

**Practical Fiber Batteries for Wearables Based on Thermally-Drawn
Zn-MnO₂**

A Thesis Presented

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Disclosure

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Abstract of the Thesis

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Dr. Joshua Gallaway and Dr. Hameed Metghalchi, Co-Advisors

The concept of the Internet-of-Things has inspired growth in the field of wearable technology, from aesthetically-pleasing color changing fabrics to practical heart rate monitors, all interwoven into any variety of clothes (i.e.: shirts, pants, hats, blankets, bags, etc.). For a continuously operating wearable system, an energy storage vessel is needed: a battery. Fabric-based systems demand that the battery be integrated in the fabric themselves. The primary challenge for such an integrated battery is rendering the active components of a battery (cathode, anode, and electrolyte) into a fiber. Existing challenges for fiber batteries include toxic/flammable materials, low power output, and complicated assembly approaches. This work seeks to address both assembly and safety issues by developing an easily manufacturable fiber battery by eventually utilizing a thermal draw tower using an inherently safe Zn-ion chemistry (Zn/MnO_2) with a gel polymer electrolyte (GPE). The GPE offers a high ionic

conductivity, mechanical properties compatible with thermal draw towers, and provides a physical separator between cathode and anode. In the end, a lab-scale fiber battery was demonstrated using a properly formulated GPE. In addition, the GPE was properly drawn through the thermal draw tower, demonstrating the feasibility of drawing the entire fiber battery.

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Chapter 1

Introduction

This work details the design and fabrication of inherently safe batteries with a fiber form factor that can be integrated into fabrics. The basis chemistry is Zn-ion, with a Zn metal anode, an MnO_2 cathode, and a gel polymer electrolyte. This work is a planned basis for eventually combining the battery materials into a polymer preform to be thermally drawn on a vertical draw tower to produce fiber batteries with a consistent size of less than 2 mm.

The overarching growth in the Internet-of-Things (IoT) concept that seeks to upgrade common items into smarter versions have led to the development of wearable technology. From color changing fabrics to fiber-sized radio antennas, the growing field of wearable technology comes with a series of unique challenges of creating micro-scale devices. Much work is devoted to micro-scale sensors and detectors as well as energy harvesting/producing nanogenerators, however, without an energy storage vessel (a battery), devices will not have power available at any given moment. Thus, for applications involving wearable devices, batteries are needed in a form-factor that can fit into common fabrics and clothes. This means the battery must be small (less than a millimeter thick) and

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offer a great amount of flexibility. Thus far, this task has been approached on multiple fronts. There have been a variety of chemistries experimented on: lithium-ion, zinc-ion, metal-air, sodium-based, etc. From sub-millimeter sized fibers to macroscale fabrics, numerous different structures and processes are also found in the literature. The presented work to follow seeks to develop a zinc-ion battery in a fiber-form factor by means of a polymer draw tower. A battery of this form-factor will enable numerous other micro-scale devices to operate without an external energy source. Being that these batteries have an end goal of integrating into clothing and fabrics, the zinc-ion battery chemistry was chosen due to the inherently safe properties, counter to many lithium-ion chemistries. In addition, due to the lack of materials that are reactive to air, a zinc-ion chemistry enables a facile method of development. Furthermore, the draw tower offers a means of producing a fiber of a precise size. Many fiber battery researchers do not offer a means of producing consistently sized fibers. Thus, the current work seeks to bridge the gap between novelty and practicality.

Chapter 2

Background

2.1 Wearable Technology

From the broadest of levels, smart-technology integration into everyday items is becoming an inevitability. The IoT is the overarching concept of integrating technology into anything and everything. One article describes the focuses required for IoT hardware as: “addressing device performance, network access, interoperability, flexibility, and reliability.”[1] With the growing concept of the internet-of-things (IOT), a wide variety of new products are transitioning into a “smart” version with inter-connectivity abilities. Smart/advanced functionality fibers and fabrics are undergoing a surge in research attention. Smart fibers cover a large breadth of technologies but can be considered anything that serves a purpose beyond aesthetics or basic clothing functionality (ie. can bend, be washed, comfortable in contact with skin). One literature review, which used the term smart wearable technology (SWT), found a slow trend upward from 28 to 94 patents for SWTs from 2006 to 2013, but a dramatic uptick to 575 patents in 2015.[2] One study found the global market for wearable devices should grow from \$30 billion in 2016 to \$150 billion by 2026.[3] Wearable

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technology is not exclusive to smart fibers/fabrics, but also ear-wear, glasses, watches, or any other rigid structure commonly found on a person. For the sake of continuity, smart wearables will be used to encompass any of: smart fibers, smart fabrics, smart textiles, smart devices, or any other small microelectronic-mechanical system being developed with wearability in mind.

2.1.1 Current Research and Applications of Wearable Technology

Wearable technology is an area of convergent research, involving electrical, mechanical, chemical, materials, and computer engineering. In addition, expertise in textile and fabric design is crucial in understanding how to physically integrate various wearable components into a wide variety of clothing items (shirts, pants, hats, gloves, socks, shoes, belts, etc.). A review work by Shi et. al., "Smart textile-integrated microelectronic systems for wearable applications," compiles several aspects of smart wearables (fabrication methods, functional components, structures/architectures, applications, and security).[4]

To start, the functional components Shi et. al. discussed include sensors, shape actuators, displays, antennas/radio frequency identification (RFID), energy harvesters, energy storage, flexible circuit boards, and memory devices. The current work will only discuss sensors, antennas. and energy harvesters in more depth to give a clearer picture of the wearable technology research field (energy storage will be covered at length later).

Sensors being developed for wearable technology purposes (with several works cited for each type) include mechanical [5, 6, 7], humidity [8, 9, 10, 11], temperature [12, 13, 14], chemical [15, 16, 17, 18], and pressure [19, 20, 21]. To serve as an example, medical applications/benefits will be used as a brief highlight/overview of the usefulness of wearable sensors.. Citing a general upward trend in life-expectancy, many articles in the literature discuss how the ever-aging population

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will require cheap, efficient, and non-invasive means of monitoring health without over-stressing healthcare systems/hospitals.[22, 23, 24] The common theme in solving this issue is wearable sensors that can track various health characteristics of a population, from walking style to heartbeat rhythm. One example is a work that developed a sensitive pressure sensor that could detect slight pressure changes on the ear canal surface to determine one's heart rate.[25] All this to say simple sensors can combine together to create highly functional and useful devices.

Crucial to integrating sensors into a wearable format is a simple way to communicate with the sensors and easily extract data while the devices are worn. This is where antenna and RFID wearable research is important. Most RFID is passive, whereas the antennas being researched for wearable technology purposes are active. The challenge of wearable antennas and RFID, as with most wearable technology, is keeping it flexible, cheap, durable, and lightweight. Antenna research is focused on polar orientation as well as a variety of different form factors, from ribbons to cloths to shoelaces.[26]

Another example of common functional components is energy harvesters, which can enable a self-contained system that powers itself. Harvesters can be generically categorized into five principles: electromagnetic, piezoelectric, triboelectric, thermoelectric, and photovoltaic. Each type of harvester simply converts one form of energy into electrical energy for use of powering a system; the only difference in each type is what the original source of energy is. The first three listed (electromagnetic, piezoelectric, and triboelectric) all rely on kinetic energy to produce electrical energy. This means that these three types of devices lose capacity if a wearer is stationary. For electromagnetic generators to come to fruition in a wearable format, more research of lightweight materials to produce conductive coils and magnetic bodies will be needed.[4] One example article

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created an electromagnetic energy harvester that could output 32 mW at a slow running speed, which is a reasonable amount of power for microelectronic devices.[27] Piezoelectric energy harvesters can produce high potentials, but are limited in power output ($1\text{--}7.5\text{ mW m}^{-2}$).[4] These types of harvesters are actually well-suited for wearable applications as piezoelectric materials are commonly flexible due to the nature of their operation. Finally, triboelectric harvesters output a higher potential than that of piezoelectric harvesters (10s-100s of volts versus 1-20 volts), however, the power density is still not quite high enough for most microelectronics at this time.[4]

The key downfall of an energy harvester is it requires an active source, such as motion, temperature gradient, or solar photons. Without the active source, no power is generated. For example, electromagnetic, piezoelectric, and triboelectric materials all allow for the conversion of mechanical energy from someone walking into electricity, but once the person sits down or simply stands still there is no way to power any devices. This is where the need for energy storage arises, to be discussed in depth later.

Applications of wearable technology are numerous, and the technology is ever-developing. For the current work, the largest market will be discussed: the health/medical market. Potentially the largest market for wearable technology in terms of economic potential lies in the health/medical field. A key corner of the market revolves around a world-wide ageing problem. According to a 2020 World Health Organization report, the population of those older than 65 is expected to double by the year 2050.[28] In 2010, it was found that medical expenses of Americans aged over 65 were 2.6 times higher than the national average while also accounting for over one-third of medical expenses despite being just 13% of the entire population.[29] The rising cost of medical care combined with this ageing population will lead to major issues in years to come. One potential answer to this

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issue is wearable technology. As previously discussed, pressure, temperature, and chemical sensors combined with an energy source and a bluetooth connection can help in early detection of potential health issues. The sensors can do basic functions such as monitoring heart rate or body temperature to something more complex such as analyzing sweat chemistry to get an indication of metabolic problems.[4] Relatively simple vitals measurements could be crucial in early detection and prevention of health issues in the ageing population, which could both keep the elderly population healthier while also enabling freeing up more physicians to treat patients with more urgent health issues.

2.2 The Essentials of a Battery

The basic elements of a battery can be found in Figure 1, a diagram of a Daniell cell. The Zn-Cu Daniell cell is composed of two electrodes, liquid electrolyte, and a porous separator. In this cell, the Zn bar can be considered the anode and the Cu bar as the cathode. During discharge (reaction in the spontaneous direction) the anode, also known as the negative or reducing electrode, releases electrons through the external circuit. The cathode, also known as the positive or oxidizing electrode, receives electrons from the external circuit. The transference of ions through the electrolyte is coupled to the flow of electrons. The electrolyte is the ion transport medium, and should possess high ionic conductivity with insulator-like electronic conductivity. The porous separator keeps the two electrolytes from mixing with each other but allows for ions to pass.

For a view of a modern engineered battery, Figure 2.2 shows a cylindrical alkaline cell. This is a common primary battery with MnO_2 as cathode and Zn powder as anode. Different from the Daniell cell, current collectors are key features of this cell. In the Daniell cell, the electrodes themselves acted as both anode/cathode and current collector. However, in the alkaline cell, the

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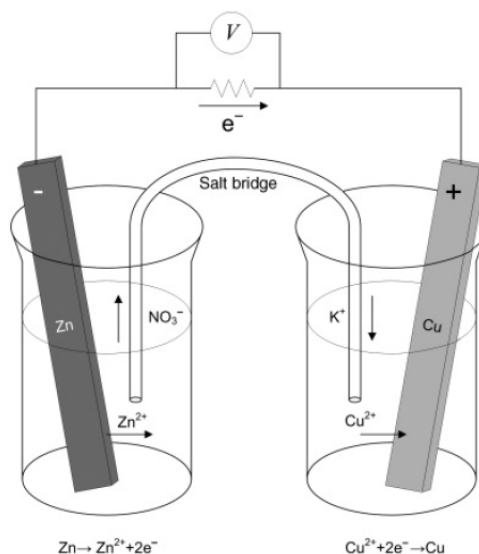


Figure 2.1: Diagram of a Daniell Cell borrowed from Fuller and Harb's *Electrochemical Engineering*. [30]

electrodes are not directly connected to the external circuit, thus the current collectors (high electronic conductivity materials) are added to collect the released electrons and bridge them to the external circuit.

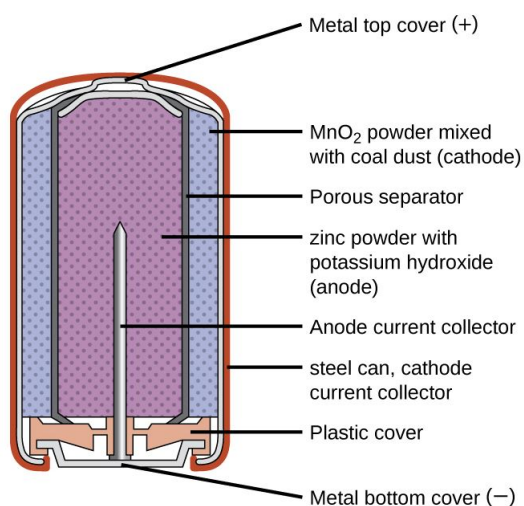


Figure 2.2: Diagram of a basic alkaline battery, adopted from [31].

2.3 Zinc-Ion Battery Developments

This project will develop rechargeable Zn-ion batteries (ZIBs) for manufacturing in a fiber form factor. This will involve several material requirements, namely reversibility of the Zn anode and MnO_2 cathode active materials, conductivity of the electrolyte, compatibility of the electrolyte with the active materials, and manufacturability. Since their commercialization in the early 1990s, lithium-ion batteries (LIBs) have been the gold standard of the secondary, or rechargeable, battery market. However, ZIBs are a topic of research interest due to several inherent benefits over LIBs: diversity of potential electrolytes, improved safety, reduced toxicity, lower cost, and higher volumetric energy density.[32] ZIBs are distinct from common alkaline primary Zn/ MnO_2 batteries because they are rechargeable, and because theoretically they involve a reversible intercalation reaction of Zn^{2+} ions at the cathode, which may also be mixed with H^+ intercalation. Alkaline primary batteries rely only on H^+ reaction at the cathode, and are non-rechargeable due to several different irreversible discharged products such as Mn_3O_4 and ZnMnO_4 . These differences are because ZIBs make use of a near-neutral aqueous electrolyte, while primary alkaline batteries use highly concentrated aqueous KOH.[33, 34]

2.3.1 Zinc-Ion Battery Electrodes

LIBs generally have anode host materials into which guest Li^+ ions intercalate, the most common being graphite, LiC_6 . This is necessary because Li metal is a problematic anode that is unstable and results in dendrites that greatly reduce cell lifetime. In contrast, ZIBs predominately use metallic Zn as the anode, which is much simpler and increases energy density. This is due to Zn being in high abundance, inherently cheap, low toxicity, and intrinsically safe.[35] Zinc has a

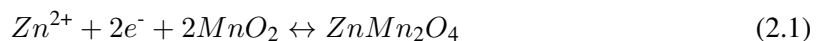
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moderate specific capacity of 820 mAh g (compared to 3860 mAh g for Li metal) but also a very high capacity density of 5855 mAh cm⁻³ (compared to 2061 mAh cm⁻³ for Li metal), which can be beneficial in a volume-limited scenario.[36]

ZIB research is often focused on cathodes based on manganese oxides. There are several other cathode materials being explored but in a much younger state of research, such as vanadium-oxides, spinel-structured oxides, Prussian blue analogues, and organic materials.[35] Manganese-oxides are the principally researched cathode material due to their relatively high abundance and high specific capacity. These manganese-oxides include MnO₂, Mn₂O₃, and Mn₃O₄. [35]

Of particular interest is MnO₂ which has various different crystal structures (α , β , γ , δ , ϵ , ν , λ , etc.) that all have structures (tunneled or layered) that allow for the hosting of foreign cations.[32] Each crystal structure offers a high theoretical specific capacity of 308 mAh g (based on the one electron redox from Mn⁴⁺ to Mn³⁺). [35] For comparison, a common LIB cathode material, lithium cobalt-oxide (LCO), has a theoretical specific capacity of 294 mAh g with a practical value of about 160 mAh g⁻¹. However, it is important to note that due to the much higher nominal working voltage offered in LIBs, compared to MnO₂ (3.7 V vs. 1.4 V, respectively), LIBs are much more energy dense.

The most researched crystal structure for ZIBs is the α form. As with β and γ MnO₂ polymorphs, the mechanism of ionic transport is theoretically the intercalation of Zn²⁺, seen below.



This reversible reaction results in a theoretical capacity of approximately 210 mAh g⁻¹. [32] One aspect of this polymorph is the remarkably high discharge rate (upwards of 126 C) it can

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accommodate.[32] The intercalation of divalent Zn^{2+} ions cannot occur this rapidly, thus leading to the belief that there must be H^+ intercalation occurring in parallel. The exact intercalation process and products are disputed in the literature.[37, 38]

In addition to the disputed mechanics of the intercalation of Zn^{2+} into MnO_2 , there is also a proposal that there may be a chemical conversion reaction occurring. Work done by Pan et. al. proposed that during discharge, MnO_2 reacts with a H^+ from water to form MnOOH . This occurred in a zinc sulfate electrolyte, and it is believed these results may not apply to other electrolytes.[39] This conversion reaction resulted in a 285 mAh observed capacity.

Another promising polymorph of MnO_2 is $\epsilon\text{-MnO}_2$, also known as akhtenskite. In this structure, H^+ and Zn^{2+} intercalation has been theorized in a work by Sun et. al.[40] In that study, Sun et. al.[40] conducted two ex situ XRD measurements at two points: once at a potential of 1.3 V and once at 1.0 V. The electrolyte used in this experiment was an aqueous solution of MnSO_4 and ZnSO_4 . This showed MnOOH peaks at 1.3 V, leading to the belief that H^+ insertion is occurring. At 1.0 V, XRD peaks were showing the presence of ZnMn_2O_4 , implying a further insertion of Zn^{2+} . This result was reinforced with data from galvanostatic intermittent titration technique (GITT), as well as electrochemical impedance spectroscopy (EIS) measurements.[40] This work resulted in a high capacity of 300 mAh g^{-1} , close to the theoretical capacity of 308 mAh g^{-1} , at a capacity fade rate of 0.007% per cycle for 10,000 cycles.[32] The exact reaction kinetics of akhtenskite is still in need of further exploration, but as it stands, offers a cyclable format of MnO_2 .

2.3.2 Common Electrolytes for Zinc-Ion Batteries

For proper functioning of the eventual fiber battery, the electrolyte must meet criteria beyond those of typical liquid electrolyte batteries. The electrolyte is the material that conducts ions

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from one electrode to the other while also preventing the flow of electrons. Therefore, electrolytes must be ionically conductive but electrically insulating.

Therefore, electrolytes must be ionically conductive but electrically insulating. The goal of the current work is to produce a rechargeable battery, thus limiting the possible electrolytes to non-alkaline electrolytes, specifically mildly-acidic electrolytes. Common alkaline batteries are primary (non-rechargeable) due to Zn dendrite growth and insulating, irreversible byproducts. However, in 1986, Yamamoto and Shoji created a MnO_2/Zn cell using an aqueous, Zn-salt electrolyte, which prevented the formation of irreversible byproducts.[41] To our knowledge, this was the first ZIB developed. These aqueous electrolytes helped suppress Zn dendritic growth and inactive by-products. However, a downside to aqueous electrolytes in ZIBs is hydrogen and oxygen evolution, which overall causes the capacity to fade and limits the cyclability.[42] Another potential issue is the dissolution of cathode material due to the water in the electrolyte. Aqueous electrolytes can cause irreversible side reactions with the electrode materials and increase dendritic growth, which degrades the cycling performance. Solid electrolytes for ZIBs can help alleviate some of these issues as well as suppress dendritic growth.

ZIB electrolytes can generally be split into aqueous and non-aqueous. Both categories use a wide variety of zinc salts such as ZnSO_4 , ZnCl_2 , and $\text{Zn}(\text{NO}_3)_2$. Non-aqueous electrolytes use an organic solvent and result in better reversibility and a larger potential window, whereas aqueous electrolytes offer greater safety, ionic conductivity, and a higher rate capacity.[35] In the current work, the focus is on one specific category of non-aqueous electrolytes: polymer electrolytes.

2.4 Polymer Electrolytes

In addition to the desired conductivity of the electrolyte, due to the process the fiber battery is to be drawn, the electrolyte cannot be liquid. In addition, the electrolyte must be moldable at temperatures in the range of 150-300 (due to the draw tower process), meaning inorganics are not an option. This limits the possible electrolytes to those possessing three characteristics: organic, solid, and allow for the recharging of the battery, which leads to polymer electrolytes (PEs).

Based on the need to use a solid electrolyte, the electrolyte used will inherently possess a lower ionic conductivity than electrolytes commonly used in commercial alkaline batteries or LIBs. For comparison purposes while discussing solid electrolytes, Figure 2.3 is provided to show the range of ionic conductivity of the aqueous electrolyte potassium hydroxide, commonly used in Zn-MnO₂ alkaline batteries. It can be seen in Figure 2.3 that the ionic conductivity is on the scale of 10⁻¹, almost reaching 10⁰. Due to the inherently higher bulk resistance of PEs, the ionic conductivity of most researched PEs are on the order of 10⁻¹⁰ to a very maximum of 10⁻².

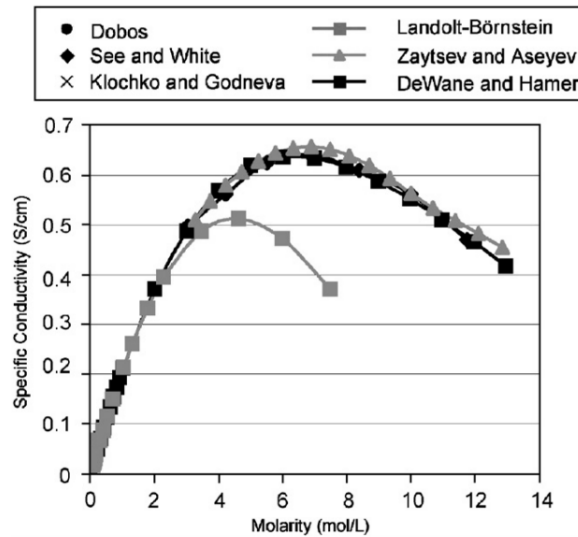


Figure 2.3: Ionic Conductivity measurements of potassium hydroxide, adopted from [43].

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A basic understanding of polymer structure is useful in understanding the way PEs function. A polymer is simply a structure made up of many repeating structural units called mers. Covalent bonds hold together the atoms of the mer, and secondary bonds hold together mers to form a polymer. Polymers are typically composed of non-metallic elements with carbon being the most common element. Polymers are composed of two main structures: a backbone and functional groups. The backbone is composed of chains of carbon atoms. Functional groups are the atoms that covalently bond to the carbon atoms and give the polymer its unique properties. The simplest polymer structure is polyethylene seen in Figure 2.4. Examples of functional groups include: alcohol, ether, alkyne, amino, or chloride.

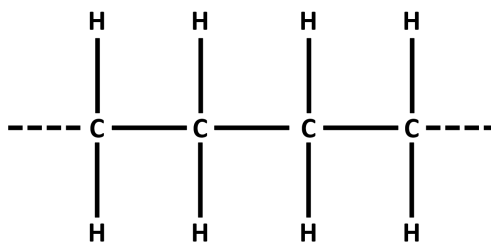


Figure 2.4: Diagram of polyethylene.

An essential trait of polymers for PEs is polarity. A polar polymer is one with a functional group that contains an element of high electronegativity. Elements with high electronegativity correlate to the upper right corner of the periodic table of elements with fluorine holding the highest electronegativity. This means the functional groups will have a higher tendency of attracting shared electrons. This means the side of the polymer chain with the high electronegative element will shift electrons away from the carbon backbone causing a negative side, which will polarize the polymer. It is important to note, however, that if the polymer's functional group is composed entirely of an atom of high electronegativity, such as polytetrafluoroethylene (PTFE) as seen in Figure 2.5, then

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the polymer is no longer polarized as the shared electrons are equally attracted to both sides of the polymer chain.

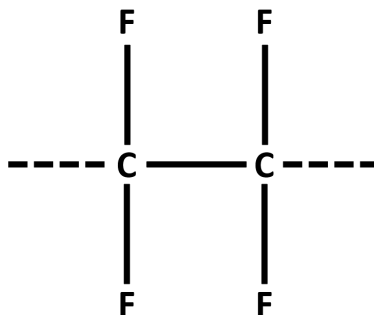


Figure 2.5: Diagram of polytetrafluoroethylene.

A good example of a polar polymer is polyvinylidene fluoride (PVDF), seen in Figure 2.6. The fluoride functional group attracts electrons causing a negative polarity towards the fluoride and away from the hydrogen atoms. While beyond the scope of the current work, it is important to note that polarity of polymers is not a set value as there may be several different conformations. This is to say that the fluoride groups may vary in positioning on the carbon backbone which could cause the polarity to cancel out, as is the case in the α -PVDF conformation.[44]

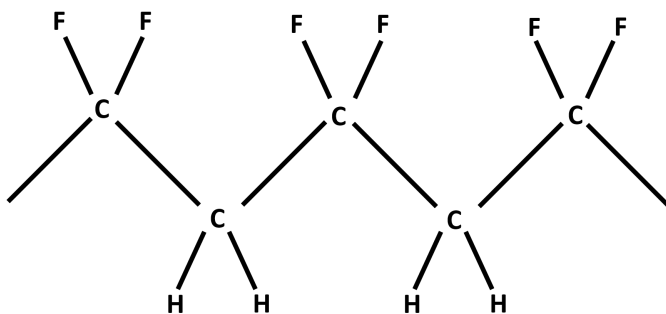


Figure 2.6: Diagram of polyvinylidene fluoride.

Before discussing the classifications of PEs, it is relevant to understand the relationship

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between ionic conductivity and temperature. Arrhenius dependency is a common model used to describe this relationship, however, PEs do not follow this model above their T_g . Instead, the Vogel-Tammann-Fulcher (VTF) model provides a better picture of PEs for those with a base polymer that has a T_g below normal operating temperatures of the eventual battery. The equation of the model is as follows,

$$\sigma = (\sigma_0/T^x)e^{(E_A/k_b(T-T_g))} \quad (2.2)$$

where the ionic conductivity, σ , depends on the operating temperature, T , and σ_0 , which "is a reference ionic conductivity value related to the frequency of events that can overcome an energy barrier E_A relative to the internal energy at that temperature by the Boltzmann number k_b and x is determined experimentally." [45] It is important to note that the VTF model only applies within temperatures 10-100 K above the polymer T_g . Deeper experimentation is necessary to determine the proper optimization of polymer to active material ratio in order to maximize ionic conductivity. The current work does not cover this area due to the most crucial factor being proper polymer viscosity at the potential loss of a higher ionic conductivity. However, it is overall important to understand that the ionic conductivity of the PE will vary with temperature fluctuations, something that is possible in a wearable, fiber battery.

It is important to distinguish between the classifications of PEs, which mostly relate to the mechanical properties of the electrolyte. There are four broad categories: dry solid polymer electrolytes (DSPEs), plasticized polymer electrolyte (PPEs), gel polymer electrolytes (GPEs), and composite polymer electrolytes (CPEs). The categories do contain some overlap in characteristics, both mechanical and electrochemical. Broadly speaking, each category is a different ratio between mechanical integrity and ionic conductivity. This trade-off is important for the success of the current

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work.

To begin, a DSPE is a PE that is prepared by complexing/dissolving ionic salts into a polymer host.[46] After dissolution, the polymer is cast into a film or membrane through normal plastic casting methods or through a hot press.[46] It is key that the polymer used is polar as the polar functional groups are what attract the ionic salts cations. DSPEs suffer from relatively low ionic conductivity at room temperature, anywhere from 10^{-9} to 10^{-4} S cm⁻¹. [47, 48, 49]

The next category of PEs is PPEs. These PEs involve introducing plasticizers or low molecular weight organic compounds such as ethylene carbonate or propylene carbonate.[50] These compounds reduce the crystallinity of the polymer allowing for an increased salt dissociation from the ionic salt, which further enhances ionic mobility in the overall PE. It is also important to note that the reduction in crystallinity lowers the T_g of the polymer. This then has the effect of improving the ionic conductivity at ambient temperatures. The ionic conductivity of PPEs are in the range of 10^{-4} to 10^{-3} S cm⁻¹ at room temperature. Thus, PPEs offer higher ionic conductivity at room temperature than DSPEs but at the cost of mechanical strength due to a more amorphous structure. Furthermore, certain plasticizers will increase the reactivity with metallic anodes thus lower the overall chemical stability of the battery.

The category of GPEs are growing in interest due to a helpful balance of mechanical integrity, electrochemical stability, and ionic conductivity. Similar to PPEs, GPEs use the polymer matrix to incorporate lots of liquid plasticizer or organic compounds to the point of swelling the polymer structure. The incorporation of liquid into the polymer allows an inherently more stable and safe electrolyte over common liquid electrolytes. Consequently, the increased use of liquid plasticizer/organic compounds increases the amorphous regions of the polymer, which allows for

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higher ionic conductivity. GPEs are very similar to PPEs in terms of ionic conductivity with slight improvements in electrochemical stability with the electrodes. At the same time, GPEs with the wrong polymer/liquid ratio can result in similarly poor electrochemical stability as liquid electrolytes as well as loss of mechanical integrity, which overall can defeat the purpose of using a PE. In brief, GPEs can be considered the boundary between PEs and liquid electrolytes.

Finally, CPEs offer a potential answer to the generally low ionic conductivity of PEs by incorporating inorganic nanoparticles. The types of nanoparticles range from inorganic oxides to ceramics. For one example, the introduction of alumina nanoparticles have been proven to improve not only the ionic conductivity but the mechanical strength as well.[51] The general effect of adding nanoparticles is an increased ionic conductivity, however, the increase is not the orders of magnitudes necessary to replicate the types of ionic conductivity offered by common liquid electrolytes. Furthermore, more research is needed to examine the exact mechanisms of ionic mobility in a CPE as well as how to properly distribute the nanoparticles in the polymer matrix.[52]

Given the various different categories of PEs, the current work will develop a GPE. (It should be noted there is some fluidity between the definitions introduced in the previous section, but for consistency purposes the PE developed in the current work will be referred to as a GPE.) The nature of the draw tower sets a very strict set of limitations/desirable attributes of the eventual GPE. As summarized in a literature review by Wu et. al., the important variables to consider are: ionic conductivity, mechanical strength, thermal/chemical stability, and solid electrode-electrolyte surface contact.[42] Based on the eventual goal of using this electrolyte in a fiber form factor, the mechanical strength and the surface contact properties will take priority at the cost of a potentially lower ionic conductivity in order to achieve the intended form-factor.

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To begin, the mechanical properties of the GPE will be chosen with the draw tower in mind. The polymer will be heated up in the range of 150-300. This means the glass transition temperature, the temperature at which the polymer rapidly transfers from a glassy state to a rubbery/viscous flow state T_g , plays an important role in controlling the way the polymer will flow on the draw tower. In addition, the melt temperature, T_m , must be considered. If the polymer experiences a temperature above its melting temperature, the behavior of its viscous flow cannot be accurately predicted. Another important feature of the mechanical properties, specifically at room temperature/operating temperature, necessary of a GPE is the ability to prevent either electrode from touching one another. The GPE removes the need of a separator. Therefore, it is vital that the GPE is indeed solid, as opposed to a viscous polymer-gel that would allow for the flow of electrodes, opening the door to a possible short.

The second most important property of the GPE for use in a fiber battery is the interfacial properties. The interfacial properties between the electrolyte and electrodes heavily influence the cycle life, coulombic efficiency, and voltage efficiency.[42] While not as effective as liquid electrolytes with inherent wetting properties, GPEs flexible properties allow for adequate surface contact with electrodes. This physical contact is key in reducing impedance caused in the electrical double layer. It is imperative that the GPE offers a stable electrochemical environment to ensure there is no ionic/electronic flux while not actively drawing energy from the battery. Furthermore, the mechanical stability of the interfaces must be tolerant of the expansion and contraction of the electrodes through multiple cycles. As the battery charges/discharges, the contact area can diminish causing an increased impedance, thus a poorer performing battery.

The mechanical properties of the GPE are key in developing a battery in fiber form, but

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most important to the electrochemical functionality of the battery is the ionic conductivity. As earlier discussed, ionic conductivity of GPEs are inherently lower than liquid counterparts. Therefore, it is crucial the GPE chosen is properly optimized (ratio of polymer to active material) to maximize ionic conductivity. In the case of the current work, the selected GPE is a PVDF base polymer, with zinc trifluoromethanesulfonate, also known as zinc triflate, and a mix of two organic compounds: propylene carbonate (PC) and ethylene carbonate (EC). This GPE is adapted from the work of Kumar and Sampath who studied the ionic conductivity in relation to the ratio of EC/PC to PVDF and zinc triflate.

The work done by Kumar and Sampath developed a GPE for a ZIB consisting of a zinc metal anode and a MnO_2 cathode.[53] Their work resulted in a GPE with a maximum ionic conductivity of $3.94 \times 10^{-3} \text{ S cm}^{-1}$. [53] As compared to the ionic conductivity of liquid electrolytes, KOH for example, found in Figure 2.3, this is still two magnitudes lower than liquid electrolytes. (But larger than the conductivity of common Li-ion electrolytes LiPF_6 in DEC, for example, has an ionic conductivity of $2.9 \times 10^{-3} \text{ S cm}^{-1}$. [45]) While this may be true, it is important to understand that this inherently lower ionic conductivity is necessary to allow for the proper mechanical properties to act as a separator between the electrodes in the fiber battery. Moreover, achieving ionic conductivity on the order of $10^{-3} \text{ S cm}^{-1}$ is no small feat. It is important to note that the highest ionic conductivity achieved involved a high PC/EC to polymer ratio, which has detrimental impacts to the mechanical integrity of the GPE.

Kumar and Sampath utilized electrochemical impedance spectroscopy (EIS) to determine the interfacial resistance as well as the interfacial stability between the GPE and Zn anode. The Nyquist plot revealed a "well-defined semicircle" which "suggests that zinc metal attains equilibrium

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with the zinc ions” of the GPE.[53] A typical Nyquist plot can be found in Figure 2.7. The ohmic resistance of an electrochemical cell is reflective by R_A in Figure 2.7; the charge transfer resistance is labeled R_{AB} . The ohmic resistance can be thought of as the bulk resistance of the electrolyte. Therefore, ohmic resistance heavily depends on the geometry of a battery; minimizing ohmic resistance requires a uniform thickness of electrolyte, or uniform distance between the entire surfaces of the electrode material. The charge transfer resistance can be thought of as the interfacial resistance between the electrolyte and the electrodes. Thus, electrochemical cells with charge transfer-limiting resistance are those with poor interfacial contact.

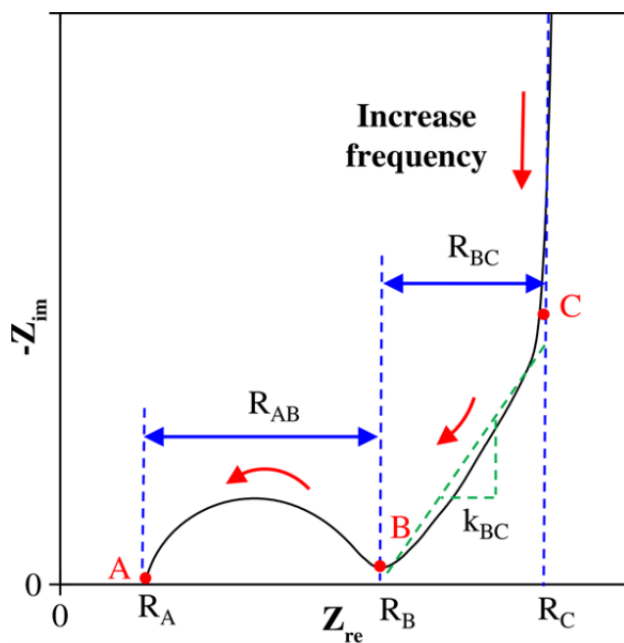


Figure 2.7: Typical Nyquist plot, adopted from [54].

For a deeper understanding of the Nyquist plot, a Randles circuit helps visualize the resistances involved in an electrochemical cell. Seen in Figure 2.8, the Randles circuit is a basic model displaying the behavior of resistances surrounding the interfacial contact between electrode and electrolyte. Moving from left to right, depicted as R_Ω , is the ohmic resistance. This is the

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resistance to current flow in the bulk electrolyte.[30] It is modeled as a simple resistor. Moving further left there are two paths: double-layer charging and faradaic current. The double-layer charging is simply represented as a capacitor; further specifics are unnecessary for this current work. The more noteworthy part of the two paths is the faradaic current, represented by R_f . This is the resistance involved in the electron-transfer occurring at the surface between the electrolyte and the electrode. The faradaic current can be described with the Butler-Volmer equation.

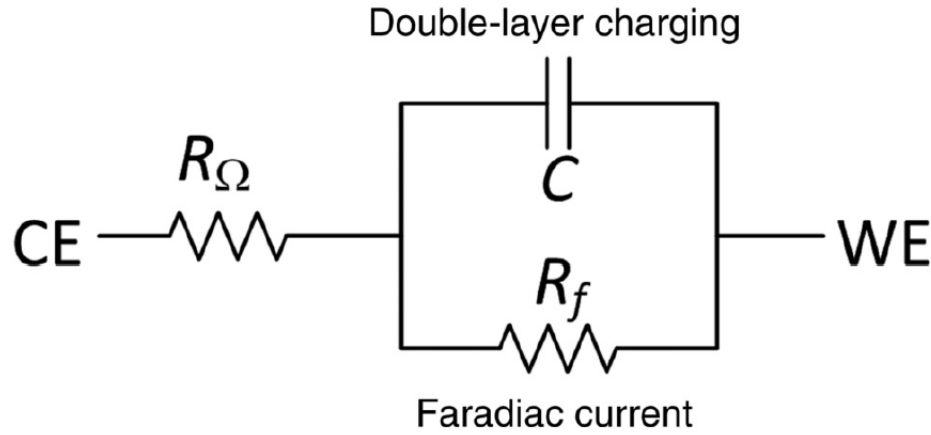


Figure 2.8: Randles circuit displaying the circuit equivalent of electrolyte/electrode resistances, adopted from [30].

The Butler-Volmer equation, seen below, describes the relationship between current density and charge transfer, where i is the current density, i_0 is the exchange current density, α_a is the anodic charge transfer coefficient, α_c is the cathodic charge transfer coefficient, F is Faraday's constant, η is the surface overpotential, R is the universal gas constant, and T is the temperature. This equation is mainly empirical with three parameters that are fitted to collected data: i_0 and the charge transfer coefficients (α_a and α_c).

$$i = i_a + i_c = i_0 \left[\frac{\exp((\alpha_a F \eta))}{RT} - \frac{\exp((- \alpha_c F \eta))}{RT} \right] \quad (2.3)$$

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Kumar and Sampath used the Butler-Volmer relationship to calculate the exchange current density of the Zn/Zn^{2+} to be $7.39 \mu\text{A cm}^{-2}$. The exchange current density, i_0 , offers an idea of the readiness of electrochemical reactions. Exchange current densities can range from several nA m^{-2} to hundreds of A m^{-2} . High exchange current densities mean the reaction readily occurs and allows for high current density. Low exchange current densities imply a sluggish reaction with limited current density possible, as is the case with this GPE.

In sum, the GPE developed by Kumar and Sampath resulted in a ZIB cell with a specific capacities of MnO_2 ranging from 37 mAh/g at higher C-rates (C/8) to 105 mAh/g at lower C-rates (C/60). The discharge curve provided in figure 2.9 shows a cell run at a C/8 rate, which cycled 65 times at a 60% capacity retention. It is important to note that the discharge does not result in any clear voltage plateaus and appears to discharge at a continually decreasing potential, implying a single-phase intercalation of species, whether Zn^{2+} or H^+ .

2.5 Fiber Batteries

Wearable technology is a growing research area with numerous different applications available. The need for on-board power is a necessity for these systems. There is much work on nanogenerators that convert any of temperature, kinetic motion, or photovoltaics into electricity for the wearable devices. However, without a dedicated energy storage vessel, i.e. a battery, power can not be guaranteed in all scenarios. Thus, the research area of fiber-form batteries is highly desirable. Important to distinguish, there is also the research field of fabric-form batteries, two-dimensional batteries on the scale of several cm^2 , that offer similar flexibility and sewability, however, the current work focuses on the fiber form as they offer the highest level of flexibility and compatibility with

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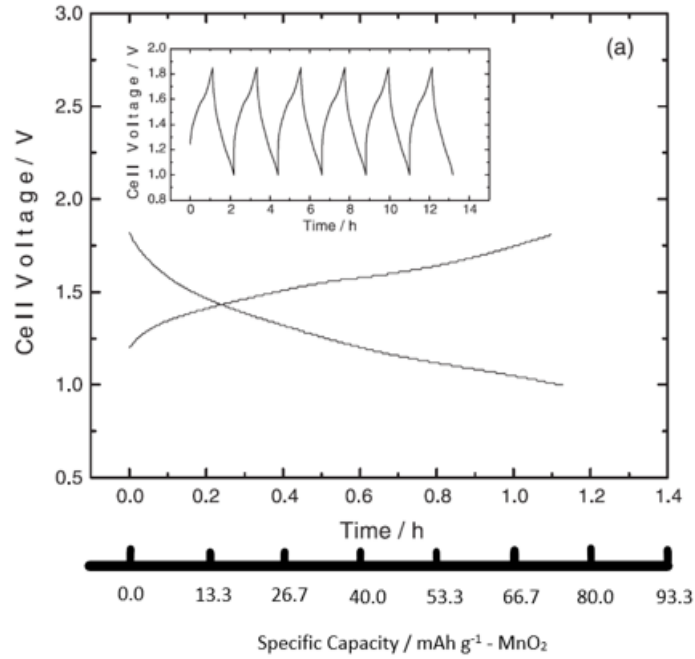


Figure 2.9: Discharge curve of Zn/GPE/MnO₂ cell operating at a current density of $200 \mu\text{A cm}^{-2}$, approximately $C/8$, with added x-axis of specific capacity of MnO₂, from the work of Kumar and Sampath.[53]

common fabrics used in most clothing.

What the current work refers to as fiber-shaped or fiber-form battery is a 1-D structure on the order of sub-1 millimeter to several millimeters thick in an elongated structure potentially several meters long. Challenges to this form-factor are numerous and non-trivial. Such challenges include: high internal resistance due to long lengths the current collectors take to deliver current, difficulty in separating the electrodes to prevent shorting, difficulty in tuning the bulk mechanical properties to enable interoperability with common fabric-weaving machines, and encapsulation issues in creating a consistently sized fiber of long lengths. Nevertheless, research is conducted on all fronts to attempt to mitigate the challenges presented by a fiber-shaped battery.

Fiber-shaped battery literature is widely varied with numerous different chemistries and

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Table 2.1: Example fiber batteries in the literature

Chemistry	Electrodes	Working Potential (V)	Battery Performance (mAh/g)	Structure	Reference
LIB	MnO ₂ /Li	1.5-4.3	218.3 @ 0.5 mA	Twisted	[56]
LIB	LCO/LTO	1.5-2.8	131 @ 1 C	Cable	[57]
LIB	LMO/LTO	1.5-3.3	138 @ 0.01 mA	Parallel	[58]
Na Battery	NaMnO ₂ /NaTi	0-1.6	46 @ 0.1 A/g	Parallel	[59]
ZIB	MnO ₂ /Zn	0.8-1.85	302.1 @ 60 mA/g	Parallel	[60]
ZIB	MnO ₂ /Zn	1.0-1.8	290 @ 0.1 A/g	Cable	[61]
ZIB	PANI/Zn	0.5-1.5	106 @ 0.5 A/g	Cable	[62]
Li-Air	CNT-LDPE-LiI/Li	2.5-3.5	1000 @ 2 A/g	Cable	[63]
Li-Air	CNT/LiSi	2.1-4.0	500 @ 0.1 mA	Coaxial	[64]
Zn-Air	Fe-N-C/Zn	1.2-2.0	800 @ 5 mA/cm ²	Coaxial	[65]

architectures/geometries being studied. Mo et al. compiled a large breadth of literature on fiber-shaped batteries.[55] The current work reviewed over 40 different fiber-shaped batteries from the past decade. The chemistries studied range from more developed lithium-ion battery (LIB) or zinc-ion battery (ZIB) chemistries, to more novel, developing chemistries, such as lithium-sulfur (Li-S) batteries, sodium-based batteries (SBs), metal-organic frameworks (MOFs) or metal-air batteries (lithium-air (LAB) or zinc-air (ZAB)). Some examples of such fiber batteries are summarized in Table 2.1 (see the work by Mo et. al. for a more complete view of previously developed fiber batteries [55]). Each of these fiber batteries are still in preliminary experimentation stages and do not yet offer an operational functionality at this time.

In addition, to varying chemistry makeup, the compilation honed in on three particularly reoccurring architectures/configurations of the fiber. These three can be found in Figure 2.10. The first two configurations (parallel and twisted) have an advantage in manufacturability, whereas the coaxial has an advantage in energy and power density, in theory, due to the highest active material to overall volume ratio. These advantages hold true for any individual battery chemistry. In practice, coaxial is not a guarantee of improved performance, in terms of battery performance (voltage and energy density).

Data compiled from the literature review by Mo et al. can be found in Figure 2.11. It is

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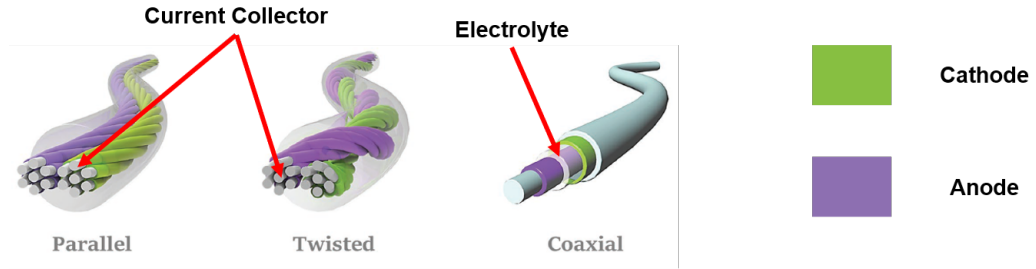


Figure 2.10: Representation of most common fiber-battery architectures, adopted from [55].

clear from this figure that coaxial does indeed tend to have a much higher energy density than the other two common configurations. Twisted configurations also trend higher than parallel. However, this is not universal across the literature. It can be seen that there are several LIB and AZB batteries with higher energy densities in the parallel configuration as opposed to the coaxial.

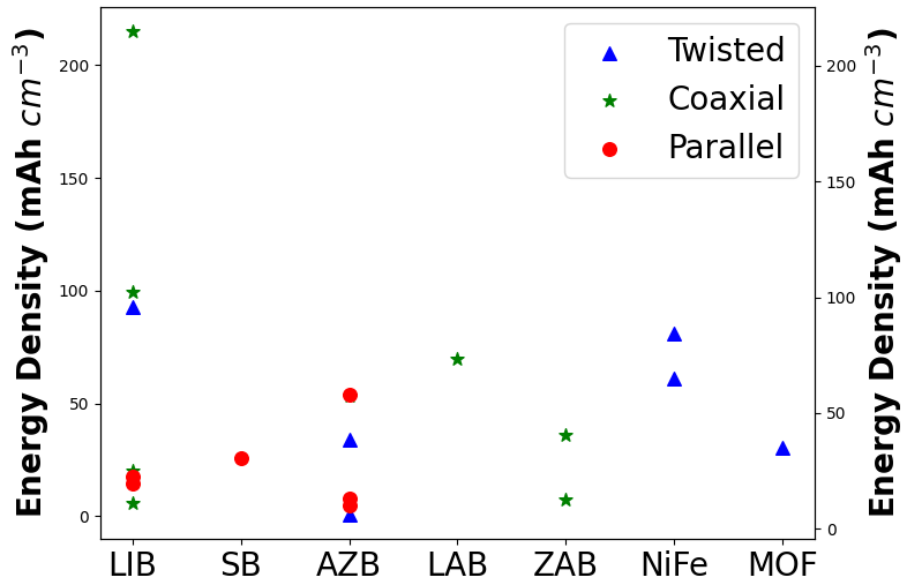


Figure 2.11: Energy density comparison of numerous different fiber-batteries from the literature, sorted by battery chemistry, adopted from [55].

Beyond the chemistry and structures of the fiber batteries developed, it is key to focus

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on the processes used to manufacture the overall fiber structure. Many fiber batteries involve one metal wire as the anode, which also acts as the current collector. A coated carbon nanotube fiber (CNT fiber) is the most common cathode setup. The coating material is the active material with the CNT fiber acting as a structural base as well as the current collector. Some of the methods used for coating consist of electrochemical deposition, chemical vapor deposition (CVD), dip-coating, and blade-coating. Each method offers some advantages and disadvantages. Generally speaking, without industrial machinery, each method of coating is a batch process, meaning it cannot be done in a continuous fashion. Dip-coating offers a high amount of active material, but at the cost of limited surface adhesion to the substrate. This can cause interfacial resistance that will cause the current flow to suffer. CVD becomes extremely expensive if needed for meters of fiber. Electrodeposition is a facile, cheap method for depositing metal-oxides but also suffers from being a batch process.

Finally, it is crucial to understand that the overall size (specifically diameter) of the fiber batteries vary from sub-millimeter to several millimeters. Seemingly insignificant, this size difference can drastically change the feasibility of sewing the fiber directly into cloth, as opposed to simply integrating a fiber into a preexisting cloth. Creating a fiber battery sub-millimeter allows for much more flexibility in the sewing process as well as the eventual wear of any clothes developed from the fibers. Fibers on the scale of 1-5 mm are possible to sew into clothes, however, result in a much more rigid product that offers very little flexibility and can mechanically stress the active battery materials more-so than a sub-millimeter fiber. This is important to note as there is a general trend in the literature that the larger the fiber, the greater the energy density. Thus, a fiber that is sewable tends to exhibit a lower energy density than some of the larger, almost cable-like, fibers.

The current work seeks to develop a sub-millimeter fiber battery. One early example

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from the literature reported a cable-like battery (several millimeters thick). Wang et. al. developed a cable-like rechargeable ZIB based on a MnO_2 electrodeposited CNT fiber ($\text{MnO}_2@\text{CNT}$) as a cathode and zinc wire as anode.[61] The key differences in the current work and the work Wang et. al. is the electrolyte and the process of manufacture. Wang et. al. used a chronoamperometry method of electrodeposition to deposit MnO_2 onto a CNT fiber. The electrolyte used for electrodeposition was a 0.1 M aqueous $\text{Mn}(\text{NO}_3)_2$ (manganese nitrate) solution. X-ray diffraction (XRD) patterns were measured to determine the crystal structure of the deposited MnO_2 . This resulted in peaks indicating Akhtenskite ($\epsilon\text{-MnO}_2$).

Wang et. al. began the study with a variety of aqueous electrolytes (2 M ZnCl_2 , 2 M ZnCl_2 - 0.2 M MnCl_2 , and 2 M ZnCl_2 - 0.4 M MnCl_2). These electrolytes required a separator, so filter paper was soaked in the electrolyte and separated the electrode wires. The next step in the work was switching to a GPE. Wang et. al. used poly(vinyl alcohol) as the base polymer and experimented with different salts (lithium chloride, manganese chloride, zinc chloride, and zinc triflate). It is important to note that the GPEs used in the work done by Wang et. al. was close to the border between aqueous electrolyte and GPE, meaning the mechanical integrity is essentially non-existent, meaning extremely low viscosity to the point that without a separator the electrodes would touch and short. The GPE was essentially a viscous fluid that would not prevent the electrodes from touching and shorting, thus a separator was necessary, which adds to higher impedance and lower overall battery performance.

The overall structure of the cable involved placing the two electrodes with the electrolyte-dipped separator into shrink wire then heated up to shrink the wire to a cable format. The end result can be found in Figure 2.12. The best functioning electrolyte incorporated MnCl_2 and resulted in a specific capacity of just over 300 mAh g^{-1} , very close to the theoretical 308 mAh g^{-1} .

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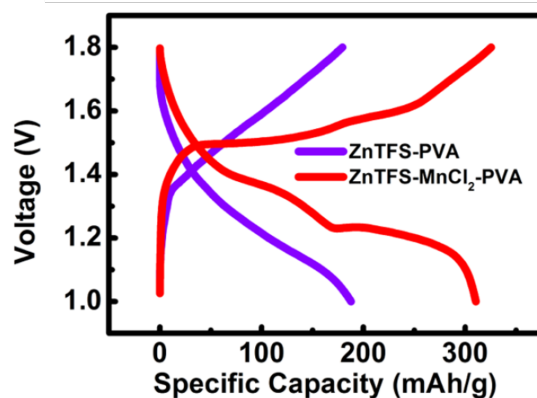


Figure 2.12: Discharge curves of cable battery by Wang et. al. comparing two different GPEs, adopted from [61].

The current work will utilize the same zinc metal wire as the anode and electrodeposited MnO_2 @CNT as cathode just as Wang et. al. used. However, as previously mentioned in discussing PEs, the current work will use a GPE as developed by Kumar and Sampath.[53] Thus our approach is novel in two ways: the pairing of electrodes and PE used and the method of manufacture. The GPE produced in the Kumar work[53] offers high mechanical strength that prevents the electrodes from touching and shorting, which in turn avoids the need for a separator. The work by Kumar and Sampath[53] was simply on the GPE, not a fiber battery. Their work used a sheet of Zn-metal and electrolytic manganese dioxide (EMD) coated onto a Ni-mesh. The method by which Wang et. al. produced their cable batteries was all by hand and results in inconsistently sized cable, which could lead to a bloated cable. The current work seeks to produce a consistently sized fiber with little to no wasted space, thus a thermal-draw tower will be utilized.

2.6 Vertical Thermal Drawing of Polymers

Thermal drawing of fibers is a cheap, scalable process that allows for hundreds of meters of fiber to be drawn from a polymer preform (dimensions roughly 12x1x0.5 inches). While numerous different methods are available to form polymer fibers, the draw tower is continuous, as opposed to more batch-process/discrete methods such as dip-coating or physical/chemical vapor deposition.[66, 67, 68]

Thermal drawing of polymers can be broken down into two broad steps: preform creation and vertical pultrusion through a furnace. The preform is crafted based on the requirements/design of the intended fiber. For an example, a preform designed for a fiber filled with LED devices can be found in Figure 2.13a. The preform can be made of a variety of polymers, such as polycarbonate (PC), polyethylene (PE), cyclic olefin copolymer (COC), poly(vinyl chloride) (PVC), or polyethylenimine (PEI), to name just a few.

The preform is made up of 2-4 smaller layers of polymer (1-10mm thick). Each layer can be milled down to create the desired pockets or slits. As can be seen in Figure 2.13a, both the top and bottom layers had small crevices milled down the middle, which serves as a space for the wires to feed into. The layer labeled '3' had many small pockets (roughly 300x300 μ m) drilled in order to place LEDs. Once each layer is properly milled, the layers are stacked and then consolidated using a hydraulic hot press. This is done in a sequential order, as in 3 gets pressed to 4, then 2 gets added on, and finally 1 is added to all 3. Teflon strips are added to the crevices to maintain the proper geometry. Each press involves an aluminum jig that holds the layers in place to ensure proper alignment. The temperature and time of the press is dependent on the materials being used, the number of layers, and the thickness of the layers. As an example, layers 3 and 4 of the preform created in Figure 2.13a

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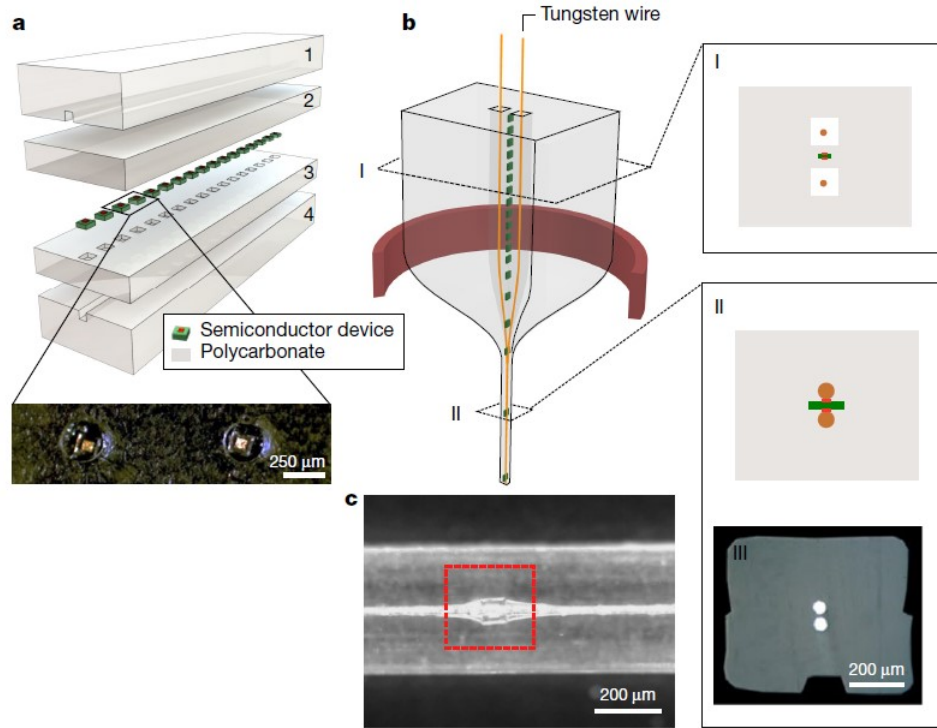


Figure 2.13: Fiber Drawing Figure a) Preform fabrication process b) Diagram of the pultrusion through furnace process c) optical micrograph of drawn fiber with photodiode, adopted from [55].

was pressed at 175 for 5 min.

The metric of success for this step is a visual assessment as well as measurements of the various dimensions. It is important the preform is pressed consistently, ensuring the thickness is consistent across the length of the preform. Minor variances in the preform can cause statistically significant variance on the final fiber. Visual inspection of the preform involves verification of layer alignment, air pocket presence (undesirable), and maintenance of milled geometries.

Once the preform is produced, any wires that belong in the final fiber are carefully fed into the crevices that were milled into the preform. The wires feed all the way through the length of the preform. At the end, the wires are tied together, and, if necessary, extra wires are added to use as a hold to pull the preform down through the furnace. Finally, the preform with spools of wire are

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placed on a jig and screwed onto the top of the draw tower.

The beginning of the second phase, vertical pultrusion, begins by attaching a weight to the tied wires at the bottom of the preform. The weight is required to begin the pulling of the polymer through the furnace until it reaches a motorized pulling mechanism. The preform is slowly lowered into the furnace by the top jig. The speed it is lowered at is called the feed speed, v_{feed} . This speed is typically $1\text{-}5 \text{ mm min}^{-1}$. The pulling mechanism pulls the fiber from the furnace at what is called the draw speed, v_{draw} (typically $1\text{-}5 \text{ m min}^{-1}$).

The initial polymer that is drawn through the furnace and pulled by a weight is called bait-off. The bait-off is distinctive in that it appears severely distorted and morphed. The beginning of the preform does not undergo a proper heating/cooling cycle, so it does not behave similarly to the rest of the fiber. Thus, the first 1-5 m of “fiber” is of no use and is simply cut off.

One of the most crucial variables of the draw tower: the draw-down ratio. This ratio, represented by β , is the ratio of the preform dimension, d_{preform} , to the fiber dimension, d_{fiber} . This applies to both the width and height of the cross section. A more practical way of representing the draw-down ratio is a square ratio of the draw and feed speed:

$$\beta = \sqrt{v_{\text{draw}}/v_{\text{feed}}} \quad (2.4)$$

The draw-down ratio is the main controller in adjusting the final fiber dimensions. Thus, the draw speed and feed speed can both be adjusted to create the desired dimensions of the final fiber.

While the draw-down ratio is crucial in forming the proper sized fiber, the temperatures of the furnace are crucial to ensure proper mechanical integrity of the final fiber. The furnace has three temperature zones. The top and bottom zones are set to temperatures significantly lower than the

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middle zone to ramp up and down the temperature of the material in a smooth transition, rather than shocking the polymer to extreme temperature fluctuations. The middle zone temperature needs to be well above the preform polymer's T_g . Above the T_g , the polymer transitions through a rubbery state and then onto a viscous flow. It is this viscous flow that allows for a moldable polymer that gets pulled and stretched out moving through the furnace. The temperatures in the furnace pose little threat to the mechanical integrity of any metal wires passing through.

As an example, the fiber draw in Figure 2.13 had a preform made of PC, which has a T_g of 150. The furnace's temperature zones were set at 150, 270, and 110. In this specific example there was no concern about the mechanical integrity of the wires, which were copper and tungsten.

2.7 Draw Tower for Fiber Battery

As opposed to the drawn fiber in Figure 2.13, which creates a fiber with embedded LEDs, the fiber developed in the current work is a fiber battery. While a significantly different purpose, the overall draw tower procedure is very similar. A literature review article by Loke et.al. provides a good overview of the current state of thermally drawn fibers. The work breaks down fibers by the number of materials comprising them and the way the fibers are fabricated. The fiber battery falls into the "4 or more" materials category: the polymer preform material, the cathode, the anode, and the electrolyte (the cathode can be considered two materials: carbon nanotube fiber and MnO_2). The other useful breakdown in the work by Loke et. al. breaks down fibers into fiber fabrication methods. The fiber battery being developed in the current work can be described as "selective material flow," meaning all of the material does not flow moving through the furnace [69]. Of the active fiber battery materials, only the electrolyte will flow. The electrodes are wires being continuously fed into the

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preform/furnace.

Rather than 4 layers of preform, the battery fiber will only involve two. A computer aided design (CAD) model can be found in Figure 2.14. The bottom layer will have two crevices: a small crevice for the anode (zinc wire) to sit in and a larger slit to hold the gel-polymer electrolyte. The top layer will simply have only one crevice for the cathode ($\text{MnO}_2\text{@CNT}$). After the proper milling on each layer, the layers will be pressed together in the hydraulic hot press.

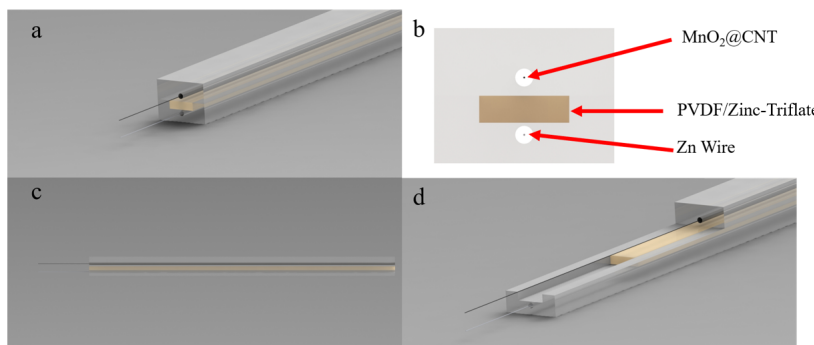


Figure 2.14: a) CAD model of fiber battery layout b) Cross-section view of fiber battery c) Side view of fiber battery d) Exploded view of the five components of the eventual fiber battery.

The electrolyte will be placed in the bottom layer of the preform and take part in the pressing between the top and bottom preform layers. Once the preform is created, the wires will be initially fed through the crevices drilled for the electrodes. As mentioned, due to the bait-off portion of the draw tower procedure, cheap copper wire is tied to the electrodes so as not to waste the CNT fibers and zinc metal during the first few meters of drawing. Once the preform is on the tower, the furnace will be set to the proper temperatures and the preform begins the pultrusion stage.

During the pultrusion stage, a set draw-down ratio, β , determines the size of the final fiber. This β value will be a difficult variable to optimize as it is a balancing act between the size and the mechanical integrity of the fiber. Drawing too fast means the polymer is in the furnace for less time,

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which could prevent either the preform polymer and/or the GPE from improperly flowing. Drawing too slow could cause potential overheating of the polymers involved, which could cause either boiling the polymers or raise the temperature of the polymer to a temperature where it becomes difficult to predict the viscoelastic properties.

2.7.1 Challenges

The challenges with the draw tower lie within the mechanical properties of the polymers involved. Rheological property matching, temperature, and draw down ratio are the three main components that affect the final fiber product.

Rheological properties of the polymers involved in the preform are the primary variables in adjusting the performance of the drawing process. Specific to the fiber battery, there are two polymers involved: the overall preform structure polymer and the polymer-gel electrolyte. The goal in selecting a proper preform structure polymer is to try to obtain similar rheological properties at the temperatures experienced in the furnace. If the preform material flows in a similar fashion with the electrolyte, there is a lower probability the two polymers mix with each other. Mixing of the two different polymers could result in the diffusion of electrolyte material that could reduce the ionic conductivity along a specific length of fiber.

The only option to adjusting the preform structure polymer is to select a different polymer. The preform polymer comes from large sheets of any given polymer. Thus, chemical adjustments to the polymer itself is not within the realm of possibility. If one polymer is not flowing properly with the electrolyte, the solution is to switch polymers. As for the GPE, the rheological properties are easier to adjust chemically. As previously mentioned, the electrolyte is a mix of PVDF, propylene carbonate, ethylene carbonate, and zinc triflate. Differing amounts of PVDF and propylene carbonate/ethylene

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carbonate can be tested to acquire the proper rheological properties that will flow in coordination with the preform structure polymer.

In the end, no matter the eventual preform structure polymer, the electrolyte will be less viscous. Thus, a preform structure polymer with a low T_g will result in the best probability of proper fiber drawing due to the lower working temperature. A polymer with a high T_g would require a higher furnace temperature and cause the GPE to behave closer to a liquid than a viscous-flowing fluid. A liquid-like flow can result in several issues, such as unequal distribution of electrolyte, air bubbles, and leakage.

Temperature is a crucial variable that is a secondary to the given rheological properties of the polymers. Critical to the temperature zones is the proper warming and cooling stages, done by the top and bottom zones of the furnace. Of the two, the cooling stage is more critical in preventing total failure of the fiber. Thermal shock of the polymer transitioning from temperatures above 200 back down to room temperature can result in cracks that could potentially snap the entire fiber (the wires would maintain its integrity). So, the bottom zone temperature is critical in slowing the decrease in temperature to acclimate the fiber to room temperature.

The other important aspect of the furnace temperature is choosing a proper middle zone temperature. Too low of a temperature could result in a snapping of the fiber due to the polymer remaining in a plastic state. Too high of a temperature could result in a very low viscosity flow, which becomes more difficult to control. The proper working temperature should be such that the polymer viscously flows in a predictable manner. The overarching regions of temperature are summarized in Figure 2.15.[70] The furnace must heat the polymer beyond the T_g to a viscous flow. However, it is imperative to remain below the melting temperature (T_m), if one exists, as temperatures beyond the

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T_m will result in unpredictable behavior of the polymers involved.

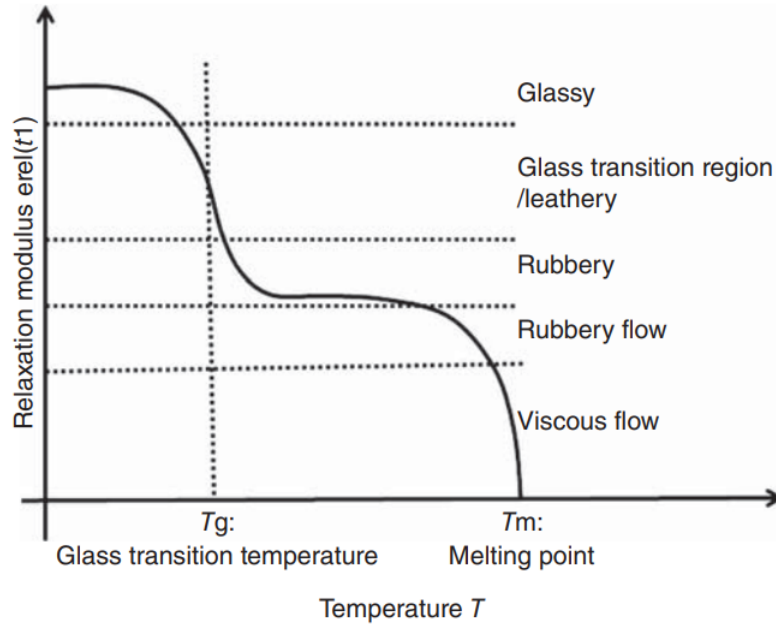


Figure 2.15: Variation of relaxation modulus with temperature after a given time t , adopted from [55].

Finally, the draw-down ratio is crucial to entire process. This ratio effects the amount of time the polymer is heated up in the furnace and how quickly it cools down. If the draw speed is too fast, the fiber can snap. If the feed speed is too slow, the polymer could be heated to a point where the polymer will begin morphing into distorted shapes. The draw-down ratio also impacts the overall dimensions of the final fiber. The higher the draw speed, the smaller the fiber will be. It takes empirical testing to determine the proper mechanical properties of the final fiber to determine whether the fiber has enough flex, or any other desired property.

Much of these three variables (rheological tuning/polymer selection, temperature, and draw-down ratio) are determined through empirical methods. The preform structure materials all have lots of draw data that can be analyzed for the mechanical strength, temperatures experienced,

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and flow properties. There is a lot of trial and error experiments as the draw tower is still in its relative infancy of scientific literature.

One helpful model of predictability is the William-Landel-Ferry (WLF) equation, found below,

$$\log\left(\frac{\eta}{\eta_g}\right) = -\frac{17.44(T - T_g)}{(51.6 + (T - T_g))} - \log\left(\frac{T_g \rho_g}{T \rho}\right) \quad (2.5)$$

where η_g and ρ_g is the polymer's viscosity and density, respectively, at T_g . [71] If the temperature of the furnace is within 100 of the polymer's T_g , the WLF equation can be used to predict the viscosity of any given polymer at any temperature. This equation is useful in predicting how the two polymers (the preform structure polymer and the electrolyte) will be flowing at any given temperature. It will allow for a more focused set of constraints to hone in on the furnace temperature zones. Of course, it is important to note that the WLF equation is based on empirical values, and the viscosity and density of the polymer at its T_g need to be known.

Overall, the draw tower offers a cheap and scalable method of producing polymer fibers. For the fiber battery, the biggest challenge is creating a polymer-gel electrolyte that has rheological properties that can properly flow through the furnace inside the preform. Most of the work on the electrolyte will be empirical data collection as the addition of the two solvents (propylene carbonate and ethylene carbonate) to PVDF may introduce minor intricacies that can greatly vary the behavior of the polymer.

Chapter 3

Experimental Section

3.1 Electrodeposition of MnO_2 for Cathode

The first step in experimentation was the electrodeposition of MnO_2 using a chronoamperometry method. This was conducted in a similar fashion as the work done by Wang et. al.[61] but with different reference, working, and counter electrodes. The setup can be found in Figure 3.1. The counter electrode is a nickel mesh; the reference electrode is silver-silver chloride; and the working electrode is a CNT fiber (used both 50 μm and 100 μm) from DexMat. Of note, initial experiments replaced the working electrode with nickel mesh to ensure proper deposition prior to using the more expensive CNT fibers.

The electrolyte solution was composed of 0.1 M $\text{Mn}(\text{NO}_3)_2$, bought from Sigma Aldrich, in 100 mL of deionized water. Electrodeposition was conducted in a chronoamperometry method for 15 minutes at 1.0 V. This resulted in a CNT fiber with MnO_2 electrodeposited layer, referred to as $\text{MnO}_2 @ \text{CNT}$.

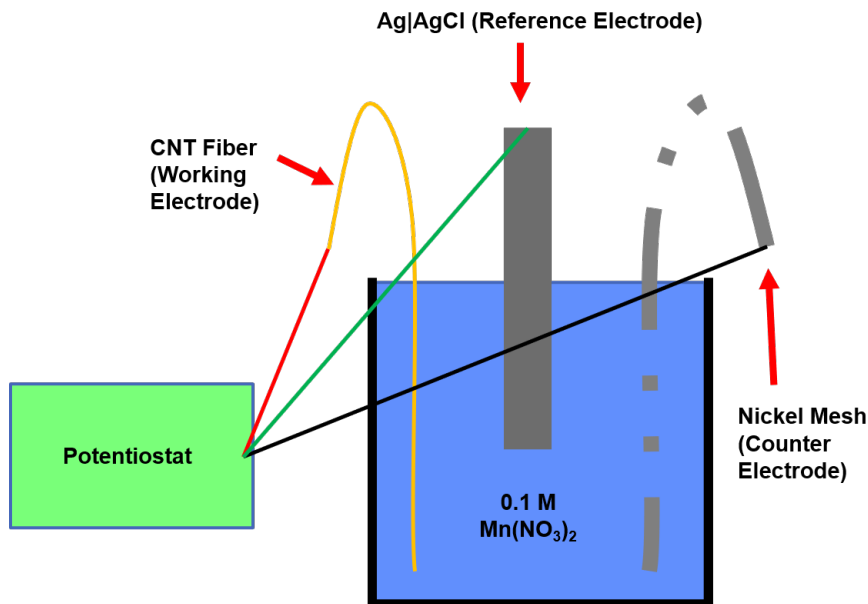


Figure 3.1: Electrodeposition setup for deposition of MnO_2 .

3.2 Aqueous-Electrolyte Cell Fabrication

After electrodeposition, verification of MnO_2 was conducted by means of a aqueous-electrolyte, primary cell. This involved the $\text{MnO}_2@\text{CNT}$ as cathode, zinc sheet metal as anode, and an aqueous, 2 M ZnCl_2 electrolyte. The zinc sheet metal was roughly 1 in². The aqueous electrolyte was produced from hand stirring 2.726 g in 10 mL of deionized water. This cell can be seen in Figure 3.2. Due to the nature of this setup, this cell only cycled once due to the lack of any pressure on the cathode to prevent expansion. However, this resulted in a nominal voltage plateau around 1.4 V, which is a good indication that MnO_2 was properly deposited onto the CNT fiber.

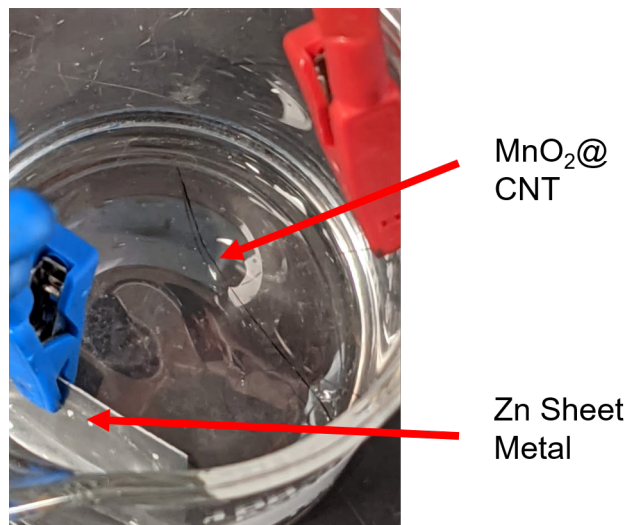


Figure 3.2: Aqueous zinc-ion battery with $\text{MnO}_2@\text{CNT}$ as cathode and zinc sheet metal as anode.

3.3 Development of PVDF Gel Polymer Electrolyte

The crux of this work revolves around the gel polymer electrolyte (GPE). Preparation of the GPE is a balancing act of mechanical integrity and ionic conductivity. GPEs with low ionic conductivity will have high mechanical integrity and vice versa. Originally, the GPE was to be based on the work of Wang et. al. who used poly(vinyl alcohol) as the base polymer combined with ZnCl_2 and LiCl_2 . However, it was quickly realized that there was not enough mechanical integrity to prevent electrodes from touching. Therefore, the GPE developed was based off a PVDF-based electrolyte developed by Kumar and Sampath.[53] The components of this GPE is PVDF (Kynar HSV 1810), ethylene carbonate (EC), propylene carbonate (PC), and zinc trifluoromethanesulfonate (zinc triflate) (the latter three purchased from Sigma Aldrich).

To vary the rheological properties, Kumar and Sampath[53] held the amount of zinc triflate and PVDF constant. EC and PC is always at a 1:1 ratio, however, the ratio between the solvents and the PVDF ranged from 1:1 up to 6:1. Higher ratios result in more liquid electrolyte; lower ratios

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results in more solid electrolytes. The current work repeated the work of Kumar and Sampath[53] in testing the various ratios. The mixing process began with the solvents: EC and PC. These are mixed on a hot plate at 70 at a 1:1 ratio, using 1.5 g of each (this was the eventual ratio chosen, but ranged from 0.5-3.0 g of each solvent). After 5 minutes of stirring, 0.4 g of zinc triflate is added. This solution is stirred until no zinc triflate particles are visible, typically 10-15 minutes of stirring. Next, 1.0 g PVDF is slowly added to the still stirring mixture. Overall, the ratio of EC:PC:PVDF:Zinc triflate is 1.5:1.5:1:0.4. This mixture is stirred for 20 minutes, or longer if PVDF powder is still visible. After 20 minutes, the temperature is slowly brought up to 120. Somewhere between 100-110 the mixture will become too viscous for the magnetic stirrer to work, therefore, the stir bar must be removed. Once the stir bar is removed, the mixture is heated further to 130. After holding at 130 for 5 minutes, the temperature is quickly ramped up to 150 and held at that temperature until the mixture is a viscous fluid. This viscous mixture is then quickly transferred out of the beaker. Of note, the mixture very rapidly solidifies into nonadjustable shapes, thus speed of transfer is crucial. If solidified too soon, the GPE can be reheated to 150. For initial experiments, the mixture is transferred to the lab counter and hand pressed with a steel platen to flatten the gel, resulting in a film as seen in Figure 3.3. The films' thicknesses range from 400 to 1000 microns thick.

For later experiments, those involving the draw, the mixture is transferred into a 3-D printed plastic mold to give the electrolyte the proper format for the draw tower, as shown in Figure 3.4. This mold shapes the GPE into a 5x5 mm block of polymer. As will be seen, the polymer must be thicker than the desired electrolyte thickness due to the draw-down ratio of the thermal draw tower.

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Figure 3.3: Gel polymer electrolyte hand pressed for lab-scale prototypes.

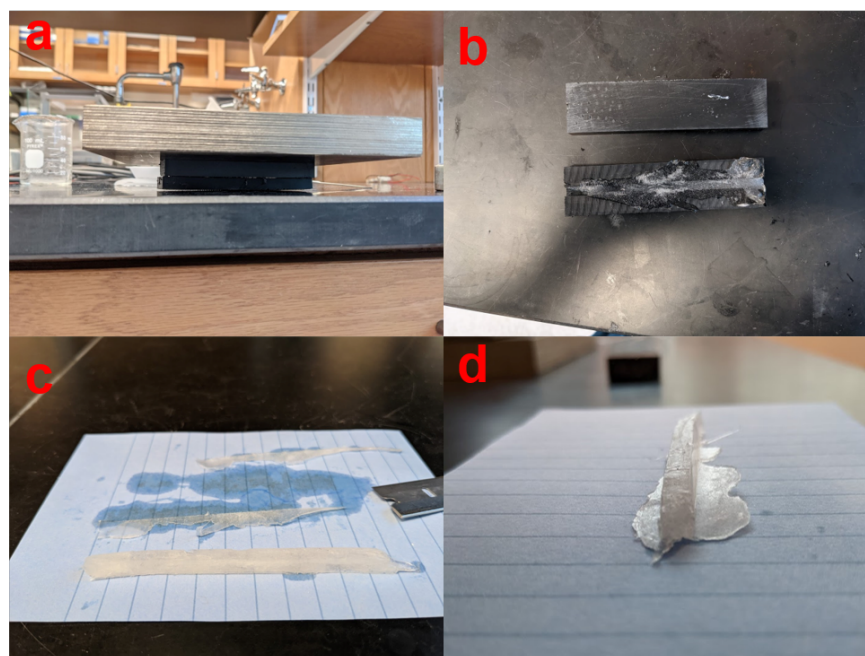


Figure 3.4: Gel polymer electrolyte mold: a) 3D printed mold with platen on top to properly form the GPE b) Image of resulting GPE c) Side view of finished GPE d) Longitudinal view of GPE.

3.4 Tabletop Prototype Cells with Gel Polymer Electrolyte

Prior to running draw tower experiments with the GPE, tabletop prototypes were produced using hand pressed GPE films with the MnO_2 @CNT cathode and Zn-wire anode. This battery can be found in Figure 3.5. The GPE is easily cut into long strips using a razor. The exact width of the GPE is not as important as the thickness, which if inconsistent can have an adverse impact on the electrochemical performance of the battery. Once cut into proper strips, the Zn-wire is placed on the bottom glass slide. The GPE film is then placed over the Zn-wire. Finally, the MnO_2 @CNT cathode is placed on top of the GPE film and then covered with another glass slide. To provide some pressure on the battery, binder clips shut the two glass slides together.

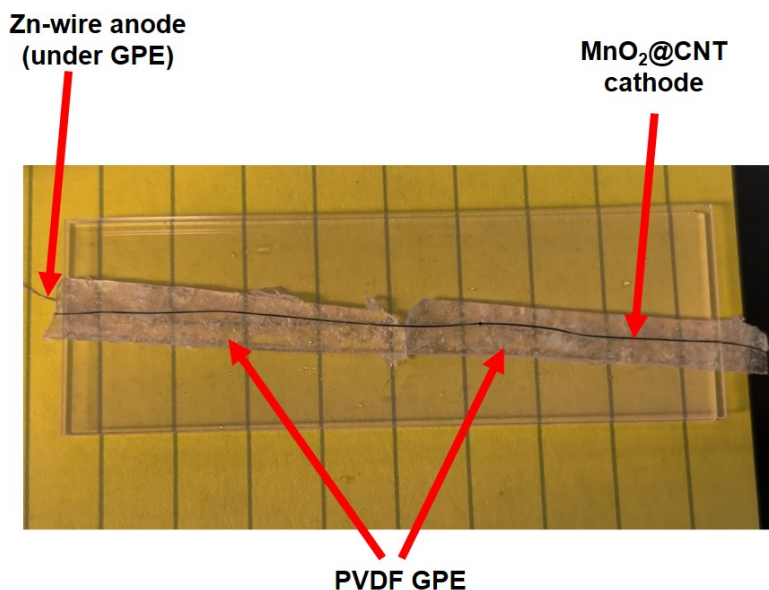


Figure 3.5: Full cell composed with MnO_2 @CNT cathode, Zn-wire anode, and PVDF GPE.

Once the cell was fully formed, it was connected to an Arbin battery cycler. Preliminary tests involved testing the batteries' open-circuit voltage (OCV) for long periods of time to determine the stability of the electrodes and electrolyte. Also on the Arbin, the batteries were cycled at various

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currents: from 1-50 μ A.

In addition to battery cycling tests, electrochemical impedance spectroscopy (EIS) was utilized to determine the internal/interfacial resistance of the GPE. EIS was conducted by simply hooking the fully formed battery up to the Biologic machine.

3.5 Draw Tower Experiments

The eventual goal of the current work is to draw the fiber battery through a thermal draw tower. In the current work, the preform used only involved the gel polymer electrolyte. The preform material used was cyclic olefin copolymer (COC). The preform was made using a 1"x1/2"x12" piece of COC with a 5x5mm channel milled down the middle of it combined with a 1"x3/16"x12" piece of COC by means of a hydraulic heat press. To prevent the channel from caving in during the press, a 5x5mm piece of Teflon was inserted as a place holder that could withstand the heat of the press.

Once pressed, the piece of Teflon was removed so that the gel polymer electrolyte could be inserted. The final preform utilized in this experiment can be found in Figure 3.6. The end of the preform shown in Figure 3.6c is the end clamped onto the top of the draw tower with the other end being the end inserted into the furnace. The channel for the gel polymer electrolyte ends 1 inch from the end first inserted into the furnace. The reasoning behind this is simply a safety measure to ensure the electrolyte does not flow/spill down from the draw tower in the case it flows more than the COC preform does.

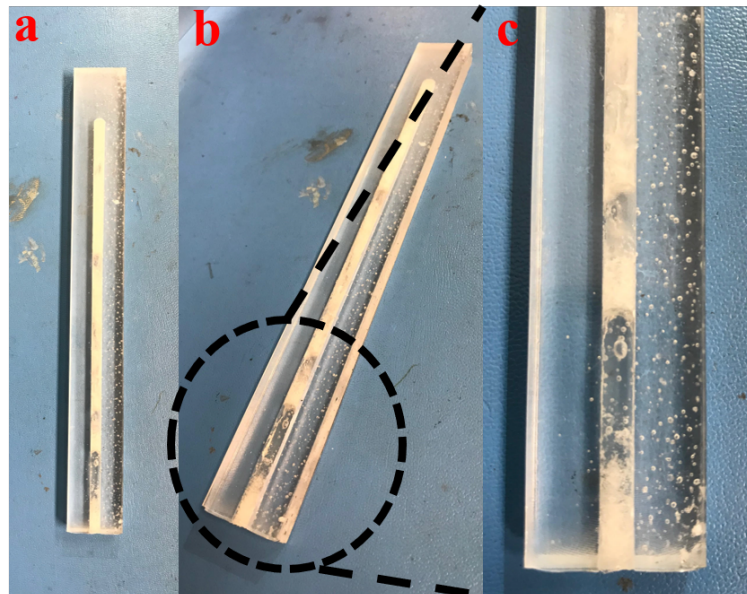


Figure 3.6: Images of preform used for draw tower experiment; a) birds-eye view b) view at an angle c) zoomed in on preform end.

Chapter 4

Results and Discussion

4.1 Electrodeposited MnO_2

Scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), and a simple electrochemical cell test was used to verify the chronoamperometric method of electrodeposition was properly coating the CNT fiber. The SEM images on nickel mesh can be found in Figure 4.1. These images offer an up close view of the deposited MnO_2 .

To further verify that these structures are indeed MnO_2 , EDS was used to determine the chemical composition of the deposited material. Spectra of the sample were taken at 9 various points on the sample. One example spectra is found in Figure 4.2 as well as various images of the sample examined. Each spectra clearly showed an approximate atomic percentage ratio of O:Mn of 2:1. Further, heat maps of the overall layout of Mn and O suggest fairly uniform coatings throughout the entire sample.

For one final verification test of the electrodeposition, a simple electrochemical cell (seen in Figure 3.2) was formed using the electrodeposited MnO_2 and Zn sheet metal in a ZnCl_2 aqueous

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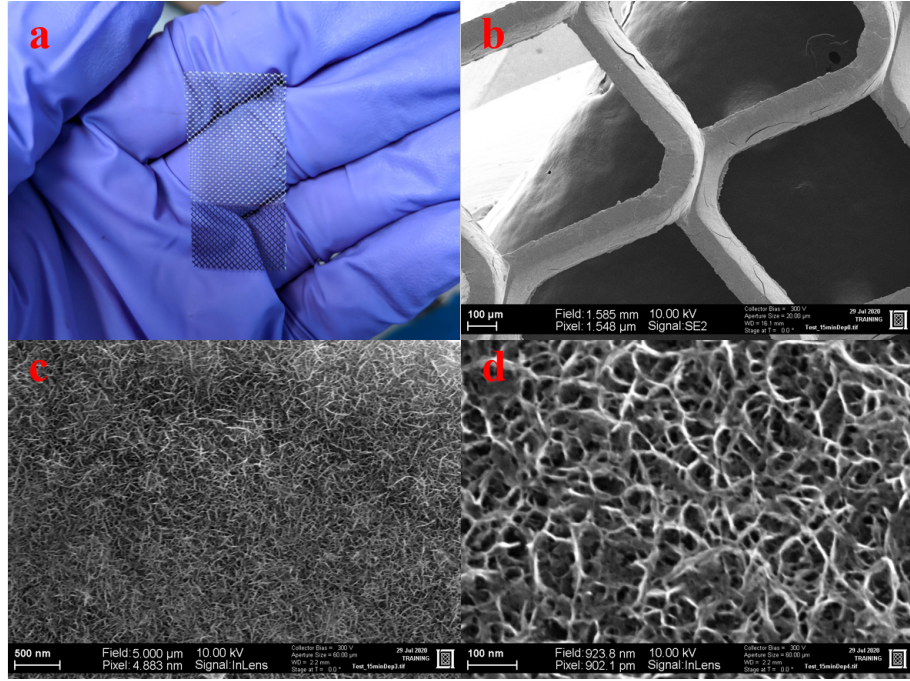


Figure 4.1: SEM images of electrodeposited MnO₂ a) picture of MnO₂ sample (lower black portion is MnO₂ ; upper silver part is the Ni-mesh); SEM images at a) 100 μm b) 500 nm and d) 100 nm scales.

electrolyte. This resulted in a discharge curve, seen in Figure 4.3, with a distinct voltage plateau of 1.4 V. This confirms that there is a proper electrochemical reaction occurring between Zn and MnO₂, based on their respective standard potentials.

In addition to verifying MnO₂ was present on the CNT fiber, the mass of deposited material needed to be calculated. This was done using Faraday's law of electrolysis, which relates the mass deposited to the total charge of the electrodeposition process. The mass can be calculated as seen below:

$$m = \frac{MQ}{zF} \quad (4.1)$$

,where M is the molar mass of the deposited material, Q is the total charge used during the

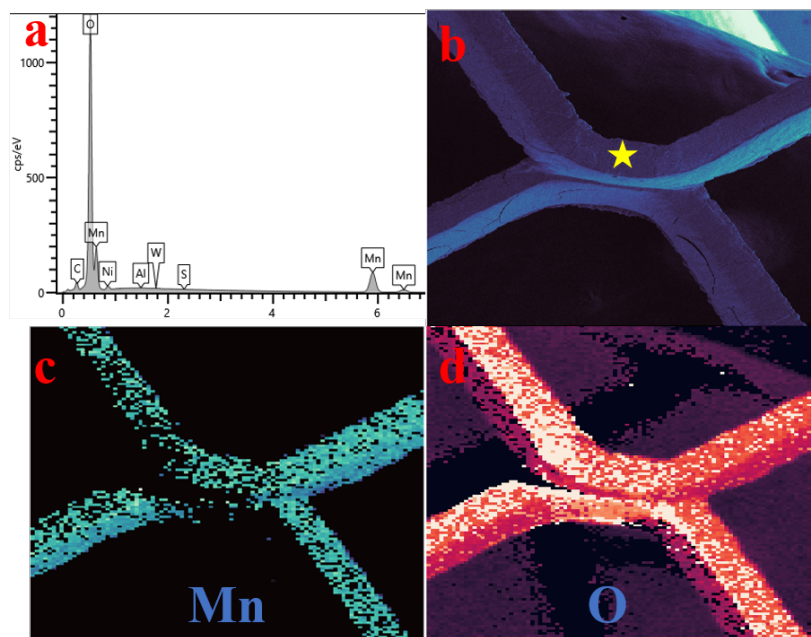


Figure 4.2: EDS data compilation a) spectra chart taken at point denoted by star in b); charts c) and d) show heat maps of Mn and O presence.

process, z is the ionic species charge, and F is Faraday's constant. The total charge, Q , is calculated by integrating the current with respect to time; resulting in Amp-seconds, or Coulombs. Using Faraday's law of electrolysis, it was calculated that the average mass deposited on a 4 inch CNT fiber was roughly $1.25 \mu\text{g}$. The mass deposited value is useful in further calculations of the specific capacity of the MnO_2 .

4.2 Gel Polymer Electrolyte Performance

After the verification of electrodeposited MnO_2 , battery cells were formed with the PVDF gel polymer electrolyte (as seen in Figure 3.5). The following data is based on a battery with a gel polymer electrolyte layer that is approximately $450 \mu\text{m}$ thick. As mentioned, electrochemical

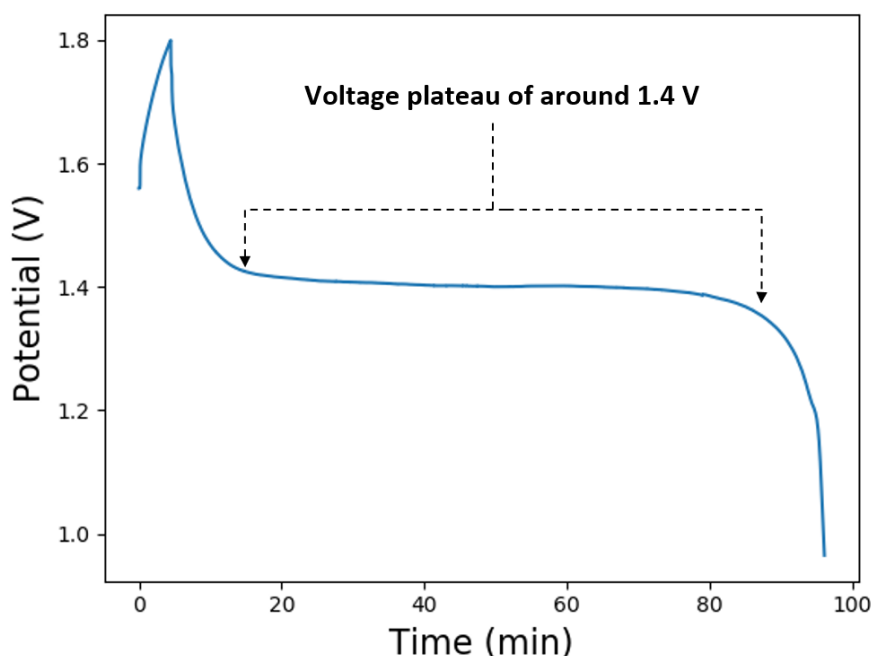


Figure 4.3: Electrochemical cell cycled once.

impedance spectroscopy (EIS) was conducted to determine the internal and interfacial (interfaces between electrolyte and either cathode or anode) resistances. The Nyquist plot shown in Figure 4.4 shows the impedance of the battery when first assembled as well as after being cycled.

The two key takeaways from this plot are the bulk and interfacial resistance. The distance between the origin and the start of the semicircle is the bulk resistance, and the diameter of the semicircle is the interfacial resistance. Unlike the interfacial resistance, the bulk resistance of the electrolyte did not drastically change between cycles and rest periods, decreasing from an initial resistance of $500\ \Omega$ to values around $400\ \Omega$. This is an expected result as the thickness of electrolyte is not changing in any noticeable way. Any slight decrease in bulk resistance could potentially be a result of the electrodes essentially flowing into the electrolyte due to minor amounts of waste heat from the electrochemical reaction occurring. This flow into the electrolyte may bring the electrodes

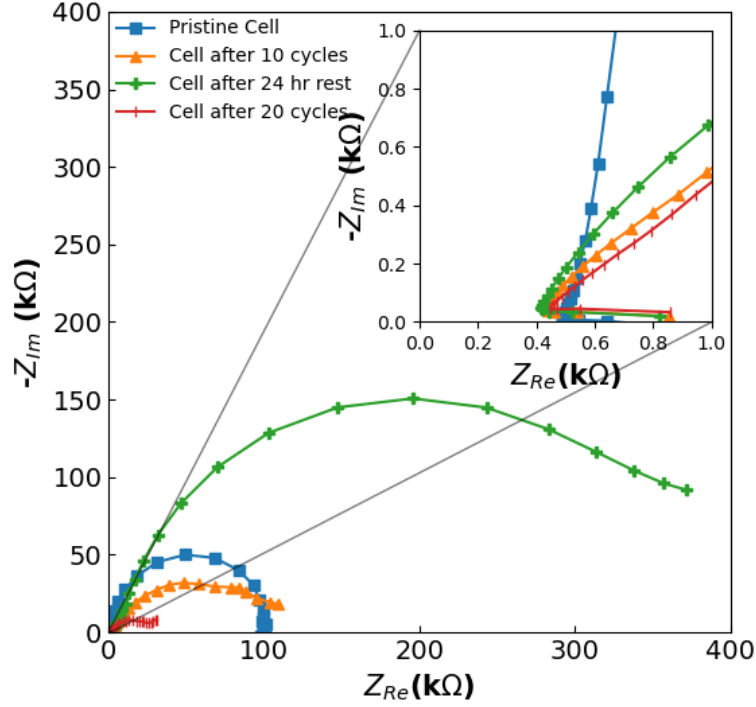


Figure 4.4: Nyquist plot of a pristine cell as well as intermittent discharge/rest cycles.

closer together, thus decreasing the distance ions must move through the electrolyte, and further, decrease the bulk resistance of the gel polymer electrolyte.

It is clear that the interfacial resistance is the much higher impedance with regards to the ionic movement. The interfacial resistance of the battery increased after cycling the battery 10 times at a roughly 1C rate (from around 100 kΩ to about 110 kΩ). This initial, minor increase in interfacial resistance may be attributed to the battery experiencing minor stress or strain that slightly adjusts the interfacial contact between the electrodes and electrolyte. These minor stress/strain differences could be the result of the paperclips holding the battery together. The larger interfacial resistance increase occurred after the battery rested for 24 hours. The resistance jumped almost four times higher, up to almost 400 kΩ. This increase can logically be attributed to the battery relaxing, allowing for a

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lessening in contact between the electrodes and electrolyte. The battery relaxes due to the materials cooling down without any electrochemical reaction occurring.

The final plotted curve is from the battery after running another 10 cycles. This resulted in a dramatic decrease in interfacial resistance from 400 k Ω to approximately 30 k Ω . This decrease is most likely attributed to the electrodes making better contact with the electrolyte. The electrochemical reaction is causing some waste heat that is most likely allowing for better electrolyte wetting of the electrodes. In other words, the electrolyte is pervading into the micropores of both the Zn wire and the MnO₂@CNT fiber. This means there is more electrode surface area making direct contact with the electrolyte, thus minimizing micro-pockets of air and overall decreasing interfacial resistance. The Nyquist plots correlate to what was observed in the discharge characteristics.

4.3 Full-Cell Electrochemical Discharge Performance

In congruence with EIS measurements, cell cycling was conducted to examine the batteries' electrochemical performance. The current work used the work by Kumar and Sampath[53] as a comparison of electrochemical performance. The main performance metric the current work is concerned with is specific capacity of the MnO₂. It is assumed throughout the experiments that the MnO₂ is the limiting electrode due to a maximum theoretical energy density of 308 mAh g⁻¹, which is less than half the theoretical energy density of Zn metal (820 mAh g⁻¹). Therefore, any references to specific capacity in the following results/discussions are referring to the capacity of MnO₂.

The specific capacities achieved by Kumar and Sampath can be found in Figure 4.5 [53]. The main takeaway from Figure 4.5 is the discharge specific capacities at the various C-rates. They achieved their best specific capacity (the line denoted as (1) in Figure 4.5) of 105 mAh g⁻¹ at a C-rate

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of C/160 (a roughly 1 week discharge cycle) [53]. At their highest C-rate (C/8), they achieved a specific capacity of 37 mAh g^{-1} (the line denoted as (4) in Figure 4.5) [53].

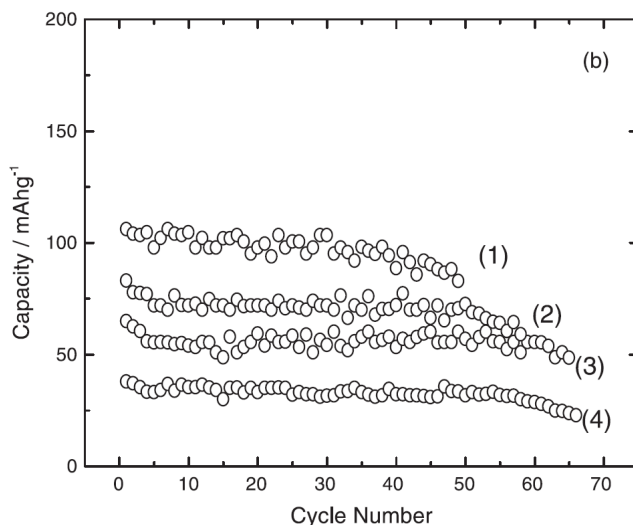


Figure 4.5: Battery cycling data from work of Kumar and Sampath; 1) $10 \mu\text{A}/\text{cm}^2$ (roughly C/8) 2) $50 \mu\text{A}/\text{cm}^2$ (roughly C/16) 3) $100 \mu\text{A}/\text{cm}^2$ (roughly C/32) 4) $200 \mu\text{A}/\text{cm}^2$ (roughly C/160), adopted from [53].

Another key takeaway from Figure 4.5 is their cycling performance. It is clear the cells ran for several dozen cycles. The specific capacity retention was not documented in the work, so ImageJ was utilized to calculate it. The scatter points denoted by (1) had the highest retention rate of roughly 78% of the original capacity after 50 cycles. This is well above the lowest retention rate of 59% that line (4) achieved after 70 cycles. The 78% capacity retention did occur in 20 less cycles than the 59% capacity, however, based on lines (2) and (3), the retention would still be highest for line (1). Overall, the data from Kumar and Sampath offer helpful insight to how the fiber batteries of the current work performed.

It must be noted that the work by Kumar and Sampath[53] was a experiment on the gel polymer electrolyte, not a fiber battery experiment. Therefore, the format of the battery was a 1

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cm² electrolytic manganese dioxide (EMD) coated Ni-mesh as cathode and Zn sheet metal as anode. This larger scale battery allowed for C-rates much lower than possibly with the fiber-form battery of the current work. This is due to the Arbin battery cycling machine with too loose a tolerance for sub-microamp cycling. The end result is that the fiber batteries in the current work needed to be cycled at higher C-rates to ensure a consistent current is charging and discharging the cells.

Table 4.1: Current work's compiled battery data.

Cell	Current (μA)	Cycles Ran	C-Rate (range)	C-Rate (Average)	Maximum Specific Capacity (mAh/g)	Avg. Specific Capacity (mAh/g)	Notes
Battery A	8	202	1C-5C	2C	90	37	
Battery B	1	17	C/24-C/8	C/15	201	119	Same battery as Battery A, lowered C-rate
Battery C	1	78	C/16-C/2	C/8	162	49	

The compiled battery data of the current work can be found in Table 4.3. The C-rates are provided as a range due to the varying nature of the capacities experienced through cycling. Due to this capacity variance, as will be discussed, the C-rate range is simply the ranges of time it took to discharge the battery throughout the cycling tests. For example, Battery A's range of 1C-5C means the battery discharged in anywhere from 12 minutes to 1 hour. The average C-rate was calculated by dividing the average specific capacity by the current per mass of MnO₂ (A/g). This gives the average time it took to discharge the battery, and then further taking the inverse of that value gives the average C-rate. Many more batteries were cycled throughout the current work, but those provided by Table 4.3 provide good insight as to the trends of all batteries' performances.

To begin, Battery A's performance will be further examined with cycle data provided by Figure 4.6. It is immediately clear that there are major differences between this battery and the batteries cycled by Kumar and Sampath.[53] To begin, the C-rate on this specific battery was 8-40

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times higher than the highest rate used by Kumar and Sampath.[53] The next notable difference is the increasing nature of the specific capacity. From cycle 1 to cycle 125, the specific capacity was linearly increasing every cycle. Then, around cycle 125, the specific capacity began increasing at a much higher rate. Subsequently, the specific capacity began fading after reaching a peak of 90 mAh g^{-1} (measured relative to the 0.130 mg of deposited MnO_2).

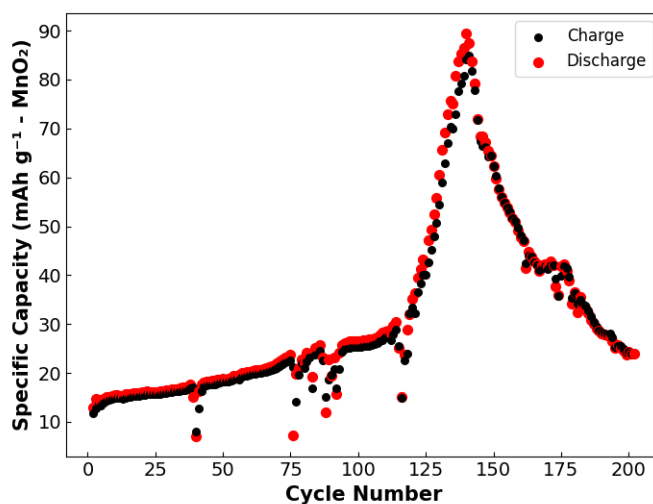


Figure 4.6: Specific capacity of battery (seen in Figure 3.5) running at $8 \mu\text{A}$ (ranging from 1C to 5C).

It is difficult to compare specific capacities of the current work's battery to those of Kumar and Sampath[53] due to drastically different C-rates. However, in general, one would expect to achieve higher capacities at lower C-rates, as is the case in the work from Kumar and Sampath.[53] Therefore, a general conclusion to be made from Figure 4.6 is that Battery A is performing well in comparison to that of Kumar and Sampath.[53] This is a fair assessment given that there was a peak capacity of 90 mAh g^{-1} , but also due to the average capacity of 31 mAh g^{-1} . This average value is slightly lower than that of Kumar and Sampath's[53] capacity of 37 mAh g^{-1} . However, there are two important differences: as mentioned the C-rate used in the current work is 8-40 times higher than

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Kumar and Sampath's[53], and secondly, the 37 mAh g^{-1} is the maximum capacity they achieved, not the average (which hovered closer to 32 mAh g^{-1}). Thus, with more context, the Battery A of the current work is performing in a similar, and temporarily better, manner while cycling at a much higher C-rate.

The reasoning behind the increasing specific capacity during cycling is not entirely clear. However, the EIS measurements, as seen in Figure 4.4, give a good insight into what is occurring in the battery. The interfacial resistance greatly decreased after 20 cycles. This indicates that better contact between the electrolyte and electrodes improved over the course of cycling. This could be the result of minor heat production as a byproduct of the electrochemical reactions occurring. This heat may be allowing for better wetting of the electrodes micropores. By filling these micropores with electrolyte, there is more active material participating in the the electrochemical reaction. Thus, due to the better wetting of the electrodes, the capacity of the battery appears to be increasing.

The specific capacity, theoretically, is not increasing. The specific capacity is calculated as the discharge capacity, measured in milliamp-hours, divided by the mass of MnO_2 , measured in grams, deposited onto the CNT fiber. In early cycling, the entire mass of MnO_2 is not taking part in the discharge. Therefore, in early cycling the discharge capacity should be divided by the mass playing an active role in the discharge, not the entire mass of MnO_2 deposited on the CNT fiber. Without further, detailed examination of interfacial contact of the electrolyte/electrodes, it is impossible to model the active material. However, future work determining these values could potentially result in a more appropriately shaped specific capacity versus cycles plot that slowly fades over time rather than increase.

The cells cycled by Kumar and Sampath[53] discharged to 1.0 V and charged to 1.8 V.

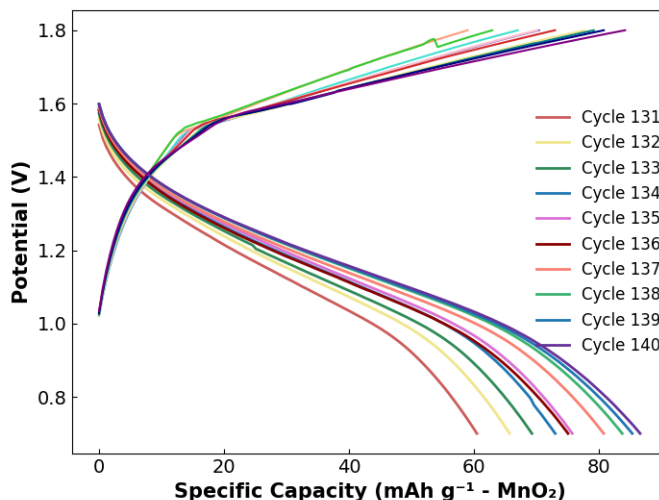


Figure 4.7: Typical discharge curves observed; cell cycled at $8 \mu\text{A}$ (ranging from 1C to 5C).

However, this work discharged the batteries to 0.7 V, while still being charged to 1.8 V. Even so, the typical discharge curves, found in Figure 4.7, appear similar to the work of Kumar and Sampath (shown in Figure 2.9).[53] The discharges do not exhibit a distinct voltage plateau, and instead, potential decreased linearly. The nominal potential was roughly centered at 1.2 V. The battery cycled in Figure 4.7 was cycled 200 times with discharge curves showing cycles 131 to 140. Over the course of the 200 cycles, the specific capacity of the MnO_2 varied between 20 and 80 mAh g^{-1} , however, the discharge curves of each cycle, whether 20 mAh g^{-1} or 90 mAh g^{-1} , are similar to the cycles displayed in Figure 4.6.

After the battery cycled 200 times at high C-rates, Battery A was lowered to a current of $1 \mu\text{A}$, becoming Battery B. This current equates to a C-rate range of C/24 to C/8, meaning at this current the battery discharged over the course of 8-24 hours. This C-rate range is more closely reflective of the rates used by Kumar and Sampath[53], who used a C/8 and C/16 rate, resulting in specific capacities of 37 and 64 mAh g^{-1} , respectively. Battery B resulted in discharge curves found

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in Figure 4.8. Cycle 1 is not included as it took place near the end of the 200th cycle of the initial $8\ \mu\text{A}$ cycling. Therefore, the battery was almost fully discharged, resulting in an extremely low capacity non-reflective of the actual performance of the battery itself.

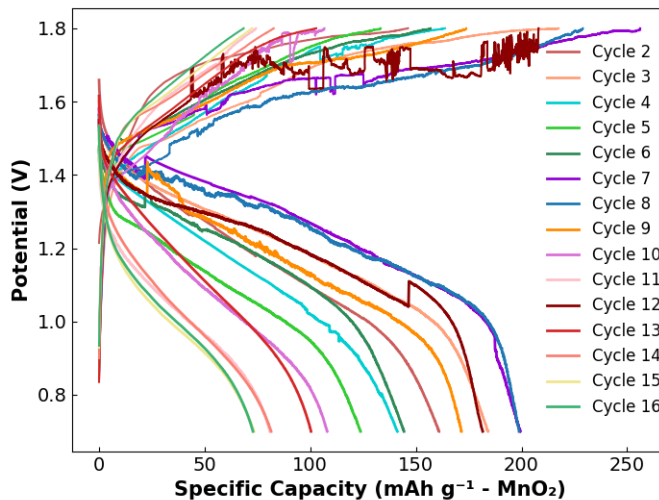


Figure 4.8: Typical discharge curves observed after 200 cycles at $8\ \mu\text{A}$; Battery B cycled at $1\ \mu\text{A}$ ($C/20$ to $C/10$).

It is seen that the discharge curves, as expected, are consistent to those of the initial $8\ \mu\text{A}$ cycling. The nominal voltage was located around $1.2\ \text{V}$ with a consistent, linearly-decreasing voltage, rather than a voltage plateau. With the fibers being so small and exposed to the laboratory environment, the leads connecting to them were slightly irritated during the cycling process (minor movement of the battery/wires being moved), which resulted in the slight noise seen in Figure 4.8, specifically cycles 8, 9, and 12. Beyond the noise, it is seen that the battery was achieving a much higher specific capacity than the $8\ \mu\text{A}$ cycling, and more importantly, higher than the work of Kumar and Sampath[53] with a high of $202\ \text{mAh g}^{-1}$ and an average specific capacity of $119\ \text{mAh g}^{-1}$. This specific capacity is higher than even the lowest C-rate ($C/160$, a week long discharge) used by Kumar

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and Sampath[53], which achieved a maximum specific capacity of 105 mAh g^{-1} .

Another key takeaway from Figures 4.6 and 4.8 is how well the battery is cycling. The subsequent cycling of Figure 4.8 all took place on the same battery that cycled 200 times. With such a varying specific capacities, it is difficult to say with certainty the coulombic efficiency (the ratio of electrons drawn from the battery during discharge to electrons inserted during the charge phase) of the battery. Figure 4.9 is provided to show why coulombic efficiency is slightly difficult to determine accurately.

The cycles represented in Figure 4.9 begin with the last dozen cycles where specific capacity was increasing and end when the C-rate was lowered to $1 \mu\text{A}$. As the specific capacity is increasing, the coulombic efficiency was always above 100%. This can be explained by the fact that the electrolyte is reaching more and more of the electrode throughout these cycles. Thus, more capacity is coming from non-cycled material, whether Zn or MnO_2 , not from the electrons being used to charge the battery. Around cycle 150, the coulombic efficiency starts to dip below 100%, however, jumps above and below 100% in later cycles. This oscillation can be attributed to two things: more active material being accessed from electrolyte wetting and from actual battery material decay due to unwanted byproducts/Zn-ions becoming trapped in the electrolyte or electrode material.

The coulombic efficiency of Battery A never dropped below 94%, which indicates that the battery should continue to operate properly, thus the current was lowered to $1 \mu\text{A}$ for further cycling. Examining Battery B's cycles, shown in Figure 4.10, it is noted that there are still several cycles where the coulombic efficiency is higher than 100%. This indicates there is still active material not being completely utilized in the previous 202 cycles. However, it is also important to note that the coulombic efficiency does drop below 90% during some of the cycles and later below 80%. It does

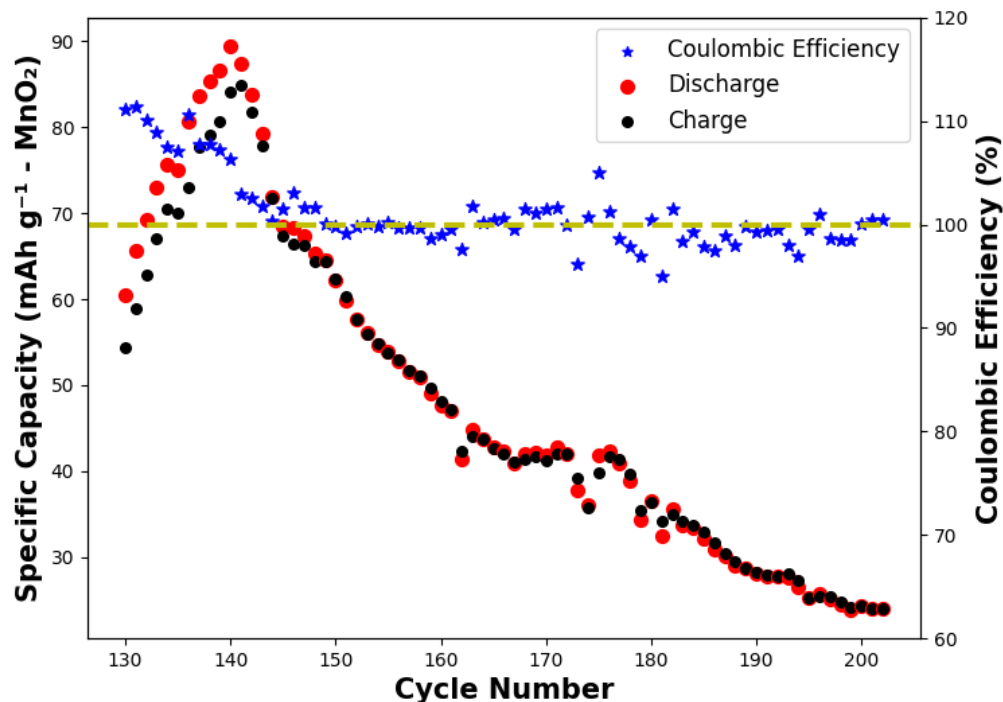


Figure 4.9: Coulombic efficiency of cycles 130-202, from Battery A. Dotted yellow line added for visualization of 100% coulombic efficiency.

later increase to above 100%, but overall, this indicates the battery is beginning to degrade faster than the electrolyte is wetting the electrodes.

Battery C, unlike Battery B, began cycling at $1 \mu\text{A}$ as a pristine cell. This battery serves to show that the reason for Battery B's improved specific capacity is not solely attributed to the lowered C-rate but also the improved wetting of the electrodes. Battery C's performance can be found in Figure 4.11. Similar to Battery A, Battery C exhibited the same increasing specific capacity over the first couple dozen cycles. These cycles had were characterized by coulombic efficiencies well above 100%, at times reaching 160%. This is again indicative that each new cycle is accessing more and more active material. Around cycle 30, the capacity ceases to continually rise and rather begins

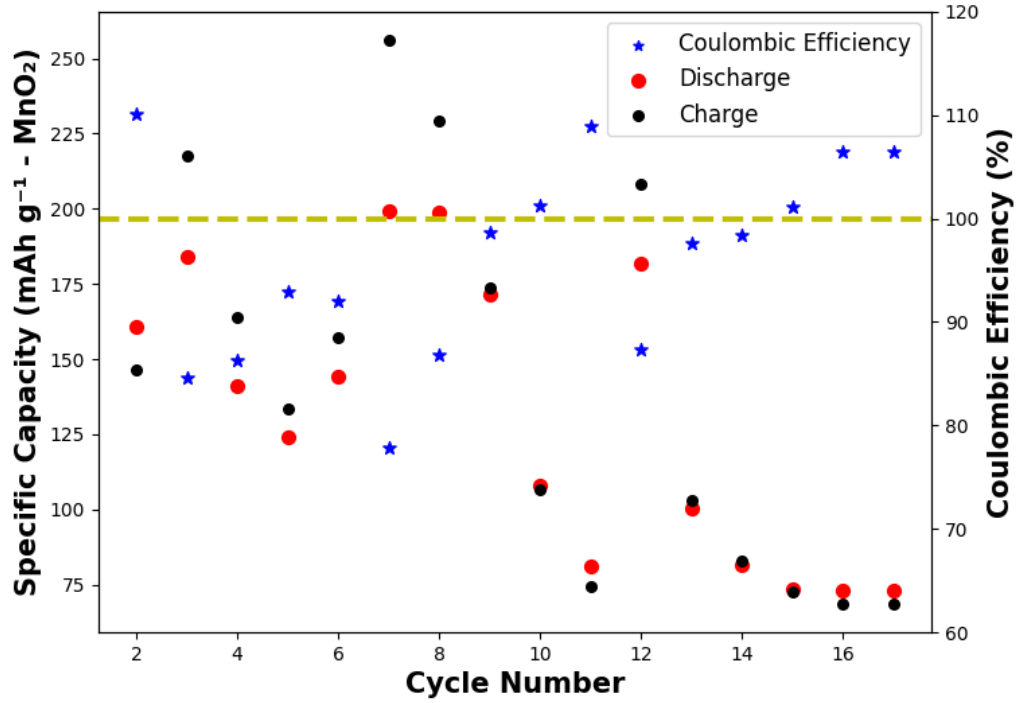


Figure 4.10: Coulombic efficiency of Battery B. Dotted yellow line added for visualization of 100% coulombic efficiency.

fluctuating anywhere from 40 mAh g⁻¹ to 160 mAh g⁻¹. This may be indicating that the contact between the electrolyte and electrodes is not consistent between each cycle. This could be the result of minor stress relaxations of the Zn wire and MnO₂@CNT fiber that occur between each cycle during the 30 second rest period.

In addition, while solid/gel polymer electrolytes help prevent MnO₂ dissolution, it is possible there is minor amounts of MnO₂ dissolution occurring. This phenomenon was observed in another work that used a PVA/ZnCl₂/MnSO₄ electrolyte.[72] This dissolution is the result of disproportionation of Mn³⁺ into Mn²⁺. [39] Essentially the structural MnO₂ on the CNT fiber gets dissolved into Mn²⁺ ions that flow into the electrolyte and becomes inactive. Eventually the dissolu-

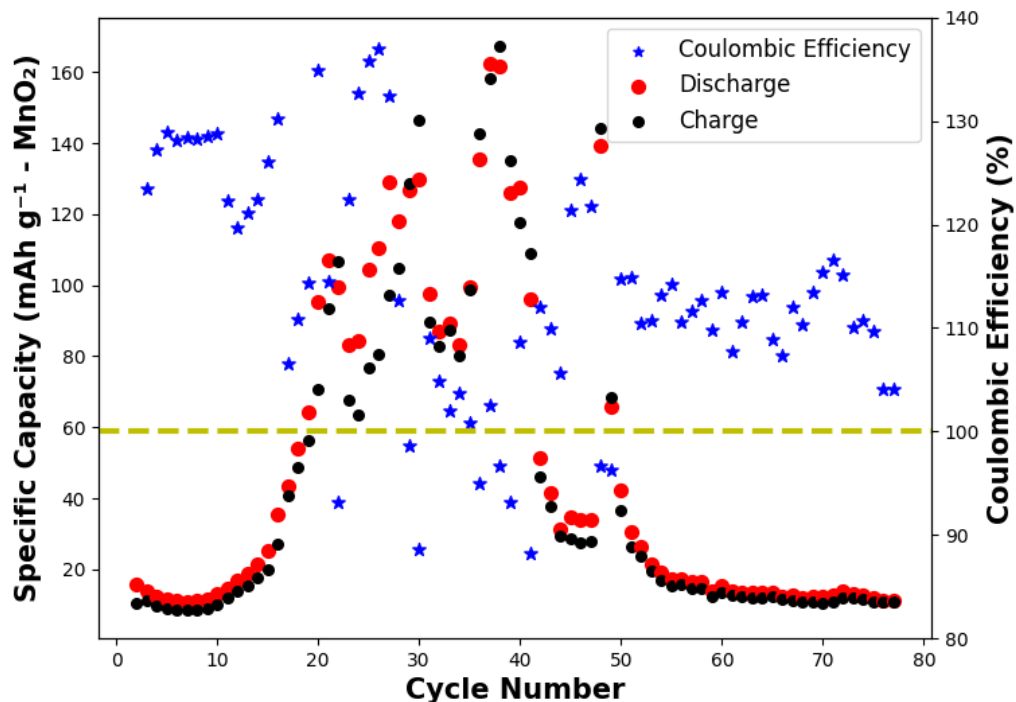


Figure 4.11: Specific capacity and coulombic efficiency of Battery C. Dotted yellow line added for visualization of 100% coulombic efficiency.

tion ceases due to an equilibrium state between the cathode MnO_2 material and the Mn^{2+} ions in the electrolyte. One way of avoiding this issue is by adding Mn^{2+} ions into the electrolyte. This changes the equilibrium state and stabilizes the cathode material.[39] This potentially helps to explain the lowering specific capacity even though the coulombic efficiency remains high.

4.4 Drawn Fiber Battery

As previously stated, the eventual goal of the current work is to draw the fiber battery through a thermal draw tower. Given the expense of CNT fiber, the current work was only able to conduct a draw experiment verifying the gel polymer electrolyte would properly flow with the

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cyclic olefin copolymer (COC) preform through the draw tower's furnace. Thus, the draw experiment conducted was more so a binary test to determine if the electrolyte possesses proper rheological properties for draw tower compatibility. In addition, temperature and tension data gave a good indication for potential settings that are conducive to the eventual drawn battery.

Analyzing the preform prior to drawing reveals clear issues that were to occur during the draw. The preform, found in Figure 3.6, clearly contains many small air bubbles. Air bubbles are present in both the COC preform material as well as the gel polymer electrolyte. The more immediate issue is the air bubbles in the electrolyte. These will greatly increase the ionic resistance of the electrolyte, thus decreasing the performance of the battery. In any further experiments, these air bubbles can be avoided by running a sonicator through the polymer prior to it cooling in the molds. Moreover, the gel polymer electrolyte was molded in a separate 3D-printed mold and then inserted into the preform. The 3D printed mold could not be heated to the temperatures that would allow air bubbles flow up and out of the electrolyte. Therefore, it would be beneficial to produce a metal preform mold so as to allow the mold to be held at high temperatures that keep the gel polymer electrolyte in a viscous state where air bubbles could escape simply through buoyancy forces.

In addition to the air bubbles within the electrolyte itself, the 3D mold was only 4 inches. This means that the preform shown in Figure 3.6 actually contains several pieces of separate polymer electrolyte. This creates minor little pockets in between each piece of electrolyte which leads to more gaps in electrolyte in the final fiber drawn. This issue is easily solved by creating a metal preform mold that is as long as the polymer preform. The metal mold would have the same dimensions (5mmx5mm) as the 3D-printed plastic part used for the electrolyte used in the preform seen in Figure 3.6. Additionally, making the mold a full 12 inches would prevent the need to place several different

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pieces of electrolyte into the preform, removing unnecessary gaps in electrolyte.

The final drawn fiber can be seen in Figure 4.12. In Figures 4.12a and 4.12b, there are several portions that clearly have large gaps in electrolyte. These gaps range from sub-millimeter to several millimeters long. These gaps in electrolyte in the fiber correlate to tiny air bubbles in the preform. Due to the draw-down ratio (as high as 30 in this draw), a air bubble of 100 micron thickness present in the preform can become a gap of 3 millimeters in the finished fiber. This clearly shows how crucial it is to remove any air bubbles in the molded electrolyte material. It is easy to detect air gaps in the fiber as highlighted in Figure 4.12c. Fiber with electrolyte clearly shows an opaque, white appearance. The air gaps are easy to see as the entire thickness of the fiber is mostly transparent.

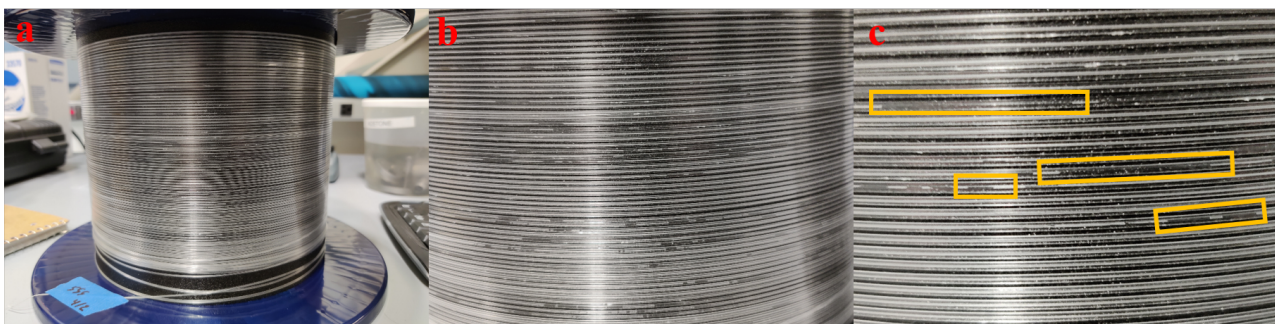


Figure 4.12: Images of drawn fiber; a) full spool of fiber b) zoomed in image showing areas of air pockets c) further zoom with boxes around example air pocket regions.

In addition to the drawn fiber, two remnants remained: the bait-off and the remaining preform, shown in Figure 4.13. The bait-off is the region of initial preform material that does not undergo the proper deformation. The bait-off section of this draw, shown in Figure 4.13a, was relatively short where useable fiber was produced within the first 2 meters. The metal wire sticking out of the bait-off is simply the means by which the preform is pulled through the furnace. The

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remaining preform, shown in Figure 4.13b, shows where the preform eventually snapped from the fiber being drawn. Difficult to see, behind the Kapton tape, the remaining electrolyte level is lower in the remaining preform material. This is a good sign that as the electrolyte flows through the furnace it begins to fill in air pockets as the air slowly rises out of the preform. Of course, this does not completely mitigate air pocket issues as seen in Figure 4.12.

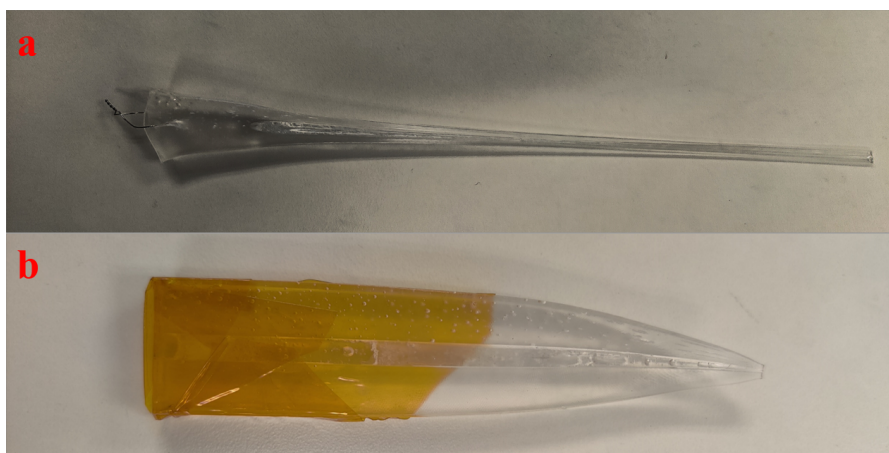


Figure 4.13: Images of drawn remnants: a) bait-off piece b) remaining preform with Kapton tape to prevent electrolyte leakage.

Temperature, stress, and tension data from the draw experiment can be found in Figure 4.14. There are three variables that can be adjusted during the draw: feed speed, draw speed, and furnace temperature. The feed speed, or the speed the polymer preform was fed into the furnace, was held constant during this experiment at 1 mm/min. Throughout the draw, the draw speed and temperature was varied to determine the limits of the fiber. Essentially, the goal when drawing fiber is to increase tension as high as possible without the fiber mechanically failing. The two ways to do this are to either use the lowest drawable temperature combined or to increase the feed speed. Increasing the tension is supposed to decrease the variance in the dimensions of the fiber. In addition, increasing the draw speed allows for smaller and smaller fibers, which is helpful in the case of the

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current work's fiber battery as the total thickness of the active battery components is only 500 μm . This thickness ties in the goal of achieving a consistent electrolyte thickness of 200 μm as opposed to the varied thicknesses from pressing the gel polymer electrolyte by hand.

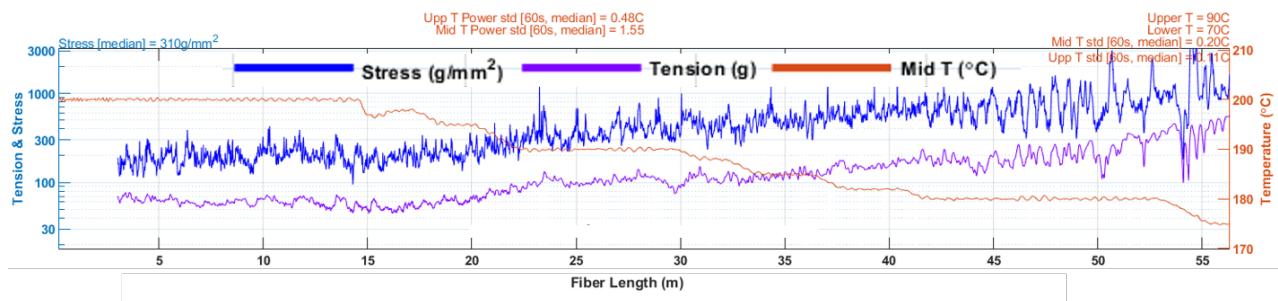


Figure 4.14: Temperature, stress, and tension data from gel polymer electrolyte draw.

It can be seen in Figure 4.14 that the mid-temperature started at 200. The "mid" distinguisher is added as there are three separate temperature zones on the draw tower furnace. The upper and lower are both held constant and simply act as a buffer/ramp towards the desired temperature found in the mid-zone of the furnace. Once the fiber became stabilized at 200, the temperature was slowly lowered in 2-5 increments until the temperature reached 175. It is a clear trend that as the temperature decreased, the tension began to slowly increase. This is due to both the polymer preform and the electrolyte becoming less viscous, which increase the amount of force the draw tower needed to exert to draw the fiber down through the furnace.

Eventually, this tension became too high for the material, which resulted in a complete snapping of the fiber from the preform. This failure is likely the result of the polymer preform material, COC, rather than the gel polymer electrolyte material. This is due to the T_g being roughly 130. As the furnace temperature is slowly lowered, the COC becomes more and more crystallized as it nears closer and closer to its T_g , making the material more brittle and unable to plastically deform. Thus, at a certain combination of tension and temperature, the material snaps.

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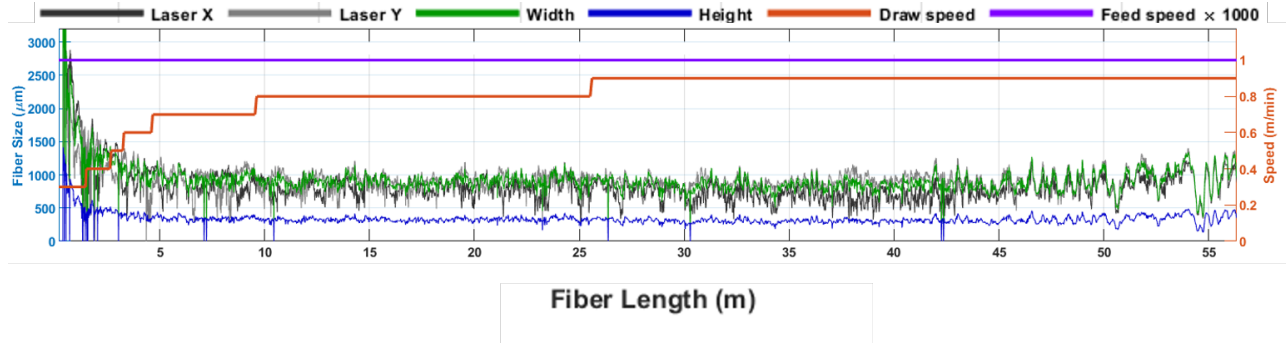


Figure 4.15: Width, height, draw speed, and feed speed data from gel polymer electrolyte draw.

In concurrence with the decreasing temperature, the draw speed began increasing to decrease the size of the fiber. This data can be found in Figure 4.15. The draw speed began at 0.3 m/min. Based on Equation 2.4, this draw speed results in a draw-down ratio of roughly 17. The draw speed was slowly ramped up to 0.9 m/min, or a draw-down ratio of 30. These draw-down ratios impact the the size of the fiber, as seen by the green line representing the width of the fiber in Figure 4.15.

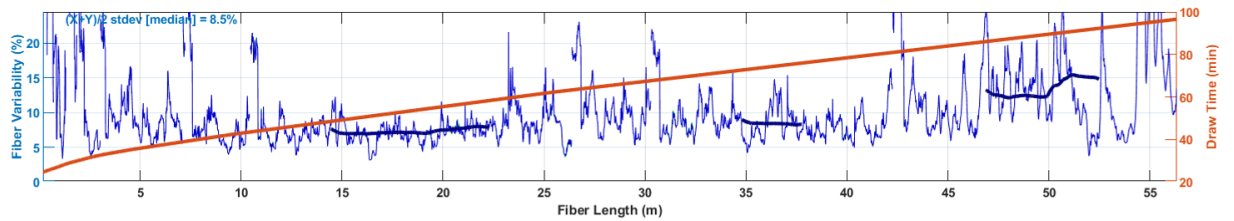


Figure 4.16: Variance data from gel polymer electrolyte draw.

A final important piece of data is the variability in the size of the fiber, found in Figure 4.16. It is clear the variance, represented by the blue line, fluctuates greatly throughout the draw. This can be partially attributed to the constant temperature and draw speed variance. In a typical, practical fiber draw, these variables are constant throughout the entire draw. Without the varying temperatures and draw speeds, it can be expected that the fiber variance will greatly lower. However,

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with a median variance of 8.5%, it cannot be ruled out that further experimentation is required to ensure the gel polymer electrolyte is properly flowing with the COC preform. If the electrolyte is not behaving rheologically similar to the COC, the variance of the fiber size could continue to present an issue.

Overall, the approximate optimal conditions for drawing the fiber can be found in Table 4.2. These are not set numbers for every future draw due to a variety of different factors affecting the draw tower. External temperature and humidity variance in the facility does play a minor role in the drawing of the fiber. In addition, future draws should, theoretically, use electrolyte with much fewer air bubbles. This may allow for either or both of decreasing the middle zone temperature or increasing the draw speed. This is because the air bubbles may assist in causing mechanical failures in the fiber that eventually causes the fiber to snap while drawing. Without the air bubbles, the fiber should theoretically be more tolerant on higher stress.

Table 4.2: Optimal conditions for drawing the fiber battery.

Top Zone Temperature (°C)	Middle Zone Temperature (°C)	Bottom Zone Temperature (°C)	Feed Speed (mm/min)	Draw Speed (m/min)
90	180	70	1	0.9

Chapter 5

Conclusion

The current work succeeded in developing a laboratory prototype fiber battery that offers a potential means of powering wearable devices. While the batteries did require numerous cycles to reach peak capacity, the fiber batteries in this work achieved better capacities than the work of Kumar and Sampath[53], even while cycling the batteries at higher C-rates. The current work does leave several important issues to be resolved through a potential, future work. The main issue that has not been discussed thus far is cost. For larger scale production, the carbon nanotube fiber, used as the cathode's current collector, will need to be replaced as it is not a cheap material (\$100/m). In any future work, time should be devoted to determining a cheaper current collector to deposit MnO_2 onto. In addition, determining precisely why the capacity takes numerous cycles to peak as well as why there are several cycles with a coulombic efficiency above 100% will be crucial for developing a practical fiber battery. Overall, the current work shows a promising basis for developing a practical fiber battery using a zinc-ion battery chemistry through use of a thermal draw tower.

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