Optimizing surface contact area and electrolyte type to develop a more effective rechargeable battery

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SUMMARY

Rechargeable batteries are playing an increasingly prominent role in our lives due to the ongoing transition from fossil energy sources to green energy. The purpose of this study was to investigate variables that impact the effectiveness of rechargeable batteries. Alkaline (non-rechargeable) and rechargeable batteries share common features that are critical for the operation of a battery. The positive and negative electrodes, also known as the cathode and anode, are where the energy of the battery is stored. The electrolyte is what facilitates the transfer of cations and anions in a battery to generate electricity. Due to the importance of these components, we felt that a systematic investigation examining the surface area of the cathode and anode as well the impact of electrolytes with different properties on battery performance was justified. Utilizing a copper cathode and aluminum anode coupled with a water in salt electrolyte, a model rechargeable battery system was developed to test two hypotheses: a) increasing the contact area between the electrodes and electrolyte would improve battery capacity, and b) more soluble salt-based electrolytes would improve battery capacity. After soaking in an electrolyte solution, the battery was charged and the capacity, starting voltage, and ending voltage of each battery were measured. The results of this study supported our hypothesis that larger anode/cathodes surface areas and more ionic electrolytes such as sodium chloride, potassium chloride and potassium sulfate resulted in superior battery capacity. Incorporating these findings can help maximize the efficiency of commercial rechargeable batteries.

INTRODUCTION

Since their invention by Alessandro Volta in the 1800s, batteries have been incorporated into our everyday lives to store chemical energy for powering electronic devices, ranging from flashlights to automobiles to cellphones (1). The growing demand for energy from renewable sources has reinvigorated the need for rechargeable batteries. Ideally, these batteries should be capable of being recharged multiple times with an adequate capacity to power a device for an extended period. Current rechargeable batteries utilize lead, nickel-cadmium, nickel metal hydride or lithium chemistries. While these types of batteries see broad use, they are limited by low capacities, low output voltages, and the use of toxic materials (2). Increasing capacity and using non-flammable designs are critical to expand the use of rechargeable batteries for everyday applications.

Although rechargeable batteries are manufactured in different shapes and sizes, they all have the same general design. Each contains a positive and negative electrode, called the cathode and anode, respectively, with an electrolyte in between that facilitates ion transfer. Charging involves applying a force to move electrons from the cathode to the anode, resulting in potential energy that is stored in the battery. This energy can be discharged to power a device when electrons move in the opposite direction (1, 3) (**Figures 1 and 2**). During both the charging and discharging process, the ions from the electrolyte move inside the battery to balance the charge of the electrons (4). The impact of the electrolyte on battery performance has been studied in the past. For example, most lithium-ion batteries can only use a fraction of their energy due to the unstable nature of their electrolyte as $LiPF_6$ reacts violently with water (5). Water in salt (WIS) electrolytes, a variant that uses water as a medium through which charge-balancing ions can flow, have recently found favor due to their increased safety and use of inexpensive materials, and they can be used in most non-lithium rechargeable batteries (6).

We used a copper cathode- and aluminum anode-based model battery system to explore the impact of the electrode surface area and the WIS electrolyte solution on the capacity of a rechargeable battery. Copper and aluminum both are inert and readily available materials that can be used safely in a home setting. During this study, we tested two hypotheses. First, we hypothesized that maximizing the surface area of the electrodes and electrolyte would improve battery capacity as capacity is likely the result of a first order chemical reaction. We also hypothesized that more ionic salt-based electrolytes would improve battery capacity due to their superior ability to transport ions. After charging for five minutes at 9 volts (V), the capacity of the battery was determined by measuring the amount of time a 1.5 V miniature lightbulb remained lit during the discharge of the battery. For each battery, four charging and discharging cycles were conducted to measure the starting voltage, capacity, and ending voltage. Three surface areas, which increased in 3-fold increments, were examined using a sodium chloride electrolyte. The results of this experiment showed a larger surface area increased the capacity of the battery. Seven different electrolytes that included salts with mono- and di-cationic/di-anionic character, that were known to dissolve in water were also tested while holding the anode and cathode surface areas constant. In general, the more electronegative electrolytes produced higher battery capacity.
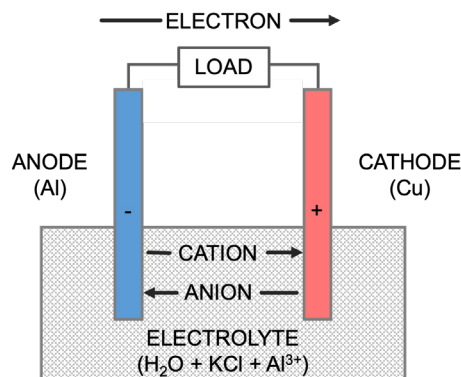
Figure 1: Diagram of a cell in operation during discharge. As electrons move from the anode to the cathode, the anode is oxidized ($2Al_{(s)} \rightarrow 2Al^{3+}_{(aq)} + 6e$), and the cathode is reduced ($3Cu^{2+}_{(aq)} + 6e \rightarrow 3Cu_{(s)}$). Anions move towards the anode, and cations move towards the cathode.

RESULTS

Surface Area

We produced different surface areas for the anode and cathode starting with a 9x10 cm metal sheet, which was folded into 1x3, 3x5 and 9x5 cm surfaces. Our use of a 9x10 cm sheet size as the common starting point kept the metal content constant and the only variable was the surface area available for reaction. The capacity of the battery, as determined by measuring the amount of time in seconds (s) a 1.5 V miniature lightbulb remained lit during the discharge of the battery, increased with surface area in a statistically significant manner ($p<0.05$). The 1x3 cm, 3x5 cm and 9x5 cm electrode sizes resulted in capacities of 19 ($\pm$1), 90 ($\pm$13) and 299 ($\pm$20) s respectively for the first charge/discharge cycle (**Figure 3A**). We found that subsequent charges and discharges preserved this trend, though the overall capacity
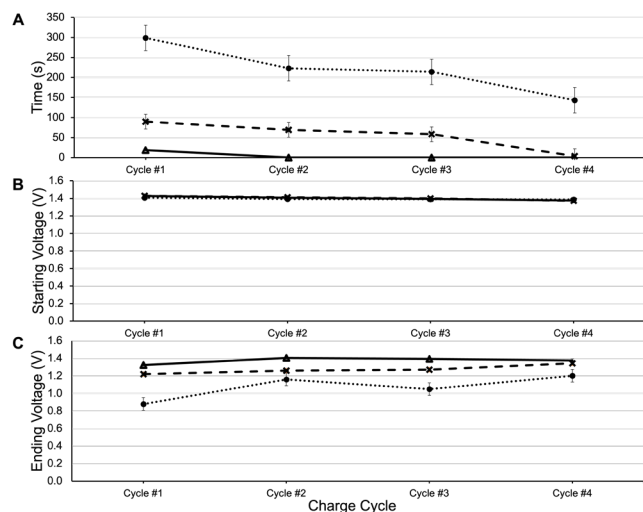
Figure 3: Surface area results. (A) The average capacity of the 9x5, 3x5, and 1x5 cm batteries. (B) The average starting voltage of each battery surface area condition. (C) The average ending voltage of each battery surface area condition. A dashed line signifies when the starting and ending voltages are the same due to no capacity. Each point represents the average of the six batteries created per the four charges for each condition, including the standard error.
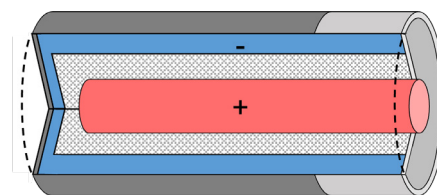
Figure 2: Standard battery cell. Contains a cathode (red) core surrounded by an electrolyte paste (grey patterned) and an anode shell (blue).

generally decreased with each cycle. The capacities for the fourth and final cycle were 0 (no capacity), 4 ($\pm$3) and 143 ($\pm$17) s respectively.

We found that the starting voltage was similar for the 1x3 cm, 3x5 cm and 9x5 cm electrode sizes at 1.43 ($\pm$0.00), 1.43 ($\pm$0.01) and 1.41 ($\pm$0.01) V respectively for the first cycle (**Figure 3B**). The ending voltage for this cycle was 1.32 ($\pm$0.01), 1.22 ($\pm$0.07) and 0.88 ($\pm$0.13) V respectively (**Figure 3C**). The trend where higher capacity was associated with lower ending voltage in this cycle was also observed for the subsequent cycles.

Electrolytes

Regarding the electrolytes, we constructed batteries utilizing a 9x5 cm electrode surface area to assess the capacity, starting voltage, and ending voltage. We chose the readily available salts potassium chloride, sodium chloride, potassium sulfate, calcium chloride, copper sulfate, copper chloride and ammonium chloride, a selection with mono- and di-cationic/di-anionic character, that were known to dissolve in water. The electrolyte solutions were made by dissolving 10g of each salt in 350mL water, and then stirring for 10 minutes until all the solid was in solution. Potassium chloride yielded the highest overall capacity of all the electrolytes for the first charge ($p<0.05$, **Figure 4A**). The capacity decreased with each subsequent cycle, with durations of 291 ($\pm$16), 190 ($\pm$1), 129 ($\pm$13) and 108 ($\pm$5) s for the first through the fourth cycles, respectively. The capacity with the sodium chloride electrolyte was slightly lower for the first and second cycles (208 ($\pm$18) and 133 ($\pm$1) s, respectively) but was similar to potassium chloride for the third and fourth cycles (114 ($\pm$3) and 105 ($\pm$ 5) s). We found that the starting and ending voltages were similar for these two electrolytes. Potassium sulfate consistently produced a slightly lower capacity for the first cycle at 143 ($\pm$2) s but was similar to sodium chloride for the subsequent cycles. Calcium chloride had an average capacity of 255 ($\pm$13) s for the first charge, 13 ($\pm$11) s for the second charge and no capacity for subsequent charges.

The starting voltage was similar between potassium chloride, sodium chloride and potassium sulfate for all four cycles (**Figure 4B**). The ending voltage following discharge was lowest for potassium chloride with the first cycle but was similar across these three electrolytes for subsequent cycles (**Figure 4C**). Interestingly, the starting voltage with the calcium chloride electrolyte was around 1.44 ($\pm$0.01) V for all four cycles, even though only the first cycle produced a meaningful capacity that resulted in an ending voltage of 0.99 ($\pm$0.06) V. Batteries utilizing copper sulfate, copper chloride,
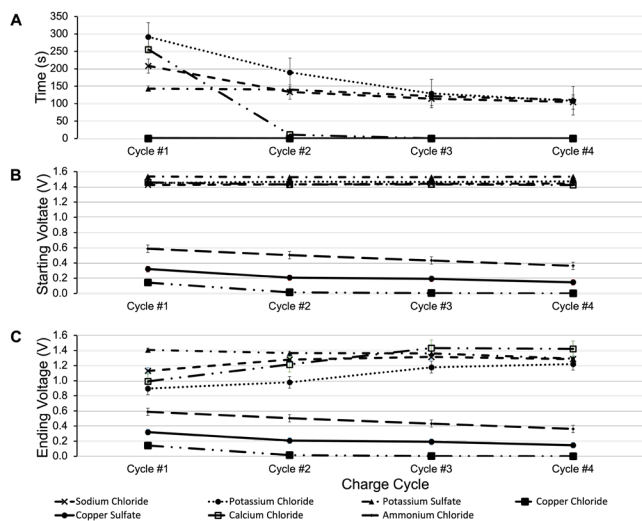
Figure 4: Electrolyte Results. (A) The average capacity of the potassium sulfate, potassium chloride, calcium chloride, sodium chloride, ammonium chloride, copper sulfate, and copper chloride electrolyte batteries. **(B)** The average starting voltage of each battery electrolyte condition. **(C)** The average ending voltage of each battery electrolyte condition. Each point represents the average of the six batteries created per the four charges for each condition, including the standard error.

and ammonium chloride were not chargeable as determined by a low starting voltage (<0.6 V) and lack of capacity.

The calculated electronegativity of the electrolyte appeared to correlate with the measured capacity. The electronegativity of each electrolyte could be estimated using the equation $\Delta X = X_B - X_A$, where X_A is the less electronegative atom, and X_B is the more electronegative atom (6, 7). These values were graphed and compared to the average capacity of the electrolytes (**Figure 5**). With the exception of the first cycle, where potassium chloride was superior ($p<0.05$), potassium chloride, sodium chloride, and potassium sulfate were the most electronegative and hence also the most effective.
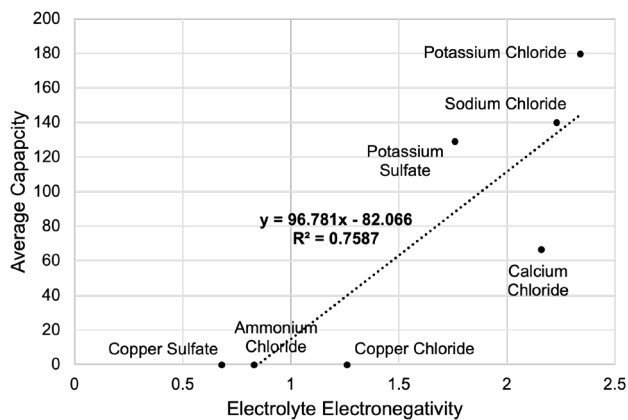
Figure 5: Electronegativity of each electrolyte. The trend shows that as the electronegativity of an electrolyte increases, battery capacity generally increases. The R2 value of 0.7587 does indicate that the correlation trends towards being linear.

DISCUSSION

We demonstrated that the capacity of a battery, as defined by the time a 1.5 V bulb was lit following charging for 5 min at 9 V, was dependent on the surface area of the anode and cathode. Note that all three anode/cathode surface area configurations were produced starting with a 9x10 cm metal sheet, which was folded to the desired surface area. As a result, the metal content was kept constant, and only the surface area was variable. In fact, we observed a close to linear relationship between the surface area and capacity. This observation is consistent with a greater surface area allowing for increased interaction between the electrolyte and electrodes, allowing better ion exchange in the redox reaction. The linear dependency can be explained by the first-order nature of the redox reaction (8).

The starting voltage for all cycles and surface areas is consistent with the maximum redox potential for this system, which is -2.00 eV (9). The reduction of capacity with each cycle can most likely be attributed to the coating of the anode with a possibly aluminum oxidized derivative, as noted by increased discoloration of this surface with each cycle. Interestingly, the voltage increases with decreasing capacity, and this is consistent with q = C*V, where q is charge, C is capacitance and V is voltage (10). When the charge is held constant, and the capacitance is reduced, the voltage increases.

We noted that the more electronegative electrolytes also produced the highest capacity. These electrolytes likely fully dissociate into their respective cations and anions in an aqueous solution (11). Therefore, a greater number of ions is available to facilitate electron transport for both charging and discharging the battery. Calcium chloride has a more moderate electronegativity and reported a capacity similar to the three more electronegative electrolytes for the first cycle, but the capacity then dropped rapidly. We speculate that this electrolyte may have undergone an irreversible chemical reaction during the first cycle, resulting in a lack of ability to function during the latter cycles. Copper chloride, copper sulfate, and ammonium chloride produced a low starting voltage upon charging, which translated to a lack of capacity. This was attributed to the low ionic nature of these compounds, which is a state that cannot support the flow of electrons.

While some of this data may be applicable to improving the efficiency of rechargeable batteries, this study does have some limitations. The capacity of the aluminum-copper battery system decreased with each cycle, which could be due to the chemical reaction of the anode. As a result, we could not draw definite conclusions regarding the impact of the variables on the performance of the battery system with multiple charges. Another limitation is that a standard mass of 10 g/350 mL of electrolyte was used to explore different electrolytes, when a better choice would have been to use a fixed molarity so that the number of ions would have been constant.

With regard to future studies, a wider variety of electrolytes should be explored to see what other properties maximize electrolyte efficiency. To help identify the physical limitations of rechargeable cells, the number of charges completed per battery could be increased.

The results from this research could be applied to modern battery designs. Optimizing the electrochemical reaction ensures that energy is stored and used to the battery's

greatest potential. Certain rechargeable batteries are inefficient, as they do not maximize the surface area between the electrodes and electrolytes. Increasing the prevalence of layered batteries that maximize surface area could create more energy-efficient batteries with greater capacities (12) (**Figure 6**). Additionally, using an electrolyte with greater ionization capabilities could increase the performance of batteries using water-based electrolytes, such as lead-acid and low-voltage lithium-ion batteries.

MATERIALS AND METHODS
Surface Area Experiment Preparations
To create batteries for the surface area experiments, sheets of aluminum foil (Household aluminum foil,99% purity, Kirkland), copper foil (100x1000 cm sheets of 0.1mm thickness, ChuDeng Ltd), and electrolyte paper (2 ply paper towel, Bounty) were cut into 9x10 cm rectangles. Six of each sheet were folded into 1 of 3 surface area measurements: 9x5 (folded in half), 3x5 (folded in half and into thirds), and 1x5 (folded in half and into ninths). This method was chosen to elicit differentiability between surface areas while preserving the total mass of the electrodes. The aluminum foil (anode), electrolyte paper, and copper foil (cathode) were layered respectively and secured with shrink tubing (2cm, HobbyKing). The aqueous electrolyte solution comprised of 10 g sodium chloride in 200 mL of water (common table salt) and mixed for 10 min with a magnetic stirrer until fully dissolved. Then, each of the 18 batteries was charged and tested individually per the "charging and discharge" procedures to explore the impact of the cathode and anode surface areas.

Electrolyte Experiment Preparations
Individual 10g measurements of sodium chloride (regular household supply), potassium chloride (NOW Supplements), potassium sulfate (99% purity, LoudWolf), copper sulfate (98.7% purity, LoudWolf), copper chloride dihydrate (Correct Scientific), ammonium chloride (Alpha Chemicals), and calcium chloride (99% purity, LoudWolf) were incorporated into separate 350 mL quantities of water (regular household supply, a volume sufficient to dissolve all the electrolytes) to create 7 unique electrolyte solutions. Each solution was mixed for 10 min until fully dissolved. Six 9x5 batteries were charged and tested per the "charging and discharge" procedures for each electrolyte.
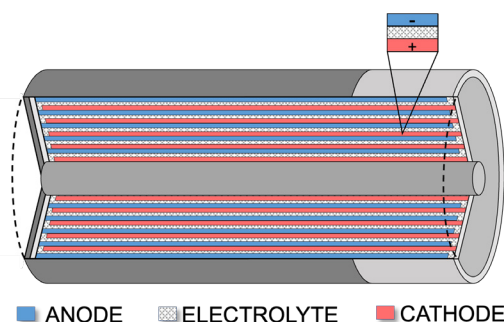
Charging and Discharge
Each battery was soaked in its respective electrolyte and removed from the solution after 1 min. A positive charging wire was attached to the battery cathode and a negative wire to the anode. After charging at 9 V (DC power source for landline phone) for 5 min, the charging alligator clips were removed, and the battery starting voltage was recorded with a voltmeter. The capacity was determined using a miniature halogen bulb (E10 screw minibulb, Amazon) and measuring how long the bulb was lit. Lastly, the ending voltage of the battery was measured. This process was repeated in four separate charges per battery, equating to 24 tests for every condition.

Statistical Analysis
A one-way ANOVA statistical test using the function built into Microsoft Excel was run to compare the different datasets for the capacities measured with the different anode and cathode surface areas as well as the capacities measured from the first charge for the different electrolytes.

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Figure 6: Layered battery cell. Contains multiple anode (blue), electrolyte (grey patterned), and cathode (red) layers, where each distinct electrode layer is connected to its respective terminal.

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