

**ANALYSIS AND PERFORMANCE METRICS OF A
CAPACITIVE MIXING ENERGY CONVERSION DEVICE**

by

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A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Bachelor of Science in Mechanical Engineering with Distinction

Spring 2019

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CAPACITIVE MIXING ENERGY CONVERSION DEVICE**

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ACKNOWLEDGMENTS

I would like to thank Dr. Roy from the department of mechanical engineering for pushing me to complete this thesis and embark on a venture that I can truly look back and be proud of. I would also like to thank Dr. Groh from the department of chemistry and Dr. Wei from the department of mechanical engineering for supporting my questions and curiosities while completing this thesis.

Lastly, I want to thank my parents for supporting me throughout my undergraduate degree and sticking by me even when times got tough. My appreciation for my professors and parents is more than I can show.

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ABSTRACT

Global warming calls engineers and scientists to work diligently to produce low-to-no emission energy production devices and processes to aid with the global sustainability agenda. Supercapacitors are devices that harvest and produce energy from clean electrochemical or electro-kinetic mechanisms. Therefore, supercapacitors are gaining interest for applications where the entropy of mixing can be utilized to control energy storage and production. This analysis will cover the fundamental mechanism, practical design aspects, and performance calculations of membrane-modified supercapacitors. These supercapacitors are to be utilized in estuaries where the entropy of mixing is proportional to energy releases on the order of common hydroelectric devices. Membrane enhanced supercapacitors utilize the free energy from mixing fresh water with salt water and capacitive Donnan potentials (CDP) to store energy via electro-kinetics. Using membranes removes the auxiliary voltage requirement needed in current capacitive mixing modules and desalination devices. Therefore, this technology presents a more direct energy storage mechanism.

Chapter 1

INTRODUCTION

1.1 Motivation

Global warming is a problem that has alarmingly announced its presence during the past few decades. We sit in a period where if we do not take a stand to reduce our greenhouse gas emissions while pursuing clean renewable energy, we will begin to pay a great price economically, with our health, and quality of life. With rising average temperatures, sea levels, and ocean acidity, scientists are observing an alarming domino effect. As a result of higher temperatures, we have increasing susceptibility of heat related illnesses as well as longer allergy seasons. Higher sea levels in conjunction with tropical storm surges will increase the frequency of flooding events which will result in more infrastructure damage in the towns and cities lining our coastlines. Lastly, ocean acidity begins to impact the wildlife that resides in our oceans, killing off species that are vital to wildlife survival food chains and valuable resources [1].

In the race towards a future with global-scale, renewable and sustainable energy infrastructure, more studies must be conducted with suggested forms of renewable energy harvesting. Significant events in the realm of climate change in attempts to lower greenhouse gas emissions such as the Kyoto Protocol in 1992, and the Paris Agreement in 2015, call scientists and engineers to action to pursue remedies for reduction of the greenhouse effect. In recent studies, engineers have come across the concept of osmotic energy harvesting or otherwise known as ‘Blue Energy’ harvesting. This method of energy harvesting highlights the potential energy extraction from diffusion across salinity gradients of salt water and fresh water.

In particular, the primary target for the field of Blue Energy is the geographical entity known as an *estuary*. Estuaries are natural formations where fresh water rivers and streams meet bodies of saline water such as ocean water in bays or lagoons. Some examples of estuaries are the Chesapeake Bay, the San Francisco Bay, and the Outer Banks [4]. The mechanism we are seeking is known as the ‘entropy of mixing’. Simply put, in thermodynamics, entropy is a physical measure of ‘randomness’ in a system. Entropy is high when events in a system are equally likely to occur (random), and low when there is a bias in the system (constrained). The change in entropy of a system is directly proportional to the energy released during the process. Thus, if we can control entropy increase, we can control the harnessable energy released by the system. With the United States housing more than 100 estuaries alone, it is completely feasible that this form of energy scale to the order of hydroelectric power generation [1][2][5].

The studies performed by Brogioli [2] and Sales¹ [7] directly suggest theoretical success and great potential in the advancement of osmotic energy harvesting with CAPMIX (Capacitor Mixing) technology. Current studies show processes done with open-loop feed systems in which the flows entering, exit as a brine without functional use. The proposed research suggests a solution that allows for a closed-loop process where the brine may be separated back into the feed salt water and fresh water streams, then fed back into the CAPMIX cell for further energy cycling. This method could drive a greater sustainability factor of osmotic energy harvesting technologies that may be implemented in vast and diverse energy system applications.

1.2 Literature Survey

The principles of energy harvesting via capacitive mixing and Donnan potentials that are of primary reference were investigated by Brogioli and Sales *et al.* Brogioli [2] (2009) introduces the idea of using electric double-layer (EDL) concepts for storing

¹ From here on, “Sales” will refer to [7].

renewable and clean energy. It was realized that free energy is dissipated at fresh water - salt water interfaces as the system entropy increases from diffusive effects. The experimental study was performed by submerging activated carbon cloth electrodes in high salinity solution and applying an external voltage. Electrostatic work is done on the sodium cations and chlorine anions as they adsorb to their counter electrode. Following this charging stage, the now brackish solution is flushed out of the cell, and fresh water is infused. Once the electrodes are switched to be in series with a load, the sodium and chlorine ions diffuse into the fresh water solution acting against the electrostatic forces, producing extractable work from the cell. Recording the data from cyclic testing, the results plotted on a voltage versus charge graph such as **Figure 1.1** resemble that of a typical engine cycle where the charging and discharging regions behave as the heating and cooling regions in a thermal engine. Thus, Brogioli's work confirmed the working principles for a practical application of EDL energy harvesting.

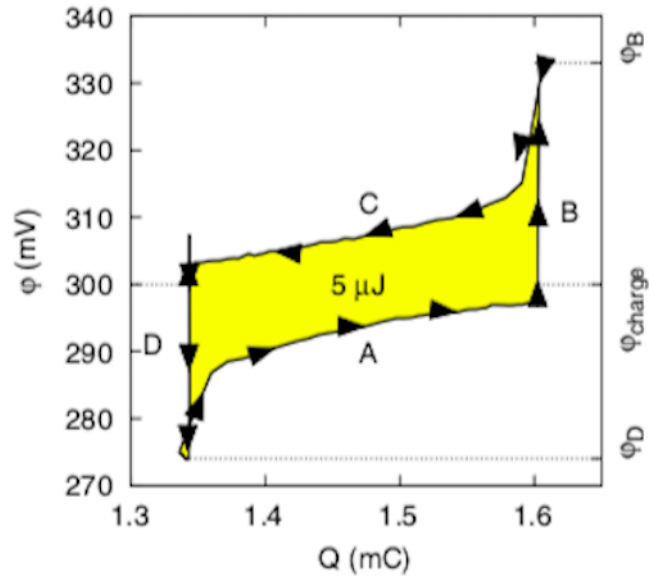


Figure 1.1: Plot of voltage versus charge for a single cell experiment from Brogioli [4].

Sales (2010) performed experimental analysis with ionic membrane modified CAPMIX modules. His objective was to reduce the complexity of the current state-of-the-art technologies by removing supplementary equipment such as turbines for pressure-retarded osmosis (PRO) systems, external voltage sources used in EDL devices or redox solutions for reverse electrodialysis (RED). The experiment consisted of eight cells connected in parallel to an external load (the cell stack configuration can be observed in **Figure 1.2**). The cells were in alternating configurations of anionic and cationic membranes. The cells and the internal components were cut in all equal geometries, compressed, and kept in a Teflon housing. Saline solution and fresh water was pumped periodically through an inlet and allowed to flow radially out of the cell. Cell voltage and power were measured versus time to obtain performance specifications of the cell. The maximum energy efficiency obtained was 56% with an external load of $11\ \Omega$, whereas the maximum power density achieved was $66\frac{\text{mW}}{\text{m}^2}$ with an external load of $1\ \Omega$. He notes that the controlled forms of mixing has yet to reach the level of entropy increase that is present in river estuaries. This is due to the limitation of the adsorbed ions and hence, stored charge, preceding the diffusion step where the ions transfer back into the fresh water solution. However, he successfully demonstrated the utilization of ionic membranes to enhance the efficiency of capacitive mixing devices by removing an external battery.

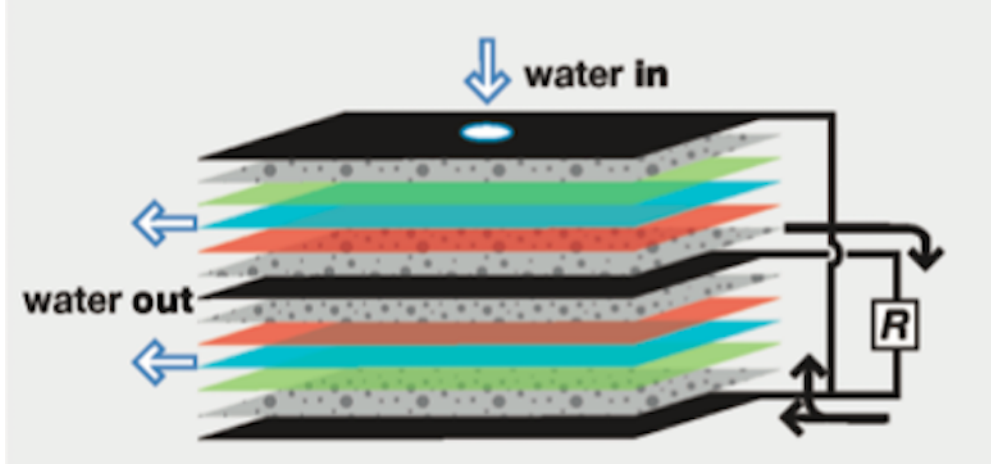


Figure 1.2: Sketch of two cells in parallel to be repeated for the full eight cell stack (from Sales [7]).

1.3 Research Scope

The scope of this investigation is to perform a thorough analysis on the mechanisms at play in a CDP (Capacitive Donnan Potential) supercapacitor. This investigation will lead to a breadth of technical questions that will influence future studies into pertinent parameters for design optimization and materials engineering.

In chapter 2, we will develop the necessary physical background for CAPMIX devices using electro-kinetics, ionic membrane theory, and electric double layer (EDL) theory. Electro-kinetics describes the transient physics of the charging and discharging stages by analyzing the dynamics of the ions (in this study, the ions of interest are Na^+ and Cl^- ions) in an electrochemical environment. Ionic membrane theory presents the origin of Donnan Equilibrium potentials. Donnan Equilibrium potentials are electrical potentials intrinsic to ionic membranes and are of interest to remove the external voltage requirement (such as power supplies or batteries) for controlled mixing mechanisms. EDL theory will describe the formation of the charge layers within the porous

electrodes and current collectors. The double layers between electrodes and current collectors generate the capacitive effect and is a fundamental component of CAPMIX device operation and performance.

In chapter 3, we will discuss the designs used for experimentation. We will discuss two designs where the first design is for prototype validation and the second design was created with higher tolerance and flow control. This chapter will go through general configuration requirements, flow design parameters, and tolerancing of internal components.

In chapter 4, we address the experiments performed and the results. Three experiments will be covered. The purpose of the first experiment is to observe the performance of the CAPMIX cell as a function of external load resistance. From Sales, the predicted outcome is increasing peak potential and power outputs with increasing resistance. The second experiment consists of studying the effect of solution flow rate on the performance of the cell. The prediction is that the charge and discharge rates will increase with increasing flow rate. The reasoning behind this prediction is that with higher flow rates, there should be more ions infused per unit time, and thus the adsorption mechanism occurs faster. In the last experiment, the CAPMIX cell performance is tested as a function of solution salinity. Increasing salinity should affect the charge and discharge rates as well as the full capacitance of the cell. Higher salinity means more ions infused per unit time, however, higher salinity does not have a continuous increase in capacitive performance due to screening length parameters as discussed in chapter 2.

In chapter 5, the performance metrics of the CAPMIX cell are stated and the data presented in chapter 4 is used to compute the metrics. In this chapter, equivalent circuit models of CAPMIX cells are presented to provide an understanding of current flow through the cell and external load. The models discussed are to accompany the cell utilized in this study and the 8 cell stack presented by Sales. Performance metrics

discussed are the maximum input energy from the charging stage, maximum output energy from the discharging stage, maximum output power density, and average efficiencies of the cell.

Finally, in Chapter 6, we will summarize the main findings of the experiments performed and qualitatively discuss the pros and cons of the experimental design. From the identified pros and cons, further research suggestions will be presented to better optimize material selection, material design, and system integration.

Chapter 2

PHYSICAL OVERVIEW

This chapter will discuss the background theory and physics applied in the Capacitive Donnan Potential (CDP) CAPMIX energy harvesting module. Fundamentally, the mechanism at play with CAPMIX devices harnesses electrical potentials near ionic membranes. The electrical potential drives the flux of ions to their respective electrode (porous material designated as an anode or cathode) where they are stored for the formation of the EDL. The formation of the EDL induces layers of electrons and holes in the current collector (metal) which is electrically connected to the external load. The first section will present the fundamental concepts in regards to electro-kinetic phenomena, while the succeeding sections will discuss ionic membrane theory for ionic exchange mechanisms, the screening effect, and the Poisson-Boltzmann distribution of ions in an EDL. This theoretical background is useful for experimental and modeling studies for material studies and device design.

2.1 Electro-kinetics and Donnan Potentials

This section will describe the principles of importance in electro-kinetic theory. The background gives foundation for the electrochemical relationships taking place in a CAPMIX device. Using thermodynamic relationships, one can obtain the ionic flux - potential relationship for an electrochemical potential environment.

$$\mathbf{J}_{ion} = -D \left(\nabla c_i + c_i \nabla \ln \gamma_i + \frac{c_i z_i F}{RT} \phi \right) \quad (2.1)$$

Equation 2.1 is known as the ***Nernst-Planck Flux Equation***. This equation defines the relationship between ionic flux, $\mathbf{J}_{ion}$, and an electrochemical potential. From this

expression we observe that the flux is proportional to the diffusivity of an ion, D (holds units of $[\text{m}^2 \cdot \text{s}^{-1}]$), the spatial gradient of concentration (∇c_i), the spatial gradient of the logarithm of the activity coefficient (γ_i), and any present electrical potential, ϕ . The electrical potential in equation 2.1 comes from ionic membrane phase potentials for a membrane enhanced supercapacitor, which is the topic of discussion for this document.

Next, we define the Donnan Potential for ions in an electrochemical potential field with ionic membranes

$$\Delta\phi_{DON,i} = \bar{\phi}_i - \phi_i = \frac{1}{z_i F} \left[RT \ln \left(\frac{a_i}{\bar{a}_i} \right) - (\bar{P}_i - P_i)v_i \right] \quad (2.2)$$

Equation 2.2 is the ***Donnan Equilibrium Potential*** for ions in an electrochemical potential with ionic exchange membranes. This equation defines the change in electrical potential when traveling from the membrane to the bulk solution. We can observe that this electrical potential is proportional to the ratio of the activity of an ionic species in the bulk solution (a_i) to the activity of the same ion in the ionic membrane phase ($\bar{a}_i$). From the rule of logarithms, if the local solution activity is higher than the membrane phase activity, the result is a positive change in potential from the membrane to the solution. However, if the potential observed is from the solution to the membrane with the same conditions, this would indicate a negative change in the potential. In a CAPMIX device, the cation concentration is higher near the cationic membrane and lower near the anionic membrane (the reverse is true for the anionic concentration). Thus, from the cationic membrane (cm) to the solution (sol), $\Delta\phi_{cm \rightarrow sol} > 0$. For $\Delta\phi_{sol \rightarrow am}$, we need to use the cation concentration near the anionic membrane (am). Since the cation concentration is low near the anionic membrane, and there is a higher concentration of cationic side-groups in the anionic membrane than in the solution, the term $RT \ln(\bar{a}_i/a_i) > 0$, indicating another step increase. Combining these two potential changes relative to the reference potential in the solution results in a potential well in the cationic membrane and a potential barrier in the anionic

membrane as seen in **Figure 2.1**.

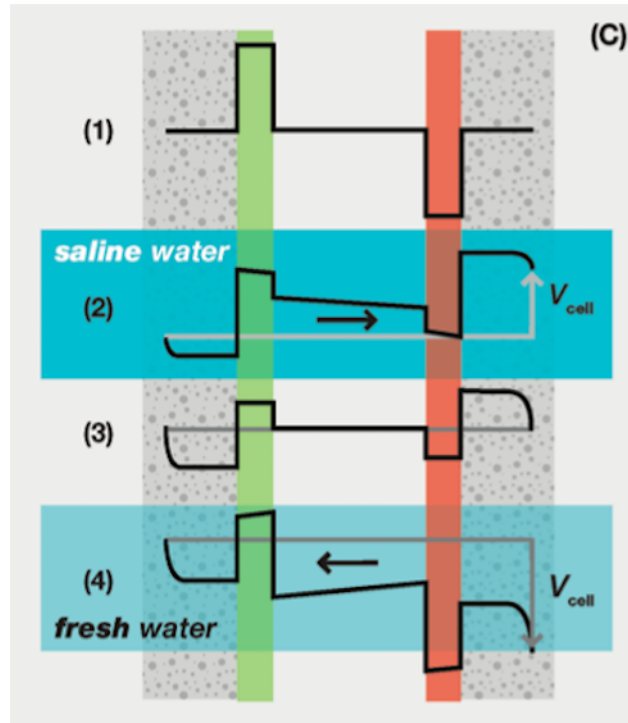


Figure 2.1: Electrical potential profile within a single CAPMIX cell during charging and discharging stages. (1) The cell is in equilibrium prior to the infusion of saline solution. (2) Saline solution is infused, and cations travel to the cationic membrane (red) and the anions travel to the anionic membrane (green). (3) The electrostatic double layer potentials form an electrical equilibrium through the cell. (4) Fresh water solution is infused and the cations and anions diffuse from the electrodes to the draw solution (from [7]).

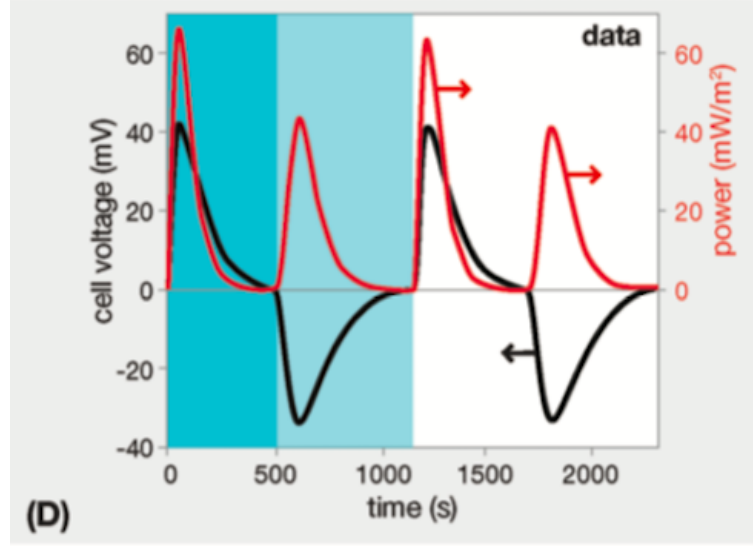


Figure 2.2: External voltage reading of Sales’ 8 cell stack as a function of time. The dark blue region indicates the charging stage where saline solution is infused. The light blue region is the discharge stage where fresh water is infused. The red line indicates the power density and the black line is the cell voltage (from [7]).

The potential profiles drive ionic flux through the membranes and electrodes within the cell. This ionic flux also drives electrical current through the external circuit, designating the charging and discharging current. As the electrical current flows through the external circuit, a voltage can be read across the external load. **Figure 2.2** is a plot of the external voltage response from Sales’ 8 cell stack. The plot is of the stack’s voltage and power density versus time, where the charging and discharging stages are indicated. The alternating voltage peaks indicate a change in polarity that is a result of the current reversing direction from the charging to discharging stages. Reproducing Sales’ plot was the initial objective of this study to validate the design. However, as we will see in chapter 4, there were further contrasts between Sales’ 8 cell stack, the cell utilized in this study, and the measurement techniques.

The Donnan Potential is also proportional to the change in pressure of the ionic species from the bulk solution to the membrane phase. However, pressure change in the membrane phase is limited to the swelling pressure limit of the membrane. The swelling pressure limit is due to the fact that the ionic membranes absorb solvent and increase in size. The amount of solvent that a membrane absorbs or the change in size from solvent absorption is a common specification for commercial ionic membranes. The pressure difference is then defined as:

$$\Pi_s = \bar{P} - P_s = \frac{RT}{v_s} \ln \left(\frac{c_s \gamma_s}{\bar{c}_s \bar{\gamma}_s} \right) \quad (2.3)$$

Now, If the electrolyte were to disassociate into x_+ moles of cations and x_- moles of anions, then the electro-neutrality implies

$$x_+ z_+ + x_- z_- = 0 \quad (2.4)$$

Then the total potential of a solute near the membranes is $x \Delta \phi_{DON}$. For a mix of dissociated cations and anions, the total potential near the membranes is $\Delta \phi_{TOT} = x_+ \Delta \phi_{DON}^+ + x_- \Delta \phi_{DON}^-$. At equilibrium it must be true that $\Delta \phi_{TOT} = 0$. Applying this, we arrive at the following

$$RT \left[x_+ \ln \left(\frac{c_+ \gamma_+}{\bar{c}_+ \bar{\gamma}_+} \right) + x_- \ln \left(\frac{c_- \gamma_-}{\bar{c}_- \bar{\gamma}_-} \right) \right] - \Pi_s (x_+ v_+ + x_- v_-) = 0 \quad (2.5)$$

Since the partial volume of the electrolyte is calculated by

$$V_{\pm} = x_+ v_+ + x_- v_- \quad (2.6)$$

one can combine this and rules of logarithms to obtain

$$\ln \left[\left(\frac{c_+ \gamma_+}{\bar{c}_+ \bar{\gamma}_+} \right)^{x_+} \left(\frac{c_- \gamma_-}{\bar{c}_- \bar{\gamma}_-} \right)^{x_-} \right] = \frac{V_{\pm}}{V_s} \ln \left(\frac{c_s \gamma_s}{\bar{c}_s \bar{\gamma}_s} \right) \quad (2.7)$$

Then if we define the activity as $a = c\gamma$ and $V_{\pm}/V_s = \beta$,

$$\left(\frac{a_+}{\bar{a}_+} \right)^{x_+} \left(\frac{a_-}{\bar{a}_-} \right)^{x_-} = \left(\frac{a_s}{\bar{a}_s} \right)^{\beta} \quad (2.8)$$

we obtain the *Donnan Equilibrium Equation*. This states an equilibrium condition as a function of the activity of the anions, cations, and the solvent both in solution and membrane phase.

2.2 The Screening Effect and Poisson-Boltzmann Distribution

This section will develop the background necessary for understanding electric double layer theory in electro-kinetics. In the CAPMIX module, understanding the adsorption characteristics as well as the membrane phase phenomena of the ions will be pertinent to the module's design. The electric double layer or the *Debye Electric Double Layer* is the polarized layer that accumulates from built up counter-ions attracting co-ions to the same surface. While there are multiple forms of surface charging at an interface between a solid surface and an aqueous electrolyte, the one of interest in this work will be ion exchange.

A fundamental characteristic of these electric double layers, is the phenomenon of *screening*. The screening effect begins at a distance away from the double layer known as the screening length or the *Debye length* commonly notated as λ_D . Screening is whether an ion is rejected or attracted because of the surface charge of the layer. For example, if the surface in question is positively charged, the concentration of cations, c_+ , is notably higher than that of the anions. This is a result of the screening effect. As one travels from the surface of the double layer, the concentration of cations and anions reach the electrolyte concentration in bulk, c_∞ . For monovalent ions, the concentrations of anions and cations are equal ($c_+ = c_- = c_\infty$).

An observation that will provide clues for developing the ion distribution is that, in equilibrium, the ionic flux has gone to zero, $\tilde{\mathbf{J}}_{ion} \rightarrow 0$. In this state, as one travels from the solid-electrolyte interface, the chemical potential becomes uniform and the

electrical potential decays to zero, $\mu_i(x)|_{x \rightarrow \infty} \rightarrow \mu_{i,\infty}$ and $\phi_i(x)|_{x \rightarrow \infty} \rightarrow 0$. Therefore, since there is no net ionic flux at the surface, nor in the bulk, we can state

$$\mu_{o,i} + RT \ln(c_i \gamma_i) + z_i F \phi_i = \mu_{o,i} + RT \ln(c_{i,\infty} \gamma_i) \quad (2.9)$$

Solving this equation for c_i gives us the concentration of species i , at the interface, $c_{s,i}$ as a function of the bulk concentration. Taking into account all i species in the system, we use a summation to give a complete description of the concentration of electrolyte. Hence we have,

$$c_s = \sum_i c_{i,\infty} \exp\left(\frac{z_i F}{RT} \phi_i\right) \quad (2.10)$$

Next, we question how the electrical potential is distributed as a function of distance from the surface. Using Gauss's Law from electrostatics, we may derive Poisson's Equation in relation to the Boltzmann distribution function, known as the ***Poisson-Boltzmann Equation***. This distribution is a tool for determining the electrical potential distribution throughout the electric double layer. Since (2.10) is the number of moles of solute per unit volume, if we multiply this expression by $z_i F$, we will obtain the charge density. Thus,

$$\rho = F \sum_i z_i c_{i,\infty} \exp\left(\frac{z_i F}{RT} \phi_i\right) \quad (2.11)$$

and so the Poisson-Boltzmann distribution in combination with Gauss' Law results in the nonlinear 2^{nd} order partial differential equation:

$$-\nabla^2 \phi = \frac{F}{\epsilon_o \epsilon_r} \sum_i z_i c_{i,\infty} \exp\left(\frac{z_i F}{RT} \phi_i\right) \quad (2.12)$$

Solutions to this equation have been evaluated both experimentally and numerically. Theories cover simplifications that are of practical use with CAPMIX modules to better understand the sodium and chlorine adsorption characteristics of the device. Two of which are discussed in the following section.

2.3 The Debye-Hückel and Guoy-Chapman Theories

Together, the Debye-Hückel and Guoy-Chapman Theories illustrate the surface phenomena occurring in an EDL system. From the Debye-Hückel theory, we will obtain the screening length using the Poisson-Boltzmann equation 2.12. First, we will make the assumption that the electric field lines emanating from the surface of an ion, $\tilde{\mathbf{E}}_{ion}$ are normal to the surface. Therefore, when ions collectively adsorb on a charged surface, the net electric field from the surface, $\tilde{\mathbf{E}}_s$, points normal to the surface. Consider only a binary electrolyte consisting of cations and anions of equal and opposite charge numbers, $z_+ = -z_-$, then apply to equation 2.11 as

$$\rho = Fz \sum_i^2 c_i = Fz(c_+ - c_-) \quad (2.13)$$

Using the Boltzmann relationship for ion concentration, and assuming that the electrolyte is electro-neutral in the bulk, equation 2.13 becomes

$$\rho = -2zFc_\infty \sinh\left(\frac{zF}{RT}\phi\right) \quad (2.14)$$

Substituting equation 2.14 for the charge density in Gauss' Law, then using the Taylor expansion to first order for small arguments of $\sinh$, $\sinh x \approx x$, we obtain the Debye-Hückel approximation

$$-\nabla^2\phi = \frac{\phi}{\lambda_D^2} \quad (2.15)$$

where λ_D is the Debye length, or screening length, defined as

$$\lambda_D = \sqrt{\frac{\epsilon_r\epsilon_o RT}{2z^2 F^2 c_\infty}} \quad (2.16)$$

A useful quantity that may be derived using the Debye length is the *charge relaxation time*, t_D . The charge relaxation time is the duration necessary for counter-ions to diffuse through the screening length. This parameter is useful to obtain a quantitative feel for the length and time scales at play during experiments. This quantity is defined as the Debye length squared divided by the diffusivity of the species, D_i , or

$$t_D \approx \frac{\lambda_D^2}{D_i} = \frac{\sigma}{\epsilon_r\epsilon_o} \quad (2.17)$$

where σ is the ionic conductivity of the diffusion layer, which in the case of this work, is the ionic membranes in the cell. Using 0.5 M as an example for calculation, $0.5 \text{ M} = 500 \frac{\text{mol}}{\text{m}^3}$, and this results in a screening length from the double layer of $\lambda_D \approx 0.44 \text{ nm}$, which is over an order of magnitude smaller than the electrode and membrane components of the CAPMIX device. Then we can calculate the relaxation time using $D_{NaCl} = 1.6 \times 10^{-9} \text{ m}^2/\text{s}$ [3], which results in a relaxation time of $t_D \approx 1.18 \times 10^{-10} \text{ s}$. This quantity is purely a transport parameter and does not constitute the time required for the formation of the EDL. However, it does give one the sense of the rate and size of the kinetics for design and configuration of the cell when conducting experimentation.

The Guoy-Chapman theory gives access to the high-resolution phenomena at the interface between the charged surface and bulk aqueous electrolyte. This model describes the potential distribution between the multiple electrical interface layers. These planes in general are defined by the ranges of distance from the charged surface. From $0 < z < \beta$, is defined as the inner compact layer or *inner Helmholtz layer*. The inner Helmholtz layer for the CDP cell is essentially the porous carbon electrode. $\beta < z < D_{onset}$, where D_{onset} is the location of the beginning of the diffusion layer from the charged surface, is known as the outer compact layer or the *outer Helmholtz layer* (the ionic membrane). The distance from the onset of the diffusion layer to the "e-plane", is defined as the *immobile layer*. The e-plane is also known as the "slip plane", the plane that distinguishes between the immobile phase of adsorbed ions and the mobile phase of ions free to move around in the bulk solution. The mobile phase is from the e-plane to infinity. The relationship between the potential at the beginning of the diffusion layer, ϕ_D , and the potential at any distance from the beginning of the diffusion layer, $\phi(x)$ is given by

$$\phi_D = \frac{2RT}{F} \ln \left[\frac{\exp(-x/\lambda_D) + \tanh(F\phi(x)/4RT)}{\exp(-x/\lambda_D) - \tanh(F\phi(x)/4RT)} \right] \quad (2.18)$$

This solution is a tool to be utilized when performing modeling studies for investigation on electrode and membrane performance for optimal energy harvesting. Multiple

approximation models are utilized to obtain more robust simulation methods for theoretical design investigations such as that done by Simoncelli *et al* in [8].

Chapter 3

MECHANICAL DESIGN AND FABRICATION

This chapter will discuss the first and second design iterations of the cells utilized in the experimental studies. The scope of the cell designs was to study electrical responses of a single cell with controlled flow patterns. In Sales study, the cell was a stack of 8 membrane modified supercapacitors pressed together with water free to flow radially out of the cell into a teflon housing [7]. Thus, the objective for this research was to generate a more practical and integrable cell design. This chapter will also serve as a general overview of practical considerations when generating further designs for future research objectives.

3.1 Materials and General Construction

The materials used in both designs were Fumasep FKE-50 cationic and FAD-55 anionic membranes (*Fuel Cell Store*, $t_{m,c} = 50 \mu\text{m}$, $t_{m,a} = 55 \mu\text{m}$), MPL double sided carbon cloth (*Fuel Cell Earth*), a square 6" and $\frac{1}{32}$ " thick food-grade multipurpose neoprene rubber sheet for gasket material, polyurethane tubing with a $\frac{1}{4}$ " ID, push-to-connect tube fittings with $\frac{1}{8}$ " NPT threads (*McMaster-Carr*), nylon $\frac{3}{8} - 16$ " hex bolts, and $\frac{1}{4} - 20$ " stainless steel bolts from the machine shop. The only extra material utilized in the second cell design that differs from the first design is the use of multi-purpose 110 copper (*McMaster-Carr*) used as current collectors rather than the use of the aluminum plates.

The assembly of this cell is to be such that the ionic membranes and carbon cloth electrodes firmly sandwich the glass fiber spacer that holds the stage solution. To

achieve this, the aluminum endplates are compressing the internal components with the aid of the bolts listed above. The nylon bolts were used to maintain electrical insulation between the two sides of the cell. After further consideration on the mechanical integrity of the nylon bolts under high torque, the nylon bolts were hollowed out and used as insulating sleeves for the stainless steel bolts. The finer thread pitch also allowed for finer control of the compression as will be discussed in a further section.

3.2 Channel Design

For the proof of concept cell, the design was inspired by the test cell construction discussed in Sales. The difference between the cells used in this work and the stack in Sales' report is that the test cell discussed here is a single cell versus an 8 cell stack. The objective for the design was to achieve maximum surface contact by compressing the ionic membranes, carbon electrodes, and glass fiber filter together via two aluminum end plates. To properly choose the flow channel geometry for a controlled sealing environment, the width-length ratio of the flow channel was derived to satisfy

$$\frac{w}{L} \geq \left(\frac{Q}{\Delta P} \right) \bigg|_{max} \frac{\mu}{\bar{\phi}^2 t} \quad (3.1)$$

where Q is the desired maximum volumetric flow rate, P is the pressure applied by the NE-1000 Syringe Pump, $\bar{\phi}$ is the average pore size of the grade D microfiber filter media from Sterlitech, μ is the approximate kinematic viscosity of the saline solution, and t is the thickness of the filter media. Defining the flow rate as $15 \frac{\text{mL}}{\text{min}}$, the pressure applied by the pump as 149.409 kPa, the kinematic viscosity as $0.00095 \frac{\text{N}\cdot\text{s}}{\text{m}^2}$, the average pore size as $2.7 \mu\text{m}$, and the thickness of the filter media as $600 \mu\text{m}$, the ratio results in $w/L \geq 1.13$. Choosing a width-length ratio of 1.15 and a width of 3cm, the resulting length dimension is 2.60cm.

3.3 Design Iterations

The first design was manufactured in the University of Delaware’s Spencer Lab Student Machine Shop. The purpose of the boss features was to aid with the alignment of the electrodes and ionic membranes. The first cell design is depicted below in **Figure 3.1**.

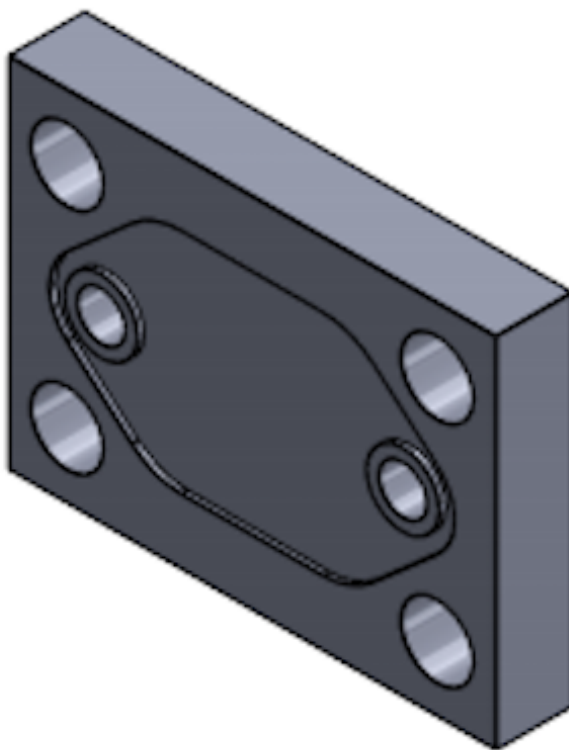


Figure 3.1: Top plate of prototype cell SolidWorks graphic. The bottom cell is a mirror image of this plate, without the inlet and outlet holes.

This cell design, while giving electrical response, had severe issues with flow control and material alignment on the inside of the channel. These flaws in the design could be observed in the “contact patches” left behind from the microporous layer on the carbon cloth electrode shown in **Figure 3.2**.

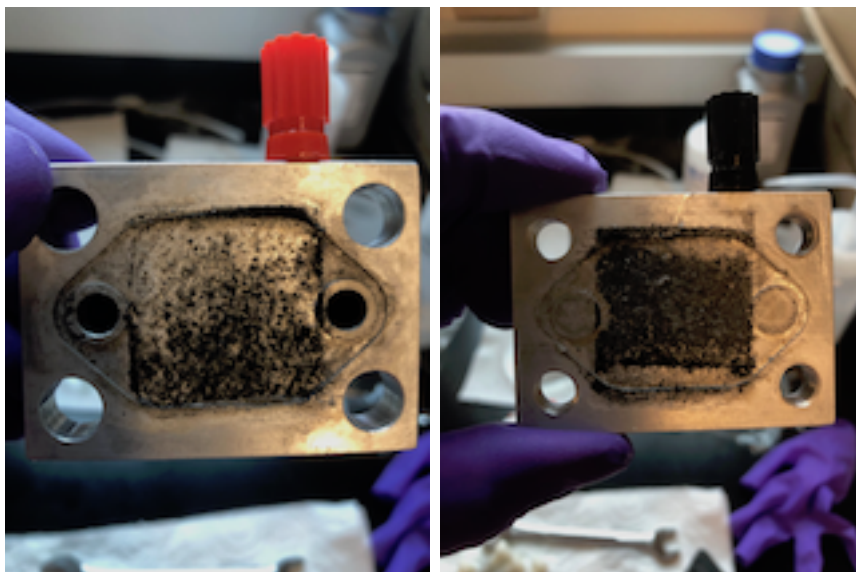


Figure 3.2: Contact patches left behind on the initial cell design after a test.

The areas with relatively lower residue can be assumed to have allowed the passage of the stage solution, thus, decreasing the contact area for the electrode to the end plate. The experimental results that lead to suspicions of the flow regime within the cell will be discussed later on in the report. The lack of flow control was due to improper spacing and fitting of the components in the cell. With the mechanisms under observation occurring on the order of a few micrometers, staying meticulous with tolerances and sizing is of the essence. It was found that misalignment of the material layers and excess material from oversized electrodes and membranes would lead to leaks from the spacer media. Excess material on the order of a millimeter caused these leaks and overall hindered the performance of the cell. At this time, it was recognized that a new design was in order to better fit the internal components and increase the flow control.

The second iteration cell design no longer utilizes the aluminum as the current

collector and solely uses them as endplates for compression. Instead, 110 copper is machined to fit the membranes and electrodes with a better tolerance. To achieve higher precision with the cell design, a new cutting procedure was considered. Instead of using the inverse profile to cut the membranes and electrode, the desired profile is placed on top of the source material, clamped down, and traced (see **Figure 3.3**). To test this method, 20 cuts of multipurpose paper were cut to obtain a statistical average for dimensioning and tolerance of the cell.



Figure 3.3: Set up of statistical tolerance test. A C-clamp is used to hold together the tracing plate (from the new channel design), the paper, and an acrylic cutting plate underneath the paper.

The results of the tests are depicted in **Table 3.1**. Using this data, the new electrode and membrane compartment was designed in the 110 copper plates.

Table 3.1: Statistical Tolerance Data

Measurement Data				
No. of Sheets	Statistic	Width (cm)	Length (cm)	Area (cm ²)
Single Sheet ($t_1 = 215.9 \mu m$)	Avg.	2.61	2.95	7.71
	Std. Dev.	0.070	0.056	0.260
Two Sheets ($t_2 = 431.8 \mu m$)	Avg.	2.61	2.94	7.66
	Std. Dev.	0.016	0.051	0.138

The copper plates were machined from a 0.062” thick sheet that was saw cut to an outer dimension of 2.355” by 2.518”. After cutting the sheets down, the outer profile and membrane-electrode pockets were machined using the Prototrak Milling Machine. The dimensions of the pockets were retrieved from the statistical testing, which resulted in a 2.948 cm (L) x 2.616 cm (W). The resulting product is shown in **Figure 3.4**.

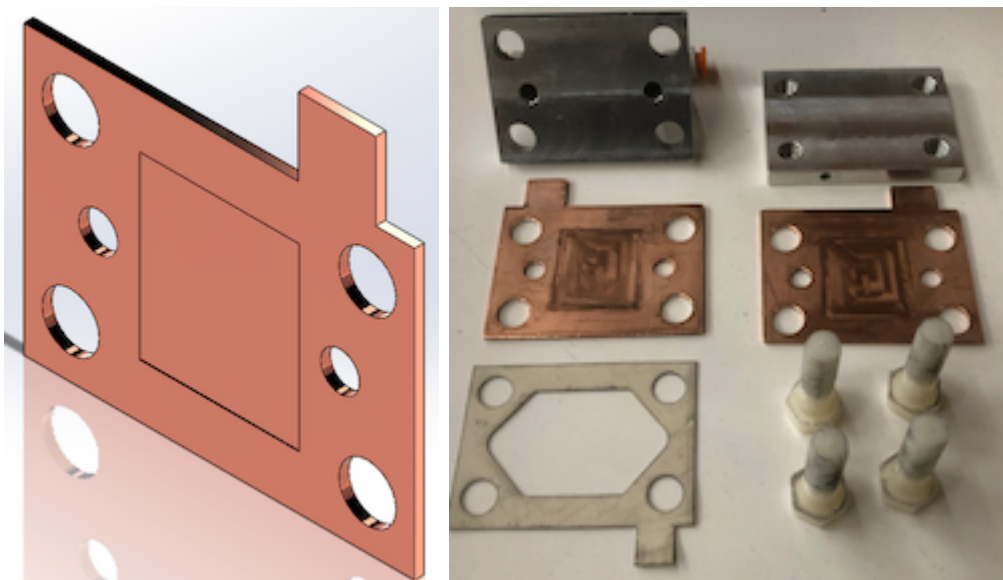


Figure 3.4: (*Left*)Solidworks isometric view of 110 copper current collector , (*Right*) all of the version 2 cell components after fabrication

With the chosen combination of materials, housekeeping items are necessary to properly maintain the condition of the cell, and attempt to uphold its intrinsic performance. These items will be addressed throughout chapter 4.

3.4 Flow Control

To achieve the necessary kinetics for the supercapacitor to operate, a focus on the characteristics and dynamics of the infused solutions is pertinent. For the capacitive effect to take place, fresh water must be infused initially, and remain in the cell channel until the system is in equilibrium. Typically the time scale required for the cell voltage to stabilize was on the order of 20-30 minutes (this can be observed in the data discussed in chapter 4). The fact that the time required for the EDL to form is approximately 11 orders of magnitude greater than the theoretically calculated relaxation time from chapter 2 section 3 shows that the building of the double layer is

not a single stage mechanism in itself. There is a fluctuation about equilibrium present as the ions travel via chemical and electrical potentials as they equal each other out. Succeeding equilibrium in fresh water, the same volume of saline solution is infused into the cell. After the transient infusion stage, the solution is left in the cell as the EDL's form. The design of the cell is such that the flow enters and exits the channel perpendicular to the spacer within the channel.

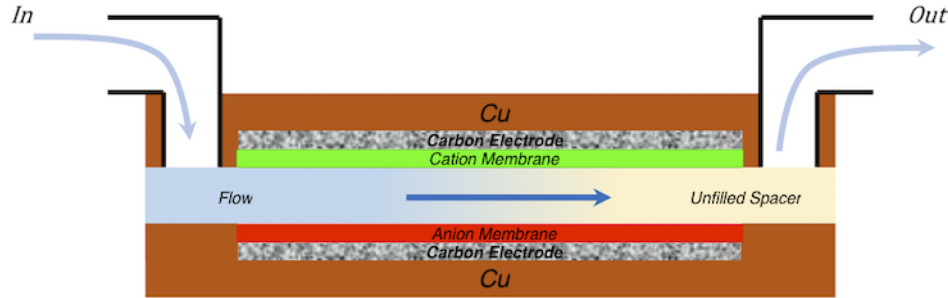


Figure 3.5: Diagram depicting how solution flows through CDP Supercapacitor cell.

Brown represents the 110 copper current collectors, *grey* resembles the porous carbon electrodes, *green* and *red* are the cationic and anionic membranes respectively. The off-white and light blue represents the glass fiber filter with water flowing through the media.

To prevent leaking, the neoprene gasket is cut so that the spacer fits snugly within the cutout profile. The thicknesses are all accounted for in the design such that the gasket and spacer are coincident. Thus, leaving any excess height, δt_g , for compression during the cell assembly.

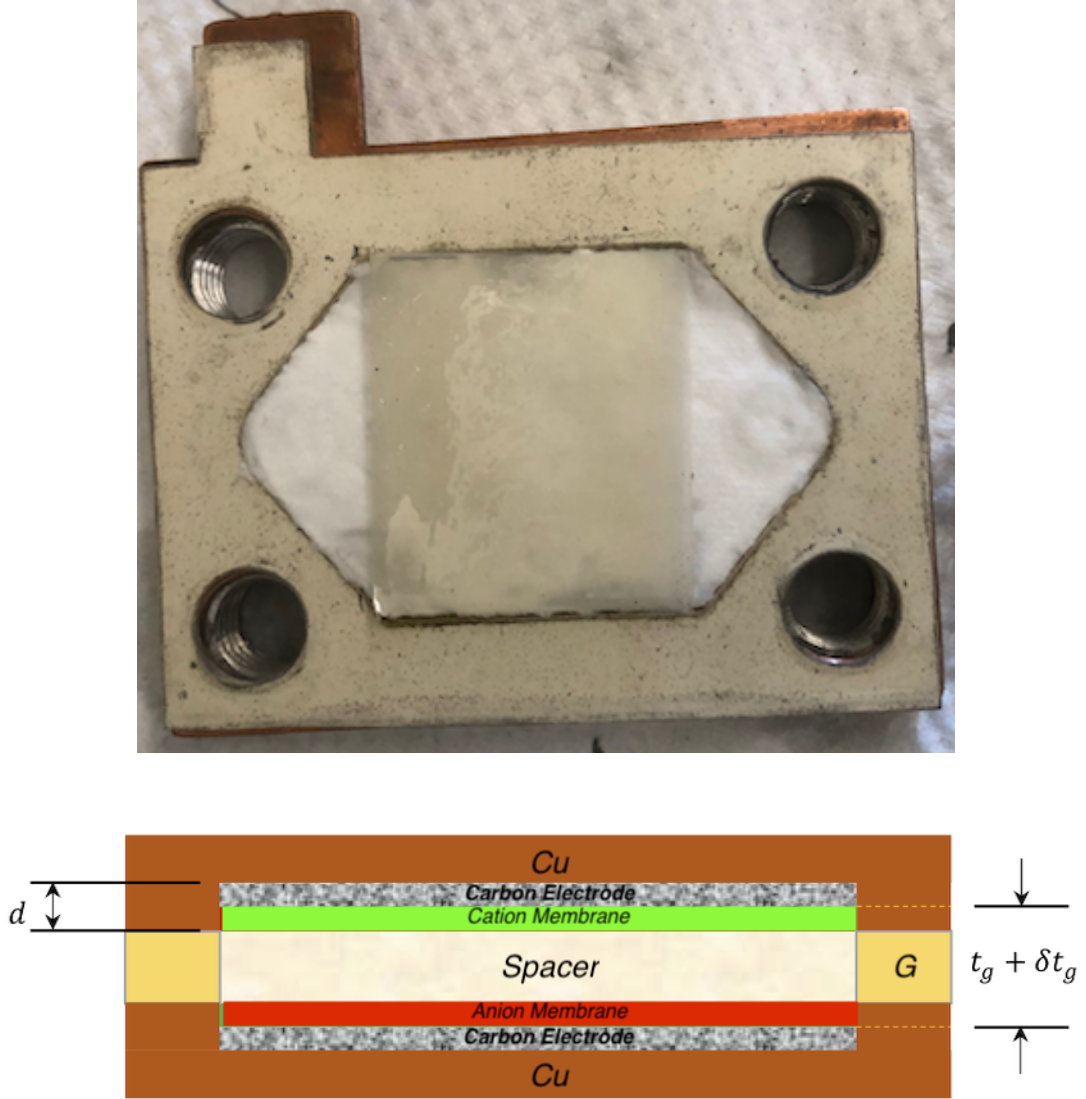


Figure 3.6: (*Top*) Picture of half-cell assembly showing the profile of the gasket surrounding the glass fiber spacer and cationic membrane. (*Bottom*) Schematic showing the cross sectional plane of the cell and the respective arrangement of materials. The *grey* corresponds to carbon electrodes, *red* corresponds to anionic membrane, *green* corresponds to cationic membrane, the off-white is the glass fiber filter, and the *brown* is copper.

One caveat to this particular configuration is that if the cell is over compressed, it will require a higher input pressure from the pumps. On the other hand, if it is not compressed enough, the flow will travel beyond the channel profile and leak out of the cell. With that being said, having knowledge of the thickness of materials is required to ensure a sufficient amount of compression for cell operation.

Chapter 4

EXPERIMENTATION & RESULTS

4.1 Methods

To test the two cell designs, the general set up consisted of the use of NE-1000HP and NE-1000X syringe pumps, a Princeton's Applied Research VersaStat 3 potentiostat / EC Lab potentiostat, and a digital multimeter (DMM). The pumps were programmed to automatically perform infusion cycles switching between pump 1 with the saline solution syringe, and pump 2 with the fresh water syringe. The potentiostat was electrically connected across a resistor that was connected externally to the cell to measure open circuit voltage during the infusion cycles. The data is recorded from the potentiostat by connection to a computer to display real-time responses of the cell. The counter-top experiment set up is shown in **Figure 4.1**.

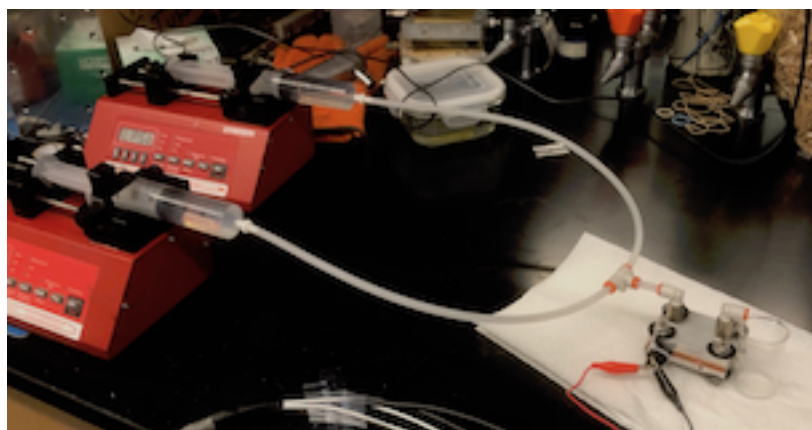


Figure 4.1: Layout of counter top experiments with the cell.

Before testing, the cell must be properly sanitized, ionic membranes should be conditioned, and solutions must be prepared. For the first cell design, the cleaning process would be simply be using acetone to scrub the aluminum surface of any crystallized salt residue, and to clear the surface of any imperfections that would add to the contact resistance of the construction. For the second cell design, the aluminum plates are again cleansed with acetone, however, the corrosion on the copper from passing water and saline can be removed using vinegar and baking soda. When conditioning the ionic membranes, the manufacturer notes to leave the membranes in 0.5 M aqueous NaCl for 24 hours. The purpose of this is to remove excess additive from the membrane. When constructing the cell, its necessary to note that after conditioning, the membranes may swell and so they may need to be re-cut in order to decrease the risk of leakage.

Finally, the preparation of the solutions is dependent on the desired molarity for the saline solution. The required amount of NaCl to be added was calculated using 50 mL of solvent. The equation used was:

$$m_{NaCl} = \overline{M}m_{MW}V_{sol} \quad (4.1)$$

where $\overline{M}$ is the desired molarity in mol/L, V_{sol} is the volume of solvent when creating the solution (which during experimentation was kept at 50 mL), and m_{MW} is the molecular weight of NaCl (58.44 g/mol).

4.2 Prototype Validation

The first experiment performed took place in the University of Delaware's Fuel Cell Laboratory. The objective for this experiment was to validate the design by observing an electrical response from the cell. The cell was fully constructed and connected to the two NE-1000 Syringe Pumps. A 60 mL syringe filled with low-concentration solution was mounted in one pump, and a 60 mL syringe filled with 0.5 M saline solution

(29.22 g/L) was mounted in the other pump.

The cell was connected to a 1.5 Ω , 10 Ω , and 100 Ω resistors during testing. The digital multi-meter was connected to the cell in parallel with the resistors to observe the voltage responses of the cell. The behavior of the sell was compared to the experimental results depicted in **Table 1** of Sales *et al* [7].

Table 4.1: Prototype Data

Experiment 0		
Load (Ω)	V_{max} / V_{min} (mV)	Max Power Density ($\frac{\text{mW}}{\text{m}^2}$)
1.5	3.1/-5.1	22.23
10	27.3/-3.6	95.55
100	77.5/-15.1	77.003

This first experiment was successful in the sense that this prototype had an electrical responses during testing. The increasing maximum voltages with increasing load resistance appears congruent with Ohm’s law, $V = IR$, where V is the voltage, I is electrical current, and R is the external load. The maximum power densities were calculated by:

$$p = \frac{V^2}{RA} \quad (4.2)$$

where V was the voltage read by the instrument, R is again the external load, and A is the planar area of the electrode which was taken to be $7.8 \times 10^{-4} \text{ m}^2$. The measurements instabilities are suspected to be a result of factors pertaining to the construction of the cell such as the island boss features, measurement error in the DMM, and uncontrolled flow patterns. The misalignment of the internal components induces leaking and therefore creates an uncontrolled dynamic, thus affecting the electro-kinetics. This

test confirmed the electro-kinetic mechanism on a first order basis, however, further improvements are necessary. Nonetheless, from here we may move on to a more formal measurement.

4.3 Experiment 1: Power vs. Resistance

The purpose of this experiment was to run the cell under a more autonomous operation and record real time data. The pumps were now programmed to run at 15 $\frac{\text{mL}}{\text{min}}$ with relaxation times in between infusion of 10 minutes, and an infused volume of 4.5 mL. The cell was run with the 1.5 Ω , 10 Ω , 330 Ω , and 510 Ω resistors while the VersaStat 3 lab potentiostat recorded the open circuit voltage. The salinity of the solution is 0.5 M (29.22 g/L).

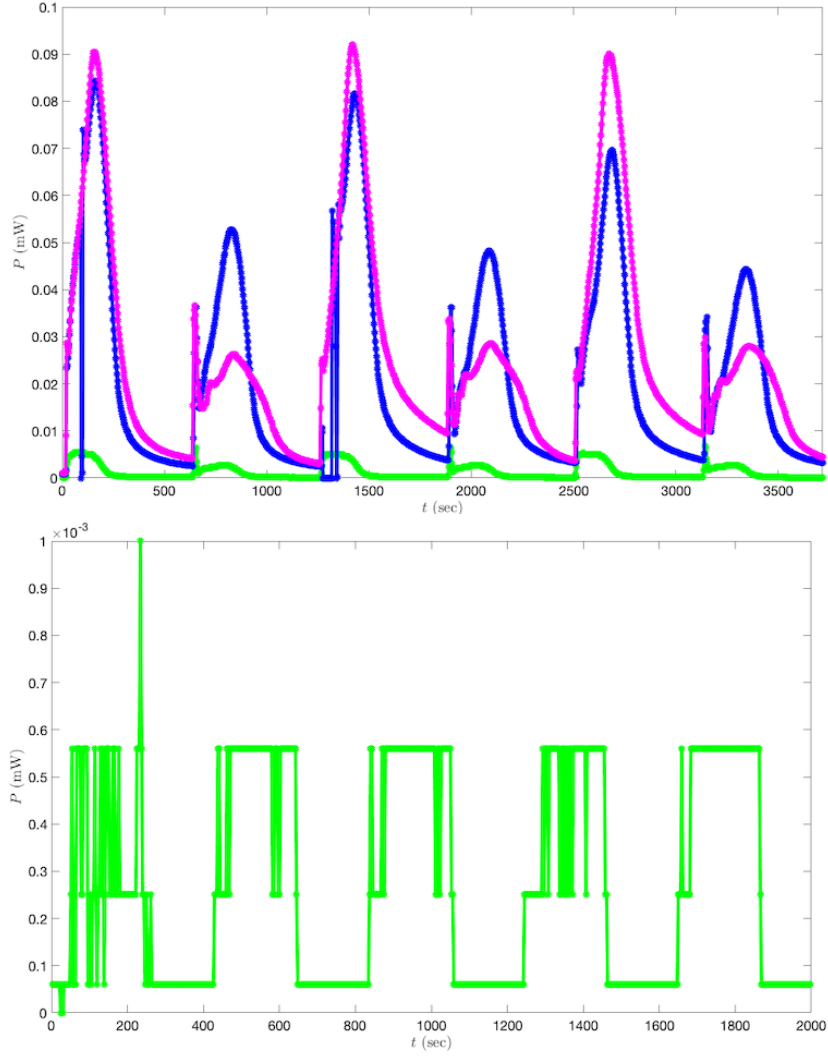


Figure 4.2: (*Top*) Power versus time plot of the cell with the 10 Ω , 330 Ω , and 550 Ω resistors (green, blue, and magenta respectively.) reproduced in MATLAB. (*Bottom*) Power versus time plot of the cell with a 1.5 Ω connected.

The results displayed in **Figure 4.2** show an unexpected feature: all of the peaks are in the same direction, without any inversions observed previously. Under the first operation (prototype validation) the cell voltage had a sign change in the voltage

upon alternating solutions. This result was in agreement with the literature, however, from measurement with the potentiostat we see that the cell voltage never changes sign. This result is not in agreement with previous experimental results as seen in [7], and indicates that there may be more to the story than previously assumed. This raised a curiosity about the system relating to the electrical integration of the testing set up.

4.4 Experiment 2: Power vs Flow Rate

After experiment 1, the concern was whether or not the flow within the cell had a positive or negative effect on the output result. The pumps were set at different flow rates for each trial. The flow rates, Q_{in} , were 5, 6, 9, 13.5 and 15 $\frac{\text{mL}}{\text{min}}$, each infusing 4.5 mL of 0.5 M solution.

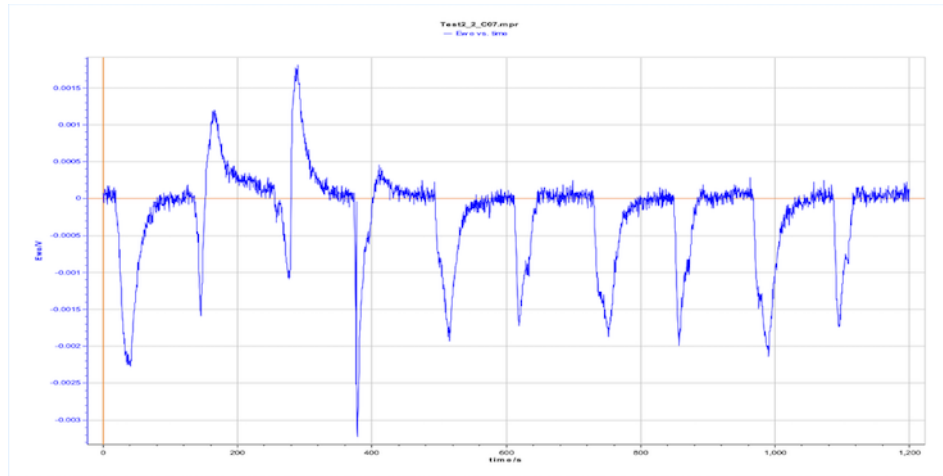


Figure 4.3: Power versus time graph of the electrical response of the cell with $Q = 8 \frac{\text{mL}}{\text{min}}$. This plot is an outlier because of the peak direction change and indicates a flow problem.

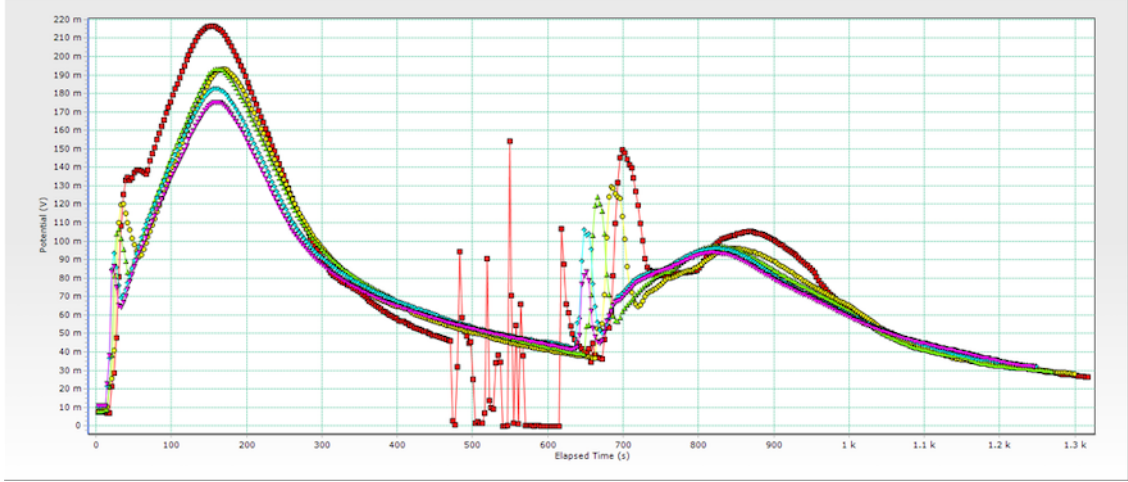


Figure 4.4: Power versus time graph of the electrical response of the cell with Q having values of 5 (red), 6 (yellow), 9 (green), 13.5 (cyan), and 15 (magenta) $\frac{\text{mL}}{\text{min}}$. The central spikes are noise from the VersaStat 3 instrument during operation.

As seen from the figures above, the majority of the data follows this same sign voltage peak where the sign of the voltage is only dependent on the location of the connecting cables relative to one another across the resistor. The outlier, **Figure 4.3**, shows a sign change in the voltage. However, this is a data point that shows behavior not consistent with the majority of the data points. This gives rise to questions about the interpretation of the data and how we are visualizing the flow within the system. The data also remains overlapped in **Figure 4.4**, showing that the different flow rates have minimal effect on the electrical response. This result is against the prediction stated in chapter 1 section 3. This result must mean that for a given infusion volume, V_{in} , there will always be a constant number of ions available to be stored for a given concentration. Thus, as long as the flow is infusing new ions on the order of, or slower, than the rate which the ions are adsorbed, then the charging characteristics will not differ significantly.

4.5 Experiment 3: Power vs Salinity

The objective of the final experiment was to observe the effect of the salt concentration in the saline on the voltage read across the resistor. The typical value of salinity in ocean water or natural saline is approximately 35 g/L, or 0.6 M [4]. From literature, we should expect to see higher ϕ_{max} points with increasing concentration until the Debye length essentially inhibits any ion adsorption, decreasing the voltage reading.

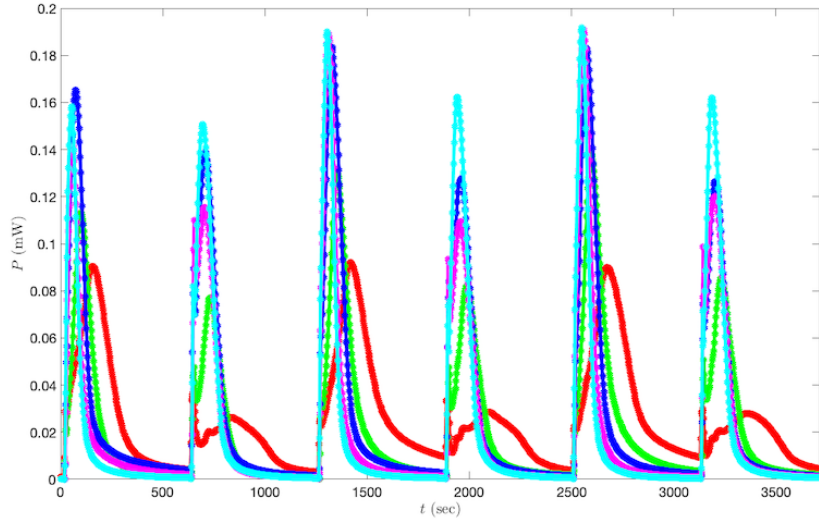


Figure 4.5: Power versus time graph of the electrical response of the cell with $Q = 15 \frac{\text{mL}}{\text{min}}$, $V_{in} = 4.5\text{mL}$, and $R_L = 510\Omega$. The concentrations are represented as red (0.5 M), green (1.0 M), blue (2.0 M), magenta (2.5 M), and cyan (3.0 M).

We can see from **Figure 4.5** that as the concentration increases, the peaks become taller and narrower, representing quicker charging and discharging rates. This agrees with intuition considering that at a higher salinity, more ions enter per unit

time, therefore, the pores in the electrode should fill quicker.

Overall, the cell has consistent performance characteristics such as alternating voltage peak magnitudes, yet the same voltage sign. These results present the framework for which an interpretation of the cell's behavior can be formed using an equivalent electrical circuit.

Chapter 5

RESULTS AND DISCUSSION

5.1 Data Assessment

As seen from the recorded data in chapter 4, it is necessary to assess the interpretation of the data has a predicted outcome consistent with the physics. The hypothesis is that the electrical connection between the cell and the resistor affects the output voltage reading. In RC circuits, the voltage read across a load resistance is dependent on whether the capacitor and resistor are in series or in parallel. To investigate this hypothesis, let us review the electrical potential profiles both within the cell, and external of the cell (the portion that is connected electrically to the resistor and potentiostat). We will begin with the potential profiles within the cell at equilibrium (fresh water infused).

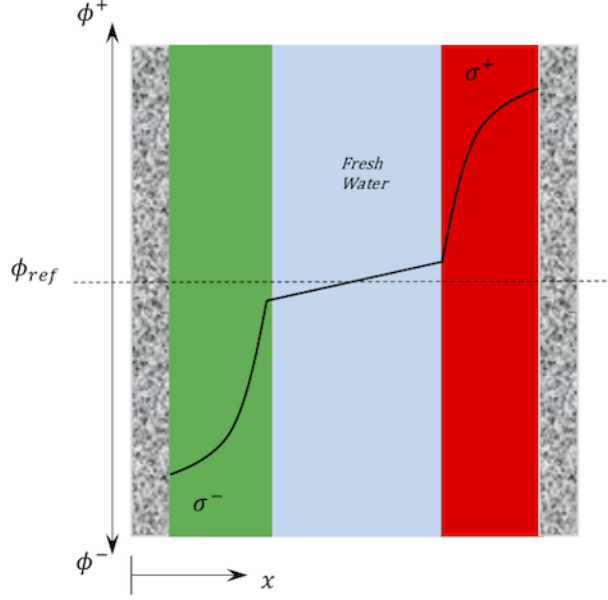


Figure 5.1: The initial potential profile of the cell with fresh water infused. The *green* represents the cationic membrane while the *red* represents the anionic membrane. The profiles are drawn arbitrarily and are not a result of an analytical expression. The purpose is for a qualitative mechanism.

The profile depicted in **Figure 5.1** is consistent with approximating the membranes as parallel plates with a surface charge, σ . For the anionic membrane, $\sigma_a > 0$ representing the positively charged sites for anion exchange. For the cationic membrane, $\sigma_c < 0$ representing the negatively charged sites for cation exchange. Next, during the charging stage in which dissociated Na^+ and Cl^- ions flow into the cell. The cations flow ‘downhill’ towards the cationic membrane (green), and the anions ‘float’ towards the anionic membrane (red) as depicted in **Figure 5.2**.

After sufficient time has passed, the accumulated charge of the stored ions in the porous electrodes forms a potential profile that grows beyond the initial voltage

profile in the membranes.

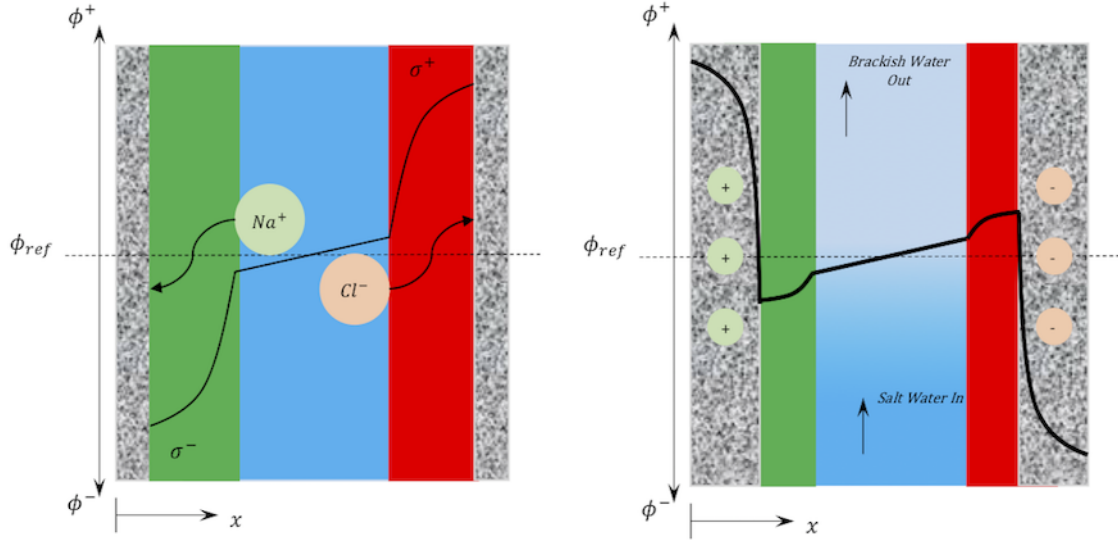


Figure 5.2: (*Left*) Ionic adsorption of Na and Cl ions during the charging stage. (*Right*) The electrical potential profile once the EDL's are formed.

The formation of the electric double layer generates a layer of electrons within the metal near the contact area with the positively charged electrode and a layer of holes near the negatively charged electrode. Now, the voltage polarity within the external circuit is the same as the polarity of the equilibrium membrane potential at the initial stage. This allows us to view the resistor as being in parallel with the initial membrane potential. The electrical connection as configured during testing can be also be represented by a capacitor in parallel with the load resistor. Thus, the final circuit can be viewed as in **Figure 5.3**.

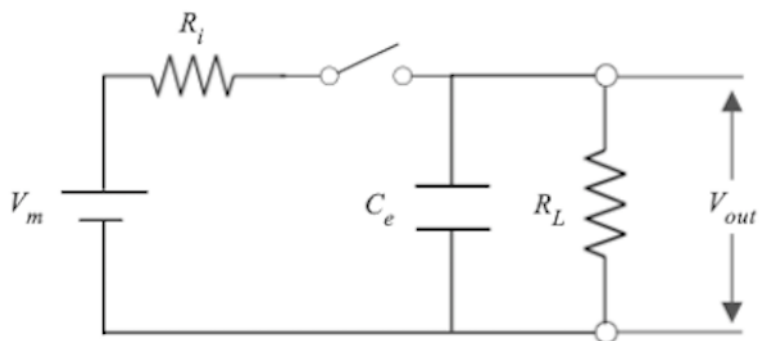


Figure 5.3: Equivalent circuit of single cell CDP Supercapacitor.

As an analogy, we look at the membrane potential as the voltage source, and V_{out} is what is read on the potentiostat. When the switch is closed, the salt water is being infused into the cell, charging the capacitor, and producing a voltage reading across the resistor. When the switch is opened, fresh water is being infused into the cell, and the capacitor is now discharging the current. When analyzing the equivalent circuit in these two stages, we recognize that the current flow through the resistor in fact never changes direction, thus the voltage read by the potentiostat should never change sign. This validates that the cell's behavior is in agreement with the prior physical descriptions of the electro-kinetic mechanisms taking place. However, it is worth discussing at this point why previous literature has voltage profiles that have alternating peak directions.

If we first look at a circuit in which the capacitor is in series with the load resistor and voltage source as in **Figure 5.4**, we can begin to analyze the difference in the experimental configurations.

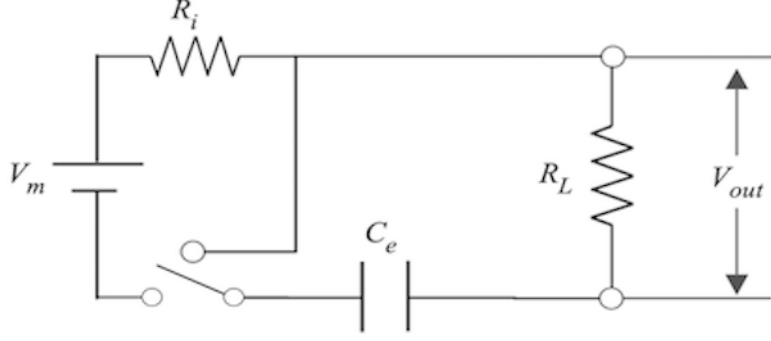


Figure 5.4: Equivalent circuit of Sales *et al* testing circuit.

In this configuration, as the switch alternates between the voltage source and the wire connection, we can say that the voltage read by the potentiostat would change polarity. The polarity changed is due to the following process: as the capacitor is charging, positive potential develops on the right plate of the capacitor (in the schematic) and a negative potential develops on the left plate. Once the capacitor is disconnected from the voltage source, the discharge from the capacitor takes on a different current direction than the current from the voltage source alone. Thus, the potentiostat reads the alternating potential, and the voltage peak sign would oppose the charging sign.

Now, we can now interpret that the cell was operating correctly, and we can evaluate the performance by integrating the power curve to obtain the energy stored and extracted from the cell.

5.2 Performance Analysis

Now that the operation of the single CDP supercapacitor cell discussed above has been validated, we can begin to compute metrics with the data. Below are tables listing the performance metrics used to evaluate the cell's performance. Using

MATLAB's **trapz** command, the data curves were numerically integrated to calculate energy stored, energy extracted, and efficiencies.

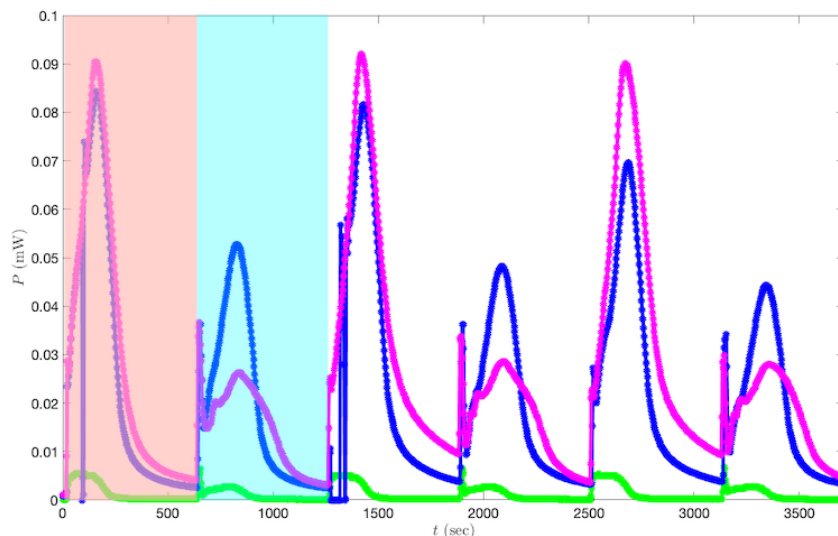


Figure 5.5: Power versus time plot with different lines corresponding to a different external load. The shaded regions highlight the first charging stage (red) and the discharging stage (blue) of the test trial. This pattern is cyclically repeated throughout the remainder of the tests. The green plot corresponds to $10\ \Omega$, the blue plot corresponds to $330\ \Omega$, and the magenta plot corresponds to $550\ \Omega$.

If we revisit the power versus time plot in **Figure 5.5** of the load test in chapter 4, the charging and discharging curves are highlighted in red and blue respectively. To compute the energy input to the system, the red region was numerically integrated to find the area underneath the curve in units of mJ. Likewise, to compute the energy output from the system, the blue region was numerically integrated. After the integration is performed, efficiency of the cycle is simply computed by taking the output energy divided by the input energy: $\eta = E_{out}/E_{in}$. This integration and efficiency computation was performed for each of the 3 cycles of the tests and then input to an

average efficiency computation defined as: $\bar{\eta} = (\sum_i^N \eta_i)/N$, where N is the number of cycles during the test (in this case 3).

Below we can see the comparison between Sales' results in **Figure 5.6** and the results of the test cell discussed throughout this document.

TABLE 1. Experimental Results for Maximum Voltage, Maximum Power Density, and Cycle Energy Efficiency

load (Ω)	max voltage (mV)	power density (mW/m ²)	energy efficiency (%)
100	119	5.3	47
11	98	32.6	56
1	42	66	27
0.5	29	72	22

Figure 5.6: Table of Sales' experimental results from [7].

Table 5.1: Load Resistance Performance Data

Energy Performance Data				
Test Condition	$E_{i,max}$ (mJ)	$E_{o,max}$ (mJ)	Max Power Density (mW/m ²)	$\bar{\eta}_{avg}$
1.5 Ω^{***}	0.09	0.09	1.3	>98%
10 Ω	3.63	0.84	8.9	46.21%
330 Ω	14.75	10.96	100	83.61%
510 Ω	33.98	28.85	100	61.95%

Table 5.2: Concentration Performance Data

Energy Performance Data				
Test Condition	$E_{i,max}$ (mJ)	$E_{o,max}$ (mJ)	Max Power Density (mW/m ²)	$\bar{\eta}_{avg}$
0.5 M	33.98	28.85	100	61.38%
1.0 M	35.05	14.17	180	67.76%
2.0 M	57.37	16.97	200	76.49%
2.5 M	70.52	13.89	130	76.01%
3.0 M	79.23	15.89	80	75.29%

We see in **Table 5.1** and **Table 5.2** that the resulting performance of this single cell has a higher average efficiency trend and power density than that listed in [7]. This shows that this controlled flow device and material selection was indeed successful and proves that CAPMIX devices can be further developed into modular and integrable

forms. The asterisks in **Table 5.1** are to signify an outlier behavior with the $1.5\ \Omega$ resistor connected as a load. During this trial, the charging and discharging behavior was that of a seemingly perfect capacitor. The potential of the cell was relatively stable until the discharge stage where it returned to the initial rest voltage. This small load limit may imply a much higher performance efficiency for smaller external loads.

Chapter 6

CONCLUSION

6.1 Summary of Main Findings

In chapter 4 and 5 we reported the results of testing a CAPMIX supercapacitor cell with variable external loads, variable flow rates, and variable saline concentrations. The objective of these tests were to observe and analyze the electrical behavior of the cell as this design differed fundamentally from Sales' 2010 study. The primary difference between the design used in this study and Sales' cell stack design was the design of a controlled flow pattern. Sales' design allowed radial flow patterns which drove the infused solution to exit the cell in a nonuniform pattern. The exit solution was captured in a teflon housing, however, in practice, this design would not be well controlled and does not allow a design engineer to properly optimize the design of the cell for proper flow characteristics. With the design used in this study, it was found that controlling the flow to enter and exit perpendicular to the cell channel is a successful design and allows a quasi two dimensional flow in the cell. This design allows the solution to sufficiently disperse throughout the glass fiber media and cover the full geometry of the ionic membrane. This aspect is crucial to the performance of the cell because any wasted contact area between the glass fiber media and the ionic membrane hinders the ionic adsorption characteristics of the cell. The less ions that are adsorbed, the lower the cell capacitance, and hence, less energy can be stored as a result. The cell as a result did have improved performance in average efficiency and peak power density in comparison to Sales 2010 study.

The experiment testing the effect of infusion flow rate on cell performance did provide insight on the sensitivity of the cell's output as a function of the construction.

The plots presented in chapter 4 depict same direction peaks for the charge and discharge stages. In Sales' study, the cell stack outputs a voltage profile that alternates in peak direction from the charging stage to the discharging stage. After the repeatable outcomes of same direction peaks, the data had to be interpreted differently than that presented in Sales. Chapter 5 section 1 discusses the equivalent circuit models that qualitatively describe the reasoning for having same direction or alternating direction voltage peaks during experimentation. Using simple RC circuit models, it was concluded that if the external load is connected to the CAPMIX device in parallel, and the open circuit voltage peaks do alternate in direction, it is a result of uncontrolled flow. The flow is uncontrolled in the sense that ions are being transported to their counter electrode (i.e. anions are forced by the cationic membrane and placed in the cathode) resulting in a change in polarity of the cell. This would occur if the membranes and electrodes are not of the same dimension, leaving bypass channels for flow to travel. Another cause is a damaged membrane or if the membrane and electrode are not properly sealed together. The electrode and membrane not properly sealed also leaves a gap for the infused solution to accumulate.

6.2 Future Research

Future investigations for this device can branch to multiple facets pertaining to a commercial level CAPMIX device. First, the performance of the module is limited by the characteristics of the ionic membranes and the porous electrode structure. Should ionic membranes have higher selectivity and ionic conductivity, this could result in quicker charge rates and higher potentials. In addition to membrane modification efforts, the effect of various porous electrode materials and configurations on ion storage capacity and overall stored energy must be tested.

Carbon cloth electrodes with microporous layer coatings were utilized in this work. However, other electrode materials must be tested for pore size, pore density,

and 2D vs 3D structures. For the designs implemented in this study and in current literature, the EDL's are formed in a 2D plane in the outermost layers of the 'sandwich' structure of the cell. In order to improve the total storage capacity, 3D construction configurations must be investigated as this has potential to significantly increase the total number of adsorbed ions in the porous electrode. With the increase in ionic storage capacity, peak voltage and power measurements can increase to the order of small commercially available batteries, thus, rendering CAPMIX devices a promising renewable energy device. Combined work on these materials will show a promising future for CAPMIX modules with speed and higher peak power outputs.

Other investigations could lead to experimenting with fully integrated CAPMIX systems. A suggested integration scheme would be utilizing pumping devices that are powered from the mechanical energy of stream currents. The system would have hydroelectric turbines both in the saline and fresh water bodies, they generate electricity and then deposit the streams into a pipeline. Following the turbine, the hydroelectric power generated would power the in-line pumps that control the infusion of the streams into the supercapacitor cell. This system would then utilize both the mechanical and chemical energy from the joining bodies of water, and thus form a clean energy production process. While this integration scheme sounds promising, lab studies must be done with small scale systems where gravitational potential energy controls the stream current.

Another integrated system would be using multiple cells in parallel with various phase shifts. Hypothetically, with multiple cells operating out of phase with one another (pumping or charge/discharge cycles are out of phase) one could control the cycle frequency and operate the cells to provide pulse-width modulated voltage signals or a fully continuous voltage, generating a DC power supply. This investigation must be done to better understand the practical scheme of using these devices in the field.

With the combined efforts of materials scientists and electrochemical researchers, CAPMIX devices could make a significant impact in the realm of clean and renewable energy sources. Progressive research to design modular and lightweight devices must be done to promote the promise of this technology when integrated efficiently.

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Appendix A
PERFORMANCE ANALYSIS CODE

```
%% Energy Integral Code
% The purpose of this code is to perform numerical integration using the
% trapezoidal rule.
```

```
% First we import the data in a .txt file from versastudio software
% IT IS KEY TO SPECIFY WHERE IN THE DATA TO END THE INTEGRATION!!!
```

```
clear all;
clear global;
clc;
P=importdata('ConcentrationCalcs.txt');
```

```
% Next we perform the numerical integration
% Initializing arrays and vectors to store localized data in plots.
```

```
P1A_1=zeros(1,length(P.data));
t1A_1=zeros(length(P.data),1);
P1B_1=zeros(1,length(P.data));
t1B_1=zeros(length(P.data),1);
P2A_1=zeros(1,length(P.data));
t2A_1=zeros(length(P.data),1);
P2B_1=zeros(1,length(P.data));
t2B_1=zeros(length(P.data),1);
P3A_1=zeros(1,length(P.data));
t3A_1=zeros(length(P.data),1);
P3B_1=zeros(1,length(P.data));
t3B_1=zeros(length(P.data),1);
```

```
P1A_2=zeros(1,length(P.data));
t1A_2=zeros(length(P.data),1);
P1B_2=zeros(1,length(P.data));
t1B_2=zeros(length(P.data),1);
P2A_2=zeros(1,length(P.data));
t2A_2=zeros(length(P.data),1);
P2B_2=zeros(1,length(P.data));
t2B_2=zeros(length(P.data),1);
P3A_2=zeros(1,length(P.data));
t3A_2=zeros(length(P.data),1);
P3B_2=zeros(1,length(P.data));
t3B_2=zeros(length(P.data),1);
```

```
P1A_3=zeros(1,length(P.data));
t1A_3=zeros(length(P.data),1);
P1B_3=zeros(1,length(P.data));
t1B_3=zeros(length(P.data),1);
P2A_3=zeros(1,length(P.data));
t2A_3=zeros(length(P.data),1);
P2B_3=zeros(1,length(P.data));
t2B_3=zeros(length(P.data),1);
P3A_3=zeros(1,length(P.data));
t3A_3=zeros(length(P.data),1);
P3B_3=zeros(1,length(P.data));
t3B_3=zeros(length(P.data),1);
```

```
P1A_4=zeros(1,length(P.data));
t1A_4=zeros(length(P.data),1);
P1B_4=zeros(1,length(P.data));
t1B_4=zeros(length(P.data),1);
P2A_4=zeros(1,length(P.data));
t2A_4=zeros(length(P.data),1);
P2B_4=zeros(1,length(P.data));
```

```

t2B_4=zeros(length(P.data),1);
P3A_4=zeros(1,length(P.data));
t3A_4=zeros(length(P.data),1);
P3B_4=zeros(1,length(P.data));
t3B_4=zeros(length(P.data),1);

```

```

P1A_5=zeros(1,length(P.data));
t1A_5=zeros(length(P.data),1);
P1B_5=zeros(1,length(P.data));
t1B_5=zeros(length(P.data),1);
P2A_5=zeros(1,length(P.data));
t2A_5=zeros(length(P.data),1);
P2B_5=zeros(1,length(P.data));
t2B_5=zeros(length(P.data),1);
P3A_5=zeros(1,length(P.data));
t3A_5=zeros(length(P.data),1);
P3B_5=zeros(1,length(P.data));
t3B_5=zeros(length(P.data),1);

```

```
% Assigning data to array and vectors
```

```

for i=1:length(P.data(:,1))
    if i==1
        Po1=P.data(i,2);
        Po2=P.data(i,3);
        Po3=P.data(i,4);
        Po4=P.data(i,5);
        Po5=P.data(i,6);
    end
    if P.data(i,1)>3 && P.data(i,1)<=624
        P1A_1(i)=P.data(i,2)-Po1;
        t1A_1(i)=P.data(i,1);

        P1A_2(i)=P.data(i,3)-Po2;
        t1A_2(i)=P.data(i,1);

        P1A_3(i)=P.data(i,4)-Po3;
        t1A_3(i)=P.data(i,1);

        P1A_4(i)=P.data(i,5)-Po4;
        t1A_4(i)=P.data(i,1);

        P1A_5(i)=P.data(i,6)-Po5;
        t1A_5(i)=P.data(i,1);

    elseif P.data(i,1)>630 && P.data(i,1)<=1248
        P1B_1(i)=P.data(i,2)-Po1;
        t1B_1(i)=P.data(i,1);

        P1B_2(i)=P.data(i,3)-Po2;
        t1B_2(i)=P.data(i,1);

        P1B_3(i)=P.data(i,4)-Po3;
        t1B_3(i)=P.data(i,1);

        P1B_4(i)=P.data(i,5)-Po4;
        t1B_4(i)=P.data(i,1);

        P1B_5(i)=P.data(i,6)-Po5;
        t1B_5(i)=P.data(i,1);
    end
end

```

```
elseif P.data(i,1)>1275 && P.data(i,1)<=1869
    P2A_1(i)=P.data(i,2)-Po1;
    t2A_1(i)=P.data(i,1);

    P2A_2(i)=P.data(i,3)-Po2;
    t2A_2(i)=P.data(i,1);

    P2A_3(i)=P.data(i,4)-Po3;
    t2A_3(i)=P.data(i,1);

    P2A_4(i)=P.data(i,5)-Po4;
    t2A_4(i)=P.data(i,1);

    P2A_5(i)=P.data(i,6)-Po5;
    t2A_5(i)=P.data(i,1);

elseif P.data(i,1)>1878 && P.data(i,1)<=2490
    P2B_1(i)=P.data(i,2)-Po1;
    t2B_1(i)=P.data(i,1);

    P2B_2(i)=P.data(i,3)-Po2;
    t2B_2(i)=P.data(i,1);

    P2B_3(i)=P.data(i,4)-Po3;
    t2B_3(i)=P.data(i,1);

    P2B_4(i)=P.data(i,5)-Po4;
    t2B_4(i)=P.data(i,1);

    P2B_5(i)=P.data(i,6)-Po5;
    t2B_5(i)=P.data(i,1);

elseif P.data(i,1)>2508 && P.data(i,1)<=3120
    P3A_1(i)=P.data(i,2)-Po1;
    t3A_1(i)=P.data(i,1);

    P3A_2(i)=P.data(i,3)-Po2;
    t3A_2(i)=P.data(i,1);

    P3A_3(i)=P.data(i,4)-Po3;
    t3A_3(i)=P.data(i,1);

    P3A_4(i)=P.data(i,5)-Po4;
    t3A_4(i)=P.data(i,1);

    P3A_5(i)=P.data(i,6)-Po5;
    t3A_5(i)=P.data(i,1);

elseif P.data(i,1)>3129 && P.data(i,1)<=3717
    P3B_1(i)=P.data(i,2)-Po1;
    t3B_1(i)=P.data(i,1);

    P3B_2(i)=P.data(i,3)-Po2;
    t3B_2(i)=P.data(i,1);

    P3B_3(i)=P.data(i,4)-Po3;
    t3B_3(i)=P.data(i,1);
```

```
P3B_4(i)=P.data(i,5)-Po4;
t3B_4(i)=P.data(i,1);
```

```
P3B_5(i)=P.data(i,6)-Po5;
t3B_5(i)=P.data(i,1);
```

```
end
```

```
end
```

```
% Now we will compute the efficiencies
```

```
E1A_1=trapz(t1A_1,P1A_1);
E1B_1=trapz(t1B_1,P1B_1);
E2A_1=trapz(t2A_1,P2A_1);
E2B_1=trapz(t2B_1,P2B_1);
E3A_1=trapz(t3A_1,P3A_1);
E3B_1=trapz(t3B_1,P3B_1);
```

```
E1A_2=trapz(t1A_2,P1A_2);
E1B_2=trapz(t1B_2,P1B_2);
E2A_2=trapz(t2A_2,P2A_2);
E2B_2=trapz(t2B_2,P2B_2);
E3A_2=trapz(t3A_2,P3A_2);
E3B_2=trapz(t3B_2,P3B_2);
```

```
E1A_3=trapz(t1A_3,P1A_3);
E1B_3=trapz(t1B_3,P1B_3);
E2A_3=trapz(t2A_3,P2A_3);
E2B_3=trapz(t2B_3,P2B_3);
E3A_3=trapz(t3A_3,P3A_3);
E3B_3=trapz(t3B_3,P3B_3);
```

```
E1A_4=trapz(t1A_4,P1A_4);
E1B_4=trapz(t1B_4,P1B_4);
E2A_4=trapz(t2A_4,P2A_4);
E2B_4=trapz(t2B_4,P2B_4);
E3A_4=trapz(t3A_4,P3A_4);
E3B_4=trapz(t3B_4,P3B_4);
```

```
E1A_5=trapz(t1A_5,P1A_5);
E1B_5=trapz(t1B_5,P1B_5);
E2A_5=trapz(t2A_5,P2A_5);
E2B_5=trapz(t2B_5,P2B_5);
E3A_5=trapz(t3A_5,P3A_5);
E3B_5=trapz(t3B_5,P3B_5);
```

```
N1_1=E1B_1/E1A_1;
N2_1=E2B_1/E2A_1;
N3_1=E3B_1/E3A_1;
N_avg_1=(1/3)*(N1_1+N2_1+N3_1);
```

```
N1_2=E1B_2/E1A_2;
N2_2=E2B_2/E2A_2;
N3_2=E3B_2/E3A_2;
N_avg_2=(1/3)*(N1_2+N2_2+N3_2);
```

```
N1_3=E1B_3/E1A_3;
N2_3=E2B_3/E2A_3;
```

```
N3_3=E3B_3/E3A_3;  
N_avg_3=(1/3)*(N1_3+N2_3+N3_3);
```

```
N1_4=E1B_4/E1A_4;  
N2_4=E2B_4/E2A_4;  
N3_4=E3B_4/E3A_4;  
N_avg_4=(1/3)*(N1_4+N2_4+N3_4);
```

```
N1_5=E1B_5/E1A_5;  
N2_5=E2B_5/E2A_5;  
N3_5=E3B_5/E3A_5;  
N_avg_5=(1/3)*(N1_5+N2_5+N3_5);
```

```
% Reproducing data in MATLAB plot
```

```
plot(P.data(1:end,1),(P.data(1:end,2)/1000),'o','Color','r','LineStyle','-','LineWidth',5)  
hold on  
plot(P.data(1:end,1),(P.data(1:end,3)/1000),'o','Color','g','LineStyle','-','LineWidth',5)  
plot(P.data(1:end,1),(P.data(1:end,4)/1000),'o','Color','b','LineStyle','-','LineWidth',5)  
plot(P.data(1:end,1),(P.data(1:end,5)/1000),'o','Color','m','LineStyle','-','LineWidth',5)  
plot(P.data(1:end,1),(P.data(1:end,6)/1000),'o','Color','c','LineStyle','-','LineWidth',5)  
hold off  
xlim([0 3717])  
xlabel('$t$ (sec)','Interpreter','latex','FontSize',24)  
ylabel('$P$ (mW)','Interpreter','latex','FontSize',24)  
set(gca,'FontSize',20)
```