>
<td>Gallium leaked through separator, through significantly less than the normal 2 zirconia cloth run</td>
<td>4 hours</td>
<td>1.5 hours</td>
</tr>
<tr>
<td>2 zirconia cloth soaked in a solution of 2.5g zirconium oxide powder and 10 mL and left to fully dry</td>
<td>No gallium leaked through the separator, but it appeared that the gallium anode was contaminated by lose zirconia powder on the surface of the separators</td>
<td>4 hours</td>
<td>1 hour</td>
</tr>
</tbody>
</table>

*Table 6: Separator Tests*

As the number of tetrabutylammonium hydroxide soaked zirconia cloth separators increases, the time to the voltage drop and the overall discharge time increases. The greater the thickness of the electrolyte layer, the longer the discharge time, which is consistent with the gallium crossover issue. For the zirconia rinsed and zirconia soaked membranes, smaller separator pores would be easier to block, which could account for the short discharge times. Another possible reason for the short discharge times is that zirconium oxide-yttria stabilized powder, used to decrease the pore sizes, could have affected the battery reaction in an unexpected and unknown
way. Additionally, any loose powder on the surface of the separators would contaminate the electrolyte and liquid metal, decrease the purity and efficiency of the battery.

It was determined that tetrabutylammonium hydroxide is a viable electrolyte for a gallium-air battery, despite the consistent issue of gallium leaking through the electrolyte separator. Due to time constraints, the ionic liquid could not be tested with the gallium-tin alloy anode.

4.7 Rechargeability

4.7.1 Gallium

Previous research had found that the gallium air battery could not hold a charge, which was verify before further rechargeability tests were performed. In order to test rechargeability, the battery was completely discharged at 2mA, charged at 0.5mA for 1 hour, and then fully discharged at 0.5mA. Figure 31 shows the results of the recharge test.

![Figure 31: Charging the gallium battery at 55°C with 6M KOH electrolyte.](image)

When charging, the voltage reached 1.8V. When water is charged above 1.2V, electrolysis of water occurs. Because of this, the discharge that took place after the charging is likely due to
the electrolysis of water in the aqueous electrolyte. Rechargeability cannot be ascertained because of electrolysis. Overall, there is no evidence that the standard gallium air battery can be recharged.

4.7.2 Slurries

To test the feasibility of recharge of the gallium battery, two electrolyte slurries were recharged at 0.5mA for three hours to see if any gallium metal would form. Ideally, if the battery were rechargeable, gallium metal would be produced from the electrolyte when the battery was charging, as explained in Section 2.2. It was already concluded that gallium oxide is the product of the pure gallium battery with 6M KOH. By creating a slurry of gallium oxide and 6M KOH, it can be tested whether a pure gallium battery is rechargeability. If there are signs of rechargeability, then other factors, such as electrolyte drying out, are preventing rechargeability of the gallium-air battery. Through simple chemical reactions, gallium nitrate can react into gallium oxide. For this reason, a slurry of gallium nitrate was also tested.

The two slurries tested were 0.094g of gallium oxide in 10M KOH and 0.095g of gallium nitrate in 10M KOH. For testing, the crucible was filled with the well mixed slurry and a catalyst was placed on top. No gasket was used, and the battery was not inverted.

After three hours of charging, the gallium oxide slurry was promptly disassembled and showed no sign of crystallization. The gallium nitrate slurry did show signs of metallization, as shown in Figure 32.

Figure 32: Result of charging a gallium nitrate and KOH.
However, the gallium nitrate slurry was not disassembled for at least 12 hours after the run has concluded. The crystals that were present are assumed to have been the 10M KOH crystallizing over time. Though no direct conclusion can be made about the gallium nitrate slurry because of the length of time before the slurry was analyzed, it is believed based on visual analysis that no gallium crystals formed. From this, it was concluded that a gallium-air battery with a KOH and gallium oxide electrolyte, or KOH and gallium nitrate electrolyte, is not going to feasibility recharge.

4.7.3 Alloy

Although the gallium-air battery was shown to not be rechargeable, nothing was known about the rechargeableness of the gallium-tin alloy. An analysis of the charging capabilities of the gallium alloy-air battery at optimal conditions was performed. First, the battery was discharged until the voltage dropped below 0.1V. It was then charged for 1 hour at 0.5mA and fully discharged, with the results shown below in Figure 33.

![Figure 33: Charging the alloy battery with 6M KOH and 0.17M Gallium Oxide](image)

During charging, the voltage increased to about 1.8V. Although the battery discharged for approximately an hour, the possibility of electrolysis of water does not allow for any conclusion
on recharging. A voltage greater than 1.23V is sufficient to cause the decomposition of water into oxygen and hydrogen gas, and could provide the unstable discharge seen after recharging. Overall, there is not sufficient evidence to conclude that this battery can, or cannot, be recharged, while an aqueous electrolyte exists in the battery cell.

4.7.4 Ionic Liquid

It was determined that the presence of water in the electrolyte led to the electrolysis of water, preventing clear evidence of charging. This indicated that an ionic liquid may be a better electrolyte option for a rechargeable battery. Since tetrabutylammonium hydroxide showed promising results as an electrolyte for the gallium-air battery (Section 4.6.3), its rechargeability was tested. However, because gallium leaks through the electrolyte separator, results would only shows viability of recharging, until electrolyte separators that prevent leaking can be tested.

Pure gallium with 2 zirconia cloth layers soaked in tetrabutylammonium hydroxide ionic liquid was fully discharged, charged at 0.5mA for one hour, then fully discharged again. The battery reached a voltage of 2V during recharging, but electrolysis of water occurring above 1.2V was not longer a concern since the electrolyte was no longer aqueous. Figure 34 below shows the recharging results.
When discharged at a current of 0.5mA, the battery sustained a voltage for 20 minutes. This result was replicated, shows a lot of promise towards the rechargeability of the gallium battery with a tetrabutylammonium hydroxide electrolyte. To further test this result, the gallium-air battery was fully discharged, then charged at 1mA for an hour and discharged. A 40 minute discharge was achieved. By doubling the charging current, the resulting discharge time also doubled. The liquid gallium-air battery with tetrabutylammonium hydroxide is thus potentially rechargeable.
Chapter 5: Conclusions and Future Work

Throughout this project, advancement of a liquid-gallium air battery was investigated, building off of two previous Major Qualifying Projects. The discharge time and rechargeability were improved by investigating different metal anode and electrolyte options. In order to being an investigation of different material options, the chemical reaction occurring in the battery cell had to be determined. Using X-ray diffraction, the reaction of the gallium-air battery with a 6M KOH electrolyte was identified to form gallium oxide, Ga$_2$O$_3$.

The viability of using a 92% gallium-8% tin alloy was proven. The optimal conditions for a liquid 92% gallium-8% tin alloy anode were determined to be 60°C with a 6M KOH and 0.17M gallium oxide electrolyte solution. Using an alloy lowered the cost of the battery, and, at optimal conditions, resulted in longer, more stable discharge runs than pure gallium.

The presence of water in the battery, as an aqueous electrolyte, prevented the battery from charging due to electrolyte evaporation and electrolysis of water. Tetrabutylammonium hydroxide ionic liquid is a feasible, non-volatile electrolyte for a gallium-air battery. Rechargeability of a gallium-air battery with a tetrabutylammonium hydroxide ionic liquid electrolyte was possibly achieved with a 20 minute discharge after recharging.

Moving forward with this research, the first area of improvement should be the electrolyte separator. Currently, a Zircar woven cloth type ZYK-15 (yttria-stabilized zirconia) with a coarse weave and large pore size is soaked in the desired electrolyte and used in the battery. While this functioned well for the aqueous electrolytes, gallium leaked through the separator when an ionic liquid electrolyte was used. This short-circuited the battery. A new separator should be investigated with the ionic liquid. A polymer electrolyte membrane, commonly used in lithium ion batteries and fuel cells, could provide the necessary barrier while still maintaining the exchange of ions.
Once the tetrabutylammonium hydroxide ionic liquid electrolyte functions well with pure gallium, it should be tested with the gallium-tin alloy. At optimal conditions with aqueous electrolytes, the gallium-tin alloy performed better than pure gallium, which could also apply to the ionic liquid electrolyte. However, no conclusions about the gallium-tin alloy and ionic liquid can be made until further tests are run.

Additionally, the liquid metal-air battery should be adapted into a flow battery configuration. This configuration decouples energy and power within the battery, which allows the battery to store more energy. By flowing liquid gallium metal through the battery, the buildup of gallium oxide on the surface of the anode would be minimized and the discharge time could increased. This would allow the gallium anode to be used to its full extent. Figure 35 shows a schematic of a flow battery configuration using liquid gallium as the anode, and 6M KOH as the electrolyte.

![Figure 35: A sample flow battery configuration for the liquid gallium-air battery.](attachment:image)
References


Na9234. (2011, November 21). Schematic of lithium-air battery charge and discharge cycles [Digital image].


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**Appendix A: Cell Assembly**

![Figure 36: Heating the gallium (left); Soaking the 1.1 cm diameter zirconia cloth separators in 6M KOH (right)](image-url)
Figure 37: The anode components (left) and final assembly (right)

Figure 38: Anode assemble (left) added to the anode/cathode connector (right)
Figure 39: Cathode assembly

Figure 40: Gallium weighing process; ~1.2g of gallium
Figure 41: Crucible assembly (left); Teflon gasket with an outer diameter of 1.4cm and an inner diameter of 0.9cm (right)

Figure 42: 2 zirconia cloth layers with diameters of 1.1cm
The BA500WIN Battery Analyzer Program:
Figure 45: Start page of the BA500WIN program with a real time plot, temperature, voltage, time, and current measurements.

Figure 46: Programs drop down menu opened. Tests can be made with the program editor. Once saved, these programs can be run by first loading them, then clicking run program.
The battery type “Primary (Non-rechargeable)” was selected to just discharge the battery and “Nickel-Cadmium” was used for charging the battery. The battery has 1 cell and a 1,000 mAh rated capacity.

Figure 48: Under the function tab, select the appropriate step for the battery program
Depending on the step function chosen before, certain parameters are required. For example, discharge tests can be conducted with a discharge current of 0.5 mA to a cut-off voltage of 0.01 V while other parameters can be ignored. The other two program editor tabs, ‘pulse details’ and ‘advanced,’ can also be ignored for typical tests. Additional steps with various functions and parameters can be added by the insert step button; typically, an open circuit voltage measurement for a period of time followed by discharge was performed. After saving the program, it can be loaded later from the programs drop down menu on the start page.
Figure 50: By selecting Options under the Analyzer tab, the data recording settings can be changed

Figure 51: The program can automatically pause after charge or discharge if desired

This function can also be added as a step in the program. This window will also allow you to change the data collection interview so you can record more or less data points. Tests were typically run collecting a data point every 5 seconds.