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Battery Design, Construction, and Characterization for Small Motor Use Focusing on Anodic Zinc for Electron Flow

Amber Veach
University of Arkansas, Fayetteville

Honor Thesis

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Amber Veach

Advisor: Tammy Lutz-Rechtin, Ph.D.

University of Arkansas Honor College
University of Arkansas
Ralph E. Martin Department of Chemical Engineering

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1. Abstract

This thesis explores the construction, characterization, and application of anodic zinc batteries for powering a small electric motor for the ChemE Car competition. Two zinc galvanic cell batteries were studied: zinc-carbon and zinc-air batteries. Prototype batteries were constructed and tested for voltage, amperage, and power production. In the zinc-carbon trials, a 3:1 mixture of manganese dioxide and graphite was determined to be the best cathode for power production. The size which allowed for sufficient power while maintaining the smallest footprint on the car was a zinc can six cm tall and two cm in diameter. Analysis of paper zinc-air battery prototypes showed insufficient voltage and amperage to power the motor. However, significant advances were made in the zinc-air battery assembly. Mixing zinc-air battery ink components with a ball mixer produced 192% more power. Additionally, novel ionic polymers and an ionic liquid were tested for use as electrolytes for increasing paper battery power production. The ionic polymers were more conductive than dry 3M NaCl impregnation in the battery membrane but less conductive than wetted 3M NaCl.

2. Introduction

Batteries are a form of energy storage and production that are becoming more vital today. At the simplest level, batteries are a way to store chemical energy and convert it to electrical energy. Advancements in battery size and efficiency have increased the portability of tools, including cellular devices, laptops, cars, and even motors. Battery innovation has led to the invention of many appliances, such as pacemakers, monitors, and flashlights, which has helped the world progress into a more mobile society. These battery-powered items have kept people out of bedridden scenarios, allowed for the movement of caregivers while maintaining a constant watch on patients, helped monitor road and weather conditions, and created a way to see in the dark where no other sources of power are located. On a larger scale, battery innovation has led to new potential renewable energy sources unaffected by weather patterns such as clouds or wind. Batteries have opened doors to a cleaner way to produce electricity while maintaining a smaller carbon footprint in the atmosphere.

The ChemE Car Competition is a contest to move and stop a small car a specific distance using only chemical reactions. The focus of this thesis will be on the chemical power supply for the motor. The chosen motor is a 12V 100 rpm motor that needs to move a 12-pound car for a distance in the 15–30-meter range. The car must reach its destination within two minutes. The exact distance will be unknown but announced at the competition. To have a reproducible run, a steady power source is required. Remote control (RC) vehicles, usually powered by batteries, were considered a model system for the ChemE Car design since the speed was highly controllable.

The next step was deciding on a specific chemical reaction to produce the redox reaction in most battery systems. When focusing on replicability, economical manageability, and nontoxic byproducts, a zinc anode offered advantages compared to other galvanic batteries such as lead. Potential battery formulations were studied for the safety of use, safety in on-site construction at the competition, hazardous waste production, and potential byproducts.

Due to proven consumer and commercial reliability, zinc-carbon battery assemblies were researched. These batteries are lightweight batteries that produce sufficient voltage and amperage. This battery style is prevalent in standard batteries such as AA, C, and D dry cell batteries. According to Davidson and the University of Florida, they have a 1.4-1.7 V voltage [9]. These batteries are low-cost, reliable, easy to manufacture, and can be produced on-site at the competition.

A paper zinc-air battery was also investigated. According to Poulin et al., this battery type is biodegradable, lightweight, and low-cost [7]. A lightweight battery would be a great source because the load on the motor would be lower, alleviating the power required from the battery. However, paper batteries are still being optimized. A study conducted by Poulin et al. showed the maximum voltage produced by a manufactured paper zinc-air battery was 1.2 V, and the maximum amperage was 0.5A [7]. This paper used a planetary mixer to maximize the homogeneity of the inks. Unfortunately, that is not a tool that this experiment had access to or could transport to the competition site. Alternative methods, including ionic polymer impregnation, were investigated in this study but found insufficient for our application.

After investigation and optimization, zinc-carbon batteries were successfully constructed and utilized for powering the ChemE Car motor.

3. Background

Electrical energy in batteries originates in the flow of electrons created via an oxidation-reduction reaction between the two electrodes. A battery comprises two terminals, a cathode and an anode. A cathode acts as the oxidizing agent, which accepts electrons, and the anode acts as the reducing agent, which releases electrons. A current is created through the flow of electrons as a byproduct of this reaction. According to Dave Roos, voltage is defined as the unit of electric potential difference between terminals, amperage is a measure of the current, or the flow of electrons moving through the loop, and resistance is the opposition to electron flow, measured in ohms [11].

There are two significant forms of batteries, galvanic cells, also known as voltaic and electrolytic cells. For this thesis, the focus will be galvanic (voltaic) cells. Galvanic batteries are not rechargeable and do not get energy from an external source. The chemical energy produced in them is formed via redox reactions separated by a semipermeable membrane. Separation is required to prevent a spontaneous and heat-producing reaction and allow the flow of electrons instead. A redox reaction occurs when electrons are transferred from one chemical substance to another. The negative terminal acts as the oxidation site and refers to the material being oxidized. The negative terminal loses electrons, which move from negative to positive, while the cathode or positive terminal gains electrons. Since most negative terminals are composed of metals, they tend to become thinner as the metal loses electrons due to oxidation of the reaction surface. The positive terminal is reduced. Figure 1 below displays a schematic of this electron flow.

A zinc-carbon battery is an example of a galvanic cell battery. In this battery, an electrolytic solution like ammonium chloride separates the cathode from the anode. The cathode in this battery is a manganese dioxide and graphite mixture, which is reduced via electron transfer.

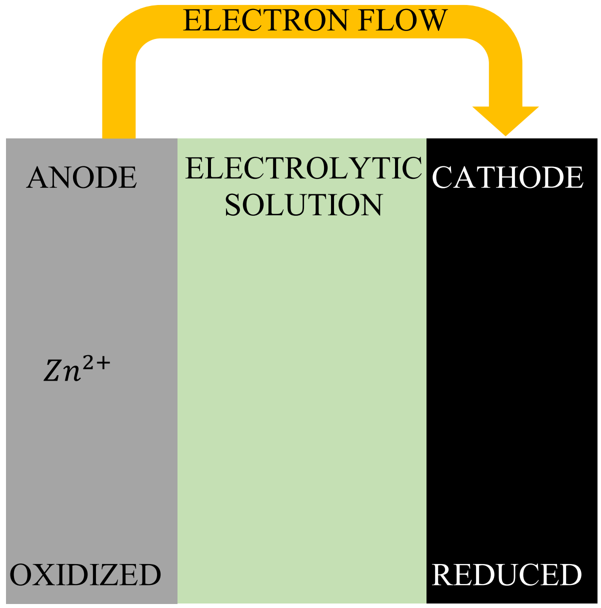


Figure 1. Electron Flow Presentation in Galvanic Battery

According to ChemEurope, the following half equations show the movement of electrons and the production of ions in this system [1]:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$
$$2MnO_{2(s)} + 2H^+_{(aq)} + 2e^- \rightarrow Mn_2O_{3(s)} + H_2O_{(l)}$$

The $H^+_{(aq)}$ in this equation comes from the aqueous ammonium that is present in the electrolytic solution. In this breakdown, it is easy to see how the zinc loses electrons and is oxidized, and the manganese dioxide gains them and is reduced.

When creating an overall reaction for this cell, the free electrons present in the half equations can be removed.

$$Zn_s + 2MnO_{2(s)} + 2NH^+_{4(aq)} \rightarrow Mn_2O_{3(s)} + Zn(NH_3)^{2+}_{2(aq)}$$

The carbon in the cathode mixture acts as an amplifier for conductivity throughout the mixture. It acts as a conductor for the flow of electrons from oxidized zinc. According to Dr. Dong Liu, graphite's molecular structure plays a significant role in its conductive properties [12]. It has four valence electrons but is only bonded to three other carbon atoms. This leaves delocalized electrons to carry a charge throughout the material.

A schematic diagram is shown below in Figure 2 of the zinc-carbon batteries:

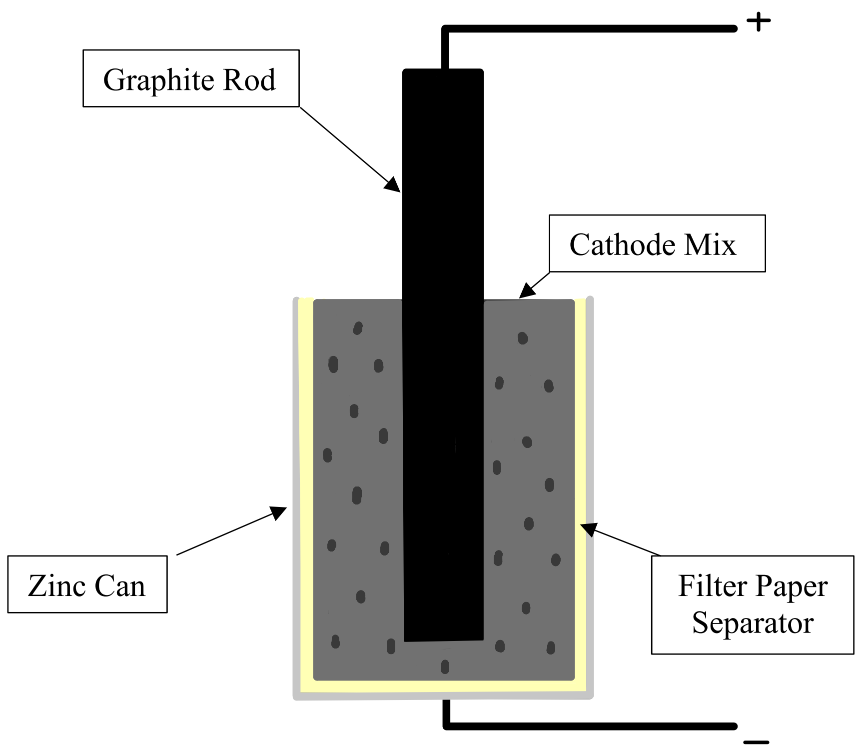


Figure 2. Schematic diagram of Zinc-Carbon Batteries

Zinc-air batteries work in a similar fashion. These batteries also rely on the oxidation of zinc, but they use a different oxidizer than the zinc-carbon batteries. The oxidizer for these cells is the oxygen in the surrounding air. When water is combined with the surrounding air, hydroxide is formed in the cathodic region when the batteries are hydrated. This molecule is then used in the anode to combine with zinc, creating the oxidation of the anode. Both the anode and cathode continue with the following reactions after the electrons have been released from the zinc. The reactions are as follows, according to Arthur Dobley et al. [6]:

$$Zn + 4(OH)^- \rightarrow Zn(OH)_4^{2-} + 2e^-$$
$$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2(OH)^-$$
$$O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$$
$$Zn + \frac{1}{2}O_2 \rightarrow ZnO$$

This flow of electrons creates the electrical energy that can be used to do work or in this case power a motor. Cellulose filter paper impregnated with NaCl acts as a separator between the two terminals while facilitating the flow of electrons. This separator acts as a barrier between the cathode and the cell's anode to keep the battery from shorting out. Once this filter paper is wetted, the battery reaction begins.

In the specific zinc-air battery described in Figure 3, cellulose filter paper, a zinc-based ink for the anode, a graphite-based ink for the cathode, and a carbon black/graphite ink for the current collector are used. This design, based on the design from Empa's water-activated disposable paper battery [7], is biodegradable and lightweight. This study aims to further their findings and point out potential future work. A paper-based design can be an eco-friendly form of electrical energy production and open the door to smaller, lighter, and more portable battery production.

A schematic diagram of the zinc-air paper batteries is shown below:

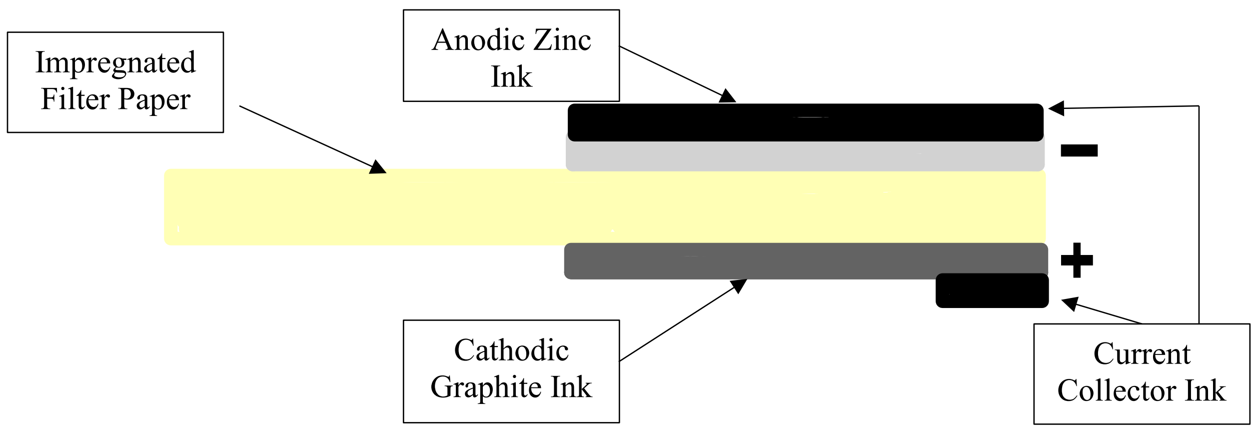


Figure 3. Schematic Diagram of Zinc-Air Paper Batteries

4. Zinc-Carbon Batteries

Section 4.1 Methods

Zinc-carbon batteries are constructed using a combination of solid and liquid materials. Both a cathode and an anode must be present for ionic transfer to occur. The anode consists of thin zinc sheets formed into tubes, and the cathode is a 3:1 mixture of manganese dioxide and graphite. A few trials were conducted to find which materials produced the car's most consistent battery power source. The materials used in the battery construction for the various prototypes included high-purity zinc sheets (99.9% pure, Micro Trader, 7440-66-6), reagent grade manganese dioxide fine powder (99% pure, LoudWolf Industrial and Scientific, 1313-13-9), ACS grade dry powder ammonium chloride (99.9% pure, LoudWolf Industrial and Scientific, 12125-02-9), 7–10-micron graphite flakes (99.9% pure, BeanTown Chemical, 7782-42-5), and medium speed 85 gsm filter paper (Eisco Labs).

Prototype 1:
The first trial used a zinc tube 10 cm tall filled with a slurry consisting of 50 wt% ammonium chloride and water surrounding a graphite rod. The zinc sheet was coated with the entire mixture of 25 g of ammonium chloride and 8.33 mL of water. On top of this slurry, a thin layer of manganese dioxide and carbon mixture was sprinkled. This mixture consisted of two g of manganese dioxide and 0.34 g of carbon. The sheet was then rolled around a graphite rod for the current collection. While this produced a sufficient voltage, it required compression and was hard to replicate. The rolling portion of the construction could have led to variations in the compression and distribution of the slurry between the zinc sheet and the carbon rod. Compression is a vital aspect of overall conductivity due to the increased interaction between

molecules accomplished through the expelling of unwanted gases caught between the reacting materials. This increased interaction leads to quicker oxidation.

Prototype II:
This prototype manufacturing was focused on a design that enables consistent reproduction. The zinc was measured into six cm (about 2.36 in) by ten cm rectangles and formed into a tube. Then, a bottom was constructed by measuring a four cm diameter circle and creating incisions around the perimeter to fold up and form a lip. This created a two-cm diameter for the zinc can. (volume = 18.85 cm^3). The exact process was done with filter paper. The filter paper was soaked in a 3M ammonium chloride solution and inserted into the zinc can. The cathode center was created by mixing a 3:1 ratio of manganese dioxide and carbon black. This mixture was dampened with 3M ammonium chloride in a 1 mL/g ratio with the cathode mix before inserting 18.2 g of the cathode mix into the battery. The last step was to insert a ten-centimeter-tall graphite rod into the center of the cathode mixture for current collection. This method, consisting of a zinc can housing loose cathode material, allowed for more extensive testing.

Prototype II in parallel:
The first multicell connection trial was a simple parallel circuit where three of the original four batteries were connected.

Prototype II in Daisy-Chain Connection:
The next attempt included a daisy-chain connection between four individual cells. This consisted of connecting two sets of two batteries in series and connecting the two new effective cells in parallel. Figure 4 below will describe the layout as well.

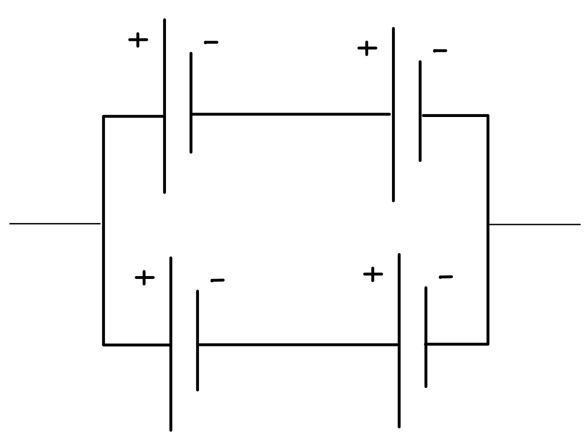


Figure 4. Daisy Chain Layout

Prototype III:
The following alteration was the replacement of carbon black with graphite flakes in the cathode mixture. This change was conducted to test all available carbon materials that could be present in the cathode mix. The size was maintained to minimize variables that could interfere with the

power produced by each battery for comparison. Prototype III was comprised of a zinc can six cm tall and two cm in diameter (volume = 18.85 cm^3).

Prototype IV:
For Prototype IV, Prototype III's cathode mix was maintained while only the size was varied to test the effect of volume on power production. Prototype IV consisted of a zinc can six cm tall and four cm in diameter (volume = 75.4 cm^3). This diameter increased the volume of the cathode mix required for the battery. The ratios of cathode to anode for each size were maintained by calculating the density of the batteries in grams of cathode mix per centimeter cubed of the zinc container. It was calculated that 24.1g of cathode mix per larger zinc container was required compared to the 18.2 g of cathode mix used for the smaller one, Prototype III.

Twelve batteries were connected via two cells of six batteries in series together with a parallel connection. In this parallel and series connection, the batteries produced enough amperage and voltage to move the car. A schematic of the connection diagram is outfitted in Figure 5.

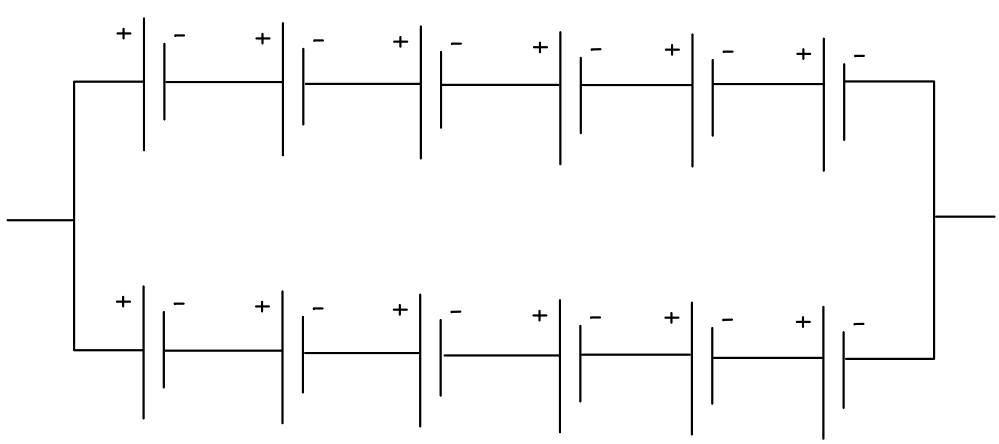


Figure 5. Schematic of Twelve Battery Connection

An image of the battery connections is shown below for both Prototype III and IV in Figure 6:

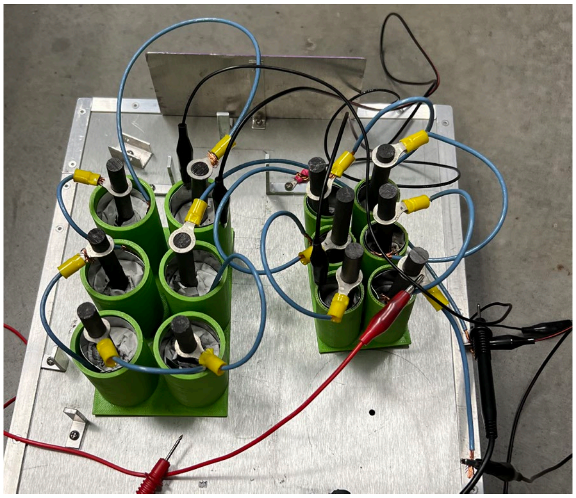


Figure 6. Image of Prototype III and IV Battery Connections

The batteries were then connected to a circuit containing the motor and a small LED light that would trigger a photosensor. This photosensor was connected to a solenoid valve to release the stopping mechanisms product, carbon dioxide, into the atmosphere. The entire electrical diagram is shown below in Figure 7:

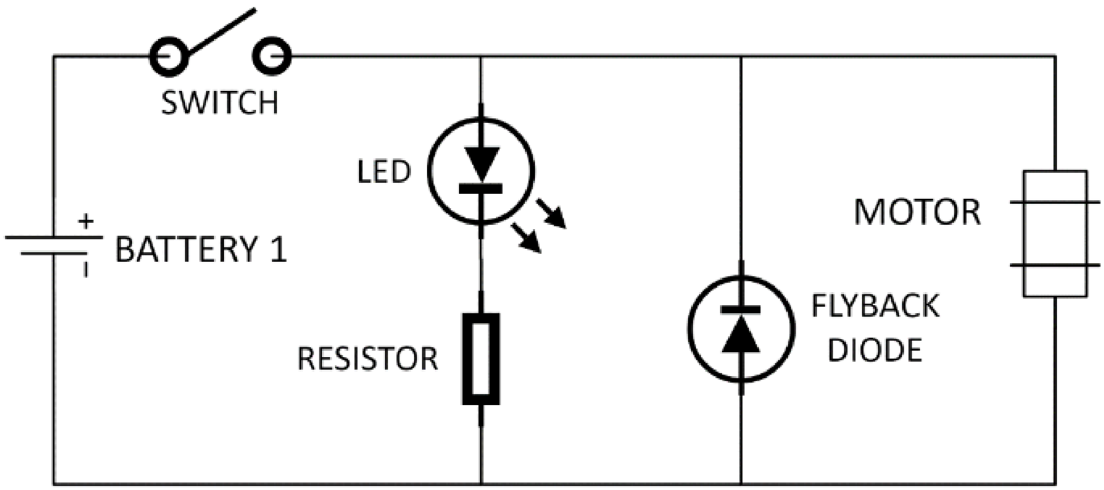


Figure 7. Electrical Diagram of Battery Connection to Motor and LED

To monitor the success of the batteries, voltage and amperage readings were taken using a BöRK MP -6050 multimeter. Volts were measured by putting the battery in series with the meter, while amps were measured by placing the battery in series with a resistor and the multimeter.

Several calculations will be used for the analysis of the batteries. These include the internal resistance, power, volume, and power density.

Internal resistance refers to the restriction of the current flow inside a battery. This is found using the following equation:

$$R = \frac{V}{I} \qquad \text{(EQ 1)}$$

Power refers to the Watt production, which is how much energy is stored in the battery. The following equation is used to calculate this:

$$P = VI \qquad \text{(EQ 2)}$$

The volume of a cylinder is found using:

$$V = \pi r^2 h \qquad \text{(EQ 3)}$$

Power density is the amount of power produced per unit volume, which is found using:

$$P_d = \frac{P}{V} \qquad \text{(EQ 4)}$$

Section 4.2 Results and Discussion

There are many ways to quantify or qualify the efficiency of a battery. Some ways to measure would be taking the voltage production from each battery, taking the amperage production from each battery, and attempting to power a source.

An image of each Prototype is displayed below in Figure 8-11.

Figure 8. Images of Top and Side View of Prototype I Zinc-Carbon Battery. From the top view, the 50 wt% ammonium chloride slurry wrapped around the graphite rod can be seen. A PVC (polyvinyl chloride) tube was slipped around the zinc can to maintain constant compression.

Figure 9. Image of Prototype II Zinc-Carbon Battery

This prototype has a wider base, a shorter zinc can, and different cathodic material. This cathode material consisted of a carbon black base with manganese dioxide in a 3:1 ratio.

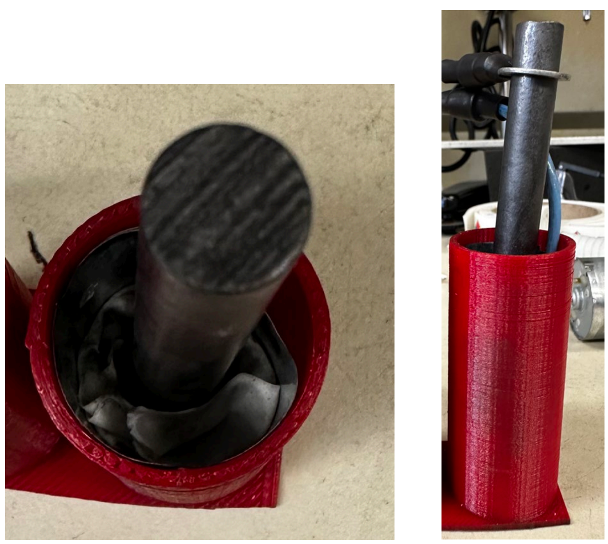


Figure 10. Image of Prototype III Zinc-Carbon Battery

Instead of PVC, an ABS (Acrylonitrile Butadiene Styrene) plastic container was printed to maintain shape and sturdiness. The same construction and size zinc can were used as Prototype II, but graphite was substituted for black carbon.

Figure 11. Image of Prototype IV Zinc-Carbon Battery
A similar ABS plastic container to Prototype III was printed for Prototype IV, but the diameter was increased from two to four centimeters.

Table 1 shows various comparable computations for each prototype for the zinc-carbon battery. All computed values were calculated based on average voltage and amperage. The average amperage was taken on the construction date for all batteries. There were no initial amperage recordings available for Prototype IV, so they are assumed to be like Prototype III since later recordings of older batteries of both Prototype III and Prototype IV have proven very similar.

Battery Comparisons						
Prototype	Average Voltage (V)	Average Amperage (A)	Resistor (ohms)	Average Internal Resistance (ohms)	Average Power (W)	Power Density (W/cm^3)
I	1.2	0.003	10	390	0.0036	0.000029
II	1.31	0.012	0.1	109.38	0.016	0.00084
II in Parallel	1.37	0.01842	0.1	74.28	0.025	-
III	1.40	1.18	0.1	1.08	1.65	0.088
IV	1.36	(1.18)	(0.1)	(1.08)	(1.65)	-

Table 1. Outline of Various Battery Comparisons for Each Prototype Zinc-Carbon

When analyzing the data and construction methods, it became evident that Prototype I would not be suitable for consistent power production. It may have boasted a large voltage production but was insufficient for the precise reproduction necessary for series connections. If this battery style had moved forward, each connection could have caused unnecessary drainage between the others due to fluctuations in manufacturing. It was also more open to the air and harder to encapsulate. The airflow was more significant to the dampened portions of the cell, causing possible dry spots. In addition, the safety of this battery was also an issue due to the increased possibility of leakage. The amperage produced with this prototype was also marginally low at 3.6 mW. The

Prototype I battery had the lowest recordable power production of all zinc-carbon batteries tested.

Prototype II was a design that yielded better results. By allowing for precise weight measurements into the can as well as organized containment sizes, the batteries manufactured in this style were far more reproducible. Each battery produced in this fashion created a consistent voltage, which was essential for the reproducible velocity needed for the car and for reducing the chance of potential draining between cells that can occur when two dissimilar batteries are connected. The voltages and amperages recorded for Prototype II, an average of 1.31 V and 12 mA, respectively, were sufficient to power the car. The batteries produced an average power of 1.6 mW. This is a 126% increase from Prototype I's power production.

Prototype III was constructed similarly to Prototype II except the carbon cathode material was replaced with graphite. Prototype III yielded slightly higher voltage productions and much higher amperage productions. Consistently providing over 1 A of current, Prototype III increased power production from Prototype II's 1.6 mW to 1.65 W. This is a drastic 196% increase in power production. When analyzing why this could have been the case, it is essential to look at the internal resistance of each battery. Internal resistance is calculated by dividing the voltage produced by the amperage produced. By doing this with Prototype II using a 0.1-ohm resistor for amperage collection, it was found that an average internal resistance of 109 ohms is present. In Prototype III, an almost 100-fold lower average internal resistance of 1.08 ohms is found. The internal resistance of Prototype IV is comparable to a store-bought AA alkaline battery, which has an internal resistance of about one ohm, according to Nustem [8].

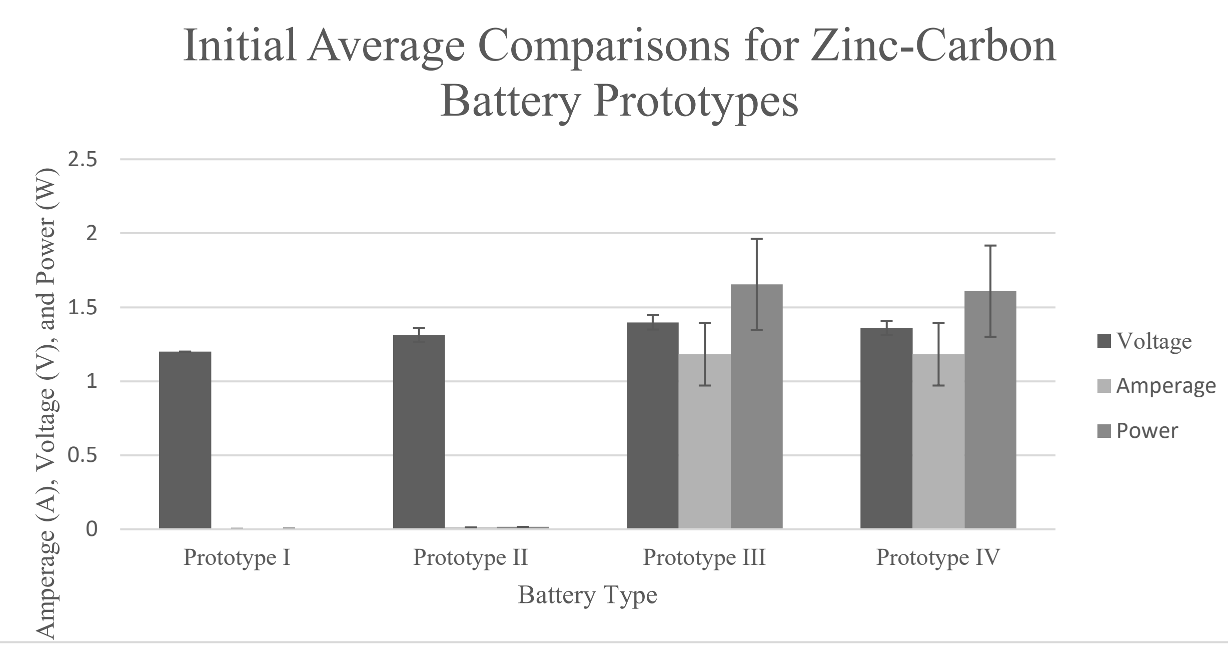


Figure 12. Initial Voltage, Amperage, and Power Comparisons for Zinc-Carbon Battery Prototypes

The batteries were also tested to see how long they could last via rehydration with the 3M ammonium chloride solution. Six large and six smaller batteries were constructed on November 19th, 2022, and kept in storage. The six large ones were connected in series separate from the series of the six small ones. The series connection containing the six large batteries produced 8.28 V, and the series connection having the six small batteries produced 8.12 V. When both series were combined for 12 batteries in series, 16.37 V was produced.

The voltages of the individual batteries were recorded over time as they were used to power the motor. The motor required 6 V and approximately 500 mA to function.

Figure 13 shows the final prototype comparisons after all six runs. The graph in Figure 14 shows the average voltages of each battery type over time, which was taken after each run. A run consisted of moving the car 30 meters.

Many factors need to be considered for using batteries on the ChemE Car including size, weight, power, and cost. The lighter the vehicle, the less voltage production would be required. On the other hand, a battery that would last the entire competition and function as predicted would be advantageous. Two sizes were considered based on the material availability. The first size, Prototype III, a zinc can that was six cm tall with a two cm diameter base, was tested. This size produced a consistent average of 1.40 V per battery with a standard deviation of $\pm$0.05 V between the twenty-three cells tested. The uniformity proves that the batteries manufactured were precise enough to maintain good connections and reduce the possibility of drainage between cells in the competition. The second size, Prototype IV, was more consistent. Six batteries were made for an initial trial. The size difference, which was the difference between a two cm diameter and a four cm diameter, was a 120% increase in volume (18.85 versus 75.40 cm^3) and a 27.7% increase in weight (18.2 versus 24.1 g) for the cathode mix. The larger battery generated 1.36 V, slightly less than the smaller Prototype III, even though the cathode was much larger.

The next step was to analyze the series connection data. The six small batteries in series connected to the six larger batteries in series via a parallel connection produced an average of 7.75 V with a standard deviation of $\pm$0.70 V. This means that both cells produced a similar value in voltage to each other since the parallel connection increases amperage production, not voltage production.

Battery longevity was tested by using them to power the car motor repeatedly. The data in Figure 14 shows that both battery sizes could produce similar voltages over multiple runs. The batteries were used in a series and parallel connection to power the small car's motor and tested after each run to monitor voltage production. The data from Figure 14 shows the result of this testing. This testing was completed over the span of multiple weeks, rehydrating the batteries with 1 mL of 3M ammonium chloride each before testing when a new day began. Prototype IV showed a strong correlation with each other throughout testing, while Prototype III showed more variation after each trial. While there was a stronger correlation between the larger battery voltages recorded, all batteries stayed in a usable range throughout the entire process. The competition will require two runs, which should remain consistent for either battery size.

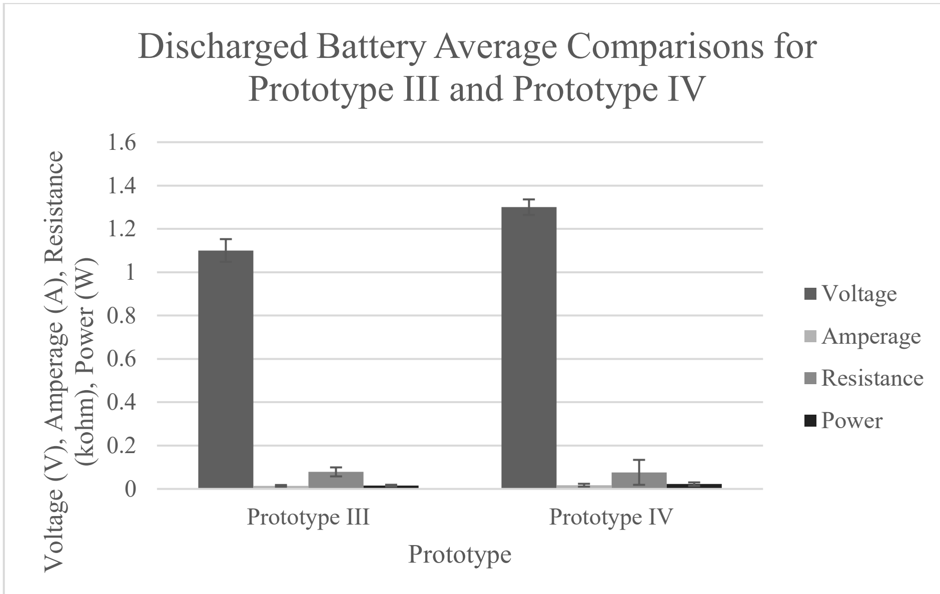


Figure 13. Discharged Battery Average Comparisons for Prototype III and Prototype IV After Six Runs

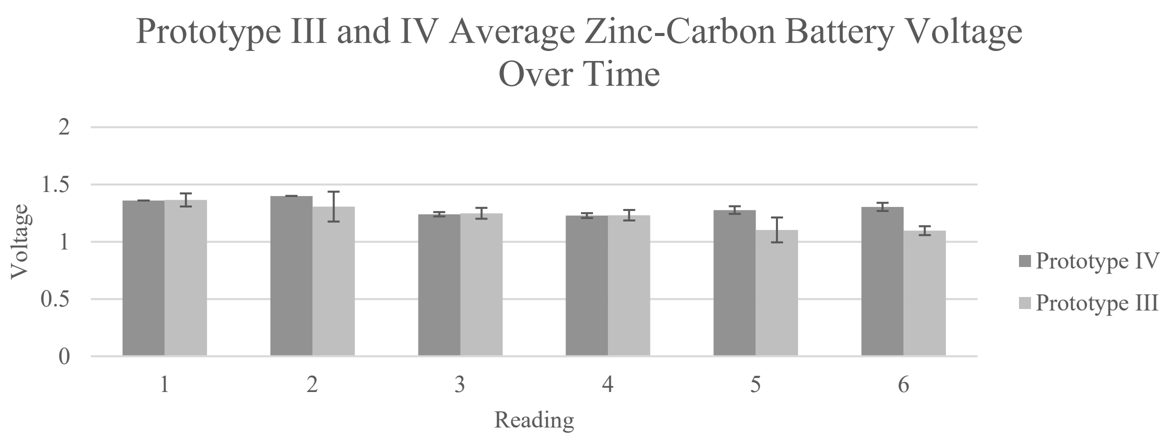


Figure 14. Voltage Variation Over Time of an Average of Individual Batteries in a Prototype III and Prototype IV 6 Battery in Series Cell

Table 2 shows the dates when each reading was recorded. At the beginning of each new date, 1 mL of 3M ammonium chloride was added to each battery. Rehydration was not required when multiple runs were completed on the same day. This is because the 3M ammonium chloride has not yet evaporated, which would leave the cell dry. On those days, the runs were completed within 15 minutes of each other.

Date	Reading Number
11/19/2022	1
11/21/2022	2
11/21/2022	3
11/21/2022	4
12/05/2023	5
1/23/2023	6

Table 2. Reading Dates for Voltages Recorded in Figure 5

Section 4.3 Conclusions

By viewing Table 1 and comparing the values, it is easy to see that Prototype III has the most power production and the least internal resistance between the first three prototypes. Power production is a vital aspect of a battery's performance because it is the value that shows how much energy can be supplied to the system from the battery. The higher this value, the more effective the battery. Internal resistance resists the flow of electrons through the battery, which lowers the possible power. Therefore, the internal resistance should be low in an effective battery. The lowest internal resistance between any tested batteries would be the one present for Prototype III. This is how the cathode mixture and initial design were chosen as the 3:1 manganese dioxide and graphite mixture with the zinc can and filter paper. The next step was to determine the scaled size of the battery between Prototype III and Prototype IV.

By comparing the differences between the two prototype sizes, it was determined that Prototype III would be best. The size increase of Prototype IV yielded only a 2.90% increase in amperage, while the volume increased by 120% and the weight by 27.5. This decision arose from the fact that the average voltage for Prototype III was greater, took up less space on the car, and weighed less than Prototype IV. Prototype III took up 108 cm^2 while Prototype IV took up 229.5 cm^2. The entire car's chassis has an area of 875 cm^2. This means that using Prototype III would use up 12% of the car's space while Prototype IV would use up 26% of the car's available space. To maintain enough space for the stopping mechanism, which takes up roughly 97 cm^2, Prototype III is the most efficient choice.

Moving on to power comparisons, Prototype IV produced 31.6% more power after six runs than Prototype III did on average, with values of 0.022 W and 0.016 W, respectively. This does not consider the extra power required to move the car due to the excess weight from Prototype IV. Increasing the car's weight will increase the torque necessary to move the motor's gears. The ideal drive torque equation, which is

$$M = F * r \qquad \text{(EQ 6)}$$

Where M is the drive torque, F is the force perpendicular, or mass, in N, and r is the radius from the distance from the axis of rotation. The distance, or r, will remain the same, so it is possible to determine the difference in drive torques required by comparing the two forces acting on the car.

This is just comparing the two masses, which differ by 27.7%. Since the torque is proportional to power, it can be concluded that the speed will only be decreased by minimal amounts if Prototype III is to be used instead of Prototype IV to make space for other mechanisms on the car.

In conclusion, Prototype III is the best-suited battery for the car.

5. Zinc-Air Batteries

Section 5.1 Methods

Paper batteries are formed using a zinc-air battery base. In this battery style, the oxygen in the surrounding air acts as the cathode, while zinc ink acts as the anode. Three separate inks are created to facilitate this electron transfer.

Prototype I
The specific materials used in manufacturing for Prototype I include shellac (ZINSSER Bulls Eye Shellac), zinc powder (100% pure, Wards Science, 7440-66-6), Ketjenblack EC-300J 100% pure carbon black (100% pure, AkzoNobel, 1333-86-4), 7–10-micron graphite flakes (99.9% pure, BeanTown Chemical, 7782-42-5), powdered polyethylene glycol, 200 proof ethanol (Deacon Labs, 64-17-5), and Whatman 4 filter paper (Sigma-Aldrich).

The anode ink was constructed using 2.5 wt% powdered polyethylene glycol, 5.5 wt% ethanol, 89.5 wt% zinc powder, and 2.5 wt% shellac. The shellac and ethanol were combined, and the zinc powder and the powdered polyethylene glycol were hand-mixed into the ink.

The cathode ink was prepared using 8 wt% powdered polyethylene glycol, 30 wt% ethanol, 47 wt% graphite flakes, and 15 wt% shellac. This was mixed in the same manner as the anode ink.

The current collector ink was made using 5.45 wt% powdered polyethylene glycol, 56.4 wt% ethanol, 8.85 wt% activated carbon, and 29.3 wt% shellac.

The Whatman. 4 Filter paper was cut into $\frac{1}{2}" \; x \; 1"$ rectangles, and then soaked in 3M NaCl. These were then dried by heat before using in the ink application. The anode ink was applied first to the upper half of one side of the filter paper via smear tactic. Then, once that side was sufficiently dry, the cell was turned over, and the cathode ink was applied to the same area on the back side using the same technique. Once both were dry, the current collector ink was printed over the entirety of the anode side and on a small section of the cathode side to allow contact with air.

To activate these batteries, the unaltered bottom half of the filter paper, where no ink was printed, is dipped into the water. This water, via capillary action, travels up the filter paper and connects the anode and cathode, beginning the oxidation process.

Prototype II
The specific materials used in manufacturing for Prototype I include shellac (Shellac Orange by Kremer Pigment, Germany, 9000-59-3), polyethylene glycol (PEG 400 by VWR, Switzerland,

BeanTown Chemical, 25322-68-3), zinc powder (100% pure, Wards Science, 7440-66-6), Ketjenblack EC-300J 100% pure carbon black (100% pure, AkzoNobel, 1333-86-4), 7-10-micron graphite flakes (99.9% pure, BeanTown Chemical, 7782-42-5), 200 proof ethanol (Deacon Labs, 64-17-5), and Whatman 597 filter paper (Sigma-Aldrich).

The anode ink was made from 2.5 wt% polyethylene glycol, 5.5 wt% ethanol, 89.5 wt% zinc powder, and 2.5 wt% shellac. Shellac and ethanol were mixed using a ball mixer, and the zinc powder and PEG were added. These continued to mix in the ball mixture until a fine ink texture was formed.

The cathode ink was constructed with 8 wt% polyethylene glycol, 30 wt% ethanol, 47 wt% graphite flakes, and 15 wt% shellac. The shellac and ethanol were remixed using a ball mixer before adding the graphite and PEG. At the end of this, 50% more ethanol and polyethylene glycol were added to create an ink-like consistency.

The current collector ink had the most significant change between the two prototypes. This ink was created using 4 wt% polyethylene glycol, 41.5 wt% ethanol, 6.5 wt% carbon black, 26.5 wt% graphite flakes, and 21.5 wt% shellac.

The preparation and activation of the batteries were maintained to exclude variables in ink comparisons.

To analyze the effectiveness of these batteries, voltages, and amperages were recorded from each construction. With these recordings, comparisons were made between the zinc-air battery prototypes. Internal resistance, power, volume, and power density were all analyzed. For these calculations, Equation 1, Equation 2, Equation 3, and Equation 4 from the methods section of the zinc-carbon batteries were consulted.

Further study into potential electrolytic bridges was carried out as well. In these trials, 3M NaCl was used for paper impregnation. Future studies should be conducted to determine the usefulness of potential ionic polymers replacing this section of the paper battery. For this thesis, a conductivity analysis was done to determine the potential uses of specific ionic polymers for this application. Two novel fluorinated polymer bases were used in conjunction with an ionic liquid, which will be referred to as Polymer I, Polymer II, and Ionic Liquid.

To conduct conductivity analysis, sections of Whatman 597 filter paper were cut into 1” x 3” sections and dissolved in 5 mL of DMF (Dimethyl Formamide). The DMF present had a concentration of 100 mg/mL. These DMF-treated filter paper samples were left overnight to solvate.

Individual DMF-coated filter paper samples were then coated with 1 mL of each of the following formulations: Polymer I, Polymer I with 40 wt% Ionic Liquid, Polymer II, and Polymer II with 40 wt% Ionic Liquid.

Conductivity was calculated using the following equation:

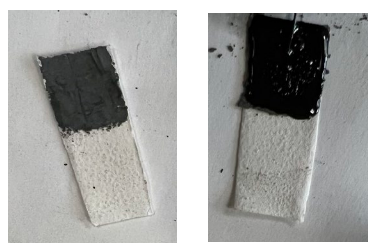
$$\sigma = \frac{L}{AR} \quad \text{(Eq. 6)}$$

The paper thickness (L) and the cross-sectional area (A) are known, and the resistance (R) is measured. The effective resistance measurements were taken at frequencies between 100 mHz and 7 Hz.

A biopsy punch was used to extract small sections of the coated filter papers to collect these measurements. These small sections were wedged into a tailor-made two-electrode cell with 316 stainless-steel blocking electrodes. Electrical Impedance Spectroscopy (EIS) on a BioLogic VSP 300 Potentiostat was used.

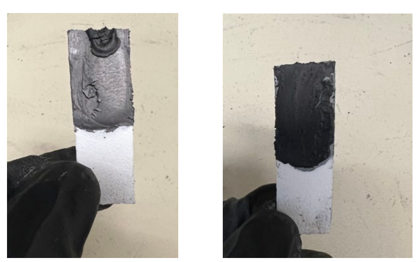
Section 5.2 Results and Discussion

Below are images of finished batteries from each prototype. Figure 15 and Figure 16 show Prototype I and Prototype II, respectively. Prototype I and Prototype II differ in the components of their inks. See the Methods section for more details. The final weights of each battery are 0.67 g for Prototype I and 0.80 g for Prototype II.



Cathode Anode

Figure 15. Image of Prototype I Zinc-Air Battery



Cathode Anode

Figure 16. Image of Prototype II Zinc-Air Battery

Table 3 below outlines the important aspects of battery comparisons for the zinc-air battery prototypes.

Battery Comparisons						
Prototype	Average Voltage (mV)	Average Amperage (μA)	Resistor (Ω)	Average Internal Resistance (Ω)	Average Power (W)	Power Density (W/cm^3)
I	0.4	6.75	0.1	1.41E03	2.70E-09	2.24E-07
II	16.12	11.43	0.1	5.93E01	1.84E-07	1.53E-05

Table 3. Outline of Various Battery Comparisons for Each Prototype Zinc-Air

Figure 17 below shows a graphical display of the voltage and amperage comparisons for the zinc-air prototypes in mV and μA, and Figure 18 shows comparisons between power production for the two prototypes in Watts.

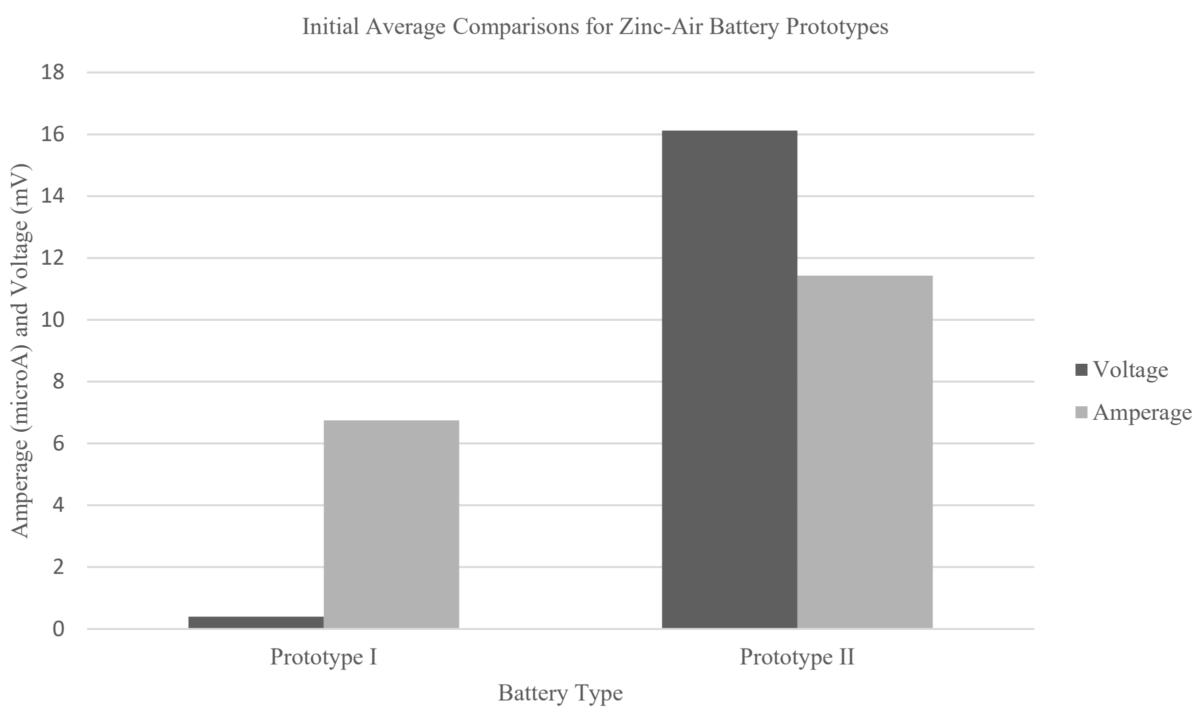


Figure 17. Initial Voltage and Amperage Comparisons for Zinc-Air Battery Prototypes

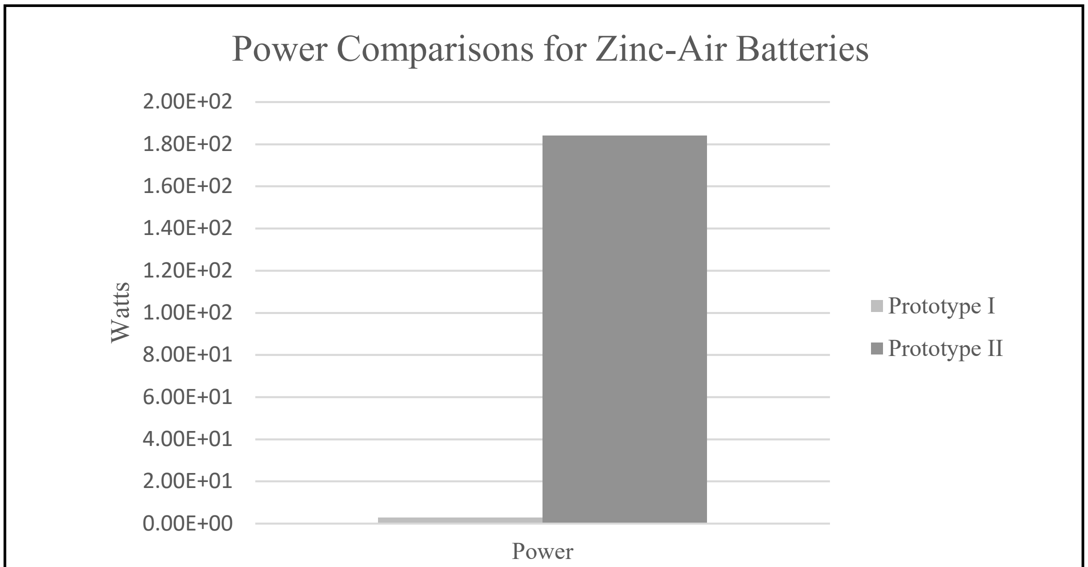


Figure 18. Average Power Comparison for Zinc-Air Batteries

Table 4 below outlines the ion conductivity comparisons for each coated filter paper. It shows the conductivity of the individual polymer coatings, each polymer mixed with 40 wt% ionic liquid and NaCl.

Coating on Cellulose Paper	EIS (mS/cm)
Polymer I	3.00E-04
Polymer I with 40wt% Ionic Liquid	2.24E-01
Polymer II	1.48E-03
Polymer II with 40wt% Ionic Liquid	1.63E-03
Dry 3M NaCl	4.3E-06
Wet 3M NaCl	10.8

Table 4. Conductivity Comparisons Between Polymers, Ionic Liquid Additions, and NaCl

Upon analysis of both prototypes, it was found that Prototype II produced more voltage, amperage, and power on average. When comparing voltage, Prototype II generated 190% more volts than Prototype I (16.12 mV and 0.4 mV, respectively). Because of this stark difference in electrical potential generated, the power production was much more significant for Prototype II.

Their amperage production was slightly more consistent, with Prototype II increasing the amperage production by 51% compared to Prototype I (11.43 μA and 6.75 μA, respectively). This also led to higher power production for Prototype II. Power, which is calculated using Equation 2 from the previous section, increased by 194%.

This large discrepancy between the two prototypes is due to many factors including more adequate mixing of the inks, more conductive and pure materials, and longer wicking periods for battery activation in Prototype II. Because of these changes in both production and materials, Prototype II is the better battery.

While Prototype II is the better battery, it is not sufficient for powering the motor of the ChemE Car. The power production is far too low. While this battery is lightweight and small, it would take too many of them attached in a combination of both series and parallel connections to be created during the two-hour preparation period at the competition. There are also many opportunities for variations in ink preparation, mixing, and application that leave room for both shortages and discrepancies that will affect the overall power supplied to the motor between each run for testing and during the competition.

When looking at the conductivity analysis for the polymers, it can be observed that Polymer I had a 133% lower conductivity than Polymer II before adding the ionic liquid (3.00E-04 mS/cm and 1.48E-03 mS/cm, respectively). When the 40 wt% Ionic Polymer is added to Polymer I, the conductivity is increased to 2.24E-01 mS/cm, a 199% increase. The Ionic Liquid did not increase Polymer II's conductivity by as much, though; its conductivity increased by 10% to 1.63E-03.

When comparing the Ionic Polymer conductivity with the dry 3M NaCl impregnation conductivity, both the polymers and the Ionic Liquid included polymers have higher conductivity rates than the dry 3M NaCl impregnation. Polymer I's conductivity was 194% greater than the dry 3M NaCl, increasing to 200% when the Ionic Liquid was included. Polymer II's conductivity was 199% higher than the dry 3M NaCl for the polymer only and the Ionic Liquid inclusion.

When analyzing the wet 3M NaCl conductivity, the ion conductivity increases higher than any polymer and ionic combination in testing. Wetting the substrate provided a 200% increase in conductivity compared to the dry 3M NaCl. When comparing the wet 3M NaCl ion conductivity to the polymers, there is a 200% increase from Polymer I and a 192% increase from Polymer I with 40 wt% Ionic Liquid. There is also a 200% increase between the wet 3M NaCl and Polymer II's ion conductivity and a similar increase between the wet 3M NaCl and Polymer II with 40 wt% Ionic Liquid. This increase in conductivity between the wet and dry 3M NaCl shows the need for activation by water for these batteries to facilitate efficient ion transfer. Future studies on the polymer substrates could lead to a paper battery that does not need to be activated before use because they remain active. The most promising polymer combination to be used in these trials would be Polymer I with 40 wt% Ionic Liquid since it has the highest conductivity tested.

Section 5.3 Conclusions

By reviewing Table 3, Prototype II is the more powerful battery. The style of mixing the inks and the ratios of specific components in the inks that were used in this prototype is better for the electron transfer required in the redox reaction. However, it is not a viable option for powering the electric motor for the ChemE Car competition. Prototype II's power output is too low, and the time it takes to manufacture is too long. This battery may have other foreseeable uses in future work, such as ionic polymer inclusion in the semipermeable substrate separating the two terminals. It could also be used in other applications where the power requirement from the battery is lower, such as remote controls or timers.

When examining the potential for ionic polymer inclusion, it can be seen in Table 4 that Polymer I would be the better choice for the specific Ionic Liquid tested. Including the Ionic Liquid greatly increased the conductivity of Polymer I on this particular filter paper. Polymer I could be a viable option for producing paper zinc-air batteries. Since the polymer trials all produced higher conductivity levels than the dry NaCl impregnations, the paper batteries created with ionic polymer impregnation produced more power than the unactivated paper battery in this style. When comparing the wet NaCl impregnations to the ionic polymer impregnations, it was found that the 3M NaCl impregnations produced higher ion conductivity. This means that the overall characteristics of the batteries will likely be better for the NaCl impregnations than the ionic polymer impregnations. It is essential to conduct further testing to say NaCl is the best, though.

6. ChemE Car

The finalized car, "Sherlock Ohms," has a steady power source and a reliable stopping mechanism. The power system, composed of Prototype III zinc-carbon batteries, supplies power to the 12 V electric motor when the circuit is closed. To stop the car, a reaction vessel containing calcium carbonate and diluted hydrochloric acid produces carbon dioxide, which is then vented through a tube into a mylar balloon. This balloon is allowed to fill up with the gas, which pushes it from a horizontal position to a vertical position. This change in position causes the balloon to contact a float-level switch. This switch is part of the circuit connecting the batteries to the motor. When this float level switch is activated, the circuit is opened, and power is cut to the motor, thus stopping the car. The time it takes for the balloon to fill is determined by controlling the carbon dioxide production reaction rate with the molarity of hydrochloric acid used in the reaction vessel. The amount of calcium carbonate remains consistent through each run.

Many fail-safes have been established in the car in pursuit of safety. One example would be releasing carbon dioxide from the mylar balloon as soon as the float level switch is activated into the atmosphere. This is accomplished by adding an LED to the battery circuit. Once the float level switch is activated, the LED powered by the batteries shuts off. When this is accomplished, a photoresistor senses that the light has turned off and signals a solenoid valve to open. This solenoid valve is connected to the carbon dioxide stream in the mylar balloon. The carbon dioxide is then allowed to safely vent to the atmosphere, removing any chances of over pressurization or popping the balloon. Other safety aspects include a pressure relief valve attached to the reaction vessel that is rated to go off before the vessel's rated pressure is met or exceeded. This precaution removes the possibility that any blockages in the tubes will lead to an overpressure of the reaction vessel. There are also many examples of primary and secondary containment throughout the entire car. These are primarily made from ABS plastic. ABS plastic is also used to house wires, relay boards, and the LED/photoresistor system to keep them safely stored under the car's chassis and cover any potential pinch points, such as the motor belt. Figure 19. Image of the Finished ChemE Car, Sherlock Ohms shows a picture of the finished car with the batteries under the larger red container.

Figure 19. Image of the Finished ChemE Car, Sherlock Ohms

7. Future Work

Many applications for future work are viable from this thesis. The starkest example of this would be in the zinc-air batteries. Data collection on this front could have been more precise using different methods. The following is a more detailed description of a proposed testing method:

> Begin with impregnating the filter paper with the chosen electrolytic solution. Ensure this filter paper is slightly larger than the desired final battery. Let dry overnight to ensure maximum dispersion throughout the substrate.
>
> Next, create the anodic ink using a planetary mixer. Once this is done, use a fabricated stencil to apply the ink to the filter paper. Allow this to dry in the same place as the impregnation was done overnight.
>
> The next day, create the cathodic ink using a planetary mixer. Apply the ink using a stencil to the other side of the filter paper as the anodic ink and allow it to dry overnight in the same place as the first two steps.

Finally, create the current collector ink using a planetary mixer and apply it using a stencil to both sides of the battery in the desired areas. Allow this to dry overnight before activating the battery.

On the last day, activate the batteries using water via capillary action. Allow the batteries to migrate water through the paper for a specific time, keeping this time consistent between each battery reading and recording the data.

Changing the experimentation process can ensure that each ink is sufficiently mixed, dried, and applied uniformly for each tested battery. The volume of water used to activate the batteries should also be kept the same throughout each trial. This process would give more consistent data and ensure no outside variables skew any data points.

Another aspect of future work for the zinc-air batteries would be to create new designs for the stencil printing process for possible series or parallel connections between batteries. The Empa experiment mentions the use of wax to separate cells on the same semipermeable substrate [7]. This could be done by rotating the cathodic and anodic directions and connecting them via the current collector ink over a wax separation (see Figure 20). The second cell would be flipped to match the first to create a parallel connection between the two cells. Due to their compact and thin nature, there are many ways to explore new connections between these paper battery cells. Screen printing could increase the surface connection between the cathode and anode in many ways.

Other future experiments could include testing batteries using ionic liquids and polymers as replacements for the NaCl impregnation on the substrate. Different semipermeable substrates could also be explored to absorb ionic liquids and polymers better. The possibilities are endless.

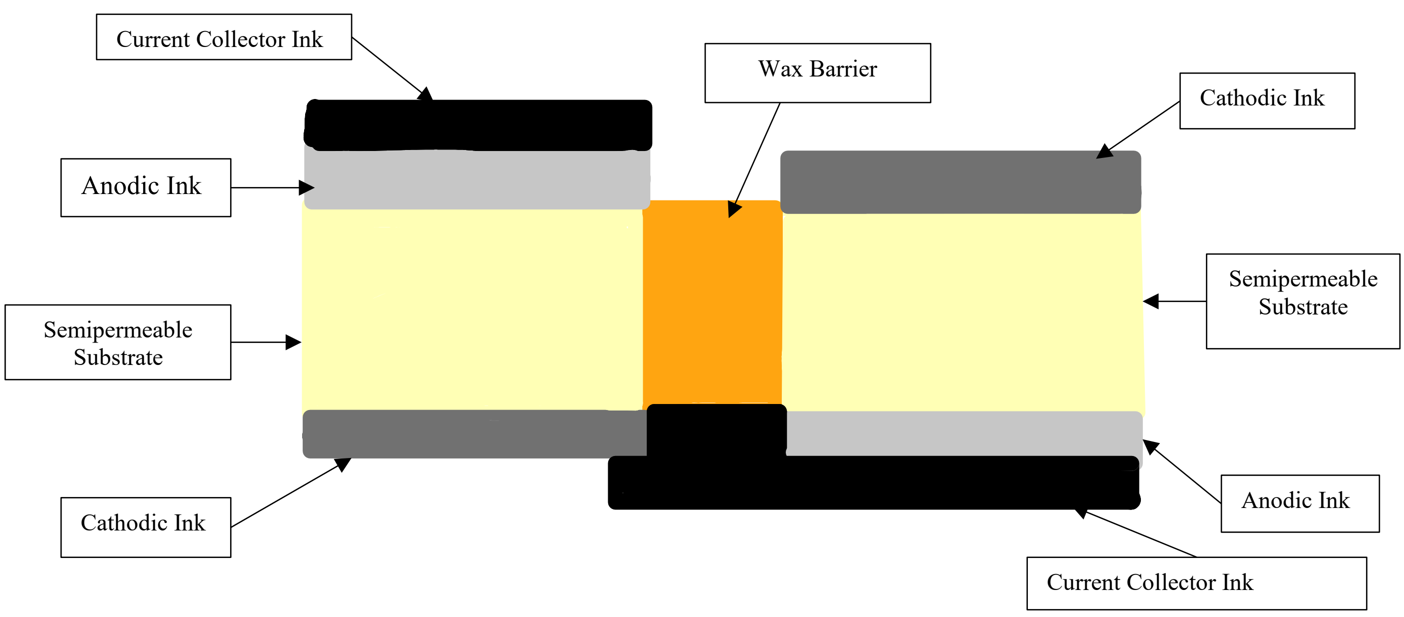


Figure 20. Diagram of Series Connection Between Two Zinc-Air Batteries on the Same Semipermeable Substrate.

8. Acknowledgments

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