Framework for the Characterization and Performance Projection of Electrochemical Capacitor Electrodes

by

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Abstract

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The objective of this thesis is to develop a framework for the characterization and performance projection of new electrochemical capacitor electrode materials. This framework was demonstrated on a new commercial electrode, called EXCELLERATOR®, from W.L. Gore & Associates, Inc. The electrode was tested in a Schlenk-type apparatus using cyclic voltammetry in a 0.5M tetrabutylammonium hexafluorophosphate in propylene carbonate solution. A macroscopic homogeneous volume averaged model was used to simulate the cyclic voltammetry response of the electrode. Subsequent fitting of the simulated response to the experimental data gave estimates of the volumetric capacitance and time constant of the electrode to be 40F/cm$^3$ and 133.4s, respectively.

Analytical solutions for the terminal voltage, energy density and power density were derived for the constant current discharging of a complete electrochemical capacitor. The evolution of the terminal voltage during discharge was explained. The energy and power densities for discharging the capacitor of different electrode thicknesses and at different current densities were investigated. The observed trends were explained by comparing the relative utilization of the electrode. The maximum energy density that can be extracted from an electrochemical capacitor during different lengths of time was simulated. It was shown that the thinner electrodes have higher energy and power densities at short times because of the lower unused active material mass. For long times, the thicker electrodes are superior because their active material mass is a larger fraction of the total mass. It was shown that the ultimate electrode geometry would involve thin electrodes with negligible non-active material masses. In this case, the thinnest electrodes would have higher energy and power densities than thicker ones even at long times.
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1.0 Introduction

There are a vast number of applications that require some form of portable electrical energy source. Conventionally, the requirements of the majority of these applications can be satisfied by the use of batteries and/or capacitors. However, many important innovations of recent years have placed ever-increasing demands on their energy supplies. An example is the continual drive of portable personal electronics, such as cellular phones and personal digital assistants, towards expanding capabilities but in smaller packages. Another important example is electric vehicles. Batteries and capacitors, by themselves, are not the optimal solutions for these and many other applications.

Electrochemical Capacitors (ECs) are a class of alternate electrical energy storage devices that promise, and in some cases have shown, to be an enabling technology for many of these applications. In the literature, ECs are also called supercapacitors, ultracapacitors, double-layer capacitors, and electrochemical double-layer capacitors. Generally, ECs have higher power densities, but lower energy densities, than batteries. If ECs can be produced that have energy densities similar to those of batteries, the utility of ECs would increase immensely. Therefore, one of the most sought after goals in EC research is the development of new electrode materials, such as nanostructured carbons, that have increased energy densities without sacrificing much power densities. However, the geometrical parameters of an electrode, such as its thickness, and the discharge conditions can drastically affect its energy and power densities. As a result, it is often
difficult to evaluate whether an EC based on a new material can satisfy the requirements of a particular application.

The aim of this thesis is to develop a framework that can be used to test prospective EC materials and subsequently predict their performances. This allows for a model-guided electrode fabrication approach to optimize the geometry of an electrode for a specific application. This framework involves first the characterization of the electrode using cyclic voltammetry. Mathematical modeling of the response will be fitted to the experimental results to give estimates of the parameters to use in the subsequent calculations. Using these parameters, the terminal voltage responses, and energy and power densities of a complete EC with different thicknesses and under different discharge conditions can be predicted. This allows for the optimization of the thickness and operation of an EC for a particular application. A new EC capacitor electrode, called EXCELLERATOR®, from W.L. Gore & Associates, Inc., will be used in this thesis to illustrate the utility of this framework.

In the next chapter, the background information needed to understand the operation of ECs is presented. Chapter 3 gives the procedure and results of the experiments performed on the EXCELLERATOR® electrode. In chapter 4, the mathematical model used is first described in detail, and then the modeling results are presented. Chapter 5 states the conclusions of this work. The last chapter lists the references used.
2.0 Background

This chapter presents some background information on ECs. In section 2.1, the physical principles of their operation are described. The second section discusses the industrial significance of ECs.

2.1 Physical Principles of EC Operation

The structure of a typical EC is depicted in figure 1. When voltage is applied, one electrode becomes positively charged while the other becomes negatively charged through charge injection. Positive ions are expelled from the positive electrode whereas negative ions are attracted towards it. On the other hand, positive ions are attracted towards the negative electrode, while negative ions are expelled from it. When the voltage source is disconnected from the electrodes, the voltage difference between the two electrodes and the energy associated with it remains due to the large forces of attraction between the stored charge in the electrode and ions in the solution.
A simple equivalent circuit representation of an EC is shown in figure 2. The two capacitors, \(C_1\) and \(C_2\), represent the capacitances of the two electrodes. The total capacitance, \(C_T\), of the device is given by:

\[
\frac{1}{C_T} = \frac{1}{C_1} + \frac{1}{C_2}.
\]

Therefore, it is important to distinguish between single electrode and total device capacitance values. \(R_i\) is the internal resistance and is the result of a combination of components. These include the electrolytic solution resistance in the pores of the electrode and the separator, the resistance of the active material and the current collector, and contact resistance between the active material and the current collector. A more elaborate model of an EC will be discussed in Chapter 4.
The stored energy in an EC is proportional to the square of the applied voltage. However, higher voltage leads to a faster rate of charge-transfer reactions, also called Faradaic reactions, at the electrodes, which is a mechanism of self-discharge. Thus, the maximum allowable applied voltage for an EC depends on the acceptable leakage. The rate of Faradaic reactions also depends on the type of electrode, electrolytic solution, and current collector used. Therefore, careful selection of all the components is necessary.

The present section describes physical principles involved in the operation of an EC. The role played by the electrodes, electrolytic solution, separator, and current collectors are discussed in turn. Then, the last part of this section presents the figure-of-merits commonly used to compare ECs.

2.1.1 Electrodes

A number of different materials can be used as the active material in an EC. A list of candidates that have been investigated heavily for this purpose and their properties are compiled in table 1. The gravimetric capacitance values listed only accounts for the active material mass.
Table 1. Materials commonly investigated as active components in ECs and their properties. Reprinted from [1], Copyright (2000), with permission from Elsevier.

The vast majority of commercial ECs are based on carbon materials because of their good performances and low costs. A number of different forms of carbon materials can be used. These include carbon powders, woven cloths, felts, and fibers. Many companies already produce these materials in large quantities. The EXCELLERATOR® electrode tested in this project also uses a carbon powder.

The energy stored in a carbon-based material is mostly stored in what is commonly known as the electrical double layer. Thus, ECs based on carbon are also often referred to as electrochemical double layer capacitors. The situation is very similar to a traditional parallel-plate capacitor, the capacitance $C$ of which is given by

$$ C = \varepsilon \frac{A}{d}, $$

where $\varepsilon$ is the dielectric constant of the medium between the plates. $A$ and $d$ are the area and separation of the electrodes, respectively. Because the charge separation distance between the surface charge and solution ion is on the order of 1nm in the electrical double layer, the per unit area capacitance of an EC is very large compared to traditional
capacitors. In a carbon-based material, the observed capacitance is on the order of 15-30\(\mu\)F/cm\(^2\) [1].

From this simple discussion, it is obvious that a criterion for a good EC electrode material is that it also has a large surface area. To increase the surface area of carbon materials, they are often subjected to an activation process that increases the carbon’s porosity. Two examples of activation processes include steam and potassium hydroxide treatment at high temperatures. A number of available activated carbon materials have specific areas and capacitances on the orders of 1000-2000m\(^2\)/g and 100-200F/g, respectively. However, there is often a tradeoff between surface area and conductivity for carbon materials. Thus, high capacitance usually comes at the expense of higher resistive losses for the EC.

A number of EC electrodes do not rely on charging of the double layer for their capacitive response. This type of observed capacitance is called pseudocapacitance. Often, these electrodes’ charge storage comes from reversible redox reactions in the active material. Although most of the measured capacitance of carbon-based ECs are attributed to the charging of the double layer, there may still be some pseudocapacitive effects that arise from redox reactions of functional groups that often exist on activated carbon surfaces [2].

One class of material based on pseudocapacitance is those based on electroactive polymers. When charges are injected into the polymer, ions move inside the bulk of the
material to compensate for the charge imbalance. Depending on the polarity of the injected charge, the polymer is classified as n- or p-type. High capacitance values in the range of 450 F/g have been reported. However, long term cycling is an issue. It is believed that the expansion and shrinkage of the polymer during cycling may be the cause of performance degradation [2].

Another class of EC electrodes based on pseudocapacitance is metal oxides. RuO₂ and IrO₂ are two such oxides that have garnered a lot of attention in recent years. The capacitance comes from the redox reactions in the material. Capacitance values as high as 650 F/g have been reported. Also, the high conductivity of these materials result in low energy dissipation. However, the high costs of these materials have been the largest hurdles to their commercialization.

2.1.2 Electrolytic Solution

The electrolytic solution used is also an important consideration in the design and operation of an EC. One way the solution affects the capabilities of the EC is through its conductivity. As shown in the EC equivalent circuit in figure 2, the internal resistance is a source of energy and power dissipation. One component of this internal resistance comes from the solution resistivity. Therefore, minimization of the resistivity of the solution is an important factor in the design of ECs.

As discussed before, the rate of Faradaic reactions at the electrode depends on the type of electrolyte used. Therefore, the maximum voltage that can be applied to the EC also
depends on the electrolytic solution. To complicate matters, the voltage window can be severely affected by the presence of moisture and other contaminants. The reduction of the voltage window in the presence of water contamination is demonstrated in [3] and [4].

The electrolyte commonly used in ECs can be divided into two classes. The first class consists of aqueous solvents. Common salts include sulphuric acid and potassium hydroxide. The advantage for this class of electrolyte is the high conductivity achievable. For example, concentrated sulphuric acid can have conductivity as high as 0.8S/cm [2]. However, the voltage window available is only about 1V.

The second class of electrolyte uses organic solvents. Typical solvents of this type that are used in ECs are propylene carbonate and acetonitrile. A common salt used is tetraethylammonium tetrafluoroborate. The advantage for using these solutions is their large voltage windows, which are generally much larger than those in aqueous solutions. Tabulations of conductivity and limiting potential data for various organic electrolytes are shown in [4] and [5]. However, the disadvantage of organic solutions is their lower conductivity. The conductivities of these solutions are at least an order of magnitude lower than that achievable in a concentrated aqueous solution. Also, because of the larger size of the ions involved, the surfaces that are accessible to charging can be affected. For example, some high surface area activated carbons show much lower capacitances in organic electrolytes, compared to aqueous ones, because their pores are too small for the ions to penetrate [1].
2.1.3 Separator

The separator is a porous material that allows an ionic current to be passed between the two active layers through the electrolyte. This completes the circuit during the charge and discharge of an EC. It is important to note that electrical contact between the two active layers through the separator is not desirable because the resulting transfer of charge would lead to losses. Therefore, the separator is ionically, but not electrically, conducting and the main consideration for selection of a suitable separator material is the effective resistance of the electrolyte through it. As discussed before, this resistance is a mechanism of energy loss in the operation of an EC and so must be minimized. The per unit area resistance, \( R_A \), of a porous material can be modeled by the relation:

\[
R_A = \frac{L_S}{\kappa_S},
\]

(3)

where \( L_S \) and \( \kappa_S \) are the separator thickness and effective solution conductivity, respectively. The effective solution conductivity in the separator is often modeled using Bruggeman's relation [6]:

\[
\kappa_S = \kappa_0 \varepsilon_S^{1.5},
\]

(4)

where \( \kappa_0 \) and \( \varepsilon_S \) are the free solution conductivity and separator porosity, respectively. Therefore, higher porosity separators have higher effective solution conductivities, which agrees with intuition. Separators with thicknesses down to about 10μm and approximately 50% porosity are already available commercially.
2.1.4 Current Collectors

The purpose of the current collectors is to make electrical contact between the active material layer and the external leads. Thus, an important consideration in the selection of the geometry and material to use as the collector is the resistance it contributes to the device. Typical current collectors are made of foils of metal, such as aluminum and nickel [1]. Because of the high conductivity of these materials, the thickness of the foil can be as thin as tens of microns thick without introducing significant bulk resistance. However, the contact resistance between the collector and the active material is much more of a concern for EC design. Another consideration in the selection of current collector is that it can also be the source of Faradaic reactions that leads to self-discharge of the device.

2.1.5 Figures-of-Merit

There are three figures-of-merit most often used for evaluating ECs. They are the mass or volume normalized specific capacitance, energy density, and power density. Energy, power and capacitance per unit mass are used because many applications of ECs require them to be integrated into a portable system where weight is important. For example, in vehicle applications, the increase in power at the cost of increased weight may be unfavorable because the extra weight becomes a physical load.

The utility of comparing ECs based on their specific capacitance is obvious since higher capacitance devices store a larger amount of energy at the same voltage. However, during discharge, the voltage evolves as a function of time. Therefore, considering the
stored energy density alone is not enough for specifying the capabilities of an EC. A common way to illustrate the performance of an EC is to use what is called a Ragone plot. In this plot, each point represents an instant in time and the power density, \( P(t) \), is plotted against the energy density, \( E(t) \). The power density is the instantaneous power density supplied at that instant, whereas the energy density is the total energy supplied up to that time. In equation form, they are expressed, in the mass normalized case, as

\[
P(t) = \frac{1}{M} I(t) V_T(t) \tag{5}
\]

\[
E(t) = \frac{1}{M} \int_0^t I(t') V_T(t') dt' \tag{6}
\]

where \( M \) is the mass of the device, \( I(t) \) is the device current at time \( t \), and \( V_T(t) \) is the device terminal voltage at time \( t \). Therefore, the Ragone plot illustrates the evolution of the supplied power as the quantity of energy withdrawn from the device increases (see Figure 21 in Chapter 4). In this thesis, energy and power densities refer to the mass normalized energy and power supplied. The calculation of the volume normalized energy and power densities would be a straightforward extension.

### 2.2 Industrial Significance

This section covers some of the application-related aspects of EC technology. Part 2.2.1 compares the capabilities of ECs to that of more conventional electrical energy supplies. In part 2.2.2, some of the commercial EC suppliers and the properties of their products are listed. The last part discusses some applications which utilize ECs today, and also opportunities where ECs are expected to make an impact in the future.


2.2.1 Performance Comparison to Other Technologies

ECs are electrochemical devices that possess energy supply capabilities different from those of conventional batteries and capacitors. A comparison of the approximate energy and power densities of various power sources are shown in figure 3. As shown in the figure, the power densities of ECs are better than batteries, but worse than capacitors. Also, ECs’ energy densities are higher than capacitors, but lower than batteries. Therefore, most promising applications of ECs are those that require higher power densities than that achievable in batteries and higher energy densities than that of capacitors.

Figure 3. Comparison of the typical energy and power densities of different electrical energy storage devices. Reprinted from [2], Copyright (2000), with permission from Elsevier.

Another reason for considering ECs is their longer lifetimes than batteries. If left unused for many months, rechargeable batteries self-discharge and degrade drastically in
performance. As pointed out before, ECs also self-discharge. However, their ability to store charge often remains, even after several years. Some ECs can be subjected to between 500,000 to 1,000,000 cycles with a relatively small degradation, about 10-20%, in capacitance and resistance [1]. The cycle life of batteries is often on the order of a few thousand cycles. Further, the components used in ECs are typically considered non-toxic and so disposal of them is simpler than for batteries.

### 2.2.2 Commercial Supplies

Several hundred million ECs are sold worldwide every year [2]. Table 2 lists some of the EC suppliers and the properties of their products. Other companies not listed in the table that invest in EC development include EPCOS, NEC, ELNA, TOKIN, Econd, and ELIT. A vast majority of these devices on the market use carbon-based electrodes because of their low cost and good performance. As shown in the table, the energy densities of most commercial ECs are in the range of several Watt-hours per kilogram.
<table>
<thead>
<tr>
<th>Capacitor Device</th>
<th>Voltage (V)</th>
<th>Ah</th>
<th>Weight (kg)</th>
<th>Resistance (mΩ)</th>
<th>W h/kg (W/kg)</th>
<th>95% Discharge Efficiency</th>
<th>Matched Impedance Discharge</th>
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<tr>
<td>Maxwell ultracapacitors</td>
<td></td>
<td></td>
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<tr>
<td>2700 F</td>
<td>3</td>
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<td>0.85</td>
<td>0.5</td>
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<tr>
<td>1000 F</td>
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<td>1.5</td>
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<td>430</td>
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<td>800 F</td>
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<td>2.0</td>
<td>3.1</td>
<td>392</td>
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<td>2000 F</td>
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<td>0.57</td>
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<td>Superfarad (250 F)</td>
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<td>0.010</td>
<td>24</td>
<td>6.0</td>
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<td>13</td>
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<td>0.015</td>
<td>10</td>
<td>833</td>
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<td>Batteries</td>
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<tr>
<td>Panasonic NiHD</td>
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<td>18</td>
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<td>498</td>
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<td>Hawker Pb-acid</td>
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</tr>
<tr>
<td>Optima Pb-acid</td>
<td>2.1</td>
<td>0.85</td>
<td>3.63</td>
<td>0.5</td>
<td>46</td>
<td>115</td>
<td>607</td>
</tr>
<tr>
<td>Horizon Pb-acid</td>
<td>2.1</td>
<td>0.0083</td>
<td>0.083</td>
<td>5.7</td>
<td>25</td>
<td>25</td>
<td>2330</td>
</tr>
<tr>
<td>Bolder Pb-acid</td>
<td>2.1</td>
<td>1.05</td>
<td>0.083</td>
<td>5.7</td>
<td>442</td>
<td>442</td>
<td>2330</td>
</tr>
</tbody>
</table>

Table 2. A list of commercial ECs and high-power batteries on the market and their characteristics. Reprinted from [1], Copyright (2000), with permission from Elsevier.

2.2.3 Applications

At the present, ECs are already used in a variety of applications. In most of these applications, the EC is used to supply high pulse power for a significant amount of time, typically on the order of $10^{-2}$ s to $10^2$ s. Examples include their use in diesel engine starting, and in rechargeable toys such as toy cars [2].

ECs are also commonly used as backup energy sources. Examples include their use in car audio, taxi meters, portable electronics, and solar-powered electronics [2]. In these cases, the EC is used as the energy source to retain critical data when the battery is disconnected. A battery could also be used to satisfy this role. However, the EC is
selected because they offer longer lifetime, faster recharging, and better environmental compatibility at a cost comparable to batteries.

One of the most promising future applications of ECs is in electric and hybrid vehicles. For typical city driving, the power required varies drastically and the tandem of a battery and an EC has been shown to form a useful solution. Ideally, the EC would supply the required energy during the high power situations such as hill climbing, accelerating and engine starting. The battery would supply energy during low power demand periods and also recharge the EC during these times. In this way, the battery can be optimally designed for maximum efficiency. Also, the high cyclability and fast recharging rates of ECs make regenerative braking possible. Regenerative braking refers to the recovery of energy of motion of a vehicle during braking. The Toyota Prius, which was the first hybrid vehicle to employ ECs, has shown fuel consumption savings of about 12.5% because of the leveled power demands and the use of regenerative braking [7]. The requirements for ECs for use in electric vehicles, as defined by the FreedomCAR ultracapacitor task force, are listed in [8].
3.0 Experiments

Cyclic voltammetry experiments were performed on the EXCELLERATOR® electrode received from W.L. Gore & Associates, Inc. In cyclic voltammetry a triangular wave voltage is applied and the resulting current is measured. The electrode consists of a 100μm thick carbon-filled polytetrafluoroethylene (PTFE) active layer laminated onto a 30μm thick aluminum current collector. The observed capacitance is expected to be derived from the carbon constituent, while the PTFE layer serves as a non-conductive binder that holds the carbon particles in place and in contact with the aluminum sheet.

The goal of the experiments is to generate experimental data that can be used to give realistic estimates of the physical parameters in the mathematical model. Furthermore, an estimation of the operating voltage window of the electrolyte was also measured.

Section 3.1 gives a brief description of the setup used for the experiments. In section 3.2, the measurement of the operating voltage window of the electrolytic solution is discussed. The last section of this chapter presents the procedure for characterizing the EXCELLERATOR® electrode and the results obtained.

3.1 Experimental Setup

As discussed earlier, the electrochemistry of many systems are greatly affected by the presence of contaminants. Therefore, a Schlenk-type apparatus was used to perform the
electrochemical tests. This apparatus is a network of glassware and tubing that allows the environment of the components under test to be filled with ultra-pure nitrogen gas. This ensures minimal exposure of the tested components to atmospheric contaminants such as moisture. Figure 4 shows the schematic of the apparatus used. The control knobs allow for the alteration of the conditions inside the electrochemical cell. The components of the cell are electrically connected to the measurement instrument using wires that feeds through the cell’s glass cap.

The salt used in these experiments was tetrabutylammonium hexafluorophosphate (TBAP), purchased from Sigma Aldrich. It was triply recrystallized before use. 99.7% anhydrous propylene carbonate (PC), also purchased from Sigma Aldrich, was used as-
received as the solvent. An Eco-Chemie µAutolab was used to perform the cyclic voltammetry experiments.

3.2 Characterization of the Electrolyte

Cyclic voltammetry experiments were performed to determine the limiting reduction and oxidation potentials of the electrolyte. A 1.0 mm diameter platinum wire was used as the working electrode. The sidewall of the wire was sealed from the solution with glass, leaving only one end of the wire exposed to solution. The exposed end was polished with alumina powder three times. A platinum mesh was used as the counter electrode. A silver wire was used as a quasi-reference electrode. Both the counter and reference electrodes were flame cleaned after previous experiments. All three electrodes were sonicated in methylene chloride three times, each time for 15 minutes with fresh solution, and left overnight at ~100°C overnight before use. A picture of the electrodes is shown in figure 5.
The electrolyte used was 0.1M TBAP in PC. The voltage scan rate used was 100mV/s from -1V to 1.2V. The measured results are shown in figure 6. As shown in the figure, the measured current stayed within about 0.05mA/cm² even at the extremes of the applied potentials. The 2.2 V measured range is very similar to that used in many commercial ECs, which often have a rated maximum voltage of 2.3V. These results show that this electrolyte is a promising choice for use in ECs.
Figure 6. CV data on the platinum wire electrode vs. silver wire quasi-reference electrode.

### 3.3 Characterization of the EXCELLERATOR® Electrode

The cyclic voltammetric response of the EXCELLERATOR® electrode was also measured. The working electrode was a 0.9x2.5cm$^2$ piece of EXCELLERATOR® electrode cut from an approximately 21.6x27.9cm$^2$ sheet received from Gore. A picture of the working electrode is shown in figure 7. The working electrode was sized so that, when the electrode is placed in solution, the electrode area exposed to solution is approximately 0.9x1.9cm$^2$. The counter electrode was composed of two pieces of Gore electrodes, approximately 1.4x2.5cm$^2$ in size each. When placed in solution, the total counter electrode area exposed to solution has an area of about 2.8x1.9cm$^2$. A silver wire was used as a quasi-reference electrode. The silver wire was cleaned using the same procedure described in Section 3.2. All three electrodes were kept at ~100°C overnight before use. The electrolytic solution used was 0.5M TBAP in PC.
The cell was tested at a scan rate of 0.2mV/s. The measured results are shown in figure 8. Simulated cyclic voltammetry responses were fitted to this data to generate realistic estimates of physical parameters for the subsequent EC modeling. Those results will be shown in the next chapter.

Figure 8. CV experimental results for the Gore EXCELLERATOR® electrode. Top: applied voltage profile. Bottom: measured current density.
4.0 Modeling

This chapter discusses the mathematical modeling that was performed for this thesis. In section 4.1, the model of the electrode is introduced. Section 4.2 presents the model equations, and the boundary and initial conditions for simulation of cyclic voltammetry experiments. The analytical solution is given and the simulated response is fitted to experimental data obtained in section 3.3 to generate physical parameters for use in the subsequent mathematical modeling. The voltage response during discharge of an EC that utilize the EXCELLERATOR® electrode is simulated in section 4.3. The simulated energy and power densities under different discharge conditions are also presented. Section 4.4 examines the effect of the change of thickness of the electrodes on the voltage response, and energy and power densities of the EC. The optimization of the thickness of the electrode to give the highest energy density for a given discharge time is shown in section 4.5. This illustrates one utilization of this framework developed in the thesis.

4.1 Electrode Model Description

Carbon-based EC discharging can be modeled by a macroscopic description of porous electrodes. This type of modeling was first used on porous electrodes in [10] and treated in greater detail in [16]. The various variables in the model are the averages over a region of the electrode small with respect to the overall dimensions but large compared to the pore structure. This accounts for the essential features of an actual electrode without having to go into exact details of the pores.
In practically all cases of interest, the thickness of the electrode is much smaller than the other two dimensions of the electrode. It is then reasonable to assume that the properties of the electrode change only with depth, and as a result, the model becomes one-dimensional. In this thesis, this depth direction is labeled as $x$. The potential and current density in the solid phase at $x$ will be labeled as $\Phi_1(x)$ and $j_1(x)$, respectively. The potential and current density of the pore-filling solution at $x$ will be labeled as $\Phi_2(x)$ and $j_2(x)$, respectively. These and other quantities are assumed to be continuous functions of the position coordinate and time as a result of macroscopic averaging. In effect, the electrode is treated as the superposition of two continua, one representing the electrolytic solution and the other representing the solid.

For the present model, concentration variations will not be considered. This is justified because for the electrodes that are tested in this thesis work, the change in the salt concentration in the electrode pores between the fully charged and discharged states is estimated to be only a few percent. Therefore, the conductivity of the solution will not be a function of charge stored and time. The numerical simulation of EC electrodes that accounts for concentration variations has been performed in [11]. We also assume that Faradaic reactions are negligible. This will be true when the voltage that is applied to the EC is kept low. The double layer capacitance is assumed to be constant with respect to potential. This assumption is typically used in the modeling of carbon-based materials because the capacitance is not expected to change drastically over the potential range of interest [9-11]. The modeled EC has the structure shown in figure 9.
The modeling of the response of an EC can proceed by examining the response of a single electrode. The thickness of the electrode is labeled as $L$. The current collector edge of the electrode will be denoted as $x=0$, while the separator edge of the electrode will be denoted as $x=L$. The behavior of the entire device can be calculated by a simple superposition that will be discussed later.

The current density in the solid phase is given by an equivalent form of Ohm’s law:

$$i_1 = -\sigma \frac{d\Phi_1}{dx},$$  \hspace{1cm} (7)

where $\sigma$ is the effective conductivity of the solid phase. Typically, this effective conductivity can be easily measured, for example in a four probe setup. The current density in the liquid phase can also be described by a similar form of Ohm’s law:

$$i_2 = -\kappa \frac{d\Phi_2}{dx},$$  \hspace{1cm} (8)
where $\kappa$ is the effective conductivity of the liquid phase. This conductivity is much more difficult to measure because it is affected by the tortuosity introduced by the carbon particles. In this thesis, this effective solution conductivity will be obtained by fitting a simulated response to the experimental cyclic voltammetry data.

All the current that transfers from one phase to another (e.g. from solid to solution, or vice versa) must do so via charging or discharging of the double layer capacitance (in the absence of Faradaic reactions). This current, denoted by $\frac{\partial i}{\partial x}$ will be called the transfer current. This transfer current is given by:

$$\frac{\partial i_1}{\partial x} = -\frac{\partial i_2}{\partial x} = -aC \frac{\partial (\Phi_1 - \Phi_2)}{\partial t}, \quad (9)$$

where $C$ is the capacitance per unit surface area of the active material, measured in $\text{F/cm}^2$, and $a$ is the surface area per unit electrode depth, measured in $\text{cm}^2/\text{cm}$. Therefore, the factor $aC$ is the capacitance per unit depth of the active material. Dividing equation (9) by the area of the electrode, $A$, gives:

$$\frac{\partial j_1}{\partial x} = -\frac{\partial j_2}{\partial x} = -\frac{aC}{A} \frac{\partial (\Phi_1 - \Phi_2)}{\partial t}, \quad (10)$$

The factor $aC/A$ is the volumetric capacitance of the active material and has units of $\text{F/cm}^3$. An equivalent circuit that can be used to represent the above equations is shown in figure 10.
Figure 10. Equivalent circuit representation for an EC electrode.

Because the current must be carried in either the solid or solution phase, the measured current density, $j_M$, at the inputs is equal to the sum of the solid and solution phase currents at any position:

$$j_M = j_1(x_1) + j_2(x_1) = j_1(x_2) + j_2(x_2),$$  \hspace{1cm} (11)

where $x_1$ and $x_2$ are any two positions inside the electrode. Also, because the solution phase terminates at $x=0$ and the solid phase terminates at $x=L$,

$$j_2(0) = 0,$$  \hspace{1cm} (12)

$$j_1(L) = 0,$$  \hspace{1cm} (13)

and

$$j_M = j_1(0) = j_2(L).$$  \hspace{1cm} (14)

### 4.2 Cyclic Voltammetry Experiment Simulation

For the porous electrodes of interest here, the physical situation is depicted in figure 11.
Combining equations (7) and (8) yields:

\[
\frac{j_1 - j_2}{\sigma \kappa} = -\frac{\partial (\Phi_1 - \Phi_2)}{\partial x},
\]

(15)

Differentiating equation (15) with respect to \(x\) and substituting equation (10) into the result gives:

\[
\frac{1}{\sigma} \left( -\frac{aC}{A} \frac{\partial (\Phi_1 - \Phi_2)}{\partial t} \right) - \frac{1}{\kappa} \left( \frac{aC}{A} \frac{\partial (\Phi_1 - \Phi_2)}{\partial t} \right) = -\frac{\partial^2 (\Phi_1 - \Phi_2)}{\partial x^2}
\]

\[
aC \left( \frac{\sigma + \kappa}{\sigma \kappa} \right) \frac{\partial (\Phi_1 - \Phi_2)}{\partial t} = \frac{\partial^2 (\Phi_1 - \Phi_2)}{\partial x^2}.
\]

(16)

A similar form of equation (16) was earlier derived in [10]. In this thesis, it is assumed that the effective solid conductivity \(\sigma\) is much greater than the effective solution...
conductivity $\kappa$. This is because the bulk solution conductivity of even a concentrated organic electrolyte is on the order of 10mS/cm, whereas the solid conductivity of an activated carbon is typically on the order of at least 1-1000S/cm [14]. Data obtained from W.L. Gore & Associates, Inc., indicates that the conductivity of the active layer in the EXCELLERATOR® electrode is approximately 300mS/cm [15], 30 times larger than the electrolyte conductivity, and thus making the approximation reasonable. However, if an aqueous electrolyte was used instead of the concentrated organic electrolyte, the electrolyte conductivity could become comparable to the electrode conductivity.

Applying the assumption, equation (16) becomes

$$\frac{aC}{\kappa A} \left( \frac{\partial (\Phi_1 - \Phi_2)}{\partial t} \right) = \frac{\partial^2 (\Phi_1 - \Phi_2)}{\partial x^2}$$

$$\tau \left( \frac{\partial \eta}{\partial t} \right) = \frac{\partial^2 \eta}{\partial \gamma^2},$$

where

$$\gamma = \frac{x}{L},$$

$$\eta = \Phi_1 - \Phi_2,$$

and

$$\tau = \frac{aCL^2}{\kappa A}. \tag{20}$$

Notice that equation (17) is now expressed in non-dimensional length $\gamma$. $\eta$ is the double layer potential (the potential difference between the electronic conducting phase and the electrolyte at a given point within the material). $\tau$ has units of seconds and can be used as a time constant for comparing different electrodes. It represents the charging time...
constant in response to a step change in applied potential. An equivalent circuit to represent the above equations is shown in figure 12.

\[ \Phi_1(0,t) \]

\[ \Phi_2(1,t) \]

**Figure 12.** Equivalent circuit representation for an EC electrode assuming the solid phase resistance is negligible.

It is also instructive to express \( \tau \) as a product of a resistance and a capacitance:

\[ \tau = \left( \frac{L}{\kappa A} \right) aCL = R_T C_T. \]  

(21)

Notice \( R_T \) and \( C_T \) are the total resistance and capacitance of the electrode, respectively.

Rewriting equations (15) and (10) in terms of \( \tau \), \( \Phi \) and \( \gamma \), and given that \( \sigma \gg \kappa \) then:

\[ \frac{j_2 L}{\kappa} = \frac{\partial \eta}{\partial \gamma}. \]  

(22)

\[ \frac{\partial j_2}{\partial \gamma} = \frac{aCL}{A} \frac{\partial \eta}{\partial t}. \]  

(22b)

These equations allow the solution phase current to be determined once the double layer potential, \( \eta(\gamma,t) \), has been determined. Assuming the resistance between the reference and working electrode can be neglected, the cyclic voltammetry experiment can be modeled using equation (17). The case where this resistance is not neglected is treated in [12].

The boundary condition at \( \gamma=1 \) is:
where \( k \) is the voltage scan rate measured in V/s and \( V_0 \) is the initial potential difference between the electrode and the solution. The boundary condition at \( \gamma = 0 \) can be derived by combining equations (12) \( J_2(0) = 0 \) and (22), which gives:

\[
\frac{\partial \eta(0,t)}{\partial \gamma} = 0. \tag{24}
\]

Assuming the electrode and solution reached equilibrium before the start of the experiment, the initial condition is given by:

\[
\eta(\gamma,0) = V_0. \tag{25}
\]

For convenience, \( V_0 \) will be assumed to be 0 from now on, which does not affect the simulated current. The solution of equation (17) subject to conditions (23)-(25) is:

\[
\eta(\gamma,t) = kt + \frac{\kappa \kappa}{2} \left( \gamma^2 - 1 \right) + \frac{16\kappa}{\pi(2m+1)} \sum_{m=0}^{\infty} \left( 16(-1)^m \right) e^{-\frac{\pi^2}{4(2m+1)^2} \tau} \cos \left[ \frac{\pi}{2} (2m+1) \gamma \right]. \tag{26}
\]

This solution of the diffusion equation is obtained using separation of variables and Fourier series. Substituting equation (26) into equation (22) gives the current density:

\[
J_2(\gamma,t) = \frac{k \kappa}{L} \left[ 1 - \sum_{m=0}^{\infty} \left( \frac{8}{\pi(2m+1)^2} \right) e^{-\frac{\pi^2}{4(2m+1)^2} \tau} \sin \left( \frac{\pi}{2} (2m+1) \gamma \right) \right]. \tag{27}
\]

Using equation (14), the total current density is then given by:

\[
J_M(t) = J_2(1,t) = \frac{k \kappa}{L} \left[ 1 - \sum_{m=0}^{\infty} \left( \frac{8}{\pi(2m+1)^2} \right) e^{-\frac{\pi^2}{4(2m+1)^2} \tau} \right]. \tag{28}
\]

Another form of the solution to this equation was earlier derived in [13]. Notice that the second term in the brackets of equation (28) dies down as \( t \) increases. At large \( t, J_M \) approaches a constant value of \( k \kappa k / L \), which is equivalent to \( k C_T \). Therefore, as \( t \)
increases, the measured current approaches the conventional value given by 
\[ i = C \frac{dV}{dt}, \]
where in this case \( \frac{dV}{dt} = k \) (equation 23).

In a cyclic voltammetry experiment, the voltage scan reverses direction after a defined period of time, \( t_0 \). So far, only the case of the positive going scan from equilibrium has been treated. For the reverse scan, equation (17) still applies, but the boundary condition at \( \gamma = 1 \) is given by:

\[ \eta(1,t) = k(t_0 - t), \]  

(29)

where \( t \) is the time after voltage reversal. Equation (24) still applies as the boundary condition at \( \gamma = 0 \). To solve equation (17) subject to these conditions is complicated for arbitrary \( t_0 \), or in other words, an arbitrary positive scan time. However, if the positive scan is allowed to proceed long enough such that the second term in the brackets of equation (28) becomes negligible (i.e. the current becomes constant), the solution of the equations for the reverse scan is much simplified. In this case, the initial condition becomes:

\[ \eta(\gamma,0) = kt_0 + \frac{\pi k}{2} (\gamma^2 - 1), \]  

(30)

which is the solution to Equation 26 when \( \tau \gg \tau \). The solution of equation (17) subject to these new conditions is:

\[ \eta(\gamma,t) = k(t_0 - t) + \frac{\pi k}{2} (1 - \gamma^2) - 2 \kappa \sum_{m=0}^{n=\infty} \left( \frac{16(-1)^n}{\pi(2m+1)} \right) \frac{\pi^2 (2m+1)^\frac{1}{2}}{\gamma^\frac{1}{2}} \cos \left[ \frac{\pi}{2}(2m+1)\gamma \right]. \]  

(31)

The electrolytic solution current density is given by:

\[ j_2(\gamma,t) = \frac{k \kappa k_t}{L} \left[ -1 + 2 \sum_{m=0}^{n=\infty} \left( \frac{8(-1)^n}{\pi(2m+1)} \right) \frac{\pi^2 (2m+1)^\frac{1}{2}}{\gamma^\frac{1}{2}} \sin \left[ \frac{\pi}{2}(2m+1)\gamma \right] \right]. \]  

(32)
The measured current density is given by:

\[ j_M(t) = \frac{\kappa \tau k}{L} \left[ -1 + 2 \sum_{m=0}^{m=\infty} \frac{8}{\pi(2m + 1)^2} e^{\frac{\pi^2}{4(2m+1)^2}} \right]. \] (33)

The double layer potential, \( \eta(\gamma t) \), the solution current density, \( j_2(\gamma t) \), and total current density, \( j_M(t) \), can also be solved for the case when the voltage scan is allowed to once again reverse to the positive direction. Assuming the negative scan was allowed to proceed for a time period of \( t_1 \), the boundary condition at \( \gamma = 1 \) now becomes:

\[ \eta(1, t) = k(t_0 - t_1 + t) \] (34)

where \( t \) is the time after the second reversal. Equation (24) once again applies at the current collector at \( \gamma = 0 \). As before, if the negative scan is allowed to proceed for long enough that the second term in the brackets of equation (33) diminishes and the current is constant, the solution becomes less complicated. Under this assumption, the initial condition becomes:

\[ \eta(\gamma, 0) = k(t_0 - t_1) + \frac{\tau k}{2} (1 - \gamma^2). \] (35)

The solution for the second scan reversal is:

\[ \eta(\gamma, t) = k(t_0 - t_1 + t) + \frac{\tau k}{2} (\gamma^2 - 1) + 2 \tau k \sum_{m=0}^{m=\infty} \left( \frac{16(-1)^m}{\pi(2m + 1)^2} e^{\frac{\pi^2}{4(2m+1)^2}} \right) \cos \left[ \frac{\pi}{2} (2m + 1) \gamma \right]. \] (36)

The electrolytic solution current density is given by:

\[ j_2(\gamma, t) = \frac{\kappa \tau k}{L} \left[ -1 + 2 \sum_{m=0}^{m=\infty} \frac{8(-1)^m}{\pi(2m + 1)^2} e^{\frac{\pi^2}{4(2m+1)^2}} \right] \sin \left[ \frac{\pi}{2} (2m + 1) \gamma \right]. \] (37)

The measured current density is given by:
Equations (28), (33), and (38) can be combined to simulate the current measured during a cyclic voltammetry experiment. In this work, these equations were visually fit to the measured cyclic voltammetry results obtained in Section 3.3. The two independent parameters that are fit are the volumetric capacitance and the time constant. The volumetric capacitance determines the limiting current while the time constant determines the rise time to steady state. The fit and experimental results are shown in figure 13.

![Voltage and current density graph](image)

**Figure 13.** Top: Voltage between the working and reference electrode during the experiment. Bottom: measured and fitted current density during the experiment.

This fit provided estimates for the volumetric capacitance \( \frac{aC}{A} \) and time constant \( \tau \) of 40F/cm\(^3\) and 133.4s, respectively. These estimates will be used in the next sections to generate performance projections for ECs that utilize the EXCELLERATOR\® electrode.
4.3 Performance Projection of an EC Built from the EXCELLERATOR® Electrode

In this section, the performance of an EC built from the EXCELLERATOR® electrode will be projected. An EC with the structure of that shown in figure 9 will be modeled.

From the discussion in section 4.2, the equivalent circuit model of the EC has the form shown in figure 14.

![Equivalent circuit model of a complete EC.](image)

ECs are often characterized in one of two ways following charging to their maximum rated voltage. The first is constant power discharging, which involves discharging the device at constant power until the voltage reaches a certain pre-defined cutoff voltage. The energy density from this discharge is useful for comparing ECs. The second method is constant current discharging, which involves discharging the EC at constant current until the voltage reaches a pre-defined cutoff voltage. The power and energy densities supplied at all stages of this discharge process are used to assess the EC’s capabilities. Because constant current discharging is much more amenable to mathematical modeling, the constant current discharge process will be modeled in this thesis.
4.3.1 The Terminal Voltage

As pointed out before, the behavior of an EC can be modeled by first calculating the response of a single electrode. Differentiating equation (22) with respect to \( t \) gives:

\[
\frac{L}{\kappa} \frac{\partial j_2}{\partial t} = \frac{\partial^2 \eta}{\partial \gamma^2}.
\]  

(39)

Differentiating equation (22b) with respect to \( \gamma \) gives:

\[
\frac{\partial^2 j_2}{\partial \gamma^2} = \frac{aCL}{A} \frac{\partial^2 \eta}{\partial \gamma^2}.
\]  

(40)

Combining equations (39) and (40) yields:

\[
\frac{\partial^2 j_2}{\partial \gamma^2} = \tau \frac{\partial j_2}{\partial t}.
\]  

(41)

For discharging current density \( J \), the boundary conditions are given by:

\[ j_2(0, t) = 0 \] (at the contact) and, \( j_2(1, t) = -J \) (at the electrode/separator interface). \( \)  

(42) \( \)  

(43)

The initial condition is:

\[ j_2(\gamma, 0) = 0. \]  

(44)

The solution to equation (41), subject to conditions (42)-(44), is:

\[
j_2(\gamma, t) = -J \gamma + \sum_{m=1}^{\infty} \frac{2J(-1)^m}{m \pi} e^{-i(m\pi)^{1/2}} \sin(m\pi \gamma).
\]  

(45)

Following from equation (22b), the double layer potential distribution throughout the electrode is described by:

\[
\eta(\gamma, t) = \frac{A}{aCL} \int_0^\gamma \frac{\partial j_2}{\partial \gamma} \, d\gamma + \eta_0
\]  

(46)
where \( \eta_0 \) is the constant of integration and is equal to the initial double layer potential (prior to discharge). This gives:

\[
\eta(\gamma, t) = \frac{L}{\kappa} \left[ \frac{-Jt}{\tau} + 2J \sum_{m=1}^{\infty} \frac{(-1)^m \cos(m\pi\gamma)}{(m\pi)^2} \left( e^{-(m\pi)^2 \tau / \tau} - 1 \right) \right] + \eta_0. \tag{47}
\]

It is important to notice from equation (47) that after discharging for any length of time, the double layer potential varies through the electrode. Therefore, when discharging is stopped, a relaxation process occurs which allows the entire electrode to come to the same potential. This relaxation process can be modeled with equation (41), using boundary conditions:

\[
j_2(0, t) = 0, \tag{48}
\]

\[
j_2(1, t) = 0. \tag{49}
\]

The initial condition is given by the current density distribution in the electrode at the termination of the discharge (i.e. when total current is stopped). For a discharge that proceeded for time \( t_0 \), the initial condition for relaxation is given by:

\[
j_2(\gamma, 0) = -J\gamma + \sum_{m=1}^{\infty} \frac{-2J(-1)^m}{m\pi} e^{-(m\pi)^2 \tau / \tau} \sin(m\pi\gamma), \tag{50}
\]

The solution to equation (41), subject to conditions (48)-(50) is given by:

\[
j_2(\gamma, t) = \sum_{m=1}^{\infty} \frac{-2J(-1)^m}{m\pi} \left( e^{-(m\pi)^2 \tau / \tau} - 1 \right) e^{-(m\pi)^2 \tau / \tau} \sin(m\pi\gamma), \tag{51}
\]

where \( t \) is the time after relaxation began. Applying equation (46) to equation (51) gives the double layer potential distribution in the electrode during relaxation:

\[
\eta(\gamma, t) = \frac{2JL}{\kappa} \sum_{m=1}^{\infty} \frac{(-1)^m \cos(m\pi\gamma)}{(m\pi)^2} \left( e^{-(m\pi)^2 \tau / \tau} - 1 \right) \left( e^{-(m\pi)^2 \tau / \tau} - 1 \right) + \eta_0(\gamma), \tag{52}
\]

37
where \( \eta_i(y) \) is the double layer potential at \( y \) before relaxation began.

So far, the current and double layer potential responses of a single electrode have been solved. It is now possible to make predictions for the voltage difference between the two leads of an entire device that is composed of two identical electrodes, separated by a separator. In this thesis, this voltage difference is called the terminal voltage. A number of separators suitable for use in ECs have been tested in the author’s laboratory. From the results obtained, one of the best performing separators is the Gen3 EXCELLERATOR® separator also supplied by W.L. Gore & Associates, Inc. These separators have a thickness of 11\( \mu \)m and a porosity of 50% and the separator model used in this work will be assumed to have these characteristics. The per unit area resistance, \( R_A \), is calculated according to equations (3) and (4).

Assuming there are no additional sources of resistance, such as contact resistance, in the device, the terminal voltage, \( V_T \), of the EC can be modeled as:

\[
V_T = 2\eta_i(1, t) - JR_A .
\]  
(53)

Therefore, by applying equation (53) to equations (47) and (52), the evolution of the terminal voltage as a function of current density and time can be modeled. The terminal voltage during discharge is given by:

\[
V_T(t) = 2\eta_i(1, t) - JR_A = \frac{2L}{K} \left[ -\frac{Jt}{\tau} + 2J \sum_{m=-\infty}^{\infty} \frac{1}{(m\pi)^2} \left( e^{-(m\pi)^2 \tau} - 1 \right) \right] + 2\eta_0 - J \frac{L_s}{K_s} .
\]  
(54)

During relaxation, the terminal voltage is given by:
The evolution of the terminal voltage during discharge from 2.3V to 0V at a constant current density of 1mA/cm² is shown in figure 15. The terminal voltage falls at a more rapid rate at first, and then continues at a constant slope until it reaches 0V. When the terminal voltage reaches 0V, the constant current discharge is terminated, and the relaxation process proceeds as discussed. The relaxation response is shown in figure 16.

\[
V_T(t) = 2\eta(1,t) - jR_A = \frac{4JL}{\kappa} \sum_{m=1}^{\infty} \frac{(-1)^m \cos(m\pi \gamma)}{(m\pi)^2} \left( e^{-(m\pi)^2 t_0/\tau} - 1 \right) \left( e^{-(m\pi)^2 t/\tau} - 1 \right) + 2\eta_i(\gamma) - J \frac{L_S}{\kappa_S} \tag{55}
\]

Figure 15. Evolution of terminal voltage during discharge from 2.3V to 0V at 1mA/cm².
Figure 16. Evolution of terminal voltage during discharge from 2.3V to 0V at 1mA/cm$^2$, and the subsequent relaxation.

This relaxation process can be explained more clearly by investigating figure 17, which is a plot of the double layer potential at different electrode positions during discharge of the EC. This figure shows that the double layer potential at $\gamma=1$ is the minimum in the electrode at all times, meaning that there is still stored energy in the electrode that hasn’t been extracted at the end of discharge. This results in a type of double layer charge redistribution. This additional energy is not normally extracted, increases with discharge rate, and is a cause of inefficiency in ECs. This recovery process is further illustrated in figure 18.
Figure 17. Evolution of Double layer potential at different positions as a function of time during discharge of terminal voltage from 2.3V to 0V.

Figure 18. Evolution of Double layer potential at different positions as a function of time during discharge of terminal voltage from 2.3V to 0V, and the subsequent relaxation.
It is useful to try to understand the shape of the terminal voltage discharge curve in figure 15 to gain additional insight into the operation of an EC. As pointed out before, the voltage declines at a more rapid rate at the beginning, and then the drop slows down to a constant rate as discharge proceeds.

The energy in an EC resides in the stored charge in the distributed capacitance. During discharge, this charge is removed from different depths of the electrode at different rates. These rates are given by the transfer current density, $\frac{\partial j_y}{\partial \gamma}$, which from equation (45) is given by:

$$\frac{\partial j_y(\gamma, t)}{\partial \gamma} = -J - 2J \sum_{m=1}^{\infty} (-1)^m e^{-(m\pi)^2 t} \cos(m\pi \gamma)$$  \hspace{1cm} (56)

The transfer current density in the electrode at different times is shown in figure 19. The observed behavior can be explained by examining the equivalent circuit of the electrode shown in figure 12. At the instant discharge begins, the transfer current density is much higher at $\gamma=1$ than anywhere else due to the low conductivity of the solution phase. The double layer potential at different positions of the electrode is related to the transfer current density by equation (22b). In combination with equation (53), this means that the terminal voltage drops rapidly while this occurs. A large double layer potential gradient results near $\gamma=1$, and it causes an increase in the liquid phase and transfer current densities at $\gamma<1$. At the same time, the transfer current density at $\gamma=1$ decreases. This process proceeds through the electrode towards $\gamma=0$ and so the discharge propagates as a front. The transfer current density eventually reaches steady state and has the same value
throughout the electrode. This type of behaviour is anticipated in a transmission line of
the kind shown in figure 12.

Since

\[-J = \int_0^\gamma \frac{\partial j_2(x)}{\partial \gamma} d\gamma,\]

the transfer current density, at its steady state, is given by:

\[\frac{\partial j_2(x)}{\partial \gamma} = -J.\] (58)

After the transfer current density reaches steady state, the rate of decline of double layer
potential throughout the electrode also reaches a constant as given by equation (22b):

\[\frac{\partial \eta}{\partial t} = \frac{-JA}{aCL}.\] (59)
This is exactly what is expected of the heat/diffusion equation in steady state. The double layer potential distribution throughout the electrode is shown in figure 20. As shown in this figure, the voltage drop at first occurs close to $\gamma=1$. As discharge proceeds, the rate of double layer potential decline is constant throughout the electrode. This explains the apparent constant terminal voltage decline shown in figure 15.

Figure 20. Evolution of double layer potential throughout the electrode during discharge.

### 4.3.2 Energy, Power and Ragone Plots

Applying equation (6) to equation (54) gives the energy density as a function of discharge time under constant current conditions:

$$E(t) = \frac{2L}{Mk} \left[ -\frac{J^2 t^2}{2\tau} - \sum_{n=1}^\infty \frac{1}{(m\pi)^2} \left\{ \frac{\tau}{(m\pi)^2} \left( e^{-(m\pi)^2 i/\tau} - 1 \right) + t \right\} \right] - 2JtI_0 - J^2 \frac{L_s t}{\kappa_S}, \quad (60)$$
where \( M \) is the mass of the device. The mass that is accounted for in the calculations in this thesis are the masses of the current collectors, active layers, separator, and the electrolytic solution that exists in the pores of the active layers and separator. No additional mass has been included for the lead connections and packaging because data on those values can vary depending on the technology. Therefore, the mass-normalized values shown in this thesis are optimistic values that need to be adjusted for when considering a real device. The power density is the time derivative of equation (60):

\[
P(t) = \frac{2L}{M\kappa} \left[ -\frac{J^2t}{\tau} + 2J^2 \sum_{m=1}^{\infty} \frac{1}{(m\pi)^2} \left( e^{-\frac{(m\pi)^2}{\tau}} - 1 \right) \right] - 2J\eta_0 - J^2 \frac{L_S}{\kappa_S}
\]  

(61)

Figure 21 plots the EC’s Ragone plot during its discharge at 1mA/cm\(^2\). As discussed before, the Ragone plot shows the evolution of the supplied power as the total amount of energy drawn from the device is increased.

![Figure 21. Ragone plot of modeled EC.](image)
4.3.3 Effect of Change of Current Density

So far, all calculations have been confined to a current density of 1mA/cm². Figure 22 shows the terminal voltage, \( V_T \), plots for different discharge current densities. The different rates of \( V_T \) decline can be explained by equation (59).

![Figure 22. Change of discharge voltage characteristics for different current densities.](image)

To gain more insight into the observed behavior shown in figure 22, equations (45) and (47) will be examined more closely. It can be seen that the solution phase current density and the rate of double layer potential decline are both proportional to the discharge current density. Therefore, at the same instant in time, the shapes of the solution phase current density and rate of double layer potential decline curves are the same for the different discharge cases here, but the magnitudes are different. Due to the separator voltage drop, the condition for the terminal voltage to reach 0V is (from equation (53)): 

\[ \text{condition for } V_T = 0 \]
\[ \eta(1,t) = \frac{JR_A}{2} \]  

Therefore, when the discharge current density is halved, the rate of fall of the double layer potential at \( \gamma = 1 \) and the final double layer potential at \( \gamma = 1 \) are both halved.

Combine this with the infinite summation term in equation (47) that slows down the rate of double layer potential drop as \( t \) is increased, the discharge time becomes more than doubled. The infinite summation term slows down the rate of double layer potential drop because of the spreading of the transfer current density in the electrode, shown in figure 19.

Figure 22 also shows that the potential recovery is greater at higher current densities. This is because there is a larger double layer potential gradient in the electrode, and a larger separator voltage drop (see equation 62) at a higher current density. Thus the stored energy that was not extracted during discharge is greater when the discharge current density is increased.

Figure 23 shows the Ragone plot for different discharge current densities. As can be seen from this figure, higher current density results in a higher maximum power density. However, this comes at a cost of reduced total energy density that can be extracted this way.
The differences between the Ragone plots for the three discharge current densities can be visualized more clearly by examining figure 24, which plots the power densities for the three discharge current densities as a function of time. At 2mA/cm\(^2\), the power density is initially double that for discharge at 1mA/cm\(^2\). However, because the terminal voltage decreases at more than twice the rate, the power density at 1mA/cm\(^2\) discharge becomes higher than at 2mA/cm\(^2\) at later times.
Figure 24. Comparison of power density as a function of discharge time for different current densities.

The energy density is given by the area under the curves shown in figure 24. As discussed before, there is a smaller separator resistive loss at lower current density. Also, because of the longer discharge time, the spreading of the transfer current density leads to a more complete discharge of the electrode at lower current density. Therefore, the energy density that can be extracted is higher, as can be seen in figure 23.

4.4 Performance Projection of ECs with Different Thicknesses

Up to this point, all the calculations have been performed on the EXCELLERATOR® electrode received from W.L. Gore & Associates, Inc. The thickness of the active layer in the electrode is 100μm. W.L. Gore & Associates, Inc., also produces EXCELLERATOR® electrodes with active layer thicknesses of 150μm and 80μm.
Using the model and parameters that have been derived in this work, the performance of the electrode with these, and other, thicknesses can be predicted. The properties, including the thicknesses, of the separator and current collectors are assumed to stay the same for the different electrode thicknesses. In this way, the tradeoffs involved in the scaling of the thickness of the active layer can be understood.

Figure 25 shows the terminal voltage evolution during discharge from 2.3V at a constant current density of 1mA/cm$^2$ for electrode thicknesses of 100µm, 75µm, and 50µm. As shown in the figure, the thicker the electrode, the longer the discharge time. This agrees with intuition because the amount of stored charge in the electrode is proportional to the thickness. Therefore, the thicker the electrode, the longer it takes to discharge given the same current density.

Figure 25. Plot of terminal voltage during discharge from 2.3V to 0V.
Since the three electrode thicknesses are discharged at the same current density, the power supplied curve would have the same shapes as those shown in figure 25. Figure 26 plots the discharge power as a function of time for the three thicknesses.

![Diagram of discharge power over time for different electrode thicknesses.](image)

Figure 26. Plot of discharge power during discharge from 2.3V to 0V at 1mA/cm².

As discussed before, the energy and power densities are often the more important figures-of-merit used to compare ECs. Figure 27 shows the power densities of the three electrode thicknesses after scaling by the mass of the devices.
As shown in figure 27, the thinnest electrode with $L=50 \mu m$ gives the highest power density at the beginning of discharge. However, as discharge proceeds, its power density decreases at a more rapid rate than the other two electrodes, and so the other electrodes possess higher power densities at later times. Also, since the energy density is the total area underneath the power density curve, it can be approximated visually that the thicker the electrode, the higher the maximum energy density. This is consistent with the behavior that is shown in the Ragone plots of the three thicknesses shown in figure 28. Therefore, from the discussion so far, it is obvious that a tradeoff exists between the power and energy densities of ECs.
A useful intuitive way to explain the data obtained is as follows. The time constant for discharge is given by: $\tau = \frac{aCL}{\kappa A}$ (equation 20). This time constant can be interpreted as the time it takes the discharging front to propagate through the electrode to $\gamma=0$. Therefore, $\tau$ is roughly the time needed to utilize the entire thickness of the electrode. At any time, $t$ (for $t<\tau$), during discharge, the effective thickness of the electrode that is utilized, $L_{eff}$, is then given by:

$$t = \frac{aCL_{eff}^2}{\kappa A}$$  \hspace{1cm} (63)

$$L_{eff} = \sqrt[3]{\frac{\kappa At}{aC}}$$  \hspace{1cm} (64)
Now comparisons can be made between the energy and power densities of the discharge of two electrodes, of different thicknesses, \( L_1 \) and \( L_2 \), at the same current density. Let's label the electrodes as \( e_1 \) and \( e_2 \), and assume \( L_2 > L_1 \). For \( L_{\text{eff}} < L_1 \), the utilization of the electrode is small, and the difference in electrode thicknesses does not matter to the energy supplied to the load. Therefore, the extra mass of the active layer of \( e_2 \) makes the energy and power densities of \( e_2 \) lower than \( e_1 \).

For \( L_{\text{eff}} >> L_1 \), the electrodes are completely utilized, and so all the energy is extracted from both electrodes. The ratio of the mass of the active material to the mass of the total device is given by:

\[
r = \frac{\text{(mass of active material)}}{\text{(mass of active material)} + \text{(mass of non-active material)}}
\]

The non-active material includes the separator, electrolytic solution in separator, and current collectors. \( r \) is smaller for \( e_1 \) than it is for \( e_2 \). Since the total energy stored in the device is proportional to the mass of the active material, the extracted energy density of \( e_1 \) is smaller than \( e_2 \).

For \( L_{\text{eff}} \sim L_1 \), the \( e_1 \) electrode is completely utilized while \( e_2 \) is not. Therefore, at times later than this, the energy density of \( e_2 \) approaches that of \( e_1 \), and eventually \( e_2 \) has a higher energy density than \( e_1 \). This explains the behavior observed in the Ragone plots in figure 28.
4.5 Optimizing the Electrode Thickness for Different Discharge Times

One way to define the optimal electrode thickness for use in a particular application is the thickness that can supply the maximum energy density within the time span of interest. Let’s call this time span the allowed time. For example, a tv cellular phone may need to acquire energy from its energy source over a span of 30 minutes, while a camera flash’s energy needs last for only a fraction of a second. The allowed time is different for different applications and can span orders of magnitude.

The maximum energy density that can be obtained from a particular electrode thickness in a certain time span is supplied when the EC is discharged at the current density that will make its $V_T$ drop from the initial voltage to 0V at the end of this time period. Higher current densities result in larger losses, while lower current densities leaves more un-extracted energy in the device. This maximum energy density is different for different electrode thicknesses and is different for different allowed times. Therefore, if the thickness of the electrode can be accurately controlled, a designer can choose the optimal EC for a specific application.

In figure 29, the maximum energy densities supplied by ECs of different thicknesses are plotted as a function of the allowed time. Each point on the curve indicates the maximum energy density that can be supplied by the device of a particular thickness during that allowed time. Figure 30 shows the same plot but with the focus on the times between 10 and 600s. As shown in the figure, in an allowed time of 10ms, the optimal EC would be
composed of, amongst all the thicknesses considered, 40μm thick electrodes. This device can supply approximately 2.15mWh per kilogram of device mass in that time frame. The 40μm electrode is the best choice for all discharge times less than about 62s. For discharge times between 62s and 88s, the 60μm electrode becomes the best one. At even longer times, 80μm is the optimal choice, and so on.

Figure 29. Plot of maximum energy density for different discharge times.
The behavior of the curves for each thickness can be explained as follows. At small allowed times, only a small portion of the electrode is discharged. As the allowed time increases, the length of the electrode that is discharged increases accordingly. From equation (64), $L_{\text{eff}}$ is proportional to $\sqrt{t}$. Since the extracted energy is approximately proportional to $L_{\text{eff}}$, the slope of the curves in figure 29 for small times is $\frac{1}{2}$. When the allowed time is increased further, the entire electrode becomes utilized and so the energy density begins to plateau. At even larger allowed times, the energy density saturates because all the stored energy has been acquired.

In figure 29, it is shown that the maximum energy density for the thinner electrode is higher than the thicker electrodes for short times. Like in section 4.4, this can be explained by the fact that only a small portion of the electrodes are utilized in both cases.
However, because of the un-used electrode mass in the thicker electrode, the maximum energy density for the thicker electrode is lower. On the other hand, at long times, the maximum energy density of the thicker electrode is higher than the thinner electrode. This is because, as was also shown in section 4.4, at these long times, the entire electrode is completely discharged, and the energy that is initially stored in the electrode is proportional to the active material mass. However, because the non-active material mass is a larger proportion of the total device mass, the thinner electrode has a lower maximum energy density. At the intermediate allowed times, the thinner electrodes are seen to reach a plateau earlier in figure 29. This is because the thinner electrode can be completely utilized in a shorter time.

From the discussion above, the maximum energy density, and as a result the maximum average power density, is higher for the thinner electrode at short times. At long times, the maximum energy density is lower for the thinner electrode because of the larger ratio of non-active mass in the device. Therefore, an approach to obtain an ultimate EC of a certain material is to decrease the mass of the separator, the electrolytic solution in the separator and the current collector. If these masses can be scaled proportional to the electrode mass, ECs made of thin electrodes will perform as well as those made of thicker electrodes even at long times. As an illustration, the calculations used to produce figure 29 above was repeated, but the masses of the separator, the electrolyte solution in the separator, and current collectors were scaled proportionally to the electrode mass. The results are plotted in figure 31. It illustrates the behavior that is expected.
Figure 31. Plot of maximum energy density as a function of allowed time.
5.0 Conclusions

The objective of this thesis is to develop a framework for the characterization and performance projection of new EC electrode materials. This framework involves first the electrochemical characterization of the electrode using cyclic voltammetry. Mathematical simulation is used to obtain a simulated response that matches the experimental results. The fitted response gives estimates of the parameters in the model for the tested electrode. Using these parameters, the terminal voltage response, energy density and power density of a complete EC can be predicted for wide a range operating conditions. Further, the effect of change in electrode geometry on the EC performance can also be projected. Examples of these changes that are anticipated to have a large effect are the thicknesses of the active layer, the current collector, and the separator, along with the porosity of the active layer and the conductivity of the electrolytic solution.

In this thesis, the procedure described above was applied to evaluate the performance of a commercial electrode, called EXCELLERATOR®, from W.L. Gore & Associates, Inc., to illustrate the utility of this framework. This electrode was tested using cyclic voltammetry in a 0.5M TBAP in PC solution. A Schlenk-type apparatus was used to ensure minimal exposure of the components to atmospheric contaminants. Moisture, for example, has been shown to adversely affect the voltage range over which Faradaic reactions are negligible. The electrolyte was also tested using a platinum wire electrode. The measured current stayed below approximately 0.5mA/cm² over a 2.2V range. This is
A good indication that the electrolytic solution employed in the tests is a suitable one for use in an EC.

A macroscopic homogeneous volume averaged model was used to simulate the cyclic voltammetry response of an electrode. The modeled active layer is 100µm thick, while its length and width are orders of magnitude larger. The model that was used assumed no variations in electrolyte concentrations within the electrode pores because the difference in electrolyte concentration between the fully charged and discharged states is calculated to be small. The capacitance and resistance of the solid phase are assumed to be independent of double layer potential. Finally, because the solid phase conductivity is many times higher than that of the electrolyte, the solid phase resistance was neglected. Faradaic reactions were assumed to be negligible. This can be assured by limiting the voltage range which the electrode is subjected to.

An analytical solution for the current in a cyclic voltammetry experiment is derived from the model. By matching the simulated curve to the experimental data, the volumetric capacitance and time constant of the electrode were estimated to be 40F/cm³ and 133.4s, respectively.

Using these values, the same model was used to project the constant current discharge performance of a complete EC that is composed of the EXCELLERATOR® electrode. The modeled device consists of a separator that is sandwiched between two electrodes. The separator was assumed to be one that is 11µm thick and 50% porous. These
properties are taken from data on the EXCELLERATOR® separator, also available from W.L. Gore & Associates, Inc.

The terminal voltage of the complete EC was solved analytically. The simulated terminal voltage curve was shown to decline rapidly initially. This can be explained by the large transfer current that exists at the separator-edge of the electrode during the early stages of discharge, which induces a large potential drop across the device. As discharge proceeds, the terminal voltage decline slows to a constant rate. This is a result of the uniform discharging of the stored charge throughout the depth of the electrode. An analytical solution for the Ragone plot, which is a plot of power density of the EC as a function of energy density drawn from it, was also derived.

The effect of the change of current density on the device’s performance was also investigated. For electrodes of the same thickness, the halving of the discharge current density was shown to lead to more than double the discharge time. This can be explained by the fact that the rate of decline of the double layer potential at the solution edge ($\gamma=1$) and the final double layer potential at the solution edge ($\gamma=1$) are both halved. This leads immediately to more than doubling of the discharge time. Further, the spreading of the transfer current density through the depth of the electrode leads to a drop in the rate of double layer potential decline as well.

At higher currents, the power density is initially higher. However, because of the rapid fall of the terminal voltage at high current density, the power density of the discharge at
lower current density becomes superior at later times. The energy density for the discharge at lower current density is higher because less of the energy is lost resistively in the separator. Also, more complete discharge of the electrode occurs because of the longer discharge time.

The tradeoffs involved in discharging of different electrode thicknesses under the same current density were investigated. An intuitive way to explain the observed results was shown. For short times, the utilization of the electrode is small, and the difference in electrode thicknesses does not make any difference to the energy extracted. For discharge times up to the complete utilization of the thinner electrode, the thinner electrode continues to have higher energy and power densities. For even longer discharge times, the thicker electrode performs better because it has more active material mass as a fraction of the total device mass.

A very important aspect of this framework is that it allows for the investigation of the effect of geometry changes of the electrode on the device performance. This leads to a modeling-based electrode design approach that can be used to evaluate and optimize an electrode for a specific application. As an example of this possibility, the maximum energy density that can be supplied from ECs of different electrode thicknesses were predicted as a function of the allowed time. Thicknesses in the range from 40\(\mu\)m to 100\(\mu\)m were considered. It is shown that for times less than 62s, the 40\(\mu\)m device can supply the largest energy density. From 62s to 88s, the highest energy density is supplied by the 60\(\mu\)m electrodes. As the time span allowed increases, different devices become
the optimal choice. This type of predictions can be very useful to a designer who is selecting an EC for a specific application, which can have a large range of time scales over which energy is demanded.

The shapes of the maximum energy density curves were also explained from the effective length of electrode utilization perspective. It was shown that the mass of the non-active material is a large factor in the lower maximum energy densities of the thinner electrodes at long times. Therefore, one of the ways to obtain the optimal response from a thin electrode is to proportionally reduce the mass of the separator, the electrolytic solution within its pores, and also the current collectors.

Therefore, this is a useful framework that can be utilized to make predictions on the capabilities of a material as an EC electrode. Also, it can be used to optimize the geometry of an electrode for a specific application. Ideally, this approach would form part of a process that makes and tests electrodes of different geometries to verify the validity of the predictions made. This would ensure that the assumptions made in the modeling were correct.
6.0 Bibliography


Appendix

This appendix shows the MATLAB® code that was used to perform the simulations for this thesis. The first piece of code, shown in part (a), is that used for modeling the cyclic voltammetry experiment. Part (b) presents the code for modeling the constant current discharge of an EC. Because of the large number of these discharge simulations that were performed, many other pieces of code were also used. However, those codes are based on that in part (b) with minor modifications.

a) Code for cyclic voltammetry data simulation

```matlab
% defining physical parameters
porosity=0.0459; % Assumed, need to contact Moire from Gore
cond_free=3.05e-3; % free solution conductivity, 0.65M TEAB (6.1e-3 for 1M TEAP) in PC from Ue et. al. Journal of Electrochemical Society, Vol. 141, No. 11, 1994
cond_electrode=cond_free*(porosity)^1.5; % solution conductivity in electrode according to Bruggeman's relation
C_vol=40; % volumetric capacitance in F/cm^3
L=100e-4; % thickness of electrode in cm
tau=C_vol*L^2/cond_electrode
porosity_separator=0.5; % Separator porosity
cond_separator=cond_free*(porosity_separator)^1.5; % solution conductivity in separator according to Bruggeman's relation
L_separator=11e-4; % separator thickness, in cm

% CV first scan simulation
k=0.2e-3; % voltage scan rate V/s
Tmax=1000/tau;
T=[0:0.1:Tmax]; % T=t/tau
tmp=zeros(1,length(T));
gamma=1;
for m=0:1000
   Am=tau*k*(16*(-1)^m/((2*m+1))^3);
   tmp=tmp-(Am*pi*(2*m+1)/2*exp(-pi^2/4*(2*m+1)^2*T)*sin(pi/2*gamma*(2*m+1))));
end
j=cond_electrode/L*(tau*k+tmp);

% CV first reversal
T2=[0:0.1:2*Tmax]; % T=t/tau
tmp2=zeros(1,length(T2));
gamma=1;
for m=0:1000
   Am=-tau*k*(32*(-1)^m/((2*m+1))^3);
   tmp2=tmp2-(Am*pi*(2*m+1)/2*exp(-pi^2/4*(2*m+1)^2*T2)*sin(pi/2*gamma*(2*m+1))));
```

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end
j2=cond_electrode/L*(-tau*k+tmp2);
% figure(2)
% plot(T2,j2)

% CV second reversal
tmp3=-1*tmp2;
j3=cond_electrode/L*(tau*k+tmp3);
% figure(3)
% plot(T2,j3)

% amalgamation
% plot([T*tau (Tmax+T2)*tau (3*Tmax+T2)*tau],[j2 j3])

% loading and overlaying experimental data
scan_rate=0.2e-3; % scan rate in Volts per second
sample_area=1.9*0.9; % in cm^2
load 'exp1.txt'
exp_potential=exp1(:,1);
max_potential=max(exp_potential);
index_max_potential=find(exp_potential==max_potential);
exp_interval=(exp_potential(2)-exp_potential(1))/scan_rate;
exp_current=[exp1(:,2)/sample_area; exp1(1:index_max_potential,3)/sample_area];
for n=1:length(exp_current)
    exp_time(n)=(n-1)*exp_interval;
end
figure(1)
subplot(2,1,1)
% voltage excursions
plot(exp_time, [exp_potential; exp_potential(1:index_max_potential)])
xlabel('time(s)')
ylabel('voltage (V)')
axis([0 5000 -0.2 0.2])
subplot(2,1,2)
plot(exp_time, 1000*exp_current, 'k', [T*tau (Tmax+T2)*tau (3*Tmax+T2)*tau], 1000*[j j2 j3], 'r')
xlabel('time (s)')
ylabel('current density (mA/cm^2)')
axis([0 5000 -2e-1 2e-1])
legend('experimental','simulated')

b) Code to simulation terminal voltage during discharge from 2.3V to 0V

clear all;
format short e
% 11 add different lengths 11: saved in data4
% defining physical parameters
porosity=0.0459; % Assumed, need to contact Moire from Gore
cond_free=3.05e-3; % free solution conductivity, 0.65M TEAB (6.1e-3 for 1M TEAP) in PC from Ue et. al. Journal of Electrochemical Society, Vol. 141, No. 11, 1994
cond_electrode=cond_free*(porosity)^1.5; % solution conductivity in electrode according to Bruggeman's relation
C_vol=40; % volumetric capacitance in F/cm^3
%L=100e-4; % thickness of electrode in cm

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porosity_separator=0.5; % Separator porosity
cond_separator=cond_free*(porosity_separator)^1.5; % solution conductivity in separator according to Bruggeman's relation
L_separator=11e-4; % separator thickness, in cm
Vmax=2.3;
V0=Vmax/2; % initial voltage before discharge (1/2 of eq voltage)
Jvalues=-1*[1e-3];
Lvalues=1e-4*[100];
tvalues=5000*Lvalues/100e-4;
for k=1:length(Lvalues)
    i=1;
    % Voltage while DISCHARGING
    %J=8.48e-4; % charging current density (A/cm^2)
    L=Lvalues(k);
    tau=C_vol*L^2/cond_electrode;
    J=Jvalues(i);
    Jfactor=J/(-1e-4);
    %10 second charging
    t_sim_int=tvalues(k);
    t_sim_final=t_sim_int/Jfactor;
    Tmax=t_sim_final/tau; % length of charging
    t_int=10^floor(log10(Tmax))-4;
    T=[0:t_int:Tmax];
    gamma=[1];
    tmp=zeros(length(gamma),length(T));
    for m=1:1000
        tmp=tmp+((-1)^m*cos(m*pi*gamma)/((m*pi)^2)*(exp(-(m*pi)^2*T)-1));
    end
    eta=L/cond_electrode*(ones(length(gamma),1)*(J.*T)-(2*J.*tmp))+V0;
V=2*(eta)+J*L_separator/cond_separator;
V_zero_index=find(V(1,:)<0);
V_plot1 =V(:,1 :V_zero_index(1)-1);
eta_plot1 =eta(:,1 :V_zero_index(1)-1);
t_plot1 =T(1,1 :V_zero_index(1)-1)*tau;
figure(1)
plot(t_plot1,V_plot1)
xlabel('time (s)')
ylabel('terminal voltage (V_T)')

% Voltage while relaxing
T2max=t_sim_final/5/tau; % length of relaxation
T2=[0:t_int:T2max];
tmp=zeros(length(gamma),length(T2));
for m=1:1000
    tmp=tmp+((-1)^m/((m*pi)^2)*(exp(-(m*pi)^2*T2)-1)*cos(m*pi*gamma)*(exp(-(m*pi)^2*T2)-1));
end
eta2=-2*J*L/cond_electrode*tmp+eta(:,V_zero_index(1)-1)*ones(1,length(T2));
V2=2*eta2;
V2_plot1=V2;
eta2_plot1=eta2;
t2_plot1=(T(1,V_zero_index(1))+T2)*tau;
figure(7)
plot(t2_plot1,eta2_plot1)
figure(2)
plot([t_plot1 t2_plot1],[V_plot1 V2_plot1])
xlabel('time (s)')
ylabel('terminal voltage (V)')
end