High Energy Density Metal Oxide and Conducting Polymer Supercapacitors

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Abstract
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Supercapacitors are electrochemical energy storage devices characterized by rapid charge-discharge speeds, high power densities, and long cycle lifetimes compared to batteries. Supercapacitors have many promising applications as energy storage devices in electric vehicles, renewable energy systems, grid energy management, as well as stationary and portable electronics. A current limitation of supercapacitors is their low energy density compared to batteries, which hinders their application as stand-alone energy storage systems. Supercapacitor energy density can be improved using pseudocapacitive materials, including conducting polymers and metal oxides, that store charge by faradaic and double layer capacitance. This dissertation explores the use of nanomaterial designs and novel fabrication methods to increase energy density of pseudocapacitor electrodes and enable more widespread application of supercapacitor energy storage.

The present work uses both experimental and modeling approaches to develop and test high energy density conducting polymer and metal oxide pseudocapacitors. Pseudocapacitor electrode performance testing was conducted using two- and three-electrode measurement techniques, including cyclic voltammetry, chronopotentiometry, and electrochemical impedance spectroscopy. Pseudocapacitor electrode material properties were characterized using electron microscopy and x-ray measurement techniques. Vertically-aligned carbon nanotubes (VACNTs) were used as high surface area, porous electrodes that are coated with pseudocapacitive materials for high energy density. Modeling work includes empirical modeling of EIS and chronoamperometry results, and the development of a simplified porous electrode model for pseudocapacitor design optimization.

For conducting polymer electrodes, a hybrid polypyrrole (PPY)-VACNT electrode design was developed in which VACNTs are uniformly coated with PPY by electrodeposition. The hybrid supercapacitor electrodes achieve a 5x increase in pseudocapacitance compared to uncoated CNT and pure PPY electrodes. Empirical modeling results confirm an increase in faradaic and double layer capacitance for the hybrid supercapacitor compared to uncoated VACNTs. For metal oxide pseudocapacitors, atomic layer deposition (ALD) was demonstrated as a novel fabrication method to achieve highly conformal and uniform pseudocapacitive coating for ruthenium oxide (RuO$_x$) electrodes. Post-ALD electrochemical oxidation increases hydrated oxide content of the ALD films, resulting in a 170x increase in pseudocapacitance for the ALD RuO$_x$-VACNT electrodes compared to uncoated CNTs. The ALD RuO$_x$ electrodes achieve an
ultra-high capacitance of 644 F/g, with performance maintained over 10,000 charge-discharge cycles and at scan rates of up to 20 V/s. Lastly, a simplified porous electrode model was developed to predict charge storage in ohmically-limited pseudocapacitor electrodes. Preliminary results show that the model is an effective tool for identifying performance-limiting factors in supercapacitor electrodes and optimizing pseudocapacitor electrode design parameters. Experimental and modeling results presented in this work highlight the importance of a comprehensive design approach for supercapacitor electrodes that considers interrelationships between material properties, design parameters, and fabrication methods.
To my parents
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Chapter 1: Introduction

“The history of man is dominated by, and reflects, the amount of available energy.” – Frederick Soddy

Energy is an integral part of our society. We depend on energy for transportation, manufacturing, food production, and communication, as well as lighting, heating and cooling, to name a few examples. Reliable and convenient access to energy is the foundation of our modern society. Of the many types of energy sources, electricity is one of the most common and convenient forms. In the United States, approximately 40% of total primary energy resources are converted to electricity for use in industrial, commercial, and residential sectors. The advantages of electricity include: ability to be generated from a wide variety of energy resources, ease of distribution, and high degree of versatility in conversion and end-use. The main challenge, however, is that electricity cannot be stored in its existing form. In the power grid, electricity generation must match demand at all times, or additional storage is required. For portable applications, such as electric vehicles and consumer electronics, electricity is typically stored electrochemically in batteries and fuel cells. Vehicle driving range and portable device lifetime are therefore limited by the capabilities of available energy storage technologies. As these examples illustrate, improving the performance of energy storage technologies is essential for all electric energy systems and applications.

The focus of this work is on supercapacitors for electrochemical energy storage. This chapter introduces the concept of supercapacitors, and their current and future applications. The current challenges in supercapacitor research are discussed, as well as the aim and scope of this dissertation in addressing these challenges. The significance of this study to the supercapacitor research field and technology sector is highlighted. The chapter concludes with an overview of the dissertation topics and chapters.

1.1 Supercapacitor fundamentals and applications

Supercapacitors store electricity by means of electrochemical energy, much like batteries and fuel cells (both types of galvanic cells). Figure 1.1 shows a simplified illustration of a supercapacitor cell. Similar to a battery, a supercapacitor cell consists of two electrodes (anode and cathode), a separator, electrolyte, and metal contacts (current collectors). When the cell is charged, a potential difference, \( V \), is established between the electrodes due to charge separation between anode and cathode. During discharge, the supercapacitor cell forms a complete circuit with electric current flowing through an external load and ionic current flowing through the electrolyte and separator.
Figure 1.1. Simplified drawing of a supercapacitor cell during charging. The cell consists of two electrodes (anode and cathode), a separator, and metal contacts. In the above diagram, the anode, cathode, and separator are assumed to be saturated with electrolyte.

A fundamental difference between supercapacitors and galvanic cells is the charge storage mechanism at the electrodes. Supercapacitors use capacitive energy storage, while galvanic cells are based on chemical reactions involving phase change. As a result, supercapacitor charge storage is faster and more highly reversible than battery electrochemical energy storage. In this regard, supercapacitors are similar to conventional, electrical capacitors. The defining principle of capacitive energy storage is that electrode potential, $\Delta V$, varies linearly with degree-of-charge, $Q$, according to equation 1.1:

$$Q = C\Delta V;$$

Equation 1.1

where $C$ is the electrode capacitance. In a galvanic cell, in contrast, cell potential is (ideally) constant, independent of degree-of-charge.$^9$ This difference has important implications for the total energy storage, $E$, of supercapacitors vs. batteries. Due to the energy required for “self charging”, supercapacitors can theoretically store only half the energy of batteries for the same potential and total charge, as indicated by comparing equations 1.2 and 1.3:$^8$

Supercapacitors: $E = \frac{1}{2} C\Delta V^2 = \frac{1}{2} Q\Delta V$

Equation 1.2

Batteries: $E = Q\Delta V$

Equation 1.3

Supercapacitors store electrochemical energy by chemical and/or physical charge storage mechanisms. Supercapacitor electrodes that use purely physical charge separation are known as “electric double layer capacitors” (EDLCs). EDLCs store charge electrostatically in the form of an electric double layer at the electrode-electrolyte interface.$^9$ Supercapacitors that store charge chemically are known as “pseudocapacitors”. The chemical charge storage mechanisms of pseudocapacitors include: adsorption, intercalation, and reduction-oxidation (redox) reactions.$^{2,10}$

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$^1$ An analogy from thermodynamics would be that of heat absorption with constant phase vs. heat absorption with a phase change. In the former, temperature increases linearly with amount of heat absorbed ($Q = mc\Delta T$; supercapacitor analogy), while in the latter, the temperature remains constant due to the phase change ($Q = mL$; galvanic cell analogy).
These chemical charge storage mechanisms are still considered capacitive because they use translation of ionic and electric charge without phase transitions, and electrode potential increases linearly with degree-of-charge.\textsuperscript{9,11} Pseudocapacitors also have an electric double layer component, but total charge storage contribution from double layer capacitance is usually small compared to pseudocapacitance (typically 10-100x smaller).\textsuperscript{8,9}

**Figure 1.2** summarizes the fundamental properties of supercapacitors by comparing supercapacitors with conventional capacitors, batteries, and fuel cells in terms of: electrical vs. electrochemical energy storage; capacitive vs. phase-change; and physical vs. chemical charge storage.

![Diagram of energy storage mechanisms](image)

**Figure 1.2.** Classification of supercapacitors, batteries, fuel cells, and conventional capacitors based on energy storage mechanisms. Electrochemical vs. electrical energy storage is indicated by green vs. red connecting lines and textbox outlines; physical vs. chemical charge storage by blue vs. orange background color; and capacitive vs. phase change mechanisms by square brackets at the bottom of the figure.

The advantages of supercapacitors for energy storage include rapid charge-discharge capabilities and high cycle lifetimes as a result of their capacitive charge storage mechanism.\textsuperscript{2,11} **Figure 1.3** compares the specific energy (Wh/kg) and specific power (kW/kg) of common storage technologies for electricity: batteries, fuel cells, flywheels, superconducting magnetic energy storage (SMES), conventional capacitors, and supercapacitors. Plots of energy vs. power are commonly known as “Ragone plots”. As described above, the specific energy of supercapacitors is lower than that of batteries and fuel cells (as well as flywheels), but their specific power is several orders of magnitude higher.\textsuperscript{2,12,13} Supercapacitors have much higher specific energy compared to conventional capacitors (10-1000x) but lower power density.\textsuperscript{13,14} As such, supercapacitors bridge an important gap between the energy storage capabilities of capacitors and those of batteries and fuel cells.\textsuperscript{1,15}
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Figure 1.4 compares the cycle lifetimes (maximum number of charge-discharge cycles) of several battery technologies (lead acid, nickel-cadmium, and lithium-ion), SMES, flywheels, and supercapacitors. Supercapacitors are attractive for electrical energy storage applications due to their long cycle lifetimes, up to one million charge-discharge cycles. In comparison, the typical cycle lifetime for batteries ranges from several hundred to several thousand charge-discharge cycles, depending on the technology. Supercapacitor cycle lifetime also exceeds that of SMES and most flywheel technologies (some flywheels have exceeded 10 million cycles).

As a result of their high power densities and long cycle lifetimes, supercapacitors have many current and promising future applications in transportation, renewable energy, grid energy management, as well as stationary and portable electronics. Current, well established uses of supercapacitors include: power load-leveling for industrial equipment, engine start modules for large vehicles, wind turbine blade control, camera flash units, backup power supplies, and rail brake energy recovery for electric trains. One of the most promising future applications of supercapacitors is electric vehicles. As part of a hybrid supercapacitor-battery system, supercapacitors could enhance electric vehicle acceleration and regenerative braking, improve charging times, and extend the life of the vehicle battery pack. In certain applications, pure supercapacitor electric vehicles may also be possible. The city of Shanghai is experimenting with prototype supercapacitor buses, known as “capabuses”, along the city’s busiest transit routes. Although total energy storage is low, the capabuses are able to recharge at bus stops while passengers are embarking and disembarking. Another promising application of supercapacitors is grid and off-grid renewable energy storage. With fast response times and cycle lifetimes comparable to those of many renewable energy systems, supercapacitors are well-suited to provide load-leveling and transient stabilization for large-scale and micro-grid renewable energy installations. Finally, consumer portable electronics is a rapidly growing area of potential applications for supercapacitors. Similar to electric vehicles, battery-supercapacitor hybrid systems in consumer electronics could reduce battery size and improve device performance, with supercapacitors meeting peak power loads for flash photography, GPS, and other high power-draw functions.

With today’s rapid pace of growth in technologies that generate and consume electrical energy, there is an urgent need for better energy storage systems. Supercapacitors have great potential to fill this need, with their unique combination of energy, power, and lifecycle characteristics. Driven by future innovations, supercapacitor technology will undoubtedly expand into new fields and applications. Research on new supercapacitor materials and designs is key to this expansion, and to the advancement of those technologies that rely on electrical energy storage.

1.2 Supercapacitor research challenges

The two main characteristics of supercapacitors that make them highly desirable for energy storage systems are their long cycle lifetimes and rapid charging ability. In these two areas, supercapacitors greatly exceed the capabilities of current battery technologies. The relatively low energy density of supercapacitors, however, inhibits their use as a stand-alone energy storage technology. Finding ways to increase the energy density of supercapacitors is key to expanding their application potential, and is widely regarded as the most significant challenge in supercapacitor research. Of the two types of supercapacitors (EDLCs and pseudocapacitors), pseudocapacitors have the highest energy densities because of their combined physical and
chemical charge storage mechanisms. As a result, increasing research efforts are focused on pseudocapacitor electrode materials, designs, and synthesis methods.  

There are two types of pseudocapacitive materials: organic pseudocapacitors using conducting polymers, and metal oxide pseudocapacitors. To maximize electrolyte contact area and minimize resistive losses, pseudocapacitor electrodes typically employ high surface area, highly conductive nanomaterials coated with a thin layer of active pseudocapacitive material. Determining the optimum design of these nanomaterial-pseudocapacitor electrodes is highly complex as many interacting processes must be considered: ion diffusion, reaction kinetics, electrical resistances, and changing electrode potentials. Optimum electrode design will vary for different materials and operating conditions. To achieve maximum utilization of the active pseudocapacitive material, a focus on pseudocapacitor electrode design optimization based on electrochemical principles is needed.

In addition to pseudocapacitor electrode design, synthesis methods are known to play an important role in determining the performance and durability of pseudocapacitor electrodes. Coating large surface area electrodes uniformly with nanoscale films of pseudocapacitive materials presents a significant fabrication challenge. To date, many of the current synthesis methods for organic and metal oxide pseudocapacitors have been unable to achieve good performance due to poor control of coating morphology and composition. In addition, pseudocapacitors often struggle to achieve the long cycle lifetimes of EDLCs, and pseudocapacitor fabrication methods can significantly affect the resulting electrode durability. To overcome these challenges, a focus on developing fabrication methods that achieve optimum physical and chemical properties for pseudocapacitive electrodes is needed.

1.3 Dissertation aim and scope

The aim of this work is to improve the energy density of pseudocapacitor electrodes through innovative fabrication methods and a study of electrochemical principles for optimum pseudocapacitor design. Electrode design and synthesis methods are both studied because of the inherent synergy between design and fabrication: while electrochemical principles can reveal optimum pseudocapacitor electrode designs, these designs are only meaningful if they can be physically achieved. Synthesis capabilities thus define the scope of design possibilities. On the other hand, new designs can motivate the search for better, more versatile fabrication methods. This work considers both conducting polymer-based pseudocapacitors and metal oxide pseudocapacitors. Innovative synthesis methods are developed, followed by a study of optimal electrode designs in the context of these methods.

The focus of this dissertation is on the electrode portion of the supercapacitor cell; other device components such as electrolyte, separator, packaging, and electrical components are not studied. The research approach is therefore based on single electrode performance measurements, as opposed to full cell construction and testing (see chapter 2). In addition, primary consideration is given to optimizing pseudocapacitor electrode performance, without in-depth consideration of cost or large-scale manufacturing potential, although these issues are discussed as they are important areas of supercapacitor research.
1.4 Significance of the study

The significance of the present study to the field of pseudocapacitor research is the demonstration of new designs and fabrication methods to improve the energy density of conducting polymer and metal oxide supercapacitors. In the work on conducting polymer pseudocapacitors, an increase in specific capacitance is achieved through a hybrid electrode design with enhanced double layer capacitance and pseudocapacitance. Although the focus of the work is on the conducting polymer polypyrrole (PPY), similar performance improvement with a hybrid supercapacitor design is expected for other conducting polymers.

The metal oxide pseudocapacitor study demonstrates the novel use of atomic layer deposition (ALD) in the fabrication of ruthenium oxide (RuO$_x$) pseudocapacitors. The research advances current understanding of the ALD process for RuO$_x$, including evidence that ALD RuO$_x$ can be deposited as a hydrated oxide. Specific capacitance values for ALD RuO$_x$ electrodes are comparable to the highest values in the literature. In addition, ALD RuO$_x$ supercapacitors are demonstrated on porous silicon (Si) electrodes, a result that greatly expands the possibilities for fabricating Si-based micro-pseudocapacitors. As in the conducting polymer work, evidence suggests that the results of the RuO$_x$ study are applicable more generally to other metal-oxide based pseudocapacitors, opening the field for further research on ALD metal oxide supercapacitors.

Finally, pseudocapacitor design optimization and modeling work conducted in this study provides valuable insight into practical design considerations for conducting polymer and metal oxide supercapacitor electrodes. Comparisons between model predictions and experimental results enable inferences into underlying electrochemical mechanisms that may be limiting pseudocapacitor energy storage. For both conducting polymer and metal oxide pseudocapacitors, optimized electrode designs can be fabricated using the synthesis methods developed in this work, thus enabling future development of supercapacitors with even greater energy storage capabilities.

1.5 Overview

Following this chapter, chapter 2 provides an overview of supercapacitor performance metrics and experimental methods used in this work. Chapter 3 focuses on the novel design of a hybrid vertically-aligned carbon nanotube (VACNT)-PPY supercapacitor electrode. The chapter introduces the theory of conducting polymer supercapacitors, and provides an overview of previous work on PPY supercapacitors. Fabrication method, materials characterization, and supercapacitor performance testing results for the VACNT-PPY supercapacitors are presented. Chapter 4 describes the use of ALD as an advanced fabrication method for RuO$_x$ pseudocapacitor electrodes. Chapter 4 discusses previous research on RuO$_x$ supercapacitors and ALD RuO$_x$, describes fabrication methods, and presents materials characterization and performance testing results for ALD RuO$_x$ supercapacitor electrodes. Chapter 5 develops a new one-dimensional porous electrode model for simulating the energy storage potential of conducting polymer and metal oxide pseudocapacitor electrodes. Model strengths and limitations are assessed by comparing predicted values with experimental results for polypyrrole and RuO$_x$ supercapacitors electrodes in chapters 3 and 4, as well as experimental values from the literature. Chapter 6 concludes the work with a summary discussion and ideas for future research.
Chapter 2: Performance Metrics and Experimental Methods

The previous chapter introduced the concept of supercapacitors, and highlighted their advantages as a high power density, long life cycle electrochemical energy storage technology. The chapter discussed the motivation for studying pseudocapacitors and the primary research challenge: increasing energy density while maintaining high cycle life with pseudocapacitive materials. Research on new pseudocapacitor designs and fabrication methods was proposed as a way to overcome these challenges, and expand the possible applications of supercapacitors. A key component of this pseudocapacitor research is performance testing and materials characterization.

The aim of this chapter is to introduce important supercapacitor performance metrics and provide background on performance testing methods. This background is necessary for understanding the pseudocapacitor experimental and modeling results presented in chapters 3 through 5. Particularly important points include the application and limitations of each experimental method, as well as possible sources of error. This chapter also introduces readers to data interpretation and methods for fitting empirical models to experimental data. As discussed in chapter 1, the focus of the experimental methods presented here is on single electrode rather than full cell performance testing.

The chapter begins with an overview of supercapacitor performance metrics, including capacitance, energy and power density, equivalent series resistance (ESR), leakage current, and cycle lifetime. This is followed by a discussion of two-electrode vs. three-electrode measurements, and the applications of each. Performance testing methods used in this work include: cyclic voltammetry, chronopotentiometry, chronoamperometry, and electrochemical impedance spectroscopy. Following these experimental methods, the chapter describes material characterization techniques to determine the physical and chemical properties of supercapacitor electrodes, including electron microscopy and x-ray measurements. The chapter concludes with a discussion of the limitations of supercapacitor performance testing methods and sources of error.

2.1 Supercapacitor performance metrics

Capacitance, power, and energy are the main performance metrics for evaluating supercapacitor electrodes. In addition to these primary metrics, leakage current, ESR, and cycle lifetime are secondary metrics that quantify supercapacitor efficiency and durability. In supercapacitor research, it is important to evaluate primary as well as secondary metrics to ensure that gains in capacitance, power, or energy do not come at the expense of supercapacitor electrode lifetime or result in high leakage currents.

Supercapacitor performance metrics including capacitance, power, energy, and leakage current can be reported on a per mass or per volume basis. The relative importance of gravimetric vs.

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ii Note that this empirical modeling work is distinct from pseudocapacitor electrode design modeling in chapter 5.

iii Per mass values are reported as “specific” or “gravimetric” values, as in specific energy or gravimetric power. Per volume metrics are reported as “density” values, as in energy density or power density.
volumetric performance depends on the energy storage application: gravimetric performance is generally important for mobility applications such as electric vehicles, while volumetric performance is often a higher priority for micro-supercapacitor applications, for example. In supercapacitor research literature, volumetric and specific performance is most often reported by including only the volume or mass of electrode active material. For gravimetric values, electrolyte mass is typically not included. As a result, it is generally not possible to directly compare the performance of research and commercial supercapacitors, as commercial supercapacitor performance values include full cell components (current collector, electrolyte, separator, and packaging). To enable comparisons with current research, this work follows literature conventions of performance values reported per mass or volume of electrode active material.

Capacitance

As described in chapter 1, supercapacitors store energy by capacitance, with ideal supercapacitors exhibiting a linear relationship between cell potential and degree-of-charge. The capacitance, $C$, of an electrode is defined as the amount of charge, $Q$, accumulated for a given change in electric potential, $\Delta V$ (see equation 1.1). For EDLCs, double layer capacitance, $C_d$, arises from physical separation of charges and is described by the electrode surface area, $A$, the charge separation distance, $d$, and the electrolyte dielectric constant, $\varepsilon$, as in a conventional capacitor:

$$C_d = \frac{\varepsilon A}{d}$$

Equation 2.1

In an EDLC, high capacitance values of 10 to 100 F/g can be achieved as a result of large surface areas and small charge separation distances (on the order of few Å), as shown in Figure 2.1.

![Figure 2.1. Conceptual illustration of charge separation and energy storage in (a) a conventional parallel-plate capacitor, and (b) a high-surface area EDLC. Typical electrode spacing for conventional capacitors is upwards of 0.1 µm, while the charge separation distance for an EDLC is on the order of a few Å. (Note that in (b) only one electrode has been drawn for simplicity. A second electrode with opposite charge configuration would comprise a complete cell, effectively forming two EDLCs in series.)

iv The effect of this omission on supercapacitor design optimization is discussed in chapter 5.
For pseudocapacitors, faradaic capacitance, $C_f$, is achieved through chemical charge storage mechanisms described by Faraday’s law:

$$C_f = \frac{F n_e}{M \Delta V}$$

Equation 2.2

where $F$ is Faraday’s constant (96,484 C/mol), $n_e$ is the number of electrons stored per active molecule, $M$ is the molar mass of the pseudocapacitive material, and $\Delta V$ is the cell voltage range.

For pseudocapacitor electrodes with a significant double layer contribution, total electrode capacitance is the sum of the double layer and faradaic capacitance since the two capacitances occur in parallel:

$$C = C_d + C_f$$

Equation 2.3

Energy and power

The maximum theoretical energy density of a supercapacitor, $E_{max}$, is proportional to the capacitance multiplied by the square of the reversible cell potential, $\Delta V_{rev}$:

$$E_{max} = \frac{1}{2} C \Delta V^2_{rev}$$

Equation 2.4

For electrochemically stable pseudocapacitor materials, the reversible cell potential is limited by the breakdown voltage of the electrolyte. For aqueous electrolytes, this corresponds to a maximum cell potential of approximately 1.0 V. Increased cell potential can be achieved using organic or ionic liquid electrolytes, though at higher cost and typically lower electrolyte conductivity. In practice, supercapacitor energy density is less than the maximum theoretical value because of internal losses that decrease cell potential. These internal losses include ohmic resistances and kinetic losses (diffusion and reaction overpotentials) that increase with higher supercapacitor discharge rates (i.e. discharge currents).

Power density for a supercapacitor depends on the discharge rate, such that it is not possible to specify a maximum theoretical power (maximum theoretical energy occurs at zero current when there are no ohmic or kinetic losses). Total power is given by $P = i \Delta V_{rev}$, where $i$ is the supercapacitor discharge current. Of this total power, some is dissipated due to supercapacitor internal resistances ($R_s$) and the remainder is power available for a load resistance ($R_L$), as shown in the circuit diagram in Figure 2.2a. The power available for the load is equal to the total power minus the power dissipated as resistive and kinetic losses:

$$P = i \left[ \Delta V_{rev} - i R_s - \sum \eta(i) \right]$$

Equation 2.5

where $i R_s$ represents ohmic losses and $\sum \eta(i)$ is the sum of reaction overpotential and concentration polarization losses.

The relationship between power and energy density for a supercapacitor is shown in the theoretical Ragone plot in Figure 2.2b. Energy density decreases continually with increasing current, while available power increases up to a maximum power $P_{max}$. At discharge rates below

\textsuperscript{\textdagger} Equation 2.4, as distinct from the general capacitor energy equation in chapter 1 (equation 1.2), indicates that maximum supercapacitor energy density is attained only for a fully reversible cell potential.

\textsuperscript{\textdagger} The use of organic electrolyte for PPY supercapacitors is discussed in chapter 3.
$P_{\text{max}}$, supercapacitor internal losses are less than the power dissipated in the load ($R_s < R_L$). Above $P_{\text{max}}$, available power decreases with further increase in discharge rate as ohmic and kinetic losses become dominant ($R_s > R_L$). $P_{\text{max}}$ can be found by solving equation 2.5 for $dP/di = 0$. Neglecting kinetic losses,\(^\text{vii}\) the maximum available power is:

$$P_{\text{max}} = \frac{(\Delta V)^2}{4R_s}$$  

Equation 2.6

which occurs at matched impedance ($R_s = R_L$). From equation 2.6, it is clear that increasing cell potential and decreasing internal resistances are two important factors in achieving high power density.

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**Figure 2.2.** (a) Circuit diagram representing changes in potential due to supercapacitor internal resistance ($R_s$) and load resistance ($R_L$). (b) Theoretical Ragone plot for supercapacitor electrodes illustrating maximum available power at the point of matched impedance. For simplicity, the plot is based only on ohmic losses (neglects kinetic losses).

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**Secondary performance metrics**

Secondary performance metrics for supercapacitor electrodes include ESR, leakage current, and cycle lifetime.\(^{39}\) ESR is the sum of all ohmic losses in the supercapacitor electrode or cell, and is equivalent to $R_s$ in equation 2.5. For supercapacitor electrodes, ESR includes: resistive losses in the electrode material, electrolyte solution resistance, contact resistance between the electrode and the metal current collector, as well as resistive losses in the current collector and external wiring. For commercial supercapacitors, ESR also includes the resistance of the separator and cell packaging. ESR is a commonly reported value in the research literature since it is a limiting factor in the maximum power output of supercapacitor electrodes (equation 2.6).\(^{39}\)

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\(^{\text{vii}}\) Kinetic losses (reaction overpotential and diffusion losses) are complicated functions of current (see chapter 5), and it is standard to neglect them when determining maximum available power.
Leakage current is an important performance metric because it results in the gradual loss of cell potential, and hence available power and energy. Ideally, a supercapacitor can maintain the potential between its two electrodes indefinitely. In reality, there will be some leakage current, or self-discharge, as a result of: diffusion of ions from the electric double layer; side reactions arising from impurities in the electrode or electrolyte; discharge of over-voltage current if the cell has been charged beyond the electrolyte decomposition limit; redistribution of charge over the electrode surface (“apparent self-discharge”); as well as internal ohmic leakage pathways within the electrode or cell.\textsuperscript{41–43} The relative importance of leakage current compared to other performance metrics depends on the application, with leakage current being a critical parameter for supercapacitors used as stand-alone or standby power sources, for example.\textsuperscript{43}

Supercapacitor cycle lifetime is defined as the number of cycles until capacitance drops below 80\% of its initial value.\textsuperscript{15} Due to the long cycle lifetime of most supercapacitor electrodes, it is common in the research literature to measure capacitance change over several thousand cycles and report the percent change from the initial value. In pseudocapacitor research, life cycle testing beyond 10,000 cycles is uncommon.\textsuperscript{44–46}

2.2 Supercapacitor performance testing

This section describes measurement techniques used to determine the above supercapacitor performance metrics. Performance tests are designed to simulate real operating conditions in terms of charging and discharging conditions, as well as to provide insight into the electrochemical processes occurring at supercapacitor electrodes. The measurement techniques described here comprise the experimental methods used in chapters 3 and 4.

Supercapacitor performance testing can be done using either a three-electrode or a two-electrode test cell configuration. A three-electrode test cell enables measurement of electrochemical reactions occurring at a single electrode, which is desirable for studies of new electrode designs and materials. The electrode under study is called the working electrode (WE). A counter electrode (CE) completes the electrochemical circuit and a reference electrode (RE) provides a constant reference point for potential measurements. A potentiostat measures the current flow between WE and CE, and the potential difference between WE and RE.\textsuperscript{47} Figure 2.3 provides a photographic illustration of a three-electrode test cell. All experimental measurements in this work use platinum wire as the CE, a Ag/AgCl RE, and a Gamry Reference 600 potentiostat. In this work, a three-electrode test cell was used for cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy measurements.

In a two-electrode cell, CE and RE are together replaced by a second supercapacitor electrode to form a full supercapacitor cell. The potentiostat measures potential difference and current flow between the two electrodes.\textsuperscript{viii} In this work, a two-electrode test cell was used for chronopotentiometry measurements, as measurement of cell voltage is needed for power and energy calculations. All two-electrode cell measurements in this work use identical supercapacitor electrodes as anode and cathode to create a symmetrical supercapacitor cell.

\textsuperscript{viii} The potential difference between the two electrodes is known as the cell voltage.
Cyclic voltammetry

Cyclic voltammetry (CV) is a three-electrode measurement in which the WE is cycled between potentials $V_1$ and $V_2$ at a constant scan rate and the resulting electrode current is measured. Figure 2.4a plots the WE potential as a function of time for a supercapacitor CV measurement between 0.2 and 1.2 V vs. Ag/AgCl at a scan rate of 100 mV/s. The resulting current-potential curve is shown in Figure 2.4b. An ideal supercapacitor has a rectangular-shaped CV curve with constant charging and discharging currents of equal magnitude.\textsuperscript{ix}

CV measurements can be used to determine electrode capacitance. Rewriting equation 1.1 in terms of the potential scan rate, $\nu$, and the measured charge or discharge current, $i$, gives an equation for capacitance:

$$C = \frac{i}{\nu}$$ \hspace{1cm} Equation 2.7

In practice, charging and discharging currents are not completely constant with electrode potential, as illustrated in Figure 2.4b. An average current can be used in equation 2.7, or a more rigorous method of determining capacitance is to first calculate “voltammetric charge” by integrating $i$ over the potential scan range, and then divide by $V_2 - V_1$. Dividing by the scan rate and the mass of active material, $m$, gives an equation for gravimetric capacitance calculated from CV measurements:

$$C = \frac{\int_{V_1}^{V_2} idV}{2(V_2 - V_1)mv}$$ \hspace{1cm} Equation 2.8

\textsuperscript{ix} For constant capacitance, electrode charge varies directly with potential according to equation 1.1. In CV measurements, electrode potential and hence electrode charge change linearly in time, resulting in constant charge and discharge currents.
The effect of supercapacitor charge and discharge rate on electrode capacitance can be studied by taking CV measurements at different scan rates and creating a plot of capacitance vs. scan rate (see chapter 4). For an ideal supercapacitor, capacitance is independent of scan rate; in practice, capacitance often decreases at higher scan rates due to increasing concentration polarization, deep electrode pores becoming inaccessible at high scan rates, or slow reaction kinetics for faradaic charge storage. In this work, CV measurements were also used for life cycle performance testing through repeated charge-discharge cycling of electrodes.

![Figure 2.4](image)

**Figure 2.4.** Example CV measurement of a supercapacitor electrode. (a) WE applied potential vs. time for one CV cycle at 100 mV/s scan rate and 1.0 V potential range. (b) Current vs. potential (“CV curve”) for the electrode in (a). Measured charging and discharging currents deviate slightly from the rectangular shape of an “ideal capacitor”.

Many supercapacitor papers in the literature report only specific or volumetric capacitance, measured by CV, as an indication of electrode performance. This is well-accepted as supercapacitor energy and power are directly related to capacitance (see equation 2.4 above and equation 2.11 in the following section). Performance testing to measure power and energy, however, is beneficial as the experimental method—chronopotentiometry—closely simulates supercapacitor operation in practical devices.

**Chronopotentiometry**

Chronopotentiometry, also known as “constant current” measurement, is a two-electrode method in which constant charging and discharging currents are applied to a supercapacitor cell and the resulting change in cell voltage is measured. **Figure 2.5a** shows the current profile for chronopotentiometry measurements of a supercapacitor test cell, and Figure 2.5b shows the measured cell voltage. The duration of charging and discharging is determined by the cell voltage, which is constrained between upper and lower bounds (typically 0-1.0 V for aqueous electrolytes). In an ideal supercapacitor, cell voltage increases linearly during charging and decreases linearly during discharging; in practice, ohmic losses can produce abrupt changes in potential at the start of supercapacitor charging and discharging, as shown in Figure 2.5b. The potential drop observed during discharge is equal to $2iR_s$, where $R_s$ is the cell ESR described above.

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$x$ The factor of two comes from having two symmetrical electrodes in the test cell.
Chronopotentiometry measurements are primarily used to determine supercapacitor cell energy and power. Energy is calculated from the familiar equation, modified to give units of Wh:

\[ E = \frac{C(\Delta V)^2}{2(3600)} \]

Equation 2.9

Capacitance in equation 2.9 is calculated from the applied discharge current, \( i_d \), and the slope of the cell voltage, \( dV/dt \), during discharge:

\[ C = \frac{i_d}{\left.dV/dt\right|_d} \]

Equation 2.10

Since chronopotentiometry is a two-electrode measurement, the capacitance calculated in equation 2.10 is the full cell capacitance, which differs from single electrode capacitance measured by CV.\(^{39}\) Available power is calculated by dividing supercapacitor energy found in equation 2.9 by the discharge time, \( t_d \):

\[ P = \frac{3600E}{t_d} \]

Equation 2.11

A Ragone plot, similar to Figure 2.2b, can be generated by calculating supercapacitor energy and power for different charge and discharge rates.

![Figure 2.5](image)

**Figure 2.5.** Chronopotentiometry measurements for a symmetrical, two-electrode test cell. (a) The applied current follows a step function, with charging and discharging times determined by the upper and lower bounds on cell voltage. (b) The resulting supercapacitor cell voltage has a fairly linear time dependence, except for abrupt changes in potential due to ohmic losses.

**Chronoamperometry**

Chronoamperometry is a three-electrode method in which constant charging and discharging potentials are applied to the WE (Figure 2.6a) and the resulting current is measured (Figure 2.6b). Although less commonly used than chronopotentiometry, chronoamperometry can provide an estimate of supercapacitor leakage current by comparing the relative magnitudes of charging and discharging currents (see chapter 3).\(^{37}\) Chronoamperometry measurements can also provide
an indication of the relative contributions of Faradaic and double layer capacitance to supercapacitor charge storage by fitting models of current vs. time to charging and discharging currents. For double layer capacitance, current from a potential step function decreases exponentially with time ($i \propto e^{-kt}$), while for Faradaic capacitance current varies with the inverse square root of time ($i \propto t^{-1/2}$).

![Figure 2.6](image.png)

**Figure 2.6.** Chronoamperometry measurements of a supercapacitor electrode using a three-electrode test cell. (a) Alternating step potentials of 1 V and 0 V are applied to the supercapacitor electrode. (b) Current vs. time measurements showing charging and discharging of the electrode.

**Electrochemical impedance spectroscopy**

Supercapacitors are complex electrochemical systems. One way to empirically model a supercapacitor electrode is using an equivalent circuit that includes resistive and capacitive elements. The most common equivalent circuit for pseudocapacitor electrodes is the Randles circuit shown in [Figure 2.7a](image.png). The Randles circuit consists of an ESR, $R_s$ (discussed previously), combined with circuit elements representing the two capacitive charge storage mechanisms—double layer capacitance and pseudocapacitance—arranged in parallel. Double layer capacitance is represented by a constant phase element (CPE) based on the electrode double layer capacitance, $C_d$, and an empirical constant $\alpha$ that accounts for non-ideal capacitor behavior:

$$Z_{CPE} = \frac{1}{(j\omega)^{\alpha} C_d}$$  

**Equation 2.12**

Pseudocapacitance is represented by two circuit elements: 1) charge transfer resistance ($R_{ct}$), which accounts for reaction overpotentials, and 2) Warburg impedance ($Z_W$), which models diffusion polarization. Warburg impedance is calculated as:

$$Z_W = \sigma (\omega)^{-1/2} (1 - j)$$  

**Equation 2.13**

where $\sigma$ is a constant that depends on diffusion coefficients. Equivalent circuit modeling in this work was done use Gamry Echem Analyst software (see chapter 3).
Electrochemical impedance spectroscopy (EIS) is a three-electrode method that measures total impedance for a supercapacitor electrode or cell. Impedance is measured at different AC frequencies such that an equivalent circuit model, like the Randles circuit, can be fit to the data. During an EIS measurement, the potentiostat applies a small AC potential to the WE over a range of frequencies and calculates cell impedance based on current measurements. EIS measurements in this work use an AC potential of 1 mV and a frequency range of 0.2 Hz to $10^5$ Hz. EIS measurements are most commonly presented as a Nyquist plot of imaginary vs. real impedance (Figure 2.7b). Measurement frequencies cannot be seen in a Nyquist plot, but have been indicated in Figure 2.7b (frequency dependence can be visually represented in a Bode plot). The semicircular component of the Nyquist plot at high frequencies results from double layer capacitance and charge transfer resistance, while the semi-linear component at low frequencies corresponds to Warburg impedance. Purely resistive circuit elements ($R_s$ and $R_{ct}$) can be deduced from the x-intercepts of the plot, as shown in Figure 2.7b.\textsuperscript{x1,53}

**Figure 2.7.** (a) Randles equivalent circuit model of a pseudocapacitor electrode representing ESR ($R_s$), double layer capacitance (constant phase element, CPE), and faradaic capacitance (charge transfer resistance, $R_{ct}$, and Warburg impedance, $W$). (b) Nyquist plot of imaginary vs. real impedance for a supercapacitor electrode measured at AC frequencies of 0.2 Hz to $10^5$ Hz. The Nyquist curve is extrapolated in the semicircular region to provide an estimate of $R_s$.

### 2.3 Materials characterization

A variety of materials characterization techniques can be used to study the physical and chemical properties of supercapacitor electrodes. Materials characterization techniques used in this work include scanning and transmission electron microscopy as well as x-ray photoelectron spectroscopy and x-ray diffraction. The following discussion focuses on the basic principles of each technique and how each method was used in this work. The reader is referred to more in-depth resources for further study.\textsuperscript{55–58}

\textsuperscript{x1} Just as capacitance measured by CV differs from capacitance measured by chronopotentiometry, $R_s$ values measured by EIS will differ from $R_s$ values measured by chronopotentiometry due to the different cell configurations used (two-electrode vs. three-electrode measurements).\textsuperscript{19}
Scanning electron microscopy

Scanning electron microscopy (SEM) imaging probes the surface of micro and nanomaterials using an electron beam generated by the high voltage acceleration of electrons from a thermionic or field-emission cathode. Images are produced from secondary electrons (sample electrons emitted from the material surface by electron-electron collisions) and backscattered electrons (beam electrons reflected from the sample surface by electron-nucleus collisions) that are collected by an electron detector within the SEM. In this work, SEM images were taken using an FEI Nova NanoSEM 650 field emission scanning electron microscope with 1.4 nm resolution. SEM images were used to compare the structure of porous electrodes before and after coating with pseudocapacitive materials to determine the quality of the coating, as well as before and after life cycle testing to identify any degradation of the electrodes or pseudocapacitive coatings.

Transmission electron microscopy

Transmission electron microscopy (TEM), in contrast to SEM, generates images from electrons that have been transmitted through the sample. TEM has greater resolution than SEM, including the ability to see the crystal structure of materials (arrangement of atoms and lattice defects) with a high resolution TEM (HRTEM). TEM imaging in this work was conducted using an FEI Tecnai 12 transmission electron microscope with 0.34 nm point resolution. HRTEM imaging was conducted off-campus by Evans Analytical Group using an FEI Tecnai TF-20 TEM. The CNT electrodes used in this work are well-suited to TEM imaging as individual nanotubes, when removed from the substrate, are transparent to the electron beam. TEM imaging was used to measure pseudocapacitor coating thicknesses on CNTs and study the crystalline structure of the pseudocapacitive materials.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a materials characterization technique for determining the types of atoms present in the surface layer of a material and how these atoms are bonded. When a material is exposed to a high energy, single wavelength x-ray source, incoming x-ray photons with sufficient energy can release an electron from an atom or ion in the material. XPS measures the kinetic energy of these emitted electrons to determine the binding energy of surface atoms in the material. By changing the incidence, or “take-off”, angle of measurement, elemental composition at different depths can be measured, from the surface of the material to approximately 10 nm depth. For elements present in multiple chemical environments (bonding states) within the material, curve fitting of high resolution XPS measurements can be used to decompose overlapping peaks and determine the relative quantities of atoms in each bonding state (see chapter 4). XPS measurements in this work were done off-campus by Evans Analytical Group using a PHI Quantum 2000 x-ray photoelectron spectrometer with high resolution capabilities. Curve fitting of high resolution XPS peaks was done by the author using XPSPEAK 4.1 peak fitting program.
X-ray diffraction

X-ray diffraction (XRD) characterizes the crystal structure of a material using interference patterns generated when a single wavelength x-ray beam is scattered off the material surface. X-rays are required for studying crystal structures because x-ray wavelengths are comparable with the interatomic spacing of crystals (approximately 0.1 Å-100 Å). XRD can be used to identify crystal phases present in polycrystalline or single crystalline materials (XRD cannot characterize amorphous materials). In this work, XRD was used to determine the chemical composition and crystal structure of pseudocapacitive films deposited on planar and nanoporous electrodes. XRD measurements were conducted using a Siemens D5000 x-ray diffractometer with copper K-alpha radiation.

2.4 Discussion

The experimental methods and materials characterization techniques discussed in this chapter are ideal for research-scale testing and rapid prototyping of supercapacitor electrodes. Maintaining high accuracy of experimental methods is critical to the supercapacitor design process, which involves frequent iteration between new designs and performance testing. The follow points discuss common sources of error in supercapacitor measurements and the steps taken to avoid such errors in this work:

- Recording electrochemical measurements before the electrode has had time to stabilize can result in over-estimation of supercapacitor performance. During the first several charge-discharge cycles, non-capacitive currents are often present due to impurities and other system instabilities. In this work, supercapacitor electrodes were stabilized by CV cycling until no change in performance between cycles was observed prior to recording electrochemical measurements.

- Testing supercapacitor electrodes outside of their stable operating range can also result in over-estimation of performance. In this case, non-capacitive currents arise from degradation of the electrolyte or other electrode materials and the measurement is not representative of true electrode performance. To avoid electrode or electrolyte degradation from over-charging, all aqueous measurements in this work use a maximum voltage range of 1.0 V. The cell voltage range was further reduced below 1.0 V if other large, non-capacitive currents were observed that suggested degradation of electrode materials.

- High solution resistance due to low concentrations of conducting ions can lead to unreasonably large ESR values and an underestimation of capacitance, power, and energy. Sufficiently high supporting electrolyte concentrations should be used such that solution resistance does not limit supercapacitor performance. In this work, reasonably concentrated electrolyte solutions (0.5 M sulfuric acid as an aqueous electrolyte and saturated sodium dodecylbenzenesulfonate in acetonitrile as an organic electrolyte) were used to avoid the effects of low solution conductance.

- Performance testing of small supercapacitor samples with minute quantities of electrode active material can result in large percent errors in gravimetric capacitance, power, and energy due to inherent difficulties quantifying the mass of active material. This
problem can be particularly challenging for research-scale testing, in which small prototype electrodes are often used because of small-scale fabrication systems or to save on material cost. In this work, supercapacitor performance results are reported per cm$^2$ to provide an accurate value based on easily measurable electrode planar surface area. When gravimetric performance values are presented in addition to planar surface area results, experimental errors relating to electrode mass measurement are quantified (see chapter 4).

- Finally, performance testing conditions should correspond to realistic operating conditions for supercapacitor cells, including charging and discharging times of a few minutes or less.$^3$ Unreasonably low discharge rates lead to capacitance values that overestimate energy storage, as reaction kinetics and diffusion limitations that would normally reduce performance are diminished. All supercapacitor performance measurements in this work were taken at CV scan rates of 100 mV/s or higher,$^{xii}$ or using charge-discharge times of one minute or less.

Following the above steps to reduce experimental errors is important for achieving consistency in results and for enabling comparisons between different supercapacitor designs and fabrication methods. In addition to internal results comparisons, it is also valuable to compare supercapacitor performance metrics measured here with results reported in the literature. Comparisons of performance values with the literature, however, must be done carefully and with knowledge of experimental conditions as there are currently no universal standards in place for supercapacitor electrode testing.$^{36,39}$ In the following chapters, experimental set-up and performance testing conditions are carefully documented to support reproducibility of results and, as much as possible, enable comparisons with other works.

2.5 Summary

Supercapacitors, as discussed in chapter 1, fill important application needs in energy storage. These application needs produce research challenges, which are quantified as performance metrics and evaluated using experimental methods. This chapter introduced primary and secondary supercapacitor performance metrics, including capacitance, power, energy, ESR, leakage current, and cycle lifetime. The relative importance of these metrics depends on the supercapacitor application. Mobility applications such as electric vehicles and portable electronics, for example, generally require high gravimetric energy (Wh/kg) and high gravimetric power (kW/kg). In standby power and load-leveling applications, the highest priority metrics are likely low leakage current and high cycle life. Although much supercapacitor research is focused on increasing energy density, it is important to evaluate both primary and secondary performance metrics to provide a complete profile of electrode performance for various applications.

$xii$ Except for capacitance vs. scan rate measurements, which are used to determine the effect of scan rate on supercapacitor performance.
The experimental methods chosen in this work enable rapid prototyping of supercapacitor designs and small-scale testing of sample electrodes. Three-electrode methods, including CV, chronoamperometry, and EIS, are well-suited for characterizing the performance of single electrodes. Chronopotentiometry, a two-electrode method, was chosen to more closely simulate supercapacitor performance in a real device and enable measurement of full cell energy and power. While such experimental methods can answer questions of how a supercapacitor electrode performs, materials characterization techniques are needed to understand why the electrode performs in this way. Electron microscopy techniques (SEM and TEM) provide insight into the physical characteristics of micro and nanomaterials, while XPS and XRD provide insight into the chemistry of these materials. In the following two chapters, the supercapacitor measurement and characterization techniques described here will be used to evaluate the performance of new designs and fabrication methods for organic (PPY) and metal oxide (RuO$_x$) supercapacitors.
Chapter 3: PPY-VACNT Hybrid Supercapacitor

Previous chapters introduced the fundamental principles of supercapacitors, including EDLCs and pseudocapacitors, and examined characterization and performance testing methods for supercapacitor electrodes. As described in chapter 1, there are two types of pseudocapacitive materials: organic pseudocapacitors using conducting polymers and metal oxide pseudocapacitors. This chapter focuses on conducting polymer pseudocapacitors, with an emphasis on polypyrrole (PPY)-based pseudocapacitor design and fabrication. The main advantages of conducting polymer supercapacitors include: simple fabrication methods, environmental and bio-compatibility, potentially high energy density, and low cost.\textsuperscript{2,11,62,63} Organic pseudocapacitors, however, often suffer from poor cycle lifetime, limited voltage range, and low rate capability which limits their use in practical applications.\textsuperscript{63–65}

To address these challenges, this chapter describes the development of a novel PPY-vertically aligned carbon nanotube (VACNT) hybrid supercapacitor electrode. The design is termed a “hybrid supercapacitor” because it combines double layer capacitance and pseudocapacitance to achieve high total capacitance. The unique features of the PPY-VACNT electrode include: 1) the use of VACNTs as a highly porous and flexible electrode material; 2) dodecylbenzenesulfonate (DBS) as a surfactant-type dopant for PPY combined with highly mobile sodium ions (Na\textsuperscript{+}) for improved rate capability; and 3) the use of organic electrolyte for increased cell voltage range. The hybrid PPY-VACNT supercapacitor achieves a 5x improvement in capacitance and a 28% decrease in ESR compared to uncoated VACNTs, as well as 92% capacitance retention over 3000 cycles. Chronoamperometry and EIS modeling confirm the hybrid (EDLC + pseudocapacitor) charge-storage mechanism of the PPY-VACNT electrode.

The chapter begins with an overview of charge storage mechanisms in conducting polymers, and a literature review of previous work on PPY-based supercapacitor electrodes. The hybrid PPY-VACNT supercapacitor electrode design is then introduced, along with fabrication details and materials characterization. Performance testing includes CV measurements, chronoamperometry, EIS, and an evaluation of cycle lifetime. The chapter concludes with a comparison to theoretical and reported performances, and a discussion of possible future improvements to the hybrid PPY-VACNT design.

3.1 Conducting polymer supercapacitors

Conducting polymers are an exciting branch of organic materials with many unique properties, including good to excellent electrical conductivity,\textsuperscript{xiii} visible light absorption, and the ability to reversibly switch between conductive and insulating states with corresponding volume changes.\textsuperscript{66} Conducting polymers were first discovered in the 1970s by Heeger, MacDiarmid, and Shirakawa, who were awarded the Nobel Prize in chemistry in 2000 for this important discovery.\textsuperscript{67} Today, conducting polymers are well-studied materials with promising applications in organic display devices and light emitting diodes as well as solar cells, photoelectrochemistry, electrocatalysis, sensors, and of course, energy storage.\textsuperscript{66,68}

\textsuperscript{xiii} Conductivities range from $10^{-4}$ S/m to $10^{7}$ S/m, depending on the polymer and fabrication method.\textsuperscript{68}
Conducting polymers are distinguished from conventional polymers by their unique conjugated bond structure (alternating double and single bonds). Figure 3.1a shows the simplest example of conjugated bonds in polyacetylene. Each carbon-carbon double bond consists of a strong, localized sigma bond, and a weaker, delocalized pi bond (Figure 3.1b). Adjacent pi bonds overlap to form a conducting path for electrons along the polymer chain (Figure 3.1c). Figure 3.1d shows the molecular structure of PPY, with the conjugated bond structure highlighted in green.

Conjugated polymers generally have low conductivity in their natural state, becoming conductive only when electrons are added or removed in a process called “doping”.* Most conjugated polymers become conducting when oxidized and are referred to as “p-type”; a few are “n-type” and become conducting when reduced. PPY, a p-type polymer, has a conductivity of less than 10⁻⁴ S/m in its neutral state vs. 10⁻³ S/m when oxidized. Doping of conjugated polymers can be achieved during polymer synthesis by chemical or electrochemical methods, or post-polymerization by ion implantation, photochemical doping, solution doping, or heat treatment. Chemical and electrochemical polymer synthesis methods with in-situ doping are the most common because they are convenient, low cost, and can be done at room temperature. During chemical doping, the polymer is exposed to a solution or vapor of the dopant, while electrochemical doping is done using a three electrode cell in a solution containing the dopant ions.

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* Doping of conducting polymers is similar to doping of semiconductors in the sense that the material’s intrinsic conductivity increases by several orders of magnitude with the addition of dopant ions. Doping of polymers, however, is reversible and generally involves much higher doping levels (doping levels of 30-40% are common for conducting polymers, while the doping level for p⁺Si is 0.1%).
Conducting polymers store charge as pseudocapacitors through the movement of dopant ions into and out of the polymer film during supercapacitor charging and discharging. Of the many types of conducting polymers, the most commonly used for pseudocapacitor applications are PPY, polyaniline, polythiophene, and poly[3,4-ethylenedioxythiophene] (PEDOT). These polymers are good candidates for pseudocapacitance because they have reasonable stability in electrochemical and ambient conditions, and have doping potentials that fall within the voltage range of common electrolytes. PPY is one of the most well-studied pseudocapacitive polymers because of its ease of fabrication, good stability, and ability to be doped without requiring hazardous oxidants. PPY was chosen for the hybrid supercapacitor electrode developed in this work because of these advantages, as well as the extensive research background available for this material.

3.2 Literature review of PPY supercapacitors

Research on the electrochemical properties of PPY began in the early 1980s with PPY deposited on platinum wire as an electrode material. Since then, much work has been done to study the effects of electrode design, synthesis method, as well as dopant and electrolyte selection on the performance of PPY supercapacitors. Significant findings, described below, include: 1) the importance of a porous electrode structure, especially VACNTs, in improving PPY pseudocapacitance; 2) the impact of chemical vs. electrochemical synthesis on PPY uniformity and porosity; and 3) the effect of electrolyte and dopant ions on PPY-CNT supercapacitor performance.

Many high surface area micro and nanomaterials have been studied as PPY supercapacitor electrodes, including CNTs, porous Si, activated carbon, electrospun nanofibers, and three dimensional ordered macroporous films (3DOMs). In all of these works, the porous electrode structure improved PPY supercapacitor performance by: 1) increasing electrode specific surface area, 2) decreasing diffusion resistance for dopant and electrolyte ions, and 3) decreasing ohmic resistance in the PPY film. Other advantages of porous electrodes have also been observed. Sharma et al. found improved adhesion of thin PPY films to porous Si electrodes compared to planar electrodes, resulting in greater durability and higher cycle lifetime. The authors also reported that depositing PPY on porous Si substrates increased the porosity of the PPY itself through the formation of “nano-porous” channels in the pseudocapacitive film. An et al. observed greater capacitance retention at high discharge rates for single-walled PPY-CNT electrodes compared to pure PPY, which they attributed to lower ESR for the porous electrode.

Besides the advantages conferred by their high surface area and porous structure, CNTs in particular have unique benefits as an electrode material for conducting polymers. One of the most significant benefits is the mechanical flexibility of CNTs, which relieves stresses in the PPY film during cycling. CNTs have also been found to increase the conductivity of PPY in its reduced (non-conducting) state by acting as an anionic dopant. Wu et al. hypothesized that delocalized electrons in the CNTs may be capable of interacting with pi bonds in conducting polymers to increase polymer conductivity. Finally, Han et al. observed enhanced thermal stability for PPY-CNT composites compared to pure PPY electrodes at elevated temperatures.
The majority of PPY-CNT works use randomly oriented CNTs, likely due to ease of fabrication.\textsuperscript{5,14,19,22,23,26,31,33} Within the research literature on PPY-CNT composites, however, growing evidence suggests that vertically aligned CNT electrodes may enhance PPY supercapacitor performance compared to randomly oriented CNTs.\textsuperscript{63} Three factors support the use of VACNTs vs. randomly oriented CNTs as PPY supercapacitor electrodes. First, aligned CNTs enable greater electrolyte ion mobility, which can improve the uniformity of PPY deposited by solution methods.\textsuperscript{63} Second, higher electrolyte conductivity in VACNT pores increases capacitance, especially at high scan rates.\textsuperscript{93} Finally, VACNTs can be grown directly on a conductive substrate with low contact resistance between the CNTs and the current collector.\textsuperscript{94} Randomly oriented PPY-CNT supercapacitors, in contrast, often require polymer binding agents to connect the CNTs to a current collector.\textsuperscript{65,81,95,96} These binding agents add weight and electrical resistance to the supercapacitor electrode. In some cases, conducting agents are even added to the binding agents, further increasing electrode mass.\textsuperscript{78,83} For randomly oriented CNT electrodes, the drawbacks of binding agents and low electrolyte conductivity can sometimes completely negate the advantages of using a PPY-CNT composite. Han et al., for example, prepared PPY-CNT electrodes by first coating the CNTs with a dodecylbenzenesulfonate sheath to help disperse the nanotubes uniformly in solution.\textsuperscript{92} The authors found no difference in supercapacitor performance for the PPY-CNT composite vs. pure PPY, likely because there was no direct bonding between conducting polymer and CNTs.

In addition to electrode structure, PPY synthesis method also has a significant impact on supercapacitor performance. The simplest method is chemical polymerization, in which the polymer is formed through oxidation of a monomer solution.\textsuperscript{69,97} Frackowiak et al. found that chemical polymerization of PPY onto CNT electrodes produces globular, irregular deposits of small PPY particles on the CNTs.\textsuperscript{63,64} During electrochemical polymerization, polymer formation and in-situ doping occurs when a potential is applied to the deposition substrate, causing oxidation and self-assembly of the monomers and dopant ions. Advantages of electrochemical deposition include: better uniformity, especially in porous electrodes; decreased contact resistance due to direct adhesion of the polymer to the electrode; and good control of conducting polymer thickness by varying electropolymerization current and deposition time.\textsuperscript{82,84,88,89,97} As a variation of electrochemical polymerization, some works have also used “electro-co-deposition” to form PPY-CNT composites. The composites form when electrodeposition is applied to a solution of monomer and dispersed CNTs, enabling the CNTs to act as an anionic dopant for the PPY (as described above).\textsuperscript{73,90}

Finally, conducting polymer pseudocapacitance also depends on the choice of electrolyte and dopant ions.\textsuperscript{69,98} Noh et al. tested the performance of PPY powders chemically synthesized in three different solvents: H$_2$O, diethyl ether, and acetonitrile. The resulting capacitance varied by a factor of 7x as a result of differences in PPY solubility in the three solutions.\textsuperscript{99} Paul et al. observed that electrolyte pH significantly affects PPY-CNT composite stability. Electrodes tested in neutral electrolyte demonstrated higher cycle lifetime compared to electrodes tested in acidic electrolyte, and much greater stability than those tested in potassium hydroxide.\textsuperscript{83} The authors also found performance differences between PPY-CNTs synthesized by chemical oxidation in water, dichloromethane, or $n$-hexane, with the dichloromethane composites exhibiting much lower specific capacitance due to decreased uniformity in the PPY coating.\textsuperscript{83}
3.3 Hybrid PPY-VACNT supercapacitor design

Previous research has demonstrated the importance of electrode structure, PPY synthesis method, as well as choice of dopant ions and electrolyte in determining the performance of PPY supercapacitors. The present work builds on previous knowledge in creating a new, hybrid PPY-VACNT electrode design for enhanced PPY supercapacitor performance. The proposed design uses a VACNT electrode with CNTs grown directly on a conducting substrate to avoid the need for binding agents. The CNTs are coated with a thin layer of PPY using electrodeposition to achieve good uniformity and control of the PPY coating. During electrodeposition, the depositing PPY film is doped with sodium dodecylbenzenesulfonate (NaDBS). DBS− is a large surfactant ion that, due to its size, becomes trapped within the PPY matrix during synthesis. As a result, instead of the traditional doping and de-doping mechanism of most conducting polymer pseudocapacitors, charge storage is achieved by highly mobile Na+ ions moving into and out of the PPY film. The PPY-VACNT supercapacitor uses an organic electrolyte to increase the cell voltage range. PPY is also known to have good stability and performance in organic electrolytes.

Figure 3.2 compares the operation of an EDLC (Figure 3.2a), a pure PPY pseudocapacitor (Figure 3.2b), and the hybrid PPY-VACNT supercapacitor (Figure 3.2c). In the EDLC, Na+ and DBS− ions store charge as an electric double layer at the supercapacitor anode and cathode, respectively. In the pure pseudocapacitor, PPY switches from its reduced (undoped) state to its oxidized (p-doped) state during charge storage. As described above, DBS− ions remain trapped in the PPY matrix as Na+ ions move into and out of the PPY. The hybrid PPY-VACNT electrode design uses both double layer capacitance and pseudocapacitance. As shown in the left side of Figure 3.2c, the hybrid supercapacitor uses pseudocapacitance at positive potentials when PPY is oxidized and conductive. The electrochemical potential for reduction of PPY is −257 mV vs. Ag/AgCl. At potentials less than −257 mV, PPY is non-conducting and the hybrid pseudocapacitor stores charge by EDLC, with Na+ ions forming an electric double layer at the surface of the PPY-coated CNTs.
**Figure 3.2.** Conceptual illustration of charge storage in an EDLC, pseudocapacitor, and hybrid supercapacitor. (a) In an EDLC, charge storage occurs as electrolyte ions move to opposite electrodes and form an electric double layer at the porous electrode surfaces. Na$^+$ and DBS$^-$ ions are represented as purple and green circles, respectively. (Although the DBS$^-$ ions are much larger than the Na$^+$ ions, the circles are drawn as equal size for clarity). (b) In the pure PPY pseudocapacitor, a thin-film PPY electrode (PPY is represented by the red lines) forms a porous matrix that enables movement of Na$^+$ ions into and out of the PPY as it switches between oxidized and reduced states. (c) In the hybrid supercapacitor, VACNTs are coated with PPY as a combined pseudocapacitor/EDLC (only one PPY-coated CNT is shown for clarity). The hybrid supercapacitor design works as a pseudocapacitor at positive voltages and an EDLC at negative voltages. Reproduced from Ref. 100 with permission from Elsevier.
3.4 PPY-VACNT supercapacitor electrode fabrication

VACNTs were first synthesized on Si substrates by a chemical vapor deposition technique described in Appendix A. The CNT growth time was 10 min in a mixture of hydrogen and ethylene gas. A molybdenum (Mo) contact layer between the CNTs and the Si substrate serves as a current collector for the supercapacitor electrodes (see Figure A.1).

Following the VACNT growth process, PPY was electrodeposited onto the CNT electrodes from a solution of 0.1 M pyrrole and 20 mM NaDBS in acetonitrile. Pyrrole (98%), acetonitrile (99.8%), and NaDBS (technical grade) were all purchased from Sigma Aldrich. No pre-treatment of the CNTs was needed for coating with PPY. Electrodeposition was conducted using a constant current density of 1 mA/cm² in a three-electrode cell with a platinum wire CE and Ag/AgCl RE. Electrodeposition times were varied from 30 s to 4 min to give a range of PPY thicknesses.

Figure 3.3 provides a conceptual illustration of the electrodeposition process for PPY on VACNTs with in-situ NaDBS doping. An anodic electrode current attracts pyrrole monomers in the electrolyte solution to the surface of the CNTs (Figure 3.3a). Monomers contacting the CNTs are oxidized and self-assemble into polymer chains that eventually become insoluble and precipitate onto the CNTs (Figure 3.3b). DBS⁻ ions are attracted to the oxidized pyrrole monomers and incorporated into the polymer chains during polymerization (Figure 3.3c). The structure of DBS⁻ is illustrated below the figure.

![Figure 3.3](image)

Figure 3.3. Conceptual illustration of electrodeposition and in-situ doping of PPY on CNTs. (a) An anodic current is applied to the CNT substrate, which attracts pyrrole monomers to the CNT surface. Na⁺ and DBS⁻ ions are also present in the electrolyte. (b) Pyrrole monomers are electrochemically oxidized and self-assemble into polymer chains. (c) Large PPY molecules are insoluble in the electrolyte and precipitate onto the CNTs. DBS⁻ ions, attracted to the oxidized pyrrole monomers, are incorporated into the polymer chains. Adapted from Ref. 100 with permission from Elsevier.
3.5 Characterization of hybrid PPY-VACNT supercapacitor electrodes

SEM and TEM imaging were used to determine the physical characteristics of uncoated VACNT and PPY-VACNT electrodes. Figure 3.4 shows cross-sectional SEM images of an uncoated VACNT electrode. The as-grown CNTs have a forest height of approximately 40 µm with well-aligned structure, and grow uniformly across the Si substrate (Figure 3.4a). A close-up view of the VACNTs in Figure 3.4b shows that the CNT forest has high porosity, which is important for uniform PPY electrodeposition and good penetration of electrolyte into the CNT forest. Figure 3.4c provides a close-up view of the CNT-Mo interface, showing good contact between the CNTs and the Mo current collector. A previous study of VACNTs grown on a Mo substrate by the same synthesis method measured a low contact resistance of approximately $5 \times 10^{-3} \ \Omega \cdot \text{cm}^2$ between the VACNTs and Mo back-contact.\(^{106}\)

![Figure 3.4. SEM images of uncoated VACNT electrodes. (a) Cross-section of the as-grown VACNT forest. (b) Close-up view of the uncoated CNTs, showing high porosity of the CNT forest. (c) Close-up view of the interface between VACNTs and the Mo/SiO$_2$/Si substrate. The uneven edge of the Mo thin film is a result of breaking the sample for cross-sectional SEM imaging. Adapted from Ref. 100 with permission from Elsevier.](image-url)
Figure 3.5 provides SEM images of PPY-coated VACNTs (1 min electrodeposition time). As shown in Figure 3.5a, the PPY-coated CNTs have aggregated to form distinct ridges of bundled CNTs. While the CNTs are still well-anchored to the substrate and retain their vertical structure, CNT forest height is significantly reduced compared to uncoated VACNTs (8.6 µm vs. 40 µm). Similar bundling has been observed in other works and is attributed to capillary forces between CNTs during evaporative drying.\textsuperscript{107–109} Although the porosity of the VACNTs is reduced by the CNT bundling, a top-view SEM image in Figure 3.5b shows that the PPY-CNTs still constitute a porous structure with voids between the CNTs for electrolyte penetration. As discussed in the following section, electrochemical surface area measurements demonstrate that the high surface area of the CNT electrode is preserved even with CNT bundling.

Figure 3.5. SEM images of a PPY-VACNT electrode. (a) Cross-sectional view of the PPY-VACNT showing aggregation of the CNTs and the formation of CNT ridges. (b) Top view of the PPY-CNT electrode. Adapted from Ref. 100 with permission from Elsevier.
While SEM images effectively characterize the structure of PPY-CNT electrodes, the nature of the PPY coating on CNTs is best seen in TEM images. Figure 3.6 compares TEM images of uncoated CNTs (Figure 3.6a) and PPY-coated CNTs (4 min electrodeposition time) (Figure 3.6b). As shown in Figure 3.6b, the PPY coating is conformal and fairly uniform over the full CNT. TEM images were used to determine the thickness of PPY electrodeposition by comparing the average outside diameters of uncoated vs. PPY-coated CNTs. Figure 3.7 provides histograms of outside diameter measurements for uncoated CNTs, 1 min PPY electrodeposition, and 4 min PPY electrodeposition. Average and standard deviation values are based on 35 measurements of distinct CNTs. Uncoated CNTs have an average outside diameter of approximately 22.5 nm (Figure 3.7a). Electrodeposition times of 1 min and 4 min give average PPY coating thicknesses of 9.7 nm and 32 nm respectively, suggesting that coating thickness varies approximately linearly with electrodeposition time. A much wider distribution of PPY-CNT outer diameter measurements is observed for 4 min PPY electrodeposition compared to both uncoated CNTs and 1 min PPY electrodeposition, indicating that the coating process becomes less uniform across the electrode area with longer deposition times.

Figure 3.6. TEM images of: (a) uncoated CNTs, and (b) a PPY-coated CNT (4 min electrodeposition time). Reproduced from Ref. 100 with permission from Elsevier.
Figure 3.7. Histograms and normal distributions of outside diameter measurements for: (a) uncoated CNTs, (b) 1 min PPY electrodeposition on CNTs, and (c) 4 min PPY electrodeposition on CNTs. TEM images (right column) show representative outer diameter measurements.
3.6 CV measurements and capacitance

CV measurements were used to compare the performance of: 1) pure PPY films of different thicknesses; 2) uncoated VACNT, pure PPY, and PPY-VACNT electrodes; and 3) PPY-VACNTs with different PPY electrodeposition times. Electrodes were tested in 20 mM NaDBS in acetonitrile using a three-electrode test cell, as described in chapter 2. The electrode scan range was -1.0 V to 1.0 V vs. Ag/AgCl, and the CV scan rate was held constant at 100 mV/s, which corresponds to a full charge-discharge cycle in 40 s.

Figure 3.8a shows CV measurements of pure PPY electrodes with three different PPY thicknesses: 50 nm, 100 nm, and 200 nm. Comparing the CV graphs of each of the three films, it is evident that the thickness of the pure PPY film has negligible influence on the total capacitance. Based on this observation, it appears that at these thicknesses (50 nm–200 nm) faradaic electron charge transfer in PPY is mostly a surface phenomenon as opposed to a volumetric phenomenon. This result suggests that for porous electrodes, thinner PPY films would be favorable because of the higher surface-area-to-volume ratio and therefore higher capacitance. From a process point of view, thinner PPY films are also advantageous because of the shorter electrodeposition times.

Figure 3.8b compares CV measurements of uncoated VACNT, pure PPY, and PPY-VACNT electrodes. The measured areal capacitance of the PPY-VACNT electrode is 5 mF/cm², which is 500% higher than that of uncoated VACNTs or pure PPY film. This result demonstrates that by combining the optimal operational voltage ranges of CNT double layer capacitance and PPY pseudocapacitance, the useful voltage range of the hybrid supercapacitor expands, and charge-discharge currents can exceed the sum of VACNTs and PPY operated individually. The 5x enhancement in capacitance with the PPY-VACNT composite electrode is likely due to increased surface area and enhanced ion diffusion in the PPY, as well as improved electrical conductivity for the thin PPY coating on conducting CNTs.

Figure 3.8c shows CV curves for PPY-VACNT electrodes with PPY deposition times of 0.5, 1, 1.5, and 2 min; Figure 3.8d compares the relative capacitance of these four electrodes as a function of electrodeposition time. The results indicate that 1 min is the optimal PPY deposition time for maximizing total capacitance of the PPY-VACNT nanocomposite. For short electrodeposition times (less than 1 min), there is likely insufficient PPY on the CNTs to achieve high pseudocapacitance. As electrodeposition time increases, total surface area of the PPY-VACNTs decreases due to the thicker PPY coating. This reduces total capacitance since both double layer capacitance and pseudocapacitance are surface phenomenon. Longer deposition times may also cause bridging of the gaps between VACNTs as PPY deposited at the top and sides of the electrode obstructs electrolyte flux through the CNT forest, resulting in non-uniform PPY deposition. Evidence of non-uniform deposition can be seen in Figure 3.7c with the wide spread in PPY thicknesses for a 4 min electrodeposition time. A 1 min electrodeposition time maximizes PPY pseudocapacitance without compromising the surface area of VACNTs that is available for double layer capacitance, thus achieving maximum hybrid supercapacitor performance.
Figure 3.8. CV measurements and capacitance of pure PPY and PPY-VACNT supercapacitor electrodes. (a) CV measurements of pure PPY films show little difference in charging and discharging currents with different PPY thicknesses (50 nm, 100 nm, and 200 nm). (b) Comparison of CV curves for uncoated VACNT, pure PPY, and PPY-VACNT electrodes. The PPY-VACNT electrode exhibits 5x greater capacitance compared to uncoated CNTs and pure PPY. (c) CV measurements of PPY-VACNT electrodes with PPY electrodeposition times of 0.5, 1, 1.5, and 2 min. (d) Capacitance vs. electrodeposition time for PPY-VACNT electrodes. Capacitance values are plotted as a fraction of maximum capacitance achieved with a 1 min electrodeposition time ($C_{\text{max}}$). Data point colors correspond to the CV curves in (c). Adapted from Ref. 100 with permission from Elsevier.

The theory that decreasing capacitance of PPY-VACNT electrodes for electrodeposition times above 1 min (Figure 3.8d) is due to lower electrode surface area can be verified by measuring the active electrochemical surface areas of PPY-VACNT electrodes. Electrochemical surface area measurement is based on comparing the double layer capacitance of two or more electrodes, since double layer capacitance is proportional to total surface area (provided that the electrodes are of the same material). CV measurements are taken at different scan rates, and double layer capacitance for each electrode is estimated from a linear fit of current vs. scan rate. Relative surface area is approximated by comparing the double layer capacitance of each electrode. It is important that the CV measurements are conducted in a scan range without pseudocapacitance so that only double layer capacitance is considered.
The electrochemical surface areas of pure PPY and PPY-VACNTs (1 min and 4 min electrodeposition times) were compared using this technique. CV measurements were conducted in the non-faradaic scan range for PPY (−0.5 V to −0.3 V) at scan rates of 2, 5, 10 and 20 mV/s. **Figure 3.9a** shows the resulting CV curves for PPY-VACNTs with 1 min electrodeposition time. Average double layer current for each scan rate was approximated as half the difference between anodic and cathodic currents at a potential of −0.4 V. **Figure 3.9b** compares current vs. scan rate measurements for pure and PPY-VACNT electrodes. Linear curve fits have good agreement with measured values, with $R^2$ values ranging from 0.89 to 0.95. **Table 3.1** summarizes double layer capacitance and relative surfaces areas for the three electrodes. The results show that the electrochemical surface area of the 1 min PPY-VACNT electrode is 5x greater than the 4 min PPY-VACNT electrode, and 17x greater than the pure PPY sample. The measurements thus confirm the theory of decreasing electrode surface area with increasing PPY electrodeposition time.

**Figure 3.9.** Electrochemical surface area measurement of pure PPY and PPY-VACNT electrodes. (a) CV curves for 1 min electrodeposited PPY-VACNT electrode at scan rates of 2, 5, 10, and 20 mV/s. (b) Double layer current vs. scan rate for pure PPY and PPY-VACNT electrodes (1 min and 4 min electrodeposition times). Linear fit equations and $R^2$ values are provided for each curve. Reproduced from Ref. 100 with permission from Elsevier.

**Table 3.1.** Comparison of double layer capacitance and relative surface areas for pure PPY, 1 min PPY-VACNT, and 4 min PPY-VACNT electrodes. Pure PPY is designated a reference surface area of “1”. Reproduced from Ref. 100 with permission from Elsevier.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Capacitance (µF/cm²)</th>
<th>Relative Surface Area</th>
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</thead>
<tbody>
<tr>
<td>Pure PPY</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>1 min PPY-VACNTs</td>
<td>500</td>
<td>17</td>
</tr>
<tr>
<td>4 min PPY-VACNTs</td>
<td>110</td>
<td>3.7</td>
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</tbody>
</table>
An interesting question is whether the PPY-VACNT composite improves the conductivity of PPY in its reduced state through anionic doping by the CNTs, as reported in some previous works.\textsuperscript{63,80,111} Table 3.2 compares the capacitance of pure PPY and PPY-VACNT electrodes in the non-conducting range of PPY (−0.3 V to −1.0 V). In this range, double layer capacitance is the primary charge storage mechanism. If PPY conductivity had increased due to anionic doping by the CNTs, one would expect the double layer capacitance contribution in the range of −0.3 V to −1.0 V to increase as a fraction of total electrode capacitance. As shown in Table 3.2, the absolute value of capacitance from −0.3 V to −1.0 V has increased for PPY-VACNTs compared to pure PPY, however the percent capacitance contribution is the same. The percent contribution from −0.3 V to −1.0 V is also similar to uncoated VACNTs. These results indicate that increased surface area, rather than enhanced conductivity, is the main factor contributing to high double layer capacitance of PPY-VACNTs in the non-pseudocapacitive range. The conductivity improvement reported in other works is not observed here, suggesting that this might be an interesting area for further study.

**Table 3.2.** Comparison of double layer capacitance contribution in the potential range of −0.3 V to −1.0 V for pure PPY, PPY-VACNT, and uncoated VACNT electrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Capacitance (mF/cm(^2)) (−0.3 V to −1.0 V)</th>
<th>% of total capacitance (−0.3 V to −1.0 V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PPY</td>
<td>0.18</td>
<td>24.1</td>
</tr>
<tr>
<td>PPY-VACNTs</td>
<td>0.54</td>
<td>25.1</td>
</tr>
<tr>
<td>Uncoated VACNTs</td>
<td>0.16</td>
<td>25.2</td>
</tr>
</tbody>
</table>

### 3.7 Chronoamperometry measurements and leakage current

Repeated chronoamperometry was used to characterize the current profile and leakage current of PPY-VACNT electrodes. Alternating charge and discharge step potentials of 0.5 V and 0 V, respectively, were applied to the sample electrode for 5 s intervals. Current measurements show that the PPY-VACNT nanocomposite undergoes highly reversible cycling over many charge-discharge cycles (first 100 s of a 500 s measurement are shown in Figure 3.10a). Figure 3.10b plots input step potential (top) and resulting current (bottom) for the PPY-VACNT electrode during a single charge-discharge cycle. To characterize charge storage for the hybrid supercapacitor as double layer capacitance vs. pseudocapacitance, the following equations were used to fit capacitive (\(i_d \propto e^{kt}\)) and faradaic (\(i_f \propto t^{1/2}\)) current models to the measured charging current:

\[
i_d = i_o e^{-0.7t} \quad \text{Equation 3.1}
\]

\[
i_f = \frac{323}{\sqrt{t}} + 150 \quad \text{Equation 3.2}
\]

where \(i_d\) is double layer current, \(i_f\) is faradaic current, \(t\) is time elapsed since the start of charging, and \(i_o\) is the initial current at time \(t = 0\). As shown in Figure 3.10b, the measured charging current initially follows an exponential decay characteristic of double layer capacitance (equation 3.1).
before transitioning to a good fit with the faradaic model (equation 3.2). This result is consistent with the faster response time of physical charge storage in EDLC vs. chemical charge storage in pseudocapacitance, and verifies the hybrid nature of the PPY-VACNT supercapacitor electrode.

For an ideal supercapacitor electrode, charge and discharge currents are symmetric about 0 A/cm$^2$. For a non-ideal electrode, leakage current results in asymmetric charge and discharge currents, with discharge current saturating to 0 A/cm$^2$ and charge current saturating to a non-zero leakage value. The difference in magnitude between chronoamperometry charge and discharge currents therefore provides an indication of supercapacitor leakage current. Figure 3.10c compares charge minus discharge currents for uncoated VACNT, 1 min PPY-VACNT, and 4 min PPY-VACNT electrodes. The 1 min PPY-VACNT electrode has the lowest leakage current compared to uncoated VACNT and 4 min PPY-VACNT electrodes. This result is likely due to better uniformity of the PPY coating for the 1 min vs. 4 min electrode, and lower exposed impurities in the 1 min PPY-VACNT electrode compared to uncoated CNTs. Non-uniform PPY deposition in the case of 4 min PPY-VACNTs increases concentration and potential gradients across the electrode that promote loss of ions from the electric double layer and reverse redox reactions in the PPY. In the case of uncoated CNTs, leakage current may arise from residual CNT fabrication impurities, including iron and aluminum catalyst particles. These impurities would have less contact with the electrolyte when coated with PPY, thus reducing leakage current in the hybrid supercapacitor. Leakage current for the 1 min VACNT-PPY electrode is approximately 5% of the total current.
Figure 3.10. Chronoamperometry measurements, capacitance modeling, and estimated leakage current for PPY-VACNT electrodes. (a) Repeated chronoamperometry measurements of a 4 min PPY-VACNT electrode. (b) Input potential (top) and resulting current measurement (bottom) for the electrode in (a) during a single charging step. Measured current initially follows a double layer capacitance model and then a faradaic model. (c) Charge minus discharge current for uncoated VACNT, 1 min PPY-VACNT, and 4 min PPY-VACNT electrodes. The saturation value of net current provides an indication of electrode leakage current. Reproduced from Ref. 100 with permission from Elsevier.

3.8 EIS measurements and equivalent circuit modeling

Figure 3.11a compares the electrochemical impedance profiles of an uncoated VACNT electrode and a PPY-VACNT electrode (4 min electrodeposition) in a Nyquist plot of real vs. imaginary impedance. Electrochemical impedance was measured using the three-electrode EIS technique described in chapter 2. EIS measurements were taken in the conducting range of PPY using an AC potential of 10 mV and 0 V DC offset. The ESR ($R_s$) of each electrode was estimated by extrapolating the Nyquist curves to their primary x-intercept, as indicated by the dashed lines in Figure 3.11a. The series resistance of the PPY-VACNT hybrid electrode is lower than that of the uncoated VACNT electrode by 28% (0.36 kΩ vs. 0.5 kΩ). This result reflects the conductivity enhancement of the pure CNT electrode with the addition of conducting PPY. As discussed in chapter 2, a low series resistance is important for high supercapacitor electrode power, suggesting the potential for enhanced maximum power output with the hybrid PPY-VACNT electrode design.
Electrochemical impedance measurements of uncoated VACNT and PPY-VACNT electrodes were modeled using the Randles equivalent circuit described in chapter 2 (Figure 2.7). **Table 3.3** summarizes Randles circuit parameters for VACNT and PPY-VACNT supercapacitors calculated using the Simplex non-linear least-squares fitting algorithm in Gamry Echem Analyst software. For both VACNT and PPY-VACNT electrodes, the series resistance of the model was fixed to match the x-intercept estimated from the Nyquist plot. Double layer capacitance is represented by the parameter $C_d$ (equation 2.12). An increase in $C_d$ for the hybrid PPY-VACNT electrode compared to uncoated VACNTs suggests that the EDLC of the PPY-VACNT supercapacitor is higher than that of pure CNTs. The model also shows an increase in Warburg impedance—indicative of diffusion resistance—for the PPY-VACNT nanocomposite. Higher Warburg impedance for the hybrid PPY-VACNT electrode is expected given: 1) the smaller pore sizes for ion diffusion in the PPY-coated CNTs, and 2) the capillary-induced bundling of PPY-VACNTs observed in SEM images (Figure 3.5). The higher charge transfer resistance for the PPY-VACNT supercapacitor shown in Table 3.3 is also expected given the additional reduction and oxidation reactions of the PPY coating. “Goodness of fit” values for both the VACNT and PPY-VACNT models are considered “good” to “fair” (between 1% and 10% error). Model fit can also be seen in the Bode plots of Figure 3.11b and Figure 3.11c for uncoated VACNT and PPY-VACNT electrodes, respectively.

**Table 3.3. Summary of Randles equivalent circuit parameters for EIS modeling of uncoated VACNT and PPY-VACNT electrodes. Reproduced from Ref. 100 with permission from Elsevier.**

<table>
<thead>
<tr>
<th>Model Parameter</th>
<th>Uncoated VACNT</th>
<th>PPY-VACNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$ (kΩ)</td>
<td>0.50</td>
<td>0.36</td>
</tr>
<tr>
<td>$C_d$ ($10^9$ Ω$^{-1} \cdot$ s$^α$)</td>
<td>8.5 ± 2.1</td>
<td>80.3 ± 15.8</td>
</tr>
<tr>
<td>$α$</td>
<td>0.84 ± 0.02</td>
<td>0.66 ± 0.02</td>
</tr>
<tr>
<td>$W$ ($10^4$ Ω$^{-1} \cdot$ s$^{1/2}$)</td>
<td>3.5 ± 0.07</td>
<td>8.2 ± 0.4</td>
</tr>
<tr>
<td>$R_{ct}$ (kΩ)</td>
<td>1.8 ± 0.01</td>
<td>2.4 ± 0.02</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>0.003</td>
<td>0.0013</td>
</tr>
</tbody>
</table>

Note that $C_d$ in the Randles circuit model is representative, rather than a true measure, of double layer capacitance. A 10x increase in the Randles $C_d$ parameter indicates an increase in double layer capacitance, though not necessary an increase of exactly 10x.
Figure 3.11. EIS measurements and equivalent circuit modeling of uncoated VACNT and 4 min PPY-VACNT supercapacitor electrodes. (a) Nyquist plot showing the reduction in ESR for the PPY-VACNT hybrid electrode compared to uncoated CNTs. (b), (c) Bode plots with Randles equivalent circuit model results ("Fit magnitude" and "Fit phase") for uncoated VACNT and PPY-VACNT electrodes, respectively. Reproduced from Ref. 100 with permission from Elsevier.
3.9 Life cycle testing

Life cycle testing of PPY-VACNT electrodes was conducted to determine stability over several thousand charge-discharge cycles. **Figure 3.12a** compares the change in capacitance of 1 min and 4 min electrodeposited PPY-VACNT electrodes cycled between ±0.5 V at a scan rate of 100 mV/s for 3000 cycles. The 4 min electrode reached its maximum capacitance after 1000 cycles. This increase in capacitance over the first 1000 cycles is likely due to electrochemical stabilization of the device, and has been observed in other PPY-based supercapacitors. After 3000 cycles, the 4 min electrodeposited PPY-VACNT nanocomposite maintained 92% of its maximum capacitance (capacitance at 1000 cycles). The 1 min electrodeposited PPY-VACNT electrode was not as stable as the 4 min electrode, with a 35% capacitance decrease over 3000 cycles. When a 1 min electrodeposited PPY-VACNT electrode was tested over a scan range of ±1.0 V, capacitance decreased by 60% over 1000 cycles, suggesting that a wider scan range is damaging to the electrode over many cycles.

Figure 3.12b compares the CV curves for the 4 min PPY-VACNT electrode after 10 and 3000 cycles, further illustrating the excellent electrode stability. SEM and TEM images of the PPY-coated CNTs after life cycle testing (Figure 3.12c and Figure 3.12d, respectively) show that the CNTs are still well coated with PPY after 3000 CV cycles. There was no observed delamination of the VACNTs from the substrate during life cycle testing, even though the electrodes were in solution for 17 hours. A previous study of VACNTs fabricated by the same method on Mo/SiO$_2$/Si substrates found that delamination of the Mo layer from the SiO$_2$/Si substrate may occur after 96 hours in solution. This delamination can be prevented using a chromium adhesion layer between the Mo and SiO$_2$ layers.
Figure 3.12. Life cycle testing of PPY-VACNT electrodes. (a) Relative capacitance vs. cycle number comparison of 1 min and 4 min PPY-VACNT electrodes tested for 3000 cycles with a voltage window of ±0.5 V, and a 1 min PPY-VACNT electrode tested for 1000 cycles with a voltage window of ±1.0 V. (b) Comparison of CV curves for the 4 min PPY-VACNT electrode after 10 and 3000 cycles. (c), (d) SEM and TEM images, respectively, of 4 min PPY-coated CNTs after 3000 charge-discharge cycles. Reproduced from Ref. 100 with permission from Elsevier.

3.10 Discussion

To evaluate the performance of the hybrid PPY-VACNT supercapacitor electrodes developed in this work, capacitance results can be compared with other PPY supercapacitor results from the literature, as well as the maximum theoretical capacitance for PPY-CNTs. Due to the wide range of supercapacitor test conditions in the literature, it is best to compare relative performance increase for PPY-CNTs vs. uncoated CNTs, rather than absolute capacitance values. Han et al., as described in the literature review (section 3.2), found no increase in capacitance for PPY-CNT electrodes compared to uncoated CNTs using randomly oriented CNTs coated with a DBS
Frackowiak et al., using randomly oriented CNT electrodes, reported 2x enhancement in capacitance for PPY-coated CNTs compared to both uncoated CNTs and pure PPY. Hughes et al. also reported a 2x increase in capacitance for PPY-CNT electrodes compared to uncoated CNTs, in this case using randomly oriented CNTs and anionic doping of the PPY by the CNTs. Chen et al. is the only work that measured greater than 5x improvement with PPY-CNTs compared to uncoated CNTs, with a 5.6x increase in performance. The 5x capacitance improvement achieved in this work is therefore comparable to—or exceeds—other works reported in the literature. Cycle lifetime of the PPY-VACNT electrodes developed here is also high compared to other works. PPY-CNT supercapacitors reported in Frackowiak et al. maintained only 80% of their initial capacitance after 2000 cycles, while the PPY-VACNT hybrid supercapacitor electrode developed in this work maintained 92% of maximum capacitance after 3000 cycles.

One possible option for improving the performance of the hybrid PPY-VACNT supercapacitor electrode developed in this work would be to prevent the bundling of CNTs observed in Figure 3.5. VACNT bundling negatively affects supercapacitor electrode performance by preventing full utilization of the CNT surface area, increasing electrolyte diffusion resistance, and causing non-uniform deposition of PPY. There are several possible methods to address CNT bundling. Chen et al. observed that aligned PPY-CNTs bundle only with thin PPY coatings; with PPY thickness above 90 nm, the CNTs retain their vertical structure. However, is likely too thick to achieve good hybrid supercapacitor performance, as indicated by the capacitance vs. PPY electrodeposition time results in Figure 3.8d (1 min electrodeposition time corresponds to 9.7 nm PPY thickness). Other investigations of CNT dispersions have found numerous polymers and surfactants that stabilize CNTs in aqueous and non-aqueous electrolytes, including polyvinylpyrrolidone (PVP) and poly(tetrafluoroethylene) (PTFE). The additional weight and electrical resistance from these additives would likely decrease supercapacitor performance, however, and may counteract the benefits of CNT stabilization. The method of Kim et al. may be the most promising for controlling the porous structure of the PPY-VACNT electrode while still maintaining high supercapacitor performance. The authors used silica nanoparticles as a sacrificial filler to maintain the porous structure of the CNTs during PPY electrodeposition, controlling pore sizes by varying the amount of silica filler. With this method, they were able to maintain the porous structure of the PPY-CNT composite up to 80 wt% addition of PPY, and reported a 140% improvement in specific capacitance for PPY-CNT composites fabricated with vs. without silica nanoparticles. Performance improvement, however, would have to be weighed against the increased process complexity.

Another approach for assessing PPY-VACNT hybrid electrode performance is to compare with the maximum theoretical capacitance, including both pseudocapacitance and double layer capacitance. The theoretical pseudocapacitance of PPY is calculated using a variation of equation 2.2 adapted for polymer pseudocapacitors:

\[ C_{pseud} = \frac{\Delta E_s}{\Delta V} \]

A theoretical value for EDLC is difficult to determine due to complexities of ion solvation and Coulomb interactions in the electric double layer, which depend on electrode material, pore sizes, and electrolyte species. For this reason, “theoretical double layer capacitance” is not reported in the literature, to the best knowledge of the author. In place of a theoretical value, one of the highest reported values for CNT double layer capacitance is used as the maximum “theoretical” value.
\[ C_{PPY} = \frac{F\alpha}{M_{PY}\Delta V} \]  

\[ \text{Equation 3.3} \]

where \( \alpha \) is the number of redox electrons per pyrrole monomer (\( \alpha = 0.3 \)),\textsuperscript{74,115} and \( M_{PY} \) is the molar mass of pyrrole (67.09 g/mol). Equation 3.3 gives a maximum theoretical capacitance for PPY of 215 F/g for \( \Delta V = 2 \) V. The capacitance of PPY-VACNT hybrid electrodes is measured in F/cm\(^2\). To compare measured vs. theoretical capacitance, the theoretical capacitance of PPY can be converted to F/cm\(^2\) using measured values of PPY thickness and electrochemical surface area. For the PPY-VACNT electrode with 1 min electrodeposition, the average PPY thickness is 9.7 nm (Figure 3.7) and the electrochemically active surface area is 17x the electrode planar surface area (Table 3.1). Using a polypyrrole density of 1.48 g/cm\(^3\),\textsuperscript{116} the theoretical maximum pseudocapacitance of PPY for the 1 min PPY-VACNT electrode is 5.2 mF/cm\(^2\). One of the highest values of double layer capacitance reported in the literature for CNTs is 240 \( \mu \)F/cm\(^2\) (total surface area),\textsuperscript{117,118} which gives a maximum double layer capacitance for the 1 min PPY-VACNT electrode of 4.1 mF/cm\(^2\). Taking the sum of pseudocapacitance and double layer capacitance, the total theoretical capacitance is 9.3 mF/cm\(^2\).\textsuperscript{xvii} Measured capacitance for the 1 min PPY-VACNT electrode is quite close to the theoretical limit at 5 mF/cm\(^2\), or 54% of the maximum theoretical value.

There are a number of possible explanations for the relatively minor difference between measured and theoretical capacitance for the PPY-VACNT hybrid electrode. First, the PPY coating may not be fully doped with DBS\(^-\) ions in all areas of the electrode. Although the PPY coating thickness appears to be fairly uniform for 1 min electrodeposition (Figure 3.7b), some of the deposited PPY may not be electrochemically active if DBS\(^-\) ions were not accessing all areas of the CNT forest (note that DBS\(^-\) is a much larger molecule than pyrrole, as shown in Figure 3.3). Second, electrolyte diffusion resistance may prevent the full pseudocapacitance of PPY from being utilized at fast charge-discharge rates. Electrochemically active surface area was measured in the double layer capacitance region at slow scan rates of 2 to 20 mV/s, while the capacitance of the hybrid PPY-VACNT electrodes was measured at scan rates of 100 mV/s. As a test of this theory, future work could measure the capacitance of PPY-VACNT electrodes as a function of scan rate to see if there are performance limitations at high charge-discharge speeds. Finally, ohmic resistance in the VACNTs and at the CNT-Mo back-contact would also contribute to reducing PPY pseudocapacitance below the theoretical value. As described in section 3.1, the electrical conductivity of oxidized PPY is approximately \( 10^3 \) S/m, compared to 50 S/m for VACNTs.\textsuperscript{119} It would be interesting in future work to test the relative importance of each of these effects in reducing the capacitance of PPY-VACNTs below the theoretical maximum.

\[ \text{xvii} \] Note that the theoretical capacitance calculated based on total (non-bundled) CNT surface area would likely be higher than 9.3 mF/cm\(^2\). By using measured electrochemically active surface area to calculate theoretical capacitance, the effects of CNT bundling are removed from consideration, enabling other performance limitations to be assessed.
3.11 Summary

This chapter detailed the development of a novel PPY-VACNT hybrid supercapacitor electrode using NaDBS dopant and organic electrolyte. By combining VACNTs and PPY to form a nanocomposite, total capacitance of the hybrid supercapacitor increases by 500% compared to its individual components (uncoated VACNTs and pure PPY). A 1 min electrodeposition time, corresponding to a PPY thickness of 9.7 nm on CNTs, was found to give optimum hybrid supercapacitor performance. In addition to an increase in charge storage via pseudocapacitance, electrochemical impedance modeling results indicate that the PPY-VACNT electrodes have higher double layer capacitance compared to uncoated VACNTs. Chronoamperometry modeling also confirms the combined double layer capacitance and pseudocapacitance charge storage mechanisms of the hybrid PPY-VACNT supercapacitor electrode.

The results of this work demonstrate significant progress in overcoming current challenges in conducting polymer pseudocapacitor research, including addressing low rate capability, limited voltage range, and poor cycle lifetime. The PPY-VACNT hybrid electrode achieves rapid charging and discharging by using highly mobile Na$^+$ ions as the pseudocapacitive charge carrier (with DBS$^-$ dopant ions trapped in the PPY matrix). Chronoamperometry measurements demonstrate the excellent response of PPY-VACNT electrodes with 5 s charge/discharge steps, with the hybrid supercapacitors even exhibiting pseudocapacitive charge storage at this ultrahigh speed (Figure 3.10b). By using an organic electrolyte, the PPY-VACNT hybrid supercapacitor is able to operate over a 2.0 V potential range, double that of most PPYPseudocapacitors. Finally, life cycle testing results show that the PPY-VACNT supercapacitor electrode maintains 92% of its maximum capacitance over 3000 charge-discharge cycles with a potential range of 1.0 V (Figure 3.12a), one of the best cycle lifetime achievements for PPY. In the following chapter, the advantages of the VACNT electrode design that lead to high PPY supercapacitor performance will be explored for RuO$_x$ supercapacitors using a novel metal oxide pseudocapacitor fabrication method.
Chapter 4: ALD RuO<sub>x</sub> Supercapacitors

A central theme of chapters 1 to 3 has been the importance of pseudocapacitor electrode design and synthesis methods in achieving high supercapacitor energy storage. The previous chapter detailed the design and performance testing of a PPY-VACNT hybrid supercapacitor electrode with combined high double layer capacitance and pseudocapacitance. This chapter explores the second category of pseudocapacitive materials: metal oxides. The advantages of metal oxide pseudocapacitors include good electrochemical stability compared to conducting polymers, as well as high theoretical capacitance and energy density. Two important challenges in metal oxide pseudocapacitor research are: 1) developing fabrication methods for coating high surface area nanomaterials with thin films of metal oxide pseudocapacitors, and 2) achieving good proton and electron conductivity within these metal oxide films to support fast and reversible charge storage.

This chapter presents the development of atomic layer deposition (ALD) metal oxide pseudocapacitors, with a focus on ALD ruthenium oxide (RuO<sub>x</sub>) supercapacitors. Specific accomplishments of this work include: (1) successful demonstration of ALD RuO<sub>x</sub> on VACNT and porous Si electrodes with uniform coating, (2) evidence of hydrated RuO<sub>x</sub> deposition at low ALD temperatures, and (3) enhanced pseudocapacitive performance of the ALD RuO<sub>x</sub> films with post-ALD electrochemical oxidation. Results show 100x and 170x higher specific capacitance with the ALD RuO<sub>x</sub> coating and further electrochemical oxidation, respectively, compared to uncoated VACNT electrodes. The measured capacitance value of 644 F/g for ALD RuO<sub>x</sub>-VACNT electrodes is close to the theoretical limit, and RuO<sub>x</sub> pseudocapacitance was demonstrated even at an ultrahigh scan rate of 20 V/s.

The chapter begins with an overview of charge storage mechanisms in metal oxide pseudocapacitors. This is followed by a literature review of previous work on RuO<sub>x</sub> supercapacitors and ALD RuO<sub>x</sub>. The ALD supercapacitor design is then introduced, along with fabrication details, materials characterization, and performance testing results. Life cycle testing showed an increase in ALD RuO<sub>x</sub> capacitance with repeated cycling, suggesting that post-ALD electrochemical oxidation might improve pseudocapacitance in ALD RuO<sub>x</sub> films. The second part of the chapter therefore focuses on ALD RuO<sub>x</sub> performance enhancement with electrochemical oxidation, including capacitance, power and energy density, and capacitance vs. scan rate results. The chapter concludes with a discussion of future improvements to the ALD RuO<sub>x</sub> supercapacitor electrode design, and the general applicability of this work to other ALD metal oxide pseudocapacitors.

4.1 Metal oxide supercapacitors

Pseudocapacitive charge storage in metal oxides occurs by reduction-oxidation (redox) reactions, similar to conducting polymers. In order for a metal oxide to be a pseudocapacitive material, the metal must have multiple oxidation states within the electrochemical range of common electrolytes, and be able to undergo reversible redox reactions without phase change. The most commonly studied metal oxide pseudocapacitors are: RuO<sub>x</sub>, manganese oxide (MnO<sub>2</sub>), iron oxide (Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub>), vanadium oxide (V<sub>2</sub>O<sub>5</sub>), nickel oxide (NiO/Ni(OH)<sub>2</sub>) and cobalt (Co<sub>3</sub>O<sub>4</sub>/Co(OH)<sub>2</sub>) oxide. Metal oxide pseudocapacitors require good proton and electron
conductivity to achieve high capacitance, as charge can be stored in sub-surface layers through proton intercalation. Amorphous, hydrated metal oxides have greater proton conductivity than crystalline oxides, resulting in more electrochemically active redox sites and higher pseudocapacitance. Improved pseudocapacitive charge storage with hydrated metal oxides has been verified for RuO$_x$, MnO$_y$, V$_2$O$_5$, mixed cobalt-nickel oxides (a-(Co+Ni)(OH)$_2$•nH$_2$O), as well as Mo and tungsten oxides.

RuO$_x$ is considered one of the best pseudocapacitive metals oxides because it has high electrical conductivity (comparable to that of metals), undergoes fast and reversible redox reactions, and has three oxidation states available between 0 and 1.0 V. The redox equation for charge storage in RuO$_x$, showing the three oxidation states, is:

$$\text{RuO}_2 + x\text{H}^+ + xe^- \leftrightarrow \text{RuO}_{2-x}(\text{OH})_x \ ; \ 0 \leq x \leq 2$$

Equation 4.1

Although RuO$_x$ is a high-cost material, it remains the most extensively researched metal oxide pseudocapacitor because of its excellent pseudocapacitive properties. In this work, RuO$_x$ was chosen as a demonstration material for ALD metal oxide supercapacitors because of its high performance and well-studied electrochemical and pseudocapacitive properties.

4.2 Literature review of RuO$_x$ supercapacitors

Electrochemical energy storage using RuO$_x$ was first studied in the 1970s by Conway et al. Despite this early beginning, interest in RuO$_x$ supercapacitors did not develop significantly until the 1990s. Initial research on RuO$_x$ supercapacitors focused primarily on planar electrodes synthesized from composite mixtures of RuO$_x$ nanoparticles, activated carbon, and polymer binding agents. Recently, there has been growing interest in achieving high surface area, porous electrodes with thin-film or nanoparticle RuO$_x$ coating, similar to the development of high surface area conducting polymer pseudocapacitors described in chapter 3. To date, research on RuO$_x$ supercapacitors has made good progress towards understanding the optimal chemical and physical properties needed for high pseudocapacitance. Achieving these optimal properties with current RuO$_x$ synthesis methods remains a challenge, especially for high surface area, porous electrodes.

As described in section 4.1, RuO$_x$ requires good proton and electron conductivity for high pseudocapacitance. This understanding developed primarily through experimental optimization of RuO$_x$ supercapacitor electrodes. Zheng et al. were among the first to demonstrate high pseudocapacitance using amorphous, hydrated RuO$_x$. The authors observed that RuO$_{2-x}$H$_2$O prepared by solution method had significantly higher performance than anhydrous RuO$_x$ prepared by thermal decomposition. The capacitance of the hydrated electrode exceeded the theoretical value for RuO$_x$, assuming charge storage occurs only on the surface of the pseudocapacitive material. This discovery led to the theory that hydrated RuO$_x$ stores charge in subsurface layers, while pseudocapacitance in anhydrous RuO$_x$ is limited to the electrode-electrolyte interface. The difference arises because hydrated, amorphous RuO$_x$ has a more accommodating lattice structure with greater proton permeability than crystalline RuO$_x$.

Following this result, many researchers began studying the effects of processing conditions on electron and proton conductivity in RuO$_x$, in an effort to optimize pseudocapacitance and advance understanding of metal oxide charge storage mechanisms. A particularly well-
studied phenomenon is the effect of annealing temperature on RuO\textsubscript{x} pseudocapacitance. Brumbach \textit{et al.} reported optimal RuO\textsubscript{x} pseudocapacitance with an annealing temperature of 150 °C, which corresponds to RuO\textsubscript{2}·0.5H\textsubscript{2}O.\textsuperscript{52} Below 150 °C, increasing annealing temperature improves electron conductivity due to the formation of polycrystalline grains. Above 150 °C, however, decreasing proton conductivity due to RuO\textsubscript{x} dehydration outweighs improvements in electron conductivity, and pseudocapacitance decreases with further increases in annealing temperature.\textsuperscript{52} Many other works also report decreasing RuO\textsubscript{x} pseudocapacitance with processing temperatures above 200 °C.\textsuperscript{128,133,139} The results of McKeown \textit{et al.} illustrate the fundamental trade-off between high electron conductivity, which requires good crystallinity, and high proton conductivity, which requires a less-crystalline and more permeable RuO\textsubscript{x} lattice.\textsuperscript{140} The authors measured similar capacitance values for RuO\textsubscript{2}·0.29H\textsubscript{2}O and RuO\textsubscript{2}·2.32H\textsubscript{2}O electrodes, noting that the two electrodes likely have a comparable balance of proton and electron conductivity (the former having better proton conductivity and the latter better electron conductivity).

To achieve high specific capacitance, RuO\textsubscript{x} fabrication methods must provide good control of electrode structure and chemical composition as well as good uniformity over high surface areas.\textsuperscript{2} The most common precursor used in RuO\textsubscript{x} synthesis is RuCl\textsubscript{3}, which undergoes thermal decomposition to form anhydrous RuO\textsubscript{2} at temperatures of 300–500 °C.\textsuperscript{52,141} More frequently, RuCl\textsubscript{3} is processed using a sol-gel method by mixing with sodium hydroxide to form hydrated RuO\textsubscript{x} nanoparticles.\textsuperscript{120,128,133–136,138,139,142} These RuO\textsubscript{x} nanoparticles are then combined with activated carbon or other high surface area carbon materials to prevent aggregation and reduce electrode material cost.\textsuperscript{133,135,142,143} Drawbacks of the RuCl\textsubscript{3}-based sol-gel method include:

- Synthesis uniformity is difficult to control, as the method requires complex stirring, filtering, washing, drying, and annealing steps.\textsuperscript{31,128,130}
- The resulting RuO\textsubscript{x} nanoparticles or RuO\textsubscript{x}-carbon nanocomposites must be mixed with a polymer binding agent to form a paste or slurry that can be spread over a current collector. The binding agent adds weight to the electrode, decreases utilization of RuO\textsubscript{x}, and increases electrode contact resistance.\textsuperscript{128,131,133–135}
- The components of RuO\textsubscript{x}-binding agent composite slurries can become segregated in the mixture, resulting in non-uniform electrode composition and poor utilization of each component.\textsuperscript{144}
- Incomplete conversion of the RuCl\textsubscript{3} precursor to RuO\textsubscript{x} results in residual chloride contaminants in the nanocomposite electrodes.\textsuperscript{145}

Many researchers have developed variations of the RuCl\textsubscript{3} sol-gel synthesis method to overcome some of the above challenges. Hu \textit{et al.}, for example, used electrochemical deposition from a RuCl\textsubscript{3} solution to obtain better control over the synthesis, although the method still required a binding agent between the electrodeposited film and the titanium electrode contact.\textsuperscript{130} Jang \textit{et al.} avoided the use of the binding agents through electrophoretic deposition,\textsuperscript{xviii} though the resulting agglomerations of RuO\textsubscript{x} nanoparticles likely yielded poor utilization of the high surface area nanoparticles.\textsuperscript{144} Kim \textit{et al.} also achieved binder-free electrodes using electrostatic spray deposition of RuO\textsubscript{x} thin films from RuCl\textsubscript{3} solution, a method which requires high voltages and

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\textsuperscript{xviii} Deposition of nanoparticles from solution using an electric field.
elevated temperatures.\textsuperscript{132} A similar spray deposition method has also been tried using ruthenium ethoxide solution.\textsuperscript{131}

Many of the RuO$_x$ synthesis methods described above are only suitable for fabricating planar supercapacitor electrodes (e.g. electrostatic spray deposition, and any method that forms a RuO$_x$ composite paste). With the many advantages of porous electrode structures, there is growing research interest in developing synthesis methods for high surface area RuO$_x$ electrodes. Several researchers have deposited RuO$_x$ nanoparticles synthesized from RuCl$_3$ or ruthenium nitrosyl nitrate solutions onto CNT electrodes or other high surface area carbon electrodes.\textsuperscript{49,138,143} The advantage of these solution methods is that the RuO$_x$ nanoparticles are hydrated, and hence have good proton conductivity. Unfortunately, the surface coverage of nanoparticles is difficult to control, and can result in non-uniform supercapacitor electrodes.\textsuperscript{146} Furthermore, due to poor contact between nanoparticles, electron conductivity is through the CNTs or other carbon materials, which have higher resistance compared to RuO$_x$.\textsuperscript{135} In a different approach, Ye \textit{et al.} used reactive magnetic sputtering to deposit RuO$_x$ onto VACNTs. RuO$_x$ deposition is limited to the tops of the CNTs, resulting in poor utilization of electrode surface area.\textsuperscript{137} Although not discussed in the work, it is also likely that the sputtered RuO$_x$ coating would be anhydrous. Other methods for achieving high surface area RuO$_x$ electrodes include: fabricating high porosity RuO$_x$ aerogels by supercritical drying of Ru-based alcogels,\textsuperscript{147} high temperature pyrolysis of an organic Ru precursor onto a highly porous carbon matrix,\textsuperscript{148} and using thiol-templated assembly of RuCl$_3$ to create an aligned porous electrode structure.\textsuperscript{52} Each of these methods require long, complicated synthesis procedures.

As a high precision nanofabrication technique, ALD has the potential to overcome many of the challenges of current RuO$_x$ synthesis methods, especially in the fabrication of large surface area, porous electrodes. To date, there have been only two studies of ALD for supercapacitor applications: vanadium oxide (VO$_x$)\textsuperscript{146} and titanium dioxide (TiO$_2$) supercapacitors.\textsuperscript{48} Although these works demonstrated conformal coating of the pseudocapacitive material, there has yet to be an investigation of optimal ALD material chemistry for maximizing pseudocapacitor performance.

### 4.3 ALD RuO$_x$

ALD is a self-limiting form of chemical vapor deposition (CVD) that enables excellent quality, highly conformal thin-film deposition.\textsuperscript{149} In a conventional CVD process, gas-phase precursor(s) flow into a heated chamber where they chemically react on the target substrate, resulting in a thin film of deposited material.\textsuperscript{150} With ALD, the gas phase precursors—termed “precursor” and “reactant” for binary reaction systems—are pulsed into the deposition chamber sequentially to produce monolayer by monolayer deposition.\textsuperscript{151} \textbf{Figure 4.1} illustrates the ALD process for RuO$_x$ using ruthenium bis(ethylcyclopentadienyl) (Ru(EtCp)$_2$) as precursor and oxygen (O$_2$) as reactant.\textsuperscript{152} In the first step of a deposition cycle, Ru(EtCp)$_2$ is pulsed into the chamber using an inert carrier gas, typically argon (Ar) (Figure 4.1a). Ru(EtCp)$_2$ adsorbs onto the deposition substrate, forming a self-limiting monolayer, and excess precursor gas is purged from the chamber by Ar flow (Figure 4.1b). O$_2$ then enters the chamber (Figure 4.1c), reacting with adsorbed Ru(EtCp)$_2$ to form a single monolayer of RuO$_x$ (Figure 4.1d). Excess O$_2$ is purged with Ar, and no further deposition can take place until the ruthenium precursor again enters the chamber. These steps are repeated until the desired film thickness is achieved (Figure 4.1e).
Figure 4.1. Conceptual illustration of ALD RuO\(_x\) deposition using Ru(EtCp)\(_2\) and O\(_2\) as precursor and reactant. (a) Ru(EtCp)\(_2\) pulse with Ar carrier gas. (b) Ru(EtCp)\(_2\) adsorbs onto the substrate in a conformal monolayer. Excess Ru(EtCp)\(_2\) is purged by Ar. (c) O\(_2\) flows into the ALD chamber, typically by Ar carrier gas. (d) O\(_2\) reacts with adsorbed Ru(EtCp)\(_2\), forming a monolayer of RuO\(_x\) on the substrate. (e) Steps (a) through (d) are repeated to give the desired thickness of RuO\(_x\).

ALD has many advantages compared to conventional CVD and other thin-film deposition methods, including:

- Angstrom-level control of film thickness simply by varying the number of deposition cycles.

- Smooth, conformal deposition since the precursor forms a saturated monolayer on the substrate, and each monolayer is fully reacted. ALD can achieve conformal deposition even on high aspect ratio geometries such as dynamic random-access memory (DRAM) trench capacitors or VACNTs.\(^{149}\)

- High quality films due to the separation of precursor and reactant gases. In a conventional CVD process, unwanted gas-phase reactions can occur as precursors are mixed in the CVD chamber. These gas-phase reactions cause particulates to be embedded in the depositing film. This problem is avoided with ALD since precursor and reactant gases enter the deposition chamber one at a time.\(^{149,151}\)

- Excellent deposition uniformity, as ALD is less sensitive to spatial variations in temperature and gas flow than conventional CVD.\(^{151}\) Unlike conventional CVD, ALD systems have a “temperature window” in which film deposition rate is independent of temperature. The ALD temperature window is defined by: 1) reaction kinetics (deposition temperature must be high enough to support reasonable reaction rates), and 2) precursor
adsorption and stability (temperatures that are too low promote precursor condensation, while temperatures that are too high cause precursor desorption or decomposition). ALD systems using organometallic ALD precursors such as Ru(EtCp)$_2$ can support moderately high reaction temperatures since precursors are chemically bonded to the substrate through a process called “chemisorption”. Unlike conventional CVD, ALD systems do not require uniform concentrations of reactant gases throughout the chamber, as only sufficient concentrations to form (or react with) a precursor monolayer are needed.

- Opportunities to use more highly reactive gases in ALD vs. CVD, since precursors and reactants remain separated throughout the ALD process. With more highly reactive gases, ALD process temperatures can be lowered compared to CVD.

A disadvantage of ALD is that it requires longer times for film deposition than conventional CVD because of the separate pulsing and purging of reactants. Processing time is therefore an important factor in deciding between CVD vs. ALD, with ALD well-suited for thin-film applications. Pseudocapacitors that use high surface area electrodes typically require only a thin coating of active pseudocapacitive material, making supercapacitors a promising application for ALD. Furthermore, the advantages of ALD described above are particularly important for supercapacitor electrodes, as chemical and physical properties greatly affect charge storage ability in pseudocapacitive materials.

There have been many recent studies of ALD Ru and RuO$_x$ systems, due to the potential applications of Ru and RuO$_x$ thin films in microelectronics, DRAM capacitors, metal-oxide-semiconductor (MOS) devices, and antiferromagnetically-coupled (AFC) magnetic recording media. Ru and RuO$_x$ are relatively challenging materials to deposit by ALD because the degree of oxidation of the film varies for different ALD conditions, with reports ranging from pure metallic Ru to pure RuO$_2$. During the ALD RuO$_x$ process shown in Figure 4.1, O$_2$ both decomposes the organic Ru precursor and oxidizes the depositing film. The oxidative decomposition of the Ru precursor is believed to occur by means of adsorbed oxygen, while Ru oxidation occurs via the accumulation of subsurface oxygen in the ALD film. ALD RuO$_x$ formation can therefore be inhibited by low rates of subsurface oxygen absorption and slow reaction kinetics for Ru oxidation. The three process variables found to most significantly affect the chemistry of ALD RuO$_x$ films are:

1. Deposition temperature. Although thermodynamically favorable for Ru to form an oxide, the reaction kinetics are slow at low temperatures. Increasing deposition temperature promotes increased oxygen adsorption, higher rates of subsurface oxygen accumulation, and hence greater RuO$_2$ vs. Ru formation.

2. Oxygen partial pressure. The importance of high oxygen partial pressure for promoting RuO$_2$ deposition has been reported in numerous works using many different ruthenium precursors. High oxygen partial pressure is believed to increase subsurface oxygen content.

3. Ruthenium precursor. Differences in ALD RuO$_x$ film composition have been observed for systems with similar temperature and oxygen exposure conditions, but different Ru

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**Footnotes:**

xix ALD systems that use physical adsorption of precursors (known as “physisorption”) require lower temperatures as precursor monolayers are held to the substrate only by van der Waals forces.
precursors. Aaltonen et al., for example, reported pure Ru deposition with ruthenium cyclopentadienyl (RuCp$_2$), while Kwon et al. and Kim et al. obtained RuO$_2$ deposition using the same temperature range (275 °C to 400 °C) and Ru(EtCp)$_2$ as precursor.\cite{154,158,160}

Besides these three main process variables, evidence suggests that number of deposition cycles may also affect the degree of oxidation of ALD RuO$_x$ films. In a recent study of ALD RuO$_x$ reaction mechanisms using bis(2,4-dimethylpentadienyl)ruthenium(II) (Ru(DMPD)$_2$) precursor, Methaapanon et al. observed that several hundred deposition cycles of Ru preceded the formation of RuO$_2$.\cite{162} The authors proposed that a minimum thickness of Ru is required to accumulate enough subsurface oxygen for RuO$_2$ formation. Although Methaapanon et al. did not specify this minimum thickness, they observed significant RuO$_2$ formation above 300 ALD cycles, which likely corresponds to a film thickness of approximately 15 nm.\cite{158}

In this study of ALD RuO$_x$ supercapacitor electrodes, the effects of deposition temperature and oxygen exposure on the pseudocapacitance of ALD RuO$_x$ films were investigated (see section 4.8). It was not possible to change the Ru precursor due to cost and lab equipment constraints. A constant number of ALD deposition cycles was used for all supercapacitor electrodes to control for possible effects on oxygen content, as reported by Methaapanon et al. Further details on the ALD RuO$_x$ process used in this work are provided in section 4.5.

### 4.4 ALD RuO$_x$ supercapacitor electrode design

The proposed supercapacitor electrode design uses a high surface area, porous electrode coated with a thin film of ALD RuO$_x$ for pseudocapacitive charge storage.\cite{163} **Figure 4.2** provides a conceptual illustration of the ALD coating process and subsequent supercapacitor electrode operation. A generic porous structure (Figure 4.2a) is coated with ALD RuO$_x$ by sequential pulsing of Ru(EtCp)$_2$ and O$_2$, as described in section 4.3 (Figure 4.2b). The as-deposited ALD RuO$_x$ coating stores charge through the adsorption of hydrogen ions and the conversion of RuO$_x$ to Ru(OH)$_2$ (equation 4.1, Figure 4.2c). The surface and near-surface charge storage mechanism of the RuO$_x$ film enables rapid supercapacitor charging and discharging, while the high surface area porous electrode structure increases power and energy density.

**Figure 4.2.** Conceptual illustration of the ALD RuO$_x$ supercapacitor electrode design. (a) A generic, uncoated porous electrode. (b) RuO$_x$ is deposited uniformly and conformally on the high surface area electrode by ALD. Monolayer by monolayer deposition is achieved by sequential pulsing of Ru(EtCp)$_2$ and O$_2$. (c) Pseudocapacitive charge storage in the ALD RuO$_x$ film by reversible adsorption of hydrogen ions and conversion of RuO$_x$ to RuO$_{2x}$(OH)$_x$. Adapted from Ref. 163 with permission from The Royal Society of Chemistry.
In this work, ALD RuO\textsubscript{x} films are deposited on VACNT forests and porous Si as electrodes. VACNTs provide a large surface area, highly porous substrate with mechanical flexibility to relieve stresses in the RuO\textsubscript{x} film as it cycles between redox states.\textsuperscript{63,164} Figure 4.3 illustrates the charging and discharging mechanisms of the ALD RuO\textsubscript{x}-VACNT supercapacitor electrode. During charging, the RuO\textsubscript{x} surface adsorbs protons from the electrolyte and electrons flow into the supercapacitor electrode from an external circuit; during discharging, the process is reversed.

While high surface area carbon materials are widely used for supercapacitor electrodes, there is growing interest in developing Si-based supercapacitors.\textsuperscript{50,53,166–170} The advantages of Si as an electrode material include: opportunities for integration as micro-energy storage for on-chip devices such as sensors and actuators; high conductivity of doped Si; and the use of a low cost, highly abundant material (similar to carbon).\textsuperscript{50,166} The electrochemical instability of Si in aqueous electrolytes, however, is a challenge for Si-based pseudocapacitors fabricated by conventional, solution-based methods.\textsuperscript{50,167} The ALD RuO\textsubscript{x}-porous Si supercapacitors developed in this work demonstrate an effective means to achieve high performance Si-based micro-supercapacitors.

### 4.5 ALD RuO\textsubscript{x} supercapacitor electrode fabrication

VACNTs were synthesized on a conducting Mo substrate by CVD using the same method as in chapter 3, which is described fully in Appendix A. Porous Si electrodes were synthesized by HF anodization using p-type Si substrates, as also described in Appendix A. RuO\textsubscript{x} was deposited using a Cambridge Fiji F200 Plasma ALD with 400 ALD cycles per deposition. Pulse times for Ru(EtCp)\textsubscript{2} and O\textsubscript{2} were 1 s and 10 s respectively, with 5 s Ar purge times. During the ALD process, substrates were heated to temperatures ranging from 270 °C to 400 °C. In addition to VACNT and porous Si substrates, ALD RuO\textsubscript{x} was also deposited on planar electrodes for materials characterization and comparison with the porous electrodes. Planar ALD RuO\textsubscript{x} electrodes were fabricated by depositing RuO\textsubscript{x} on a Si substrate coated with 30 nm chromium (Cr) and 70 nm gold (Au) by thermal evaporation. The Cr and Au layers provide a better nucleation surface for ALD RuO\textsubscript{x} compared to pure Si.\textsuperscript{160}
4.6 Characterization of ALD RuO$_x$ supercapacitor electrodes

ALD RuO$_x$ supercapacitor electrode properties were investigated using electron microscopy and x-ray materials characterization techniques, as described in chapter 2. SEM and TEM images were used to characterize the physical properties of ALD RuO$_x$ supercapacitor electrodes. Chemical and material properties were investigated using XPS and XRD measurements.

**SEM and TEM imaging**

**Figure 4.4** compares SEM and TEM images of uncoated VACNTs (Figure 4.4a-c) and ALD RuO$_x$-VACNTs (Figure 4.4d-f). The uncoated VACNT forest is highly porous (Figure 4.4a, b), which is beneficial for achieving good flow of ALD precursor and reactant gases into the CNTs. A TEM image of an uncoated CNT in Figure 4.4c shows that the CNTs are multi-walled with an outer diameter of approximately 20 nm. The ALD RuO$_x$-coated CNTs perfectly maintain their vertically aligned structure, and are uniformly coated over the entire length of the CNTs (Figure 4.4d). A close-up SEM image of the ALD RuO$_x$-coated CNTs (Figure 4.4e) shows a uniform and complete ALD coating around each CNT, with a more highly textured surface compared to uncoated CNTs. A TEM image of a RuO$_x$-coated CNT (Figure 4.4f) confirms that the RuO$_x$ coating is highly conformal, with good adhesion to the CNT surface. The thickness of the ALD coating is approximately 20 nm.

**Figure 4.4.** Electron microscopy images of uncoated and ALD RuO$_x$-coated CNTs. (a) SEM image of uncoated VACNTs. (b) Close-up SEM image of the uncoated CNTs in (a). (c) TEM image of an uncoated CNT. (d) SEM image of ALD RuO$_x$-VACNTs. (e) Close-up SEM image of the ALD RuO$_x$-coated CNTs in (d). (f) TEM image of an ALD RuO$_x$-coated CNT. Adapted from Ref. 163 with permission from The Royal Society of Chemistry.
Figure 4.5 compares SEM images of uncoated porous Si (Figure 4.5a-c) and ALD RuO$_x$-porous Si (Figure 4.5d-f) electrodes. The Si pores are tightly packed, with some variability in pore depth and size across the electrode (Figure 4.5a, b). The average pore diameter is approximately 13 µm, the average pore center-to-center distance is 17 µm, and pore depths range from 34 µm to over 127 µm (average pore depth of 75 µm), as measured from SEM images. The Si surface inside the pores has a rough texture resulting from the pore synthesis process (Figure 4.5c). For porous Si electrodes, ALD RuO$_x$ is deposited over the entire depth of the pores, but with less uniformity than on VACNTs due to poor nucleation of ALD RuO$_x$ on Si-H terminated surfaces. Figures 4.5d and 4.5e show light and dark surface areas in the pores of an ALD RuO$_x$-porous Si electrode. The light areas, which have greater surface texture (Figure 4.5e), are regions coated with ALD RuO$_x$. High magnification cross-sectional views of the electrode surface in these lighter, coated regions show an ALD RuO$_x$ film thickness of approximately 40 nm (Figure 4.5f).

Figure 4.5. SEM images of uncoated (a-c) and ALD RuO$_x$-coated (d-f) porous Si. (a) Side view of uncoated Si pores. (b) Top view of uncoated Si pores. (c) Close-up side view of an uncoated Si pore wall. (d) Side view of ALD RuO$_x$-coated porous Si. (e) Side view of the bottom of a Si pore coated with ALD RuO$_x$ (127 µm pore depth). (f) Close-up side view of an ALD RuO$_x$-coated Si pore wall showing an ALD thickness of 40 nm. Adapted from Ref. 163 with permission from The Royal Society of Chemistry.
High-resolution TEM imaging

**Figure 4.6** provides high-resolution TEM images of ALD RuOₓ on CNTs. From Figure 4.6a, it appears that the ALD RuOₓ coating is formed by droplet-type nucleation on the CNT surface, rather than by the homogeneous adsorption of precursors characteristic of an ideal ALD process. Previous studies of other ALD materials deposited on CNTs have also reported difficulties attaining uniform film nucleation, as the relatively inert surface of the CNTs inhibits precursor adsorption.¹⁴⁹,¹⁷² RuOₓ nucleation sites in Figure 4.6a most likely correspond to defect locations on the CNTs where Ru(EtCp)₂ chemisorption can occur.¹⁴⁹ CNT functionalization by wet chemistry methods can improve the reactivity of CNT surfaces, though often with negative impacts to CNT properties.¹⁷²–¹⁷⁴ An *in-situ* method for ALD functionalization of CNTs has also been reported.¹⁷²,¹⁷⁵ By exposing CNTs to NO₂ and trimethylaluminum (TMA) pulses in the ALD prior to film deposition, a methyl-terminated surface layer forms that promotes uniform deposition of ALD aluminum oxide (Al₂O₃) on CNTs.¹⁷² A future study could test whether this method also enables uniform RuOₓ deposition on CNTs. In Figure 4.6b, a high-resolution TEM image of the ALD RuOₓ coating, Moiré interference patterns visible in the center of the image indicate the presence of an ordered, crystalline structure in the ALD RuOₓ film. A grain boundary clearly visible in the top right of the image confirms that the ALD RuOₓ film is polycrystalline.⁵⁶

![Figure 4.6](image)

**Figure 4.6.** High-resolution TEM images of ALD RuOₓ deposited on CNTs. (a) Droplets of RuOₓ form at ALD nucleation sites on the CNT surface. (b) Grain boundaries and Moiré interference patterns are visible in the polycrystalline ALD RuOₓ film.

XPS measurements

XPS measurements were used to characterize the surface chemistry of ALD RuOₓ films deposited on planar and VACNT substrates. **Figure 4.7** presents high-resolution XPS measurements of Ru 3d binding energies for ALD RuOₓ films deposited on planar (Figure 4.7a) and VACNT electrodes (Figure 4.7b) at an ALD temperature of 350 °C. XPS measurements were conducted at take-off angles of 15°, 30°, and 75°, corresponding to measurement depths of approximately 2.5 nm, 5 nm, and 10 nm, respectively. Reference data for Ru metal is provided
for comparison. For both planar and VACNT electrodes, Ru 3d binding energies for ALD RuOₓ films show a shift to higher binding energies, and hence higher oxidation states, compared to Ru metal. Since Ru does not form a native oxide at room temperature,¹⁷⁶ these results indicate that RuO₂ is formed during the ALD process. For the planar substrate, Ru 3d measurements at smaller take-off angles show a greater shift to higher binding energies, suggesting that the surface regions of the ALD film are more oxidized compared to deeper layers. For VACNTs, it is not possible to distinguish material properties at different take-off angles due to the complex geometry of the CNT substrate.

![Figure 4.7](image)

**Figure 4.7.** High-resolution XPS measurements of Ru 3d binding energy for RuOₓ films deposited on (a) planar and (b) VACNT substrates. Data for Ru metal is provided as a reference. Adapted from Ref. 163 with permission from The Royal Society of Chemistry.

**Figure 4.8a** provides high-resolution XPS measurements of O 1s binding energy for ALD RuOₓ films deposited on planar and VACNT substrates (350 °C deposition temperature). Previous XPS studies of RuOₓ have found oxygen present in three different bonding states: O²⁻, OH⁻, and H₂O, with binding energies of 529.5 eV, 530.8 eV, and 532.4 eV, respectively.¹⁷⁷,¹⁷⁸ Figure 4.8b compares O 1s measurements for planar ALD RuOₓ with an XPS curve fit composed of these three oxygen bonding states. XPS curve fitting was done using XPSPEAK 4.1 peak fitting program. The “cumulative fit” (sum of the composite peaks) closely matches measured values, indicating that the curve fit is a good approximation of oxygen bonding in ALD RuOₓ. The relative distribution of O²⁻, OH⁻, and H₂O peaks in Figure 4.8b closely resembles that reported by Mun et al. for hydrous RuO₂, with a prominent OH⁻ peak (exceeding that of O²⁻) and substantial presence of H₂O.¹⁷⁸ O 1s binding energy curve fit results reported by Mun et al. for anhydrous RuO₂, in contrast, have an O²⁻ peak exceeding OH⁻, and a smaller H₂O contribution. XPS results in Figure 4.8 therefore indicate that ALD RuOₓ films can be deposited in a hydrated state, with RuOₓ, a hygroscopic oxide, likely absorbing residual water in the ALD chamber during deposition.¹⁷⁹,¹⁸⁰ The deposition of hydrated metal oxides by ALD is highly beneficial for pseudocapacitor applications. *In-situ* hydration of ALD metal oxides has not yet been studied or reported, to the best knowledge of the author.

Note that measurements of H₂O contribution are limited by the ultrahigh vacuum conditions used in XPS.¹⁷⁸
Figure 4.8. High-resolution XPS measurements of ALD RuO$_x$ O 1s binding energy. (a) O 1s curves for ALD RuO$_x$ deposited on planar and VACNT substrates (30° take-off angle). (b) Curve fit of O 1s measurements for planar ALD RuO$_x$, using Gaussian-Lorentz models of O$^{2-}$, OH$^-$, and H$_2$O peaks. Background intensity is estimated with a Tougaard fit in XPSPEAK 4.1. Experimental error for the high-resolution XPS measurements is less than ± 0.2 eV. Adapted from Ref. 163 with permission from The Royal Society of Chemistry.

XPS measurements of planar ALD RuO$_x$ films deposited at different ALD temperatures confirm that oxygen content increases with ALD temperature, as noted in section 4.3. Figure 4.9 plots percent O, percent Ru, and O:Ru ratio as a function of deposition temperature for planar ALD films deposited at 300 °C, 350 °C, and 400 °C. At an ALD temperature of 400 °C, the RuO$_x$ film is approximately stoichiometric RuO$_2$.

Figure 4.9. Temperature dependence of O and Ru concentrations as well as O:Ru ratio for planar ALD RuO$_x$.

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xvi Atomic percentage measurements in XPS are calculated based on relative peak areas. 268
XRD measurements

XRD measurements were used to characterize the bulk crystal structure of ALD RuO$_x$ films deposited on planar and VACNT substrates (Figure 4.10). For ALD RuO$_x$ films deposited on planar substrates, the dominant crystal phase changes with deposition temperature, from Ru(100) at 270 °C, to Ru(002) and Ru(101) at 350 °C, and Ru(002) at 400 °C (Figure 4.10a). These results are in good agreement with XRD measurements reported by Matsui et al. and Aaltonen et al. The lack of RuO$_2$ XRD peaks suggests that the ALD films are not fully oxidized, and that any RuO$_2$ present is in an amorphous phase. XRD measurements of ALD RuO$_x$ on VACNTs also show predominantly Ru peaks, without the temperature dependence observed for planar ALD RuO$_x$ (Figure 4.10b).

![XRD measurements of (a) planar ALD RuO$_x$, and (b) ALD RuO$_x$-VACNTs. Peaks at 34° and 48° in (b) correspond to uncoated VACNTs. Adapted from Ref. 163 with permission from The Royal Society of Chemistry.](image)

4.7 Supercapacitor electrode mass measurement

Most RuO$_x$ supercapacitor works in the literature report electrode performance (capacitance, power, and energy) on a per mass basis. This section describes methods used to estimate the mass of ALD RuO$_x$-VACNT and ALD RuO$_x$-porous Si electrodes. Due to the small quantities of active materials and the small sizes of test electrodes, direct mass measurement of supercapacitor electrode components was not always feasible. In such cases, SEM and TEM images were used to estimate RuO$_x$ coating thicknesses and electrode surface areas to obtain an approximate electrode mass. Recognizing the potential for errors in these mass estimates (see section 2.4), ALD RuO$_x$ supercapacitor test results in this chapter are also reported per unit of electrode area. Measurement uncertainties given below are based on the range of measured values; uncertainty analysis for calculated values follows the standard method for statistical analysis of small data sets.

ALD RuO$_x$-VACNT electrodes

For VACNT electrodes, the mass of uncoated CNTs was directly measured using before-and-after mass measurements. The photograph in Figure 4.11a shows four, large-surface area
samples that were weighed before and after CNT growth to determine the average mass of uncoated VACNTs (Figure 4.11b shows sample A after CNT growth). Mass measurements were taken using a Sartorius Analytic Type A2005 balance, with each recorded mass averaged from five individual measurements. To account for differences in CNT height between samples, the average mass of VACNTs was calculated per µm of CNT height and per cm$^2$ of electrode area. Substrate areas were measured using an image processing and analysis software called ImageJ. The average height of the VACNTs in samples A through D, measured from cross-sectional SEM images, is 14.6 ± 0.3 µm (Figure 4.11c). Table 4.1 summarizes sample area, before-and-after CNT mass measurements, and height-normalized CNT mass for samples A–D. The average mass of uncoated VACNTs for the four samples is 9.0 ± 1.0 µg/(cm$^2$-µm).

![Image](image1.png)

Figure 4.11. Mass measurement of uncoated VACNT electrodes. (a) Samples A–D before CNT growth (Si substrates with CNT catalyst layers). (b) Sample A after CNT growth. (c) Histogram of VACNT heights measured from cross-sectional SEM images of Samples A–D, with normal distribution. Adapted from Ref. 163 with permission from The Royal Society of Chemistry.

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<th>C</th>
<th>D</th>
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<td>2.2 ± 0.3</td>
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<td>CNT mass (µg/cm$^2$-µm)</td>
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<tr>
<td>Average CNT mass (µg/cm$^2$-µm)</td>
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</table>

Table 4.1. Summary of calculated CNT mass per cm$^2$-µm for samples A–D. Adapted from Ref. 163 with permission from The Royal Society of Chemistry.

The mass of ALD RuO$_x$ on VACNT electrodes was calculated by estimating the volume of RuO$_x$ deposited on each CNT and the density of CNTs per electrode area. First, outer diameters of uncoated CNTs and ALD RuO$_x$-CNTs were measured from TEM images to determine the average thickness of RuO$_x$ deposited on the CNTs. Measurement results are shown in the histograms of Figure 4.12 (a and b). The calculated average thickness of 15.7 ± 1.7 nm is
assumed to be constant for all VACNT electrodes, as the number of ALD cycles was kept constant at 400 cycles. The number density of CNTs per cm$^2$ of electrode area was then estimated by counting “CNT footprints” left on the electrode surface after carefully removing the CNTs (Figure 4.12c).\textsuperscript{117} The estimated density of CNTs is $(4.1 \pm 1.0) \times 10^9$ CNTs/cm$^2$, in the same range as other reported values (Figure 4.12d).\textsuperscript{117,182} Finally, the calculated volume of RuO$_x$ deposited per cm$^2$ of electrode area and per µm of CNT height was converted to mass of RuO$_x$ using the density of Ru to give an average value of µg/(cm$^2$-µm).\textsuperscript{xxii} For a typical VACNT height of 15 µm, the total mass of electrode active materials (CNTs + RuO$_x$) is approximately 1.3 ± 0.3 mg/cm$^2$. Table 4.2 summarizes average values of ALD RuO$_x$ thickness, CNT density, and ALD RuO$_x$-VACNT electrode mass, with uncertainties.

Table 4.2 summarizes average values of ALD RuO$_x$ thickness, CNT density, and ALD RuO$_x$-VACNT electrode mass, with uncertainties.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.12.png}
\caption{Mass measurement of ALD RuO$_x$-VACNT electrodes. (a), (b) Histograms of uncoated CNT and ALD RuO$_x$-CNT outer diameter, respectively, as measured from TEM images. (c) SEM image of CNT footprints. (d) VACNT density measurements based on CNT footprint images. Adapted from Ref. 163 with permission from The Royal Society of Chemistry.}
\end{figure}

\textsuperscript{xxii} The density of Ru, rather than RuO$_2$, was chosen based on XRD measurements indicating a predominantly Ru film composition, and to provide a more conservative estimate of gravimetric performance results (the density of Ru is 12.45 g/cm$^3$ vs. 6.97 g/cm$^3$ for RuO$_2$).
Table 4.2. Summary of ALD RuO$_x$-VACNT supercapacitor electrode mass calculations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD RuO$_x$ thickness</td>
<td>15.7 ± 1.7 nm</td>
</tr>
<tr>
<td>VACNT density</td>
<td>(4.1 ± 1.0) x 10$^9$ CNTs/cm$^2$</td>
</tr>
<tr>
<td>ALD RuO$_x$ coating mass</td>
<td>78.7 ± 22.4 µg/(cm$^2$-µm)</td>
</tr>
<tr>
<td>ALD RuO$_x$-VACNT mass</td>
<td>87.7 ± 22.4 µg/(cm$^2$-µm)</td>
</tr>
</tbody>
</table>

ALD RuO$_x$-porous Si electrodes

The mass of ALD RuO$_x$-porous Si electrodes was calculated by estimating the mass of the active region of porous Si and the mass of the ALD RuO$_x$ coating. Figure 4.13 defines the active region of porous Si as the volume above the average pore depth. The mass of the underlying, non-porous Si substrate was excluded from the calculated electrode mass. The average pore depth of 74.8 ± 10.2 µm is assumed to be the same for all porous Si samples, as all the substrates were fabricated by the same method. The mass of the active porous region was determined by measuring the total mass of the uncoated porous Si electrode and subtracting the mass of the supporting Si substrate (calculated from the thickness of the supporting Si region and the density of Si). The average mass of the active porous Si region is 20.5 ± 2.4 mg/cm$^2$.

Figure 4.13. Cross-sectional SEM image of an uncoated porous Si electrode with average pore depth, active porous region, and supporting Si substrate regions defined. Adapted from Ref. 163 with permission from The Royal Society of Chemistry.

The mass of ALD RuO$_x$ deposited on porous Si electrodes was estimated based on the thickness of the ALD coating (approximately 40 nm, as shown in Figure 4.5f), and the surface area of porous Si coated with RuO$_x$. The total surface area of the porous Si electrodes was first calculated from SEM measurements of average pore depth, diameter, and spacing. The surface area of the porous Si electrode is estimated to be 11.4 ± 2.1 times that of a planar electrode. As described in section 4.6, the porous Si electrodes are not fully coated with ALD RuO$_x$. The average fraction of the Si pores coated with RuO$_x$ was estimated from cross-sectional SEM images (Figure 4.5d, e), using ImageJ to calculate coated and non-coated areas for four different Si pores. On average, approximately 63.6 ± 3.6% of the porous Si surface area is coated with
RuO\textsubscript{x}. From these measurements, the mass of ALD RuO\textsubscript{x} was calculated using the density of Ru metal, similar to the VACNT electrodes. Table 4.3 summarizes average values used to calculate the mass of uncoated and ALD RuO\textsubscript{x}-coated porous Si electrodes. For porous Si electrodes, unlike VACNT electrodes, the mass of the ALD RuO\textsubscript{x} coating is negligible compared to the mass of the electrode substrate.

**Table 4.3.** Summary of values for porous Si-based supercapacitor electrode mass calculations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore depth</td>
<td>74.8 ± 10.2 µm</td>
</tr>
<tr>
<td><strong>Uncoated porous Si mass</strong></td>
<td>20.5 ± 2.4 mg/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>Porous Si surface area (per unit planar electrode area)</td>
<td>11.4 ± 2.1 cm\textsuperscript{2}/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>ALD RuO\textsubscript{x} coating thickness\textsuperscript{xxiii}</td>
<td>39.9 nm</td>
</tr>
<tr>
<td>ALD RuO\textsubscript{x} coating efficiency</td>
<td>63.6 ± 3.6%</td>
</tr>
<tr>
<td><strong>ALD RuO\textsubscript{x}-porous Si mass</strong></td>
<td>20.9 ± 2.4 mg/cm\textsuperscript{2}</td>
</tr>
</tbody>
</table>

### 4.8 CV measurements and capacitance

Cyclic voltammetry (CV) measurements were conducted to determine the capacitance of ALD RuO\textsubscript{x}-coated VACNT and porous Si electrodes. All CV measurements use 0.5 M H\textsubscript{2}SO\textsubscript{4} electrolyte, a Pt CE, and a Ag/AgCl RE. Figure 4.14 presents CV measurements of uncoated VACNT (Figure 4.14a), uncoated porous Si (Figure 4.14b), ALD RuO\textsubscript{x}-VACNT (Figure 4.14c) and ALD RuO\textsubscript{x}-porous Si (Figure 4.14d) electrodes. Uncoated VACNTs have much higher double layer capacitance than uncoated porous Si (roughly 1000x greater). This difference is likely due to both the larger surface area and higher electrical conductivity of VACNTs compared to porous Si. Oxidation of uncoated porous Si in aqueous electrolyte is a well-known cause of low porous Si capacitance.\textsuperscript{183,184} With the ALD RuO\textsubscript{x} coating, there is a substantial increase in capacitance for both VACNT and porous Si electrodes. The shape of the CV curves for ALD RuO\textsubscript{x} electrodes in Figures 4.14c and 4.14d is characteristic of RuO\textsubscript{2} supercapacitors reported in other works, providing further evidence that the surface layer of the ALD films is hydrated RuO\textsubscript{2}.\textsuperscript{129,134}

A comparison of ALD RuO\textsubscript{x}-VACNT electrodes fabricated at different ALD temperatures indicates that ALD RuO\textsubscript{x} pseudocapacitance is highly dependent on deposition temperature, with lower ALD temperatures corresponding to higher CV currents (Figure 4.14c). This result is likely due to differences in the degree of hydration of the ALD films, as hydration affects proton conductivity in RuO\textsubscript{x} (see section 4.2).\textsuperscript{52,139} Previous studies report that RuO\textsubscript{x} dehydration begins at temperatures above 150 °C, with increasing temperature accelerating water loss until full

\textsuperscript{xxiii} It was only possible to obtain one measurement of ALD RuO\textsubscript{x} coating thickness for the porous Si electrode due to the difficulty of taking cross-sectional SEM images of the ALD coating on the porous Si walls.
dehydration occurs at 400 °C. As discussed in section 4.6, XPS measurements of RuO$_x$ deposited at 350 °C show evidence of hydration of the ALD film (Figure 4.8b). To further investigate the theory of RuO$_x$ dehydration with increasing ALD temperature, a future study could compare XPS measurements of RuO$_x$ films deposited at different ALD temperatures to see if there are measureable differences in O 1s bonding states.

Specific capacitance values of uncoated and ALD RuO$_x$-coated electrodes were calculated from CV measurements according to the method described in chapter 2 (equation 2.8). There is a large, two-order of magnitude increase in specific capacitance for VACNT electrodes with the ALD RuO$_x$ coating, from 3.4 F/g (0.47 mF/cm$^2$) for uncoated VACNTs to a maximum of 363 F/g (23.6 mF/cm$^2$) for ALD RuO$_x$-VACNTs deposited at 270 °C. ALD RuO$_x$-VACNT specific capacitance increases by 2.4x and 4.4x for ALD films deposited at 350 °C and 270 °C, respectively, compared to 400 °C (Figure 4.14c). For porous Si electrodes, specific capacitance increases nearly 4900x with the ALD RuO$_x$ coating, from 0.39 mF/g (15.4 µF/cm$^2$) to 1.88 F/g (38.2 mF/cm$^2$).

**Figure 4.14.** CV measurements of: (a) uncoated VACNT, (b) uncoated porous Si, (c) ALD RuO$_x$-VACNT, and (d) ALD RuO$_x$-porous Si electrodes. As shown in (c), ALD RuO$_x$-VACNT electrodes deposited at temperatures ranging from 270 °C to 400 °C demonstrate enhanced pseudocapacitance at lower ALD temperatures (capacitance increases by 2.4x and 4.4x for ALD temperatures of 350 °C and 270 °C, respectively, compared to 400 °C deposition temperature). All CV measurements were taken at a scan rate of 100 mV/s. Adapted from Ref. 163 with permission from The Royal Society of Chemistry.
**Figure 4.15** compares CV curves for ALD RuO$_x$-VACNT electrodes deposited with varying ALD O$_2$ precursor conditions (deposition temperature was held constant at 350 °C). The standard O$_2$ exposure time for the “Thermal Ru” recipe in the Cambridge Fiji F200 ALD is 10 s. Increasing O$_2$ exposure time to 35 s results in a decrease in capacitive current by a factor of approximately 3x. An SEM image of the ALD RuO$_x$-VACNTs with 35 s O$_2$ exposure shows that the increased O$_2$ pulse time results in damage to the VACNT electrode, a likely cause of the decreased capacitance (Figure 4.16a). To increase the reactivity of reactant gases, the Cambridge Fiji F200 ALD is equipped with a plasma system of up to 250 W. The effect of O$_2$ plasma on ALD RuO$_x$ pseudocapacitance was investigated based on the hypothesis that higher O$_2$ reactivity might increase RuO$_2$ vs. Ru formation, and hence increase pseudocapacitance. As shown in Figure 4.15, ALD RuO$_x$ deposition with a 50 W O$_2$ plasma decreases RuO$_x$ pseudocapacitance compared to non-plasma ALD. No structural damage to the VACNT electrode was observed (Figure 4.16b), however Saito and Kuramasu have reported RuO$_2$ etching at a rate of several nm/min using O$_2$ plasma. Although 50 W is a relatively low power plasma, it is possible that RuO$_x$ pseudocapacitance decreases as a result of RuO$_2$ etching when using plasma ALD.

**Figure 4.15.** CV measurements of ALD RuO$_x$-VACNT electrodes deposited with varying O$_2$ conditions. Increasing O$_2$ exposure time from 10 s to 35 s decreases CV current a factor of 3. Adding a 50 W O$_2$ plasma decreases CV current by 1.3x compared to 10 s O$_2$ exposure with no plasma. ALD temperature was held constant at 350°C for all samples.
Figure 4.16. Cross-sectional SEM images of ALD RuO$_x$-VACNT electrodes deposited with: (a) 35 s O$_2$ exposure, and (b) 50 W O$_2$ plasma (see Figure 4.4d for comparison with ALD RuO$_x$-VACNT electrodes deposited with 10 s O$_2$ exposure and 0 W plasma).

4.9 EIS measurements and equivalent series resistance

Figure 4.17 compares Nyquist plots of uncoated and ALD RuO$_x$-coated VACNT and porous Si electrodes. The x-intercept of a Nyquist plot is equal to the electrode ESR, as described in chapter 2. The uncoated VACNT electrode (Figure 4.17a) has a low ESR of 24 $\Omega$, which further decreases to 7.1 $\Omega$ with the ALD RuO$_x$ coating (Figure 4.17a, b). Uncoated porous Si has a much higher ESR compared to VACNTs, at 71 $\Omega$ (Figure 4.17c). With the ALD RuO$_x$ coating, porous Si ESR decreases to a low value of 4.9 $\Omega$ (Figure 4.17d). These results demonstrate: 1) the low contact resistance of VACNTs synthesized directly on a conductive substrate, and 2) the excellent conductivity of the thin-film ALD RuO$_x$ coating. Arabale et al., in comparison, measured an ESR of 300 $\Omega$ for randomly dispersed CNTs deposited on a glassy carbon electrode by dropwise addition from a CNT solution. ESR further increased to 1.1 k$\Omega$ for their RuO$_x$-CNT composite electrodes synthesized from RuCl$_3$ solution (EIS measurements in Arabale et al. were conducted using the same 0.5 M H$_2$SO$_4$ electrolyte and 10 mV AC signal used in this work).

Nyquist curves for ALD RuO$_x$-VACNT and porous Si electrodes (Figure 4.17b and d, respectively) show only a partly-defined semicircular region. This indicates that the ALD RuO$_x$ coating has low charge-transfer resistance and small double layer capacitance compared to pseudocapacitance. A low charge-transfer resistance is characteristic of RuO$_x$ supercapacitors because of their fast reaction kinetics. The Nyquist curves for the ALD RuO$_x$ electrodes also show a quick transition from the semicircular, capacitive region to the semi-linear region, suggesting that electrochemical impedance is dominated by diffusion resistance (Warburg impedance in the Randles equivalent circuit model of Figure 2.7a).

xxiv The higher ESR value measured for uncoated VACNT electrodes in chapter 3 is likely due to the use of a low conductivity organic electrolyte (20 mM NaDBS in acetonitrile) for PPY-based supercapacitor electrodes compared to a high conductivity aqueous electrolyte (0.5 M H$_2$SO$_4$) for RuO$_x$ electrodes.
Figure 4.17. Nyquist plots of imaginary vs. real impedance for: (a) uncoated VACNT, (b) ALD RuO$_x$-VACNT, (c) uncoated porous Si, and (d) ALD RuO$_x$-porous Si electrodes.

4.10 Life cycle testing

Figure 4.18 presents life cycle performance testing results for ALD RuO$_x$-VACNT and planar ALD RuO$_x$ supercapacitor electrodes. Life cycle testing was conducted by repeated CV scans over the full supercapacitor operating range (0.2–1.2 V vs. Ag/AgCl). Remarkably, the specific capacitance of the ALD RuO$_x$-VACNT electrode increased by 17% over 10,000 CV cycles (Figure 4.18a), while the capacitance of the planar ALD RuO$_x$ electrode increased by 250% over 3000 cycles (Figure 4.18b). The durability of the planar electrode, however, is much lower than that of VACNTs. As shown in the inset photograph of Figure 4.18b, the planar electrode suffered considerable damage after 3000 cycles, likely due to stresses in the RuO$_x$ film from repeated cycling on an inflexible substrate. For both planar and VACNT electrodes, changes in the shape of the CV curves after repetitive cycling (Figure 4.18c, d) indicate a non-reversible change in electrode chemistry, with evidence of the formation of RuO$_2$ peaks.$^{129,134}$
Figure 4.18. Life-cycle testing of ALD RuO$_x$-VACNT and planar ALD RuO$_x$ supercapacitor electrodes. (a) Change in capacitance of ALD RuO$_x$-VACNTs over 10,000 CV cycles. (b) Change in capacitance of planar ALD RuO$_x$ over 3000 cycles (Inset: photograph showing delamination of the RuO$_x$ film from the planar electrode after 3000 cycles). (c) Comparison of ALD RuO$_x$-VACNT CV curves at 10 vs. 10,000 cycles. (d) Comparison of planar ALD RuO$_x$ CV curves at 10 vs. 3000 cycles. Adapted from Ref. 163 with permission from The Royal Society of Chemistry.

A possible explanation of the observed capacitance improvement and changing CV curve shape is that the ALD RuO$_x$ coating is becoming electrochemically oxidized with repeated cycling. As described in section 4.6. XRD measurements of as-deposited ALD RuO$_x$ films show significant amounts of polycrystalline Ru (Figure 4.10). Although XPS measurements indicate that the ALD films have some hydrated RuO$_2$ (Figure 4.8), ALD deposition conditions—especially the low vacuum environment (mTorr base pressure) and elevated temperature (270 °C–400 °C)—are not as conducive for forming hydrated oxides as solution-based methods. Previous electrochemical studies have reported electrochemical oxidation of Ru metal by potential sweep methods. Hadzi-Jordanov et al. observed irreversible Ru oxidation by repeated CV cycling in H$_2$SO$_4$ electrolyte. The authors note that 0–0.8 V $E_{\text{H}}$ (0.2–1.0 V vs. Ag/AgCl) is a region of nearly reversible oxide formation and reduction, while CV cycling from 0–1.4 V $E_{\text{H}}$ (0.2–1.6 V vs. Ag/AgCl) causes irreversible Ru oxidation. Burke et al. also observed irreversible RuO$_x$
formation with potential sweeps of Ru metal electrodes in aqueous electrolyte.\textsuperscript{187} The authors report that electrolyte pH significantly influences the resulting oxide chemistry, with more highly protonated (and hence porous) oxides formed in acidic vs. basic conditions.

Life cycle testing results in Figure 4.18 suggest that post-ALD electrochemical oxidation could be used to increase capacitance of as-deposited ALD RuO\textsubscript{x} supercapacitor electrodes. In the following sections of this chapter, ALD RuO\textsubscript{x}-VACNT and porous Si electrodes are electrochemically oxidized and performance testing results compared with as-deposited ALD RuO\textsubscript{x} electrodes. Materials characterization confirms an increase in hydrated oxide content of the ALD films, and electrochemically oxidized supercapacitor electrodes show even greater pseudocapacitance improvement than observed in Figure 4.18.

4.11 Electrochemical oxidation of ALD RuO\textsubscript{x} supercapacitors

Figure 4.19, an extension of Figure 4.2, illustrates the theory of enhanced charge storage with electrochemically oxidized ALD RuO\textsubscript{x} supercapacitor electrodes. The as-deposited ALD RuO\textsubscript{x} coating is converted to a hydrated oxide by electrochemical oxidation in aqueous electrolyte (Figure 4.19a). Figure 4.19b shows the hypothesized increase in charge storage through enhanced proton diffusion into deeper layers of the RuO\textsubscript{x}, thus enabling greater utilization of the ALD RuO\textsubscript{x} compared to Figure 4.2c.

**Figure 4.19.** Conceptual illustration of the electrochemically oxidized, porous ALD RuO\textsubscript{x} supercapacitor electrode design. (a) Electrochemical oxidation of the as-deposited ALD RuO\textsubscript{x} coating results in a hydrated amorphous oxide. (b) Enhanced proton conductivity of the hydrated oxide enables greater utilization of the ALD RuO\textsubscript{x} coating (compare with Figure 4.2c). Adapted from Ref. 163 with permission from The Royal Society of Chemistry.

Electrochemically oxidized ALD RuO\textsubscript{x} supercapacitor electrode fabrication

ALD RuO\textsubscript{x} supercapacitor electrodes (planar, VACNT, and porous Si) were fabricated as described in section 4.5. Following ALD RuO\textsubscript{x} deposition, electrodes were oxidized via controlled potential coulometry\textsuperscript{xxv} at 1.3 V vs. Ag/AgCl for times ranging from 3 min to 120 min. Electrochemical oxidation was conducted in 0.5 M H\textsubscript{2}SO\textsubscript{4} electrolyte to promote the

\textsuperscript{xxv} Three-electrode method in which the WE is held at a constant potential.
formation of a hydrated oxide with good proton conductivity, as reported by Burke et al. (see section 4.10). In addition to electrochemical oxidation, thermal oxidation of ALD RuOₓ supercapacitor electrodes was conducted to determine the relative impact of increased oxidation vs. hydration of the ALD films. Post-ALD thermal oxidation was achieved by placing the supercapacitor electrodes in a horizontal tube furnace at 600 °C for 30 min with 70 sccm O₂ flow.

Materials characterization

Figure 4.20 compares XRD results for as-deposited, thermally oxidized, and electrochemically oxidized planar ALD RuOₓ. With thermal oxidation, the ALD film changes from Ru(100) composition for as-deposited RuOₓ to RuO₂(210) composition. The electrochemically oxidized film displays a broad peak centered around RuO₂(101), suggesting that the film is partly amorphous. The greater amorphous character of the electrochemically oxidized electrode is likely due to its hydrated structure. In their study of RuO₂ films prepared with different hydration levels, McKeown et al. observed that more hydrated samples showed greater amorphous character as incorporated water molecules tend to distort the RuO₂ polycrystalline structure.

![Figure 4.20](image)

Changes in RuOₓ film thickness also provide evidence of oxidation and hydration processes occurring in thermally and electrochemically oxidized supercapacitors. Table 4.4 compares average outer diameters of uncoated CNTs, as-deposited ALD RuOₓ-CNTs, and electrochemically vs. thermally oxidized ALD RuOₓ-CNTs, as measured from TEM images. Thermally and electrochemically oxidized samples show 44% and 53% increase in RuOₓ coating thickness, respectively, compared to as-deposited ALD RuOₓ films. The greater increase in RuOₓ thickness with electrochemical vs. thermal oxidation further supports the theory that electrochemical oxidation produces a hydrated oxide (assuming both films are fully oxidized). For gravimetric performance testing results, changes in RuOₓ mass with electrochemical and thermal oxidation were taken into account by: 1) using revised RuOₓ thickness measurements (Table 4.4), and 2) calculating mass using RuO₂ density instead of Ru density (see section 4.7).
Table 4.4. Average outer diameter of uncoated CNTs, as-deposited ALD RuO$_x$-CNTs, and thermally and electrochemically oxidized ALD RuO$_x$-CNTs, as measured from TEM images.

<table>
<thead>
<tr>
<th>CNT supercapacitor electrode</th>
<th>Average outer diameter (nm)</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated CNTs</td>
<td>15.7 ± 1.0</td>
<td>25</td>
</tr>
<tr>
<td>ALD RuO$_x$-CNTs</td>
<td>47.0 ± 3.3</td>
<td>12</td>
</tr>
<tr>
<td>Thermally oxidized ALD RuO$_x$-CNTs</td>
<td>60.7 ± 3.0</td>
<td>10</td>
</tr>
<tr>
<td>Electrochemically oxidized ALD RuO$_x$-CNTs (9 min oxidation)</td>
<td>63.6 ± 3.2</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 4.21 compares cross-sectional SEM images of as-deposited, thermally oxidized, and electrochemically oxidized ALD RuO$_x$-VACNT electrodes. No damage to the VACNT structure was observed with thermal or electrochemical oxidation, as VACNTs provide a highly flexible substrate that can accommodate volume changes in the ALD RuO$_x$ film.$^{188}$ SEM images of an ALD RuO$_x$-porous Si electrode after 18 min of electrochemical oxidation show substantial degradation of both the ALD RuO$_x$ film and porous Si substrate (Figure 4.22). During electrochemical oxidation, both porous Si and RuO$_x$ are oxidized, resulting in significant volume changes and stresses that likely caused the observed degradation.$^{189}$
Figure 4.21. Cross-sectional SEM images of ALD RuO$_x$-VACNT supercapacitor electrodes: (a) as-deposited ALD RuO$_x$, (b) thermally oxidized ALD RuO$_x$, and (c) electrochemically oxidized ALD RuO$_x$ (120 min oxidation). Reproduced from Ref. 163 with permission from The Royal Society of Chemistry.
Figure 4.22. SEM images of electrochemically oxidized ALD RuO$_x$-porous Si electrodes showing degradation of the porous Si structure and ALD RuO$_x$ coating (18 min oxidation). Adapted from Ref. 163 with permission from The Royal Society of Chemistry.

CV measurements and capacitance

Figure 4.23 compares CV measurements of as-deposited, thermally oxidized, and electrochemically oxidized ALD RuO$_x$ supercapacitor electrodes on VACNT and porous Si substrates. The results show a substantial increase in supercapacitor charging and discharging currents with post-ALD electrochemical oxidation for both VACNT (Figure 4.23a) and porous Si (Figure 4.23b) electrodes. Gravimetric specific capacitance of the as-deposited ALD RuO$_x$-VACNT electrode increases by 30% after 15 min of electrochemical oxidation and by 60% after 120 min of electrochemical oxidation. The highest measured specific capacitance of the ALD RuO$_x$-VACNT electrode is 578 F/g (37.7 mF/cm$^2$), an increase of 170x compared to uncoated CNTs. In contrast, thermal oxidation of the ALD RuO$_x$-VACNT electrodes results in a decrease in specific capacitance by 55%. The decrease in supercapacitor performance with thermal oxidation is most likely due to dehydration of the RuO$_x$ coating, despite the increase in oxide content of the ALD film (Figure 4.20).$^{52,139}$ For porous Si electrodes, capacitance increases by a maximum of 28% with electrochemical oxidation compared to as-deposited ALD RuO$_x$. Maximum gravimetric specific capacitance for the electrochemically oxidized ALD RuO$_x$-porous Si electrode is 2.42 F/g—a 6200x increase compared to uncoated porous Si and the highest value of gravimetric specific capacitance reported to date for porous Si-based electrodes.$^{166,183}$
Figure 4.23c and 4.23d show the effects of increasing electrochemical oxidation time on the gravimetric specific capacitance of ALD RuO$_x$-VACNT and ALD RuO$_x$-porous Si electrodes, respectively. Gravimetric capacitance values in Figure 4.23c and 4.23d are calculated including only the mass of RuO$_x$, to enable comparison of RuO$_x$ pseudocapacitance when deposited on VACNT vs. porous Si electrodes. The capacitance of the ALD RuO$_x$-VACNT electrode increases steadily over 120 min of electrochemical oxidation (Figure 4.23c). Porous Si electrode capacitance, in contrast, increases during the first 3 min of electrochemical oxidation, then decreases with further oxidation (Figure 4.23d). These results are likely due to differences in each electrode’s ability to accommodate stresses in the ALD RuO$_x$ film arising from simultaneous oxidation and hydration, with the porous Si electrode sustaining significant damage during electrochemical oxidation (Figure 4.22). Another important observation is that RuO$_x$ gravimetric capacitance is approximately 4–5x higher with the VACNT electrode compared to porous Si, likely due to the higher electrical conductivity and larger surface area of the VACNT electrode.\textsuperscript{119,190}
An interesting question is whether electrochemical oxidation of ALD RuO\textsubscript{x} supercapacitor electrodes enables charge storage in deeper layers of the RuO\textsubscript{x} film, as reported in other works.\textsuperscript{52,129} One method of exploring this question is to calculate the minimum thickness of active RuO\textsubscript{x}, $x$, needed to produce measured capacitance, $C$, for a given electrode specific surface area, $A$, using equation 4.2 (a variation of equation 2.2):

$$x = \frac{CM\Delta V}{AFn_e\rho}$$

Equation 4.2
Planar ALD RuO\(_x\) samples were used for this analysis, since their specific surface area is easily measured. **Figure 4.24a** shows CV results for a planar electrode with 40 nm ALD film thickness. Changes in planar electrode capacitance with thermal and electrochemical oxidation are similar to those observed for VACNT electrodes (Figure 4.23a), confirming repeatability of results for different substrates. As with porous Si electrodes, electrochemical oxidation of planar ALD RuO\(_x\) is limited by damage to the sample during oxidation. After 3 min of electrochemical oxidation, the 40 nm RuO\(_x\) film delaminated from the planar electrode substrate. To increase the durability of the planar electrode, ALD RuO\(_x\) film thickness was increased to 150 nm.\(^{xxvi}\) Figure 4.24b compares CV measurements of the as-deposited and electrochemically oxidized ALD film for the 150 nm planar sample, which survived 18 min of oxidation. Specific capacitance of the 150 nm planar electrode increased from 0.15 mF/cm\(^2\) to 4.9 mF/cm\(^2\) with electrochemical oxidation, a 33x improvement. Active RuO\(_x\) thickness, calculated using equation 4.2, increased from 1.3 Å for the as-deposited film to 4.3 nm with 18 min of electrochemical oxidation.\(^{xxvii}\)

Structural studies of RuO\(_2\) have determined the lattice parameters of RuO\(_2\) to be approximately 3–4 Å, similar to the calculated active thickness for as-deposited ALD RuO\(_x\).\(^{191}\) This result suggests that only the surface layer of the as-deposited ALD RuO\(_x\) film is used for pseudocapacitance. Electrochemical oxidation enables sub-surface charge storage to greater than 4 nm depth. The maximum possible thickness of RuO\(_x\) that can be utilized for pseudocapacitance unfortunately cannot be determined using the current planar ALD RuO\(_x\) films, due to degradation of the electrode before reaching maximum capacitance. To the best knowledge of the author, this question has not been explored in any previous works, and would be an interesting line of future investigation.

Comparing Figure 4.24b (CV measurements of planar electrodes) and Figure 4.23a (CV measurements of VACNT electrodes), one observes that the relative increase in capacitance after 18 min of electrochemical oxidation is much greater for the planar electrode (33x) than for the VACNT electrode (1.3x). This difference arises because VACNTs have much higher surface area than planar electrodes, and hence require longer oxidation times to convert the same fraction of RuO\(_x\) to hydrated RuO\(_2\). Figure 4.24c plots the change in capacitance of planar and ALD RuO\(_x\)-VACNT electrodes as a function of total charge transferred during electrochemical oxidation, with both capacitance and charge calculated per mass of ALD RuO\(_x\). The rate of change of capacitance with electrochemical oxidation is a constant value of approximately 0.01 F/C, independent of RuO\(_x\) film thickness or substrate. This result confirms that capacitance improvement is by the same mechanism for each electrode.

Figure 4.24d provides a photograph of the 150 nm planar electrode after 18 min of electrochemical oxidation. As-deposited ALD RuO\(_x\) is shiny metallic color, as seen in the top half of the sample which was not exposed to the electrolyte. With electrochemical oxidation, the ALD RuO\(_x\) film changes to a black color characteristic of RuO\(_2\).\(^{128}\) During the oxidation process, the stress in a thin film deposited on a thick substrate is given by Stoney’s equation:

\[
\sigma = \frac{E}{(1-\nu)} \left( \frac{h^2}{6Rt} \right),
\]

where \(E\) is the Young’s modulus, \(\nu\) is Poisson’s ratio, \(h\) the substrate thickness, \(R\) is the radius of curvature of the substrate, and \(t\) is the film thickness.\(^{269}\) Increasing film thickness \(t\) reduces stress \(\sigma\) in the thin film layer.

\(^{xxvi}\) The stress in a thin film deposited on a thick substrate is given by Stoney’s equation: \(\sigma = \frac{E}{(1-\nu)} \left( \frac{h^2}{6Rt} \right)\), where \(E\) is the Young’s modulus, \(\nu\) is Poisson’s ratio, \(h\) the substrate thickness, \(R\) is the radius of curvature of the substrate, and \(t\) is the film thickness.\(^{269}\) Increasing film thickness \(t\) reduces stress \(\sigma\) in the thin film layer.

\(^{xxvii}\) Note that these values are minimum thicknesses which assume 100% pseudocapacitive efficiency for the RuO\(_x\) coating.
the electrode surface bubbled vigorously due to oxygen evolution and the co-production of RuO$_4^{2-}$ gas.$^{192}$ The round purple spots in Figure 4.24d are regions where the RuO$_x$ film delaminated from the substrate due to bubble formation, with the purple color presumably resulting from oxidation of the underlying Si substrate. The green color seen around the edges of the sample is likely chromium oxide, as the ALD RuO$_x$ film is deposited on a Si-Cr-Au substrate (see section 4.5).$^{193}$

Figure 4.24. Electrochemical and thermal oxidation of planar ALD RuO$_x$ supercapacitor electrodes. (a) CV measurements of a 40 nm thick planar ALD RuO$_x$ electrode (as-deposited ALD RuO$_x$, thermally oxidized, and 3 min electrochemically oxidized samples). (b) CV measurements of a 150 nm thick planar ALD RuO$_x$ electrode (as-deposited ALD RuO$_x$, and 9 min and 18 min electrochemically oxidized samples). (c) Rate of change of capacitance of ALD RuO$_x$ supercapacitors as a function of electrochemical oxidation charge, normalized by ALD RuO$_x$ mass. (d) Photograph of the 150 nm planar ALD RuO$_x$ electrode after 18 min of electrochemical oxidation.
Life cycle testing

Figure 4.25 provides life cycle performance testing results for an electrochemically oxidized ALD RuO$_x$-VACNT electrode (120 min oxidation time). In contrast to the capacitance increase measured with life cycle testing of as-deposited ALD RuO$_x$ electrodes (Figure 4.18), a gradual, 19% decrease in capacitance over 1500 CV cycles is observed for the electrochemically oxidized ALD RuO$_x$ electrode. This result confirms that the electrochemical oxidation process has fully oxidized the ALD RuO$_x$-VACNT electrode. Potential causes of the decrease in capacitance over 1500 cycles include: gradual delamination of the Mo layer and VACNTs from the Si substrate, faradaic reaction irreversibilities, electrochemical oxidation of the Mo electrical contact layer, or electrolyte polarization causing the formation of insulating layers at the electrode-electrolyte interface.

![Figure 4.25](image)

**Figure 4.25.** Life cycle testing of electrochemically oxidized ALD RuO$_x$-VACNT electrode (120 min oxidation time). Charge-discharge cycling was conducted by repeated CV scans at 100 mV/s over a potential range of 0.2 V to 1.2 V vs. Ag/AgCl. Reproduced from Ref. 163 with permission from The Royal Society of Chemistry.

4.12 Chronopotentiometry measurements, power and energy

Two-electrode chronopotentiometry measurements were used to determine the energy and power density of ALD RuO$_x$ supercapacitor electrodes, according to the method described in section 2.2. Figure 4.26 shows charge-discharge curves for planar and VACNT ALD RuO$_x$ supercapacitor electrodes. Charge-discharge curves for planar ALD RuO$_x$ electrodes have good linearity with low resistance drop for both as-deposited (Figure 4.26a) and electrochemically oxidized ALD films (Figure 4.26b). ALD RuO$_x$-VACNT chronopotentiometry measurements, in contrast, have greater non-linearity and higher resistance losses for as-deposited (Figure 4.26c) and electrochemically oxidized samples (Figure 4.26d). Similar non-linearities and high resistance losses are observed for an uncoated VACNT electrode (Figure 4.26e), suggesting that the non-ideal supercapacitor behavior of ALD RuO$_x$-VACNT electrodes can be attributed primarily to the VACNT substrate rather than the ALD RuO$_x$ coating. Possible sources of non-linearities in the VACNT electrodes include: side reactions from impurities such as iron and aluminum CNT growth catalysts, or electrolyte polarization losses due to diffusion resistance.
Figure 4.26. Constant current charge-discharge measurements of: (a) planar, as-deposited ALD RuO\textsubscript{x} (150 nm thickness), (b) electrochemically oxidized planar ALD RuO\textsubscript{x} (150 nm thickness; 9 min oxidation time), (c) as-deposited ALD RuO\textsubscript{x}-VACNT, (d) electrochemically oxidized ALD RuO\textsubscript{x}-VACNT (9 min oxidation time) and (e) uncoated VACNT electrodes. Measurements were conducted using a symmetrical two-electrode test cell. Reproduced from Ref. 163 with permission from The Royal Society of Chemistry.
Figure 4.27 compares calculated values of gravimetric power and energy for as-deposited and electrochemically oxidized ALD RuO$_x$ supercapacitor electrodes. For planar electrodes, electrochemical oxidation results in a substantial improvement in both energy and power density compared to as-deposited ALD RuO$_x$ (17x increase in maximum power and 14x increase in maximum energy). For VACNT electrodes, energy density is also highest with the electrochemically oxidized ALD RuO$_x$ coating at 4.0 Wh/kg. Power density, in contrast, is greatest for uncoated VACNT electrodes as a result of the faster charge/discharge mechanism for double layer capacitance compared to pseudocapacitance. Electrochemical oxidation further decreases the power density of ALD RuO$_x$-VACNT electrodes, likely due to an increase in pseudocapacitance vs. double layer capacitance as the primary energy storage mechanism of the electrochemically oxidized VACNT electrodes. The highest gravimetric power achieved with RuO$_x$ pseudocapacitance is 17 kW/kg for electrochemically oxidized planar RuO$_x$.

![Ragone plot comparing gravimetric power and energy density of: planar ALD RuO$_x$ (150 nm thickness); electrochemically oxidized planar ALD RuO$_x$ (150 nm thickness, 9 min oxidation); uncoated VACNT; ALD RuO$_x$-VACNT; and electrochemically oxidized ALD RuO$_x$-VACNT (9 min oxidation) supercapacitor electrodes. Adapted from Ref. 163 with permission from The Royal Society of Chemistry.](image)

4.13 Capacitance vs. scan rate performance testing

Charge-discharge cycling of ALD RuO$_x$ electrodes was conducted over a range of CV scan rates to characterize supercapacitor performance at different charge-discharge speeds (Figure 4.28). Figure 4.28a compares capacitance vs. scan rate results for planar ALD RuO$_x$ electrodes (as-deposited and electrochemically oxidized). Planar, as-deposited electrodes exhibit exceptional capacitance retention at high scan rates, maintaining the same specific capacitance at 10 mV/s and 20 V/s—one of the fastest scan rates reported. Electrochemically oxidized planar ALD RuO$_x$ retains high capacitance up to 1000 mV/s, equivalent to full supercapacitor charge and discharge in 2 s. Above 1000 mV/s the capacitance of the electrochemically oxidized sample likely decreases because the scan rate exceeds the rate of H$^+$ ion diffusion into the RuO$_x$ film. The as-deposited planar ALD RuO$_x$ electrode, in contrast, uses just the surface layer of RuO$_x$ for pseudocapacitance, and charge-discharge speed is limited only by reaction kinetics. For VACNT
electrodes, electrochemical oxidation improves capacitance retention compared to as-deposited ALD RuO$_x$-VACNT and uncoated VACNT electrodes at scan rates up to 500 mV/s (Figure 4.28b). Increasing electrochemical oxidation time of ALD RuO$_x$-VACNT electrodes from 18 min to 120 min increases capacitance retention at 500 mV/s from 25% to 49%, as shown in Figure 4.28c (capacitance at 500 mV/s calculated as a percentage of capacitance at 10 mV/s). This performance improvement is most likely due to improved proton conductivity in the RuO$_x$ coating resulting from increased electrochemical oxidation. Figure 4.28d shows capacitance vs. scan rate results for as-deposited ALD RuO$_x$-porous Si. The porous Si electrode has better capacitance retention compared to VACNTs, with ALD RuO$_x$-porous Si capacitance decreasing by 33% when the scan rate increases from 10 mV/s to 100 mV/s compared to a 48% decrease in capacitance for ALD RuO$_x$-VACNTs over the same range. The enhanced performance of the porous Si electrode at high scan rates probably results from the larger pore structure, and hence lower electrolyte diffusion resistance, compared to VACNTs.$^{196}$$^n$
4.14 Discussion

The ALD RuO$_x$ supercapacitor electrodes developed in this work have high capacitance compared to other RuO$_x$ supercapacitor results reported in the literature. Gravimetric capacitance values for the ALD supercapacitors are highest with VACNT electrodes at 363 F/g for as-deposited ALD RuO$_x$ and 578 F/g for electrochemically oxidized ALD RuO$_x$, as described in sections 4.8 and 4.11, respectively. To enable better comparisons between RuO$_x$ films deposited on different substrates, it is common in the literature to report gravimetric capacitance in terms of only the mass of the RuO$_x$ coating. This also enables comparison with the theoretical capacitance for RuO$_2$. The maximum capacitance of electrochemically oxidized ALD RuO$_x$ films deposited on VACNT electrodes is 650 F/g (including only the mass of RuO$_x$). This value is comparable to the highest values of RuO$_x$ capacitance reported in the literature, which range from 900–950 F/g.$^{138,140}$ Electrochemically oxidized ALD RuO$_x$ capacitance is also in the same order of magnitude as the maximum theoretical capacitance for RuO$_2$ at 1450 F/g (calculated using equation 2.2 for a voltage range of 1 V). These comparisons demonstrate that the electrochemically oxidized ALD RuO$_x$ films have good chemical properties for achieving high pseudocapacitance (comparable to solution-based synthesis methods). In addition, the high surface area and good electrical conductivity of the VACNT electrode enables the ALD RuO$_x$ coating to approach its maximum theoretical capacitance.

Despite the high capacitance of ALD RuO$_x$-VACNT electrodes, measured values of power and energy are surprisingly low compared to other works. As described in section 4.12, maximum energy density for ALD RuO$_x$-VACNT electrodes is 4.0 Wh/kg (electrochemically oxidized ALD RuO$_x$), and maximum power density is 17 kW/kg (as-deposited ALD RuO$_x$). The highest reported values, in contrast, are in the range of 10–30 Wh/kg for energy density and 50–100 kW/kg for power density under similar test conditions (aqueous electrolyte and 1 V cell voltage range).$^{129,138,197,198}$ Although supercapacitor energy is most commonly calculated from chronopotentiometry measurements (as in section 4.12), energy can also be estimated using capacitance values calculated from CV measurements (equation 2.4).$^{xxviii}$ For electrochemically oxidized ALD RuO$_x$-VACNTs, this gives an energy density of 40 Wh/kg using the CV capacitance of 578 F/g. The large difference between energy densities calculated from chronopotentiometry vs. CV measurements could be due to limitations in the measurement set-up used for chronopotentiometry, which consisted of two symmetric electrodes clipped to potentiostat leads and placed in a beaker of electrolyte (similar to Figure 2.2). To further investigate the low power and energy values obtained with two-electrode measurements, chronopotentiometry measurements could be repeated using a fully-fabricated supercapacitor test cell, including an electrolyte-saturated separator and assembled with stainless steel plates and Mylar insulated bolts according to the diagram in Stoller et al.$^{39}$ Since the goal of the present work is to provide a first demonstration of ALD RuO$_x$ supercapacitor electrodes, a high capacitance measurement is a good indication that the electrodes could achieve high energy and power density when assembled into a full supercapacitor cell.

$^{xxviii}$ To compare energy densities calculated from chronopotentiometry vs. CV measurements, CV capacitance must be divided by 2 to account for the fact that the two-electrode test cell has two symmetric capacitors in series, and hence half the capacitance of a three-electrode cell.
To improve the performance of ALD RuO\textsubscript{x} supercapacitor electrodes, future work could focus on: 1) post-processing steps to optimize ALD RuO\textsubscript{x} proton and electron conductivity, and 2) determining electrode design parameters that achieve maximum pseudocapacitance. As discussed in section 4.2, good proton and electron conductivity are needed to achieve high RuO\textsubscript{x} pseudocapacitance. The current work focused primarily on optimizing proton conductivity of ALD RuO\textsubscript{x} films by decreasing ALD reaction temperature (Figure 4.14c) and with post-ALD electrochemical oxidation (Figure 4.23). Future work is needed to optimize the electron conductivity of ALD RuO\textsubscript{x} films through methods such as low temperature thermal annealing. In their study of hydrous RuO\textsubscript{x} supercapacitors, McKeown et al. increased the capacitance of RuO\textsubscript{x} electrodes from 577 F/g to 900 F/g by thermal annealing at 150 °C.\textsuperscript{140} The low temperature annealing step improved electron conductivity without dehydrating the RuO\textsubscript{x} film. To avoid the need for post-ALD electrochemical oxidation and thermal annealing steps, a more practical approach would be to optimize pseudocapacitive film properties during the ALD process. Methaapanon et al. report mixed Ru/RuO\textsubscript{2} films at an ALD temperature of 185 °C, close to the optimum annealing temperature of 150 °C identified by McKeown et al.\textsuperscript{161,162} This result suggests that it may be possible to develop a single step ALD process for fabricating hydrated RuO\textsubscript{x} films with high proton and electron conductivity. Another promising approach to increase ALD RuO\textsubscript{x} pseudocapacitance is to optimize the supercapacitor electrode design. Previous studies of electric double layer capacitors have determined that porous electrode geometry, including surface area and pore size, is critical to attaining high supercapacitor performance.\textsuperscript{199–201} A significant advantage of ALD is that it can deposit films on a wide variety of electrode materials and geometries. Important design parameters for ALD RuO\textsubscript{x} supercapacitors include the thickness of ALD film, as well as the density and height of VACNTs (or similar porous electrode material). The following chapter (chapter 5) explores the use of electrochemical modeling to optimize porous electrode geometry for pseudocapacitive materials, including RuO\textsubscript{x}.

A significant challenge to the feasibility of RuO\textsubscript{x} supercapacitors is the high cost of Ru, a platinum group element. One common approach to decrease the cost of RuO\textsubscript{x}-based supercapacitor electrodes is to combine RuO\textsubscript{x} with highly porous carbon materials, such as CNTs or active carbon.\textsuperscript{31,49,138,202} The ALD method is well-suited for coating high surface area carbon materials, as demonstrated in this work. Some researchers, however, believe that RuO\textsubscript{x} is too expensive to find practical application even in composite supercapacitor electrodes.\textsuperscript{146,203–205} Other promising metal oxide pseudocapacitors include V\textsubscript{2}O\textsubscript{5}, MnO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, NiO, and Co\textsubscript{3}O\textsubscript{4}.\textsuperscript{53,122,123,126,203,204,206} Like RuO\textsubscript{x}, these metal oxides store charge by redox reactions with proton intercalation, as described in section 4.1. In addition, all these metal oxides can be deposited by ALD. As shown in Table 4.5, ALD reactions for these metal oxides typically occur in the temperature range of metal oxide dehydration, similar to RuO\textsubscript{x}. The results of this study can therefore potentially be applied to the development of many different ALD metal oxide pseudocapacitors.
Table 4.5. Comparison of dehydration temperatures and typical ALD temperature ranges for pseudocapacitive metal oxides.

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>Dehydration temperature</th>
<th>Typical ALD temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50% dehydrated</td>
<td>Fully dehydrated</td>
</tr>
<tr>
<td>Ruthenium oxide</td>
<td>130 °C\textsuperscript{129}</td>
<td>400 °C\textsuperscript{129}</td>
</tr>
<tr>
<td>Vanadium oxide</td>
<td>90 °C\textsuperscript{207}</td>
<td>350 °C\textsuperscript{207}</td>
</tr>
<tr>
<td>Manganese oxide</td>
<td>190 °C\textsuperscript{204}</td>
<td>400 °C\textsuperscript{204}</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>100 °C\textsuperscript{211}</td>
<td>200 °C\textsuperscript{211}</td>
</tr>
<tr>
<td>Nickel oxide</td>
<td>200 °C\textsuperscript{214,216}</td>
<td>300 °C\textsuperscript{214,216}</td>
</tr>
<tr>
<td>Cobalt oxide</td>
<td>160 °C\textsuperscript{203}</td>
<td>170 °C\textsuperscript{203}</td>
</tr>
</tbody>
</table>

Having demonstrated the high performance of ALD RuO\textsubscript{x} supercapacitor electrodes, and established the potential applicability of ALD to metal oxide pseudocapacitors in general, it is important to consider the feasibility of using ALD in large-scale supercapacitor manufacturing. To date, ALD has found commercial application in the fabrication of DRAM metal-insulator-metal capacitors, and in depositing the gate oxide layer of complementary metal-oxide-semiconductor (CMOS) transistors.\textsuperscript{219} The current use of ALD for DRAM and CMOS commercial technologies suggests the potential of ALD to be scalable and cost-effective in the future.\textsuperscript{219} There has also been growing interest in the use of ALD for a wider variety of applications, including catalysis, sensing, photovoltaics, thin-film transistors, and display technologies.\textsuperscript{146,220–224} As a result, many companies and researchers are developing new ALD systems with higher efficiency and throughput.\textsuperscript{225–229} Advanced ALD technologies currently under development include: multiple-wafer batch processing systems, “spatial” ALD reactors in which the substrate moves between separate precursor and reactant gas zones, as well as “roll-to-roll” ALD for applications in flexible electronics.\textsuperscript{230} Levitech, a semiconductor company in the Netherlands, produces a spatial ALD with a floating wafer track that enables fast motion of substrates through the system.\textsuperscript{231} These examples demonstrate that ALD technology has excellent future potential as a scalable, high through-put, industrial level process that could be feasible for supercapacitor electrode fabrication.
4.15 Summary

This chapter demonstrates the use of ALD to fabricate high-performance RuO$_x$ supercapacitors, achieving conformal coating of high surface area electrodes and nanoscale control of film thickness. The as-deposited ALD RuO$_x$ films are mixed Ru/RuO$_2$, with some hydration at lower ALD reaction temperatures. Supercapacitor performance of as-deposited ALD RuO$_x$ films is maintained over 10,000 charge-discharge cycles with gradually improved capacitance of 17% higher than the starting value, and at ultra-high scan rates of up to 20 V/s. Post-ALD electrochemical oxidation improves capacitance, power, energy, and high scan rate performance of the ALD RuO$_x$ supercapacitors by creating a hydrated, amorphous oxide with enhanced proton conductivity. Electrochemically oxidized ALD RuO$_x$ films on VACNTs achieve a high specific capacitance of 644 F/g, comparable to the best reported values and the theoretical maximum capacitance of RuO$_2$.

The results of this work demonstrate the advantages of ALD in overcoming current fabrication challenges for RuO$_x$ supercapacitors, especially in obtaining good uniformity and high utilization of RuO$_x$ without the use of binding agents. The results of this work are generally applicable to other pseudocapacitive metal oxides—including vanadium, manganese, iron, nickel, and cobalt oxides—which can be deposited by ALD and in which charge storage efficiency depends on achieving highly uniform electrode coating with enhanced proton conductivity. This chapter focuses primarily on optimizing hydration and proton conductivity of ALD RuO$_x$ supercapacitor electrodes. In addition to good pseudocapacitive material chemistry, the physical design of supercapacitor electrodes is important for achieving high capacitance. The following chapter explores the use of porous electrode modeling to determine the optimum design of metal oxide and conducting polymer-based pseudocapacitor electrodes.
Chapter 5: Pseudocapacitor Modeling

The previous two chapters describe the use of novel porous electrode designs and fabrication methods to achieve high-performance conducting polymer and metal oxide supercapacitors. The design process in chapters 3 and 4 is primarily experimental: supercapacitor electrodes with different properties are fabricated, tested, and compared to determine the effects of each design parameter. The current chapter develops an electrochemical model toward the optimizations of pseudocapacitor electrode design. The advantages of modeling include: 1) rapid prediction of pseudocapacitor performance without the need to fabricate and test a large number of different designs; 2) ability to identify the most significant variables affecting supercapacitor performance; and 3) improved understanding of the fundamental processes and limiting factors governing pseudocapacitor charge storage.

The electrochemical model presented in this chapter simulates the performance of porous electrodes coated with metal oxide or conducting polymer pseudocapacitive materials. The primary objective of the model is optimization of supercapacitor electrode design parameters to achieve maximum current density. Many supercapacitor models in the literature aim to accurately simulate interacting electrical, faradaic, and diffusion processes in pseudocapacitor electrodes. As a result, these models are often highly complex and are not typically used as part of the pseudocapacitor electrode design process. The present model follows a simplified approach by considering the case of ohmically-limited supercapacitor electrode performance; the model is therefore called a “resistive-capacitive” model. By following a simplified approach, it is anticipated that the resistive-capacitive model may become an easily integrated and commonly-used tool in the design of conducting polymer and metal oxide pseudocapacitors.

The chapter begins with a literature review of previous pseudocapacitor electrode models. This is followed by a description of the one-dimensional (1-D), macroscale porous electrode model developed by Euler and Nonnenmacher, and Newman and Tobias, that forms the basis of the simplified resistive-capacitive model. Resistive-capacitive model predictions for metal oxide pseudocapacitors (high and low conductivity oxides) and conducting polymer pseudocapacitors are compared with experimental results to determine the validity of model assumptions. The resistive-capacitive model is found to apply well to low conductivity metal oxide supercapacitors with thin pseudocapacitive coating. The chapter concludes with a discussion of possible methods to expand the current model for reaction- and diffusion-limited supercapacitor electrodes.

5.1 Literature review of pseudocapacitor modeling

Supercapacitors use high surface area, porous electrodes to achieve high power and energy density, as described in chapter 1. Pseudocapacitor electrode modeling therefore involves simulating electrochemical processes occurring in porous electrodes. Porous electrodes have several unique features compared to planar electrodes that must be considered in supercapacitor modeling, including:

1) Electrode and electrolyte conductivities are affected by the porosity and tortuosity of the pores.
2) The close contact between electrode and electrolyte in porous electrodes results in series and parallel combinations of mass transfer, chemical reactions, and electrical charge transport throughout the electrode;\textsuperscript{237} and

3) Current and reaction rates are often non-uniform in porous electrodes, with the degree of non-uniformity depending on electrode geometry and materials.\textsuperscript{34,233}

As a result of these differences, porous electrodes require unique modeling approaches compared to planar electrodes.\textsuperscript{238} There are two basic approaches to modeling porous electrodes: the microscale modeling approach and the macroscale modeling approach.\textsuperscript{34}

The microscale modeling approach simulates electrochemical processes occurring in individual pores of supercapacitor electrodes. Microscale porous electrode modeling is most commonly used to simulate double layer capacitance in nanoporous carbon electrodes.\textsuperscript{239–241} The goal of these models is to understand the effects of pore size and shape on the atomic-scale interactions between ions in the electric double layer.\textsuperscript{200,242,243} Due to the complexities of nanoporous electrode geometry and the large number of atomic interactions, microscale double layer capacitor models require sophisticated numerical approaches such as molecular dynamics,\textsuperscript{244,245} density functional theory,\textsuperscript{246} and Monte Carlo simulations.\textsuperscript{243,247} An example of the microscale modeling approach for pseudocapacitor electrodes is De Levie’s cylindrical pore model. In this work, De Levie approximates electrode pores as semi-infinite cylinders of uniform diameter.\textsuperscript{248} The model assumes no electrolyte flow between pores, and the resistance of the electrode material is neglected. De Levie’s cylindrical pore model provides important insight into the effects of pore diameter distribution on charge storage dynamics in pseudocapacitors. A significant limitation of the model, however, is the difficulty correlating the physical properties of porous electrodes—which typically feature a wide range of pore sizes and shapes—with the uniform cylinder model.\textsuperscript{249,250} As de Levie notes, increasing the complexity of the cylindrical pore model by using an “effective” pore diameter would not necessarily improve the model’s accuracy due to the inherent difficulties in determining this parameter.\textsuperscript{248} Although there are many microscale porous electrode models of double layer capacitors, De Levie’s cylindrical pore model is one of the only microscale porous electrode models for pseudocapacitors.

The macroscale modeling approach uses average physical parameters for the porous electrode, without considering individual pore geometries.\textsuperscript{236} In the macroscale porous electrode model, matrix and electrolyte phases are modeled as parallel, interrelated systems. The governing equations of the macroscale porous electrode model for pseudocapacitors are:

1) Ohm’s law for matrix and electrolyte,
2) Electrolyte mass transfer (Nernst-Planck equation),
3) Electroneutrality for matrix and electrolyte,
4) Conservation of charge for matrix and electrolyte, and
5) Reaction kinetics (Tafel or Butler-Volmer equation).\textsuperscript{34}

Macro model parameters are easily measured quantities, such as electrode porosity, electrode length, and matrix and electrolyte conductivities.\textsuperscript{233,238} The most common macroscale porous electrode models are 1-D models, in which current flow is assumed to be parallel to the electrode length.\textsuperscript{34,232,235,236} Among the first 1-D porous electrode models developed were those
of Euler and Nonnenmacher,\textsuperscript{235} and Newman and Tobias.\textsuperscript{236} Both models assume constant electrolyte properties throughout the porous electrode and neglect double layer capacitance. Despite these simplifying assumptions, the 1-D porous electrode models of Euler and Nonnenmacher, and Newman and Tobias are mathematically complex: analytical solutions require solving eight nonlinear, dependent, partial differential equations.\textsuperscript{236} Since the early work of Euler and Nonnenmacher, and Newman and Tobias, many variations of the 1-D, macroscale porous electrode model have been developed to more accurately simulate ohmic resistance, reaction kinetics, and diffusion resistance in porous electrodes. Grens \textit{et al.} and Lin \textit{et al.} for example, include spatial variations in electrolyte properties in their porous electrode models.\textsuperscript{232,251} Other variations of the 1-D macroscale electrode model incorporate more detailed equations for electrode reaction kinetics;\textsuperscript{71,251} include the effects of double layer capacitance;\textsuperscript{71,234,252} and/or provide transient analysis of electrode properties.\textsuperscript{232,234} Although these models provide more accurate simulations of porous electrodes, they are even more mathematically complex than the original models of Euler and Nonnenmacher, and Newman and Tobias (most require numerical solutions).\textsuperscript{71,232,252}

In contrast to the highly complex pseudocapacitor models described above, there is a need to develop simple, macroscale models for use in rapid prototyping and design of supercapacitor electrodes. Tiedemann and Newman, in their study of porous electrodes for electrochemical battery cells, considered the case of ohmically-limited charge storage.\textsuperscript{253} Their model provides a much simpler version of the full, macroscale electrode model by neglecting diffusion and reaction kinetics. Using the ohmically-limited model, Tiedemann and Newman determine the optimum electrode length and porosity for charge storage in electrochemical battery cells. The promising results of the ohmically-limited model of electrochemical battery cells suggest that a similar approach could be used to develop a simple, porous electrode model for pseudocapacitor electrodes. This chapter considers the development of an ohmically-limited, macroscale, porous electrode model for pseudocapacitors. The following sections describe in more detail the theory of the 1-D, macroscale porous electrode model (section 5.2), and the development of an ohmically-limited model for pseudocapacitor electrodes (section 5.3).

### 5.2 1-D macroscale porous electrode model

Figure 5.1 provides a conceptual illustration of a generic electrochemical system described by the 1-D macroscale porous electrode model.\textsuperscript{236} The electrode is in contact with the free electrolyte solution at $x = 0$, and with a metal current collector at $x = L$. The basic assumptions of the porous electrode model are:

- Potential, current, and concentration gradients occur only along the electrode $x$-axis (1-D model);
- The external surface area of the electrode is small compared to the inner porous structure, such that edge and side effects can be neglected;
- The electrode region under consideration is large compared to individual pore dimensions, enabling average parameters to be specified; and
- The porous electrode is fully immersed in electrolyte (no gas-phase components).\textsuperscript{34,232,233}
The above assumptions are common to all 1-D, macroscale porous electrode models; additional assumptions such as uniform electrolyte concentration, or neglecting double layer capacitance, are specific to individual models.

**Figure 5.1.** Conceptual illustration of a porous electrode described by the 1-D macroscale porous electrode model. The electrode consists of a matrix phase uniformly saturated with electrolyte. The electrode is in contact with the free electrolyte solution at \(x = 0\) and with a metal current collector at \(x = L\).

Physical parameters used in the 1-D macroscale porous electrode model are as follows:

- Length of the porous electrode, \(L\) (Figure 5.1).

- Electrode porosity, \(\varepsilon\), defined as the volume fraction of the electrode occupied by the electrolyte:

  \[
  \varepsilon = \frac{V_{electrolyte}}{V_{total}} = \frac{V_{total} - V_{matrix}}{V_{total}} \tag{5.1}
  \]

- Electrode tortuosity factor, \(\alpha\) (also known as the Bruggeman exponent), which accounts for the complexity of the porous structure.\(^{254}\) Electrode tortuosity factors typically range from \(\alpha = 1\) to \(\alpha = 3\), with increasing values of \(\alpha\) corresponding to more highly complex pore structures.\(^{253}\) The electrode tortuosity factor is used in calculating effective conductivities, as described below.

- Matrix conductivity, \(\sigma\), defined as the effective conductivity of the porous electrode matrix phase. Matrix conductivity is calculated based on the bulk conductivity of the matrix material, \(\sigma_o\), the electrode porosity, and the tortuosity factor:\(^{253}\)

  \[
  \sigma = \sigma_o (1 - \varepsilon)^\alpha \tag{5.2}
  \]

- Electrolyte conductivity, \(\kappa\), defined as the effective conductivity of the solution phase in the porous electrode. Electrolyte conductivity is calculated based on the electrolyte free solution conductivity, \(\kappa_o\), electrode porosity, and tortuosity factor:\(^{253}\)

  \[
  \kappa = \kappa_o \varepsilon^\alpha \tag{5.3}
  \]
For models that consider reaction kinetics and diffusion, additional electrode parameters include exchange current density, Tafel parameters, and the electrolyte diffusion coefficient. These parameters are described in more detail in section 5.7.

Figure 5.2 illustrates the effects of electrode porosity and tortuosity on matrix and electrolyte conductivities by plotting equations 5.2 and 5.3, respectively. For a highly porous electrode ($\varepsilon = 0.99$), electrolyte conductivity is approximately equal to the free solution conductivity. As shown in Figure 5.2a, decreasing electrode porosity to $\varepsilon = 0.5$ reduces electrolyte conductivity to $\kappa = 0.5\kappa_o$, $0.25\kappa_o$, and $0.125\kappa_o$ for electrode tortuosity factors of 1, 2, and 3, respectively. While reducing electrode porosity improves matrix conductivity (Figure 5.2b), high values of electrode tortuosity are detrimental to both electrolyte and matrix conductivities. These results demonstrate the importance of considering effective conductivities of matrix and electrolyte when designing porous supercapacitor electrodes.

![Figure 5.2. Effect of electrode porosity and tortuosity on (a) electrolyte conductivity, $\kappa$, and (b) matrix conductivity, $\sigma$.](image)

### 5.3 Resistive-capacitive porous electrode model

This section describes the development of an ohmically-limited, 1-D, macroscale porous electrode model for pseudocapacitor electrodes. In their ohmically-limited model of an electrochemical battery cell, Tiedemann and Newman consider an electrochemical cell that discharges its maximum capacity, $Q$, just as the electrode potential reaches its minimum value (typically 0 V). This condition corresponds to the maximum possible discharge of the electrochemical battery cell. Electrode potential is represented by Ohm’s law:

$$\Delta V = iR(i, \Delta t)$$  \hspace{1cm} Equation 5.4

where the electrode resistance $R$ is a function of the discharge current, $i$, and cell discharge time, $\Delta t$, due to changes in cell properties during discharge.

The resistive-capacitive model developed here considers the case of ohmically-limited pseudocapacitor electrodes. The model simulates constant current discharge of pseudocapacitor electrodes, as this is a common operating condition for supercapacitors. Unlike
electrochemical battery cells, supercapacitor electrode potential depends on state-of-charge, as described in chapter 1 (equation 1.1). During discharge, pseudocapacitor electrode potential decreases due to both resistive losses and capacitive discharging:

$$ \Delta V = iR + \frac{Q}{C} $$

Equation 5.5

Re-writing $Q$ in terms of the discharge time $\Delta t$ and current $i$, maximum pseudocapacitor electrode current can be calculated for a given cell voltage range $\Delta V$ by solving for $i$ in equation 5.5:

$$ i = \frac{C\Delta V}{(RC + \Delta t)} $$

Equation 5.6

In the resistive-capacitive model developed here, electrode capacitance in equation 5.6 is assumed to be only faradaic capacitance, thereby neglecting double layer capacitance. For most pseudocapacitive materials, faradaic capacitance is 10-100x larger than double layer capacitance.\(^{37}\) Faradaic capacitance for a given pseudocapacitor electrode design is calculated using equation 2.2 (Faraday’s law). Total pseudocapacitor electrode resistance is calculated by assuming the matrix and solution phases are parallel resistances:

$$ R = \frac{L}{(\sigma + \kappa)A} $$

Equation 5.7

where $\sigma$ and $\kappa$ are calculated according to equations 5.2 and 5.3, respectively; $L$ is the length of the porous electrode (Figure 5.1); and $A$ is the electrode planar surface area.

Resistive-capacitive model simulations in this chapter are based on physical parameters for a VACNT porous electrode structure. The 1-D macroscale porous electrode model is well-suited for simulating VACNT electrodes because VACNT forests are uniform across large areas, and the porous structure of VACNTs is highly one dimensional (Figure 3.4 and Figure 4.4). The porosity of a VACNT electrode coated with pseudocapacitive material is calculated based on the VACNT density, $n_{CNT}$, CNT outer diameter, $d_o$, and pseudocapacitive coating thickness, $T$:

$$ \varepsilon = 1 - n_{CNT} \pi \left( \frac{d_o}{2} + T \right)^2 $$

Equation 5.8

VACNT electrodes in chapter 4 have a CNT density of $4.1 \times 10^9$ CNTs/cm$^2$ (Table 4.2) and an average outer diameter of 15.7 nm (Figure 4.12a). These values give an uncoated VACNT porosity of 0.99 using equation 5.8. For comparison, a “carbon nanotube sponge” developed by Gui \textit{et al.} reported a porosity exceeding 0.99,\(^{256}\) while Cao \textit{et al.} measured a porosity of 0.87 for vertically aligned CNTs grown by CVD.\(^{257}\)

In the model developed here, the bulk conductivity of the matrix, $\sigma_o$, is assumed to be the pseudocapacitive material conductivity. Electrolyte free solution conductivity, $\kappa_o$, for a single salt electrolyte is calculated according to the equation:

$$ \kappa_o = \Lambda z \nu_c c $$

Equation 5.9

where $\Lambda$ is the solution equivalent conductance, $z_+$ is the cation charge number, $\nu_+$ is the number of cations per molecule of solute, and $c$ the solute concentration.\(^{34}\) Measured values of solution
equivalent conductance can be found in the literature, either for the full salt or for cation and anion components ($\Lambda = \lambda_+ + \lambda_-\). For 0.5 M H$_2$SO$_4$ electrolyte (used for RuO$_x$ supercapacitors in chapter 4), the electrolyte free solution conductivity is 43 S/m. The free solution conductivity of 20 mM NaDBS electrolyte (used for PPY supercapacitors in chapter 3) is 0.25 S/m.$^{258}$

**Figure 5.3** summarizes resistive-capacitive model input parameters and calculations in an equation flow chart. Model input parameters include:

- VACNT height, $L$;
- Density of VACNTs, $\rho_{VACNT}$;
- VACNT electrode tortuosity factor, $\alpha$;
- Pseudocapacitive material properties (density $\rho_{pseudo}$, conductivity $\sigma_0$, molar mass $M$, and electron storage $n_e$);  
- Pseudocapacitive coating thickness, $T$;
- Electrolyte properties (density $\rho_{electrolyte}$, and free solution conductivity, $\kappa_0$);
- Supercapacitor electrode discharge time, $\Delta t$; and
- Supercapacitor electrode voltage range, $\Delta V$.

From these input parameters, dependent parameters are calculated, including: electrode porosity; effective conductivities, $\sigma$ and $\kappa$; faradaic capacitance, $C$; and electrode resistance, $R$. Maximum supercapacitor current can be calculated as either gravimetric or volumetric current density.

The following sections present resistive-capacitive model simulation results for three types of pseudocapacitive materials: 1) high conductivity metal oxide pseudocapacitors (section 5.4); 2) conducting polymer pseudocapacitors (section 5.5), and 3) low conductivity metal oxide pseudocapacitors (section 5.6). Each simulation assumes a supercapacitor discharge time of 30 s and a voltage range of 1 V. Resistive-capacitive models of high and low conductivity metal oxides use the equation flow chart in Figure 5.3. For conducting polymer simulations, the resistive-capacitive model is modified to account for changes in polymer properties between reduced and oxidized states.
Figure 5.3. Flow chart of input parameters and calculations in the resistive-capacitive model. Note that $d_o$ and $d_i$ refer to CNT outer and inner diameters, respectively. All other variables are explained in the figure.
5.4 High conductivity metal oxide simulation

The resistive-capacitive model was first used to simulate the performance of RuO$_x$-VACNT supercapacitor electrodes. To assess the applicability of the model to high-conductivity metal oxide pseudocapacitors, resistive-capacitive model results were compared with experimental results for electrochemically oxidized ALD RuO$_x$-VACNT electrodes from chapter 4. Model input parameters match those of the experimental electrode: VACNT height 15 µm (Figure 4.11); VACNT density $4.1 \times 10^9$ CNTs/cm$^2$ (Table 4.2); RuO$_x$ pseudocapacitive material properties (density 7 g/cm$^3$, bulk conductivity $2.8 \times 10^6$ S/m, $n_{e^-} = 2$, and molar mass 133.1 g/mol); and 0.5 M H$_2$SO$_4$ electrolyte. VACNT electrode tortuosity factor was estimated to be 1.5.$^{254}$

Figure 5.4 plots resistive-capacitive model predictions for RuO$_x$-CNT gravimetric current density as a function of RuO$_x$ coating thickness. For a RuO$_x$ thickness of 24 nm (Figure 5.4a), the model predicts a current density of 28 A/g, not including the mass of the electrolyte. The experimentally measured current from chapter 4, however, is only 2 A/g (similarly neglecting electrolyte mass). One possibility for the much lower experimental current is that the total thickness of RuO$_x$ is not being utilized for pseudocapacitance. Figure 5.4b compares model and experimental results assuming the active thickness of RuO$_x$ is only 4.3 nm (the active thickness value estimated in section 4.11). Even considering a thinner layer of active RuO$_x$, the model greatly overestimates current density compared to experimental results, likely due to the model neglecting reaction kinetics and diffusion. These results suggest that ohmic losses for RuO$_x$-VACNT pseudocapacitor electrodes are small compared to diffusion and reaction kinetic losses. The resistive-capacitive model is therefore not a good fit for high conductivity metal oxide pseudocapacitors.

![Figure 5.4](image)

**Figure 5.4.** Comparison of resistive-capacitive model and experimental results for RuO$_x$-VACNT supercapacitor electrodes. (a) For a RuO$_x$ coating thickness of 24 nm, the model predicts a current of 28 A/g compared to a measured current of 2 A/g. (b) Assuming only 4.3 nm of RuO$_x$ coating are utilized for charge storage, the model prediction of 23.5 A/g is still much higher than experimental results.
5.5 Conducting polymer simulation

The resistive-capacitive model described in section 5.3 assumes constant electrode properties during supercapacitor discharge. While this assumption is valid for metal oxide pseudocapacitors, conducting polymer properties change substantially between oxidized and reduced states. One of the most significant property changes is polymer electrical conductivity. Conducting (oxidized) PPY has a conductivity of approximately $10^4$ S/m, depending on the anion dopant. Insulating (reduced) PPY, in contrast, has a conductivity of less than $10^{-5}$ S/m. In addition to conductivity, conducting polymers undergo substantial volume changes between oxidized and reduced states. In PPY electrodes using NaDBS dopant ions, highly mobile Na$^+$ ions (along with their solvation shell) enter and exit the PPY film during reduction and oxidation, respectively (Figure 3.2). Volume changes of up to 40% have been reported for PPY electrodes with NaDBS dopant. For PPY-VACNT composite electrodes, these volume changes result in potentially large differences in electrode porosity between reduced and oxidized states, as shown in Figure 5.5.

![Figure 5.5. Changes in PPY-VACNT electrode porosity with PPY oxidation and reduction as a function of PPY coating thickness. Electrode porosity is calculated using equation 5.8 assuming a PPY volume change of 40% (CNT density of 4.1 x 10^9 CNTs/cm²).](image)

Figure 5.6 provides a conceptual illustration and equivalent circuit diagram of a modified resistive-capacitive model that takes into account property changes in conducting polymer electrodes. The model simulates the supercapacitor cathode, which transitions from oxidized to reduced state during discharge. Changing electrode properties are accounted for by considering the fraction of the electrode, $\Delta(i,t)$, that has been reduced at time $t$, for a given discharge current, $i$ (Figure 5.6a). This method closely follows the analysis by Tiedemann and Newman for the ohmically-limited battery electrode model with changing matrix properties. In the reduced fraction of the electrode, porosity, matrix conductivity, and electrolyte conductivity have

---

**Note** that a 40% volume change was measured using an aqueous electrolyte; PPY volume change with NaDBS dopant in acetonitrile has not been reported, to the best knowledge of the author.
adjusted property values: $\varepsilon'$, $\sigma'$, and $\kappa'$, respectively. In the non-discharged fraction of the electrode, $L - \Delta(i,t)$, electrode properties are those of the oxidized polymer ($\varepsilon$, $\sigma$, and $\kappa$). The electrode equivalent circuit shown in Figure 5.6b consists of a series combination of matrix-electrolyte parallel resistances for reduced and oxidized portions of the electrode.

**Figure 5.6.** Resistive-capacitive pseudocapacitor electrode model for conducting polymers. (a) Conceptual illustration of a conducting polymer porous electrode showing the fraction of the electrode, $\Delta$, that has been reduced, with the remaining fraction, $L - \Delta$, still in the oxidized state. (b) Equivalent circuit diagram of the conducting polymer resistive-capacitive model consisting of reduced and oxidized electrode resistances arranged in series.

From the equivalent circuit diagram in Figure 5.6b, the resistance of the conducting polymer-based porous electrode as a function of current, $i$, and time, $t$, is:

$$R(i,t) = \frac{L - \Delta(i,t)}{(\kappa' + \sigma')A} + \frac{\Delta(i,t)}{(\kappa + \sigma)A}$$

Equation 5.10

where $\kappa' = \kappa_o(\varepsilon')^{\alpha}$ and $\sigma' = \sigma_o(1 - \varepsilon')^{\alpha}$ (assuming $\kappa_o' = \kappa_o$). An expression for $\Delta(i,t)$ is found by first determining the mass of polymer, $m_{py}$, that is reduced after time $t$:

$$m_{py} = \frac{it}{n_eF}M_{py}$$

Equation 5.11

where $n_e$ is the number of electrons exchanged per monomer, and $M_{py}$ is the molar mass of the monomer. Assuming that the entire thickness of the conductive polymer coating is reduced during discharge, the mass of reduced conducting polymer is related to the geometry of the VACNT electrode as follows:

$$m_{py} = \pi\Delta(i,t)\left(\frac{d}{2} + r\right)^2 - \frac{d_e^2}{4}\rho_{py}n_{CNT}$$

Equation 5.12

xxx Although electrolyte properties are assumed not to change during conducting polymer supercapacitor discharge, electrolyte conductivity varies due to changes in electrode porosity (equation 5.3).
Solving equations 5.11 and 5.12 for $\Delta(i,t)$:

$$\Delta(i,t) = \frac{iM_{PY}}{\pi n_e F \rho_{PY} n_{CNT} (2d_C T + T^2)}$$

Equation 5.13

Inserting equation 5.13 into equation 5.10 provides a complete expression for electrode resistance as a function of current and material properties. From this complete expression, it can be seen that conducting polymer electrode resistance varies linearly with time during supercapacitor discharge. The effective electrode resistance over the time interval $\Delta t$ is therefore equivalent to the resistance at time $t = \Delta t/2$. To determine the electrode maximum discharge current, equations 5.6 and 5.10 are solved iteratively for $i$ and $R$.

The accuracy of the resistive-capacitive model for conducting polymer electrodes was evaluated by comparing model vs. experimental results for PPY-VACNT supercapacitor electrodes. Figure 5.7 compares model predictions with CV current measurements for the 1 min electrodeposited PPY-VACNT supercapacitor electrode from chapter 3 (Figure 3.8). Similar to the high conductivity metal oxide model for RuO$_x$ supercapacitors, the conducting polymer resistive-capacitive model over-predicts discharge current compared to the measured value. This discrepancy is likely due to the high conductivity of PPY in its conducting state, such that ohmic losses are small compared to diffusion and reaction kinetic losses. The disagreement between model and experimental results shown in Figure 5.7 may also be due in part to CNT bundling, which lowers PPY utilization and increases electrode diffusion resistance (Figure 3.5).

![Figure 5.7](image)

**Figure 5.7.** Conducting polymer resistive-capacitive model predictions for PPY-VACNT current as a function of PPY thickness. For a PPY thickness of 9.7 nm (corresponding to the 1 min electrodeposited PPY-VACNT electrode in chapter 3), the model predicts a current of 40 mA/cm$^2$, compared to an experimental result of 0.6 mA/cm$^2$.

A second check of conducting polymer resistive-capacitive model accuracy compares model predictions with experimental results reported in the literature. In their work on PPY-VACNT electrodes, Chen et al. uniformly coated VACNT electrodes (10 µm CNT height) with thin (9 nm) and thick (90 nm) PPY films, using LiClO$_4$ as a dopant. Figure 5.8 compares model predictions with experimental results from Chen et al. for the 90 nm (Figure 5.8a) and 9 nm (Figure 5.8b) PPY-VACNT electrodes. Experimental results are based on CV measurements,
similar to the above comparison with chapter 3. The authors did not specify VACNT density; a rough estimate based on an SEM image in Chen et al. suggests that the CNT density is close to $4 \times 10^8$ CNTs/cm$^2$. For the thinner PPY coating (Figure 5.8b), the model is approaching a more reasonable agreement with experimental results, though still over-predicting current by almost 4x. The model still over-predicts current for thicker PPY films (Figure 5.8a), which suggests that the ohmically-limited pseudocapacitor model is not well-suited to conducting polymer electrodes. The following section tests the applicability of the ohmically-limited model to the final category of pseudocapacitive materials: low conductivity metal oxides.

![Figure 5.8. Comparison of conducting polymer resistive-capacitive model with experimental results reported in Chen et al. for PPY-VACNT electrodes.](image)

(a) Experimental vs. resistive-capacitive model results for 90 nm PPY thickness. (b) Experimental vs. resistive-capacitive model results for 9 nm PPY thickness.

### 5.6 Low conductivity metal oxide simulation

In addition to high conductivity materials such as RuO$_x$ and conducting polymers, many low conductivity metal oxides are also of great interest for supercapacitor applications. Table 5.1 compares the electrical conductivity of several well-studied metal oxide pseudocapacitive materials. Low conductivity metal oxides have electrical conductivities several orders of magnitude below that of RuO$_x$, suggesting that ohmic losses could be significant for these materials when used in supercapacitor electrodes. The range of conductivity values reported for some materials in Table 5.1 reflects the fact that electrical conductivity is highly dependent on fabrication method.$^{261}$
Table 5.1. Electrical conductivity of metal oxide pseudocapacitive materials.

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>Electrical conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ruthenium oxide (RuO$_x$)$^{205}$</td>
<td>$2.8 \times 10^6$</td>
</tr>
<tr>
<td>Manganese oxide (MnO$_2$)$^{262}$</td>
<td>$10^6$–$10^3$</td>
</tr>
<tr>
<td>Nickel oxide (NiO)$^{263}$</td>
<td>$2.6 \times 10^4$–$2.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>Iron oxide (Fe$_2$O$_3$)$^{261}$</td>
<td>$9 \times 10^9$–$5 \times 10^{-2}$</td>
</tr>
<tr>
<td>Vanadium oxide (V$_2$O$_5$)$^{205}$</td>
<td>$1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

The resistive capacitive model was used to simulate the performance of low conductivity metal oxide pseudocapacitors, using V$_2$O$_5$ as an example material. Model predictions were compared with chronopotentiometry results for ALD V$_2$O$_5$-CNT electrodes reported by Boukhalfa et al.$^{146}$ The ALD V$_2$O$_5$-CNT electrodes use randomly-oriented CNT films of approximately 80 µm thickness. In the resistive-capacitive model, an electrode tortuosity factor of $\alpha = 3$ was chosen to account for the non-vertically aligned structure of the CNTs. CNT density was not specified in Boukhalfa et al., so the measured density of $4.1 \times 10^9$ CNTs/cm$^2$ from chapter 4 was used in the resistive-capacitive model as an approximate value. In their work, Boukhalfa et al. provide chronopotentiometry results for three different ALD V$_2$O$_5$ coating thicknesses: 10 nm, 25 nm, and 53 nm. The authors use 8 M LiCl electrolyte for V$_2$O$_5$-CNT performance testing, which has a free solution conductivity of 92 S/m (calculated using equation 5.9).

Figure 5.9 plots resistive-capacitive model predictions vs. experimental results for the 10 nm V$_2$O$_5$-CNT electrodes from Boukhalfa et al. The resistive-capacitive model has excellent agreement with experimental results for gravimetric current densities ranging from 1–10 A/g, with the model slightly under-predicting experimental results. For V$_2$O$_5$ thickness of 25 nm and 53 nm, the model over-predicts electrode current with large errors. Boukhalfa et al. observed a decrease in specific capacitance with increasing V$_2$O$_5$ thickness above 10 nm, suggesting that only the surface layer of V$_2$O$_5$ is utilized for pseudocapacitance in the ALD V$_2$O$_5$-CNT supercapacitor electrodes. The resistive-capacitive model assumes that the full thickness of V$_2$O$_5$ is active for charge storage, which explains the over-prediction of electrode current for 25 nm and 53 nm V$_2$O$_5$ electrodes. To provide more accurate performance predictions for thick pseudocapacitive films, a future version of the resistive-capacitive model could be developed that considers only surface layer charging.
**Figure 5.9.** Comparison of resistive-capacitive model vs. experimental results for ALD V$_2$O$_5$-CNT electrodes. Experimental data is from Boukhalfa *et al.* (10 nm thick V$_2$O$_5$). The model has excellent agreement with experimental results at discharge currents of 1, 2, 5, and 10 A/g.

**Figure 5.10** demonstrates the use of the resistive-capacitive model to optimize pseudocapacitive coating thickness for V$_2$O$_5$-CNT electrodes. Figure 5.10a plots gravimetric current density (not including the mass of the electrolyte) as a function of V$_2$O$_5$ thickness for CNT heights ranging from 10 µm to 500 µm. The results indicate that: 1) gravimetric current density is a continuously increasing function of V$_2$O$_5$ thickness, and 2) CNT height does not affect gravimetric current density (all CNT heights follow the same curve). Figure 5.10a uses a VACNT density of $10^{13}$ CNTs/m$^2$, which corresponds to electrode porosities greater than 94% for V$_2$O$_5$ thicknesses up to 30 nm. For high values of electrode porosity, model results show that the electrolyte maintains good ion mobility irrespective of CNT height.

Figure 5.10b plots gravimetric current density (not including the mass of the electrolyte) as a function of V$_2$O$_5$ thickness using a CNT density of $5 \times 10^{14}$ CNTs/m$^2$. With a high CNT density, the results indicate that: 1) there is an optimum V$_2$O$_5$ thickness for maximizing gravimetric current, and 2) optimum thickness varies with CNT height. For low values of electrode porosity, model results show that ion mobility decreases with increasing CNT height. The differences between Figure 5.10a and 5.10b can be explained mathematically based on the relative magnitudes of denominator terms in equation 5.6. For low CNT densities, electrolyte conductivity is high, such that $RC \ll \Delta t$. Gravimetric current can therefore be approximated as:

\[
i = \frac{CV}{(RC + t)(m_{\text{CNT}} + m_{V_2O_5})} \approx \frac{CV}{t(m_{\text{CNT}} + m_{V_2O_5})}
\]  

Equation 5.14

Since $C$, $m_{\text{CNT}}$, and $m_{V_2O_5}$ in equation 5.14 all depend linearly on $L$, gravimetric current for low CNT densities is independent of CNT height. For high CNT densities, electrolyte conductivity decreases, resulting in large values of electrode resistance, $R$. Gravimetric current for high CNT densities is proportional to CNT height through an equation of the form:

\[
i \propto \frac{a}{L+b}
\]  

Equation 5.15

where $a$ and $b$ are calculated from other pseudocapacitor electrode parameters (Figure 5.3). Gravimetric current density decreases with increasing CNT height, as shown in Figure 5.10b.
Figure 5.10c plots gravimetric current as a function of V$_2$O$_5$ thickness using the same model parameters as in Figure 5.10b, this time including the mass of the electrolyte in the gravimetric current calculation. The results in Figure 5.10c are based on 8 M LiCl electrolyte, as used in Boukhalfa et al. for V$_2$O$_5$-CNT electrodes. Besides reducing overall gravimetric current density, including the mass of the electrolyte also affects the optimum V$_2$O$_5$ coating thickness predicted by the resistive-capacitive model for a given CNT height. Most supercapacitor studies in the literature do not include electrolyte mass when designing pseudocapacitor electrodes or reporting gravimetric current density. The results of Figure 5.10c highlight the importance of considering electrolyte mass in the design of supercapacitor electrodes to obtain maximum gravimetric current for the full supercapacitor cell.

The resistive-capacitive model can also be used to simulate the effect of different electrolytes on pseudocapacitor performance and design optimization. For low conductivity metal oxide pseudocapacitors, the choice of electrolyte has a significant effect on performance as current flow in the porous electrode is predominantly through the electrolyte. Figure 5.10d plots gravimetric current density as a function of V$_2$O$_5$ thickness for 0.5 M H$_2$SO$_4$ electrolyte using the same model parameters as in Figure 5.10c for 8 M LiCl electrolyte. With 0.5 M H$_2$SO$_4$ electrolyte there is a slight decrease in gravimetric current, as well as a change in shape of current vs. V$_2$O$_5$ thickness curves compared to 8 M LiCl electrolyte. Figure 5.10e directly compares optimum V$_2$O$_5$ thickness for 8 M LiCl vs. 0.5 M H$_2$SO$_4$ electrolyte as a function of CNT height. The free solution conductivity of 8 M LiCl electrolyte is approximately double that of 0.5 M H$_2$SO$_4$ electrolyte (92 S/m vs. 43 S/m). As shown in Figure 5.10e, the model indicates that V$_2$O$_5$ thickness should be decreased when using a lower conductivity electrolyte such as 0.5 M H$_2$SO$_4$ in order to minimize electrolyte resistance and maintain high current densities.

Figure 5.10f plots optimum V$_2$O$_5$ thickness as a function of CNT height for different values of electrode tortuosity factor. For low conductivity metal oxides, pseudocapacitive coating thickness can be increased when using highly ordered porous electrodes (α = 1.5). Figure 5.10f also compares maximum gravimetric current densities for different values of α at a CNT height of 500 µm (values indicated in blue on the plot). Values range from 5.8 A/g for α = 3 to 8.4 A/g for α = 1.5. These results confirm the advantage of using well-aligned CNT electrodes to achieve high values of gravimetric current.
Figure 5.10. Resistive-capacitive model results for $V_2O_5$-CNT electrodes. (a) Gravimetric current (not including the mass of the electrolyte) vs. $V_2O_5$ thickness for a CNT density of $10^{13}$ CNTs/m$^2$ and 8 M LiCl electrolyte. (b) Same as (a), with a CNT density of $5 \times 10^{14}$ CNTs/m$^2$. (c) Gravimetric current (including the mass of the electrolyte) vs. $V_2O_5$ thickness for a CNT density of $5 \times 10^{14}$ CNTs/m$^2$ and 8 M LiCl electrolyte. (d) Same as (c) with 0.5 M H$_2$SO$_4$ electrolyte. (e) Optimum $V_2O_5$ thickness as a function of CNT height for 8 M LiCl vs. 0.5 M H$_2$SO$_4$ electrolyte ($5 \times 10^{14}$ CNTs/m$^2$). (f) Optimum $V_2O_5$ thickness vs. CNT height for electrode tortuosity factors of 1.5, 2, and 3 (8 M LiCl electrolyte, $5 \times 10^{14}$ CNTs/m$^2$).
5.7 Discussion

The resistive-capacitive model developed in this chapter considers the case of ohmically-limited pseudocapacitor electrodes. The model has good agreement with experimental results for low conductivity metal oxide supercapacitors, but over-predicts charge storage in high conductivity pseudocapacitive materials such as RuO$_x$ and conducting polymers. For high conductivity pseudocapacitive materials, charge storage is limited by reaction kinetics and diffusion, rather than ohmic resistance. To more accurately simulate charge storage in high conductivity materials, the resistive-capacitive model must be expanded to include the effects of all three factors—ohmic resistance, reaction kinetics, and diffusion—on supercapacitor performance.\textsuperscript{34}

Many existing porous electrode models simultaneously consider the effects of ohmic resistance, reaction kinetics, and diffusion.\textsuperscript{234,255,264} These models are highly complex and generally require numerical solutions, as described in section 5.1.\textsuperscript{232,236,251} The primary advantage of the resistive-capacitive model is its inherent simplicity. To expand the capabilities of the current model while still maintaining a high degree of simplicity, the model could simulate three scenarios independently: 1) ohmically-limited, 2) reaction kinetics-limited, and 3) diffusion-limited supercapacitor performance. The ohmically-limited branch of the model is the resistive-capacitive model developed and described in this chapter. The following paragraphs describe possible methods of developing the reaction kinetics and diffusion branches of the model. Note that the discussions below represent only preliminary ideas for possible solution approaches to the reaction- and diffusion-limited branches of the supercapacitor electrode model. Once developed, each of these branches of the model would need to be tested against experimental results to confirm the validity of assumptions and solution approaches.

Reaction kinetics-limited model

Reaction kinetics in electrochemistry are described using the concept of reaction overpotential. Reaction overpotential, $\eta$, is defined as the deviation of electrode potential, $E$, from the reaction equilibrium potential, $E_{\text{equilibrium}}$,\textsuperscript{xxxi} because of a net current:\textsuperscript{47}

$$\eta = E - E_{\text{equilibrium}}$$ \hspace{1cm} \text{Equation 5.16}

The relationship between electrode current and reaction overpotential is described by the Tafel polarization equation:

$$\eta = a + b \log_{10}(i)$$ \hspace{1cm} \text{Equation 5.17}

where $a$ is a constant calculated from known reaction properties and $b$ is the Tafel slope.\textsuperscript{47} Using equations 5.16 and 5.17, pseudocapacitive (faradaic) current can be calculated for a given electrode potential based on reaction kinetics.

One approach to modeling reaction kinetics in supercapacitor electrodes could be to calculate the electrode voltage $\Delta V$ as the sum of capacitance ($Q/C$) and overpotential contributions:

$$\Delta V = \frac{Q}{C} + \eta(E, i)$$ \hspace{1cm} \text{Equation 5.18}

\textsuperscript{xxxi} Equilibrium potentials for a given pseudocapacitive material can be determined from a Pourbaix diagram.
where $\eta$ is a function of electrode potential and current, according to equations 5.16 and 5.17. For small values of electrode polarization, there is a linear relationship between current and polarization:

$$i = \frac{i_o F}{RT} \eta$$

Equation 5.19

where $i_o$ is the exchange current density (equilibrium current). In this case, reaction overpotential losses can be expressed as an equivalent resistance, known as the charge transfer resistance (see section 2.2):

$$R_{ct} = \frac{RT}{i_o F}$$

Equation 5.20

In the linear case, equation 5.18 becomes:

$$\Delta V = \frac{it}{C} + iR_{ct}$$

Equation 5.21

which closely resembles equation 5.5 for the ohmically-limited model. Using either equation 5.18 or equation 5.21, a similar solution method to that described in section 5.3 for the ohmically-limited model could be developed for simulating supercapacitor electrodes with reaction-limited charged storage.

**Diffusion-limited model**

Pseudocapacitor charge storage is diffusion-limited when the faradaic reaction rate exceeds the rate at which reactant ions can reach the electrode-electrolyte interface by means of diffusion. In this case, maximum electrode current is determined by the diffusion rate of reactants to the electrode surface. Diffusion rate is described by Fick’s first law:

$$J = -D \frac{\partial C}{\partial x}$$

Equation 5.22

where $D$ is the diffusion coefficient, and $\partial C/\partial x$ is the concentration gradient. Bard and Faulkner define a concentration overpotential, $\eta_{conc} = E - E_{equilibrium}$, as:

$$\eta_{conc} = \frac{RT}{nF} \ln \left( \frac{i_i - i}{i_i} \right)$$

Equation 5.23

The term $i_i$ in equation 5.23 is the “limiting current”, given by:

$$i_i = nFAmO C_O^*$$

Equation 5.24

where $A$ is the electrode surface area, $m_O$ is the mass-transfer coefficient (proportional to the diffusion coefficient in equation 5.22) and $C_O^*$ is the bulk reactant concentration. For small concentration overpotentials, $\eta_{conc}$ can be expressed as a linear function of $i_i$, and a mass transfer resistance, $R_{mt}$, can be defined:

$$R_{mt} = \frac{RT}{nF|i_i|}$$

Equation 5.25
As in ohmically-limited and reaction-limited models, $R_{mt}$ could then be incorporated into an equation for pseudocapacitor electrode potential:

$$\Delta V = \frac{it}{C} + iR_{mt}$$

Equation 5.26

with a similar solution method as described in section 5.3.

### 5.8 Summary

This chapter describes the development of a simplified macroscale porous model for pseudocapacitor electrodes. In its current stage, the resistive-capacitive model simulates constant current discharge in ohmically-limited supercapacitor electrodes. The model has good agreement with experimental results for low conductivity pseudocapacitive materials, in which ohmic losses are significant compared to reaction overpotential and diffusion resistance. In future work, the model can be expanded to include pseudocapacitor electrodes in which charge storage is limited by reaction kinetics or diffusion, such as RuO$_x$ and conducting polymer supercapacitors. Preliminary demonstrations of model capability show that the simplified macroscale model can be used to predict optimum pseudocapacitor design parameters for porous electrodes of varying thickness, density, and material properties, as well as for different electrolytes. The model is also an important tool for increasing understanding of performance-limiting factors in supercapacitor electrodes and identifying critical design parameters. The concluding chapter of this work considers the interrelationship between design, fabrication, experimental testing, and modeling of supercapacitor electrodes.
Chapter 6: Conclusion

The principal research challenge in the field of supercapacitor energy storage, identified in chapter 1, is increasing supercapacitor energy density. This research challenge motivated the current study of conducting polymer and metal oxide pseudocapacitors. The overall aim of this study, as defined in chapter 1, is to increase supercapacitor energy density by optimizing pseudocapacitor electrode design and fabrication. This chapter summarizes important achievements that address the dissertation aim. A future research direction is proposed that considers the sustainable design of supercapacitor devices. The chapter concludes with a summary of the research implications of this dissertation.

6.1 Present accomplishments

The present work considers two approaches for increasing pseudocapacitor energy density: 1) optimizing pseudocapacitor electrode design, and 2) developing novel methods for pseudocapacitor electrode fabrication. Pseudocapacitor electrode design optimization was achieved through both modeling and experimental work:

- PPY-VACNT hybrid supercapacitor electrodes presented in chapter 3 exhibit a 5x increase in charge storage compared to uncoated VACNT and pure PPY electrodes. Experimental testing was used to optimize electrodeposition time for PPY-VACNT electrodes. Empirical modeling confirmed an increase in both double layer and faradaic capacitance compared to uncoated VACNT electrodes.

- ALD RuO$_x$-VACNT supercapacitor electrodes described in chapter 4 achieve an ultra-high specific capacitance of 644 F/g, with performance maintained over 10,000 charge-discharge cycles and at scan rates of up to 20 V/s. Supercapacitor performance was optimized experimentally by testing the effects of ALD temperature and post-ALD electrochemical oxidation on pseudocapacitor charge storage.

- The simplified porous electrode model developed in chapter 5 is a promising tool for identifying performance-limiting factors in pseudocapacitor electrodes. Optimization of design parameters is demonstrated for low conductivity metal oxide pseudocapacitor electrodes with the ohmically-limited resistive-capacitive model.

Novel fabrication methods developed to increase pseudocapacitor energy density include:

- A non-aqueous electrodeposition technique using NaDBS dopant for conducting polymer pseudocapacitors (chapter 3);

- ALD combined with electrochemical oxidation for metal oxide pseudocapacitors (chapter 4). ALD RuO$_x$ pseudocapacitor electrodes are fabricated using both VACNT and porous Si substrates. Materials characterization and performance testing results show that ALD RuO$_x$ films can be deposited in a hydrated state.

As a result of these design optimizations and novel fabrication techniques, performance testing results in chapters 3 and 4 show substantial improvement in PPY and RuO$_x$ pseudocapacitor charge storage compared to previous reports in the literature.
In addition to the excellent performance testing results described above, the present work demonstrates important interconnections between supercapacitor electrode design parameters, material properties, and fabrication methods, as shown in Figure 6.1. Resistive-capacitive model simulations in chapter 5, for example, show that optimum electrode design parameters depend on pseudocapacitive material properties, which determine the relative importance of ohmic, reaction kinetic, and diffusion resistances in supercapacitor electrodes (line (a) in Figure 6.1). In chapter 3, a problem with CNT bundling was encountered when using the electrodeposition fabrication method with a VACNT electrode design (line (b) in Figure 6.1). In chapter 4, ALD fabrication parameters affected the hydration level—and hence supercapacitor performance—of RuO$_x$ films (line (c) in Figure 6.1). The implication of these observations is that supercapacitor electrode design should consider interrelationships between design parameters, material properties, and fabrication methods to achieve high performance. It is well-known that supercapacitors should use high surface area, porous electrodes to achieve high energy density. This general principle, however, is often incorrectly treated as the sole factor in designing supercapacitor electrodes. Based on the results of this work, it is clear that a more comprehensive design strategy should be followed that: determines optimum design parameters based on material properties; chooses appropriate fabrication methods for a specific electrode design; and anticipates the influence of electrode fabrication methods on material properties.

![Figure 6.1. Interrelationships between supercapacitor electrode design parameters, material properties, and fabrication method.](image)

### 6.2 Future research direction

Most supercapacitor research, including the present work, focuses primarily on increasing the power and energy density of supercapacitor electrodes. As electrochemical energy storage devices become increasingly widespread, it is important to also consider the environmental impacts of supercapacitor materials and manufacturing. Renewable energy storage and electric vehicles are among the most promising applications of supercapacitors, as described in chapter 1; for these applications in particular, it is important that supercapacitors contribute to reducing net environmental impact compared to fossil fuels. To date, little work has been done to assess and improve the environmental sustainability of supercapacitor materials and manufacturing.
Figure 6.2 shows opportunities to incorporate sustainable design principles into supercapacitor devices, from innovations in materials and manufacturing, to improvements in the use and end-of-life phases. This future research direction could open up many avenues for exploring new pseudocapacitive materials, decreasing energy and resource needs of fabrication methods, and finding ways to reuse or recycle supercapacitors. Methods of quantifying and testing sustainability improvements, such as life cycle assessment metrics, will also need to be developed.

6.3 Summary

Supercapacitors are a promising technology for electrochemical energy storage. The current work has demonstrated novel design and fabrication methods for enhancing energy storage in supercapacitor electrodes. These include: hybrid PPY-VACNT supercapacitor electrodes with 5x energy storage compared to uncoated CNTs; and ALD RuO$_2$-VACNT electrodes with post-ALD electrochemical oxidation that achieve ultra-high specific capacitance. In addition, a simplified, 1-D porous electrode model was developed for design optimization of ohmically-limited supercapacitor electrodes. Through modeling and experimental studies of conducting polymer and metal oxide supercapacitors, this dissertation advances fundamental understanding of charge storage-limiting factors in pseudocapacitor electrodes, and calls attention to the importance of a comprehensive design approach to achieve maximum energy storage. An important future research direction is assessing and improving the environmental sustainability of supercapacitors. As electrochemical energy storage becomes increasingly important in today’s society, supercapacitors will undoubtedly have an important role as a long life cycle, high power, and rapidly rechargeable energy storage technology.
References


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Appendix A: VACNT and Porous Si Synthesis

The following sections describe synthesis methods for VACNT and porous Si electrodes used in this work.

A.1 VACNT synthesis

VACNT electrodes used in chapters 3 and 4 were synthesized by chemical vapor deposition in a horizontal tube furnace, according to the method of Jiang et al.\textsuperscript{265} Figure A.1 provides a schematic illustration of the VACNT growth process. Si substrates are first cleaned in piranha solution (heated mixture of sulfuric acid and hydrogen peroxide), then coated with 100 µm thermally grown silicon dioxide (SiO\textsubscript{2}) as a barrier against metal diffusion into the Si. A 50 nm molybdenum (Mo) electrical contact layer is deposited by electron beam evaporation, followed by the metal catalyst layers (10 nm Al and 5 nm Fe by thermal evaporation). CNTs are grown in a horizontal tube furnace at 720 °C and atmospheric pressure in a mixture of 7:1 hydrogen-to-ethylene gas. A growth time of 10 min produces CNT heights of approximately 10 µm.

**Figure A.1.** VACNT electrode fabrication by chemical vapor deposition using Fe and Al catalyst layers and a Mo electrical contact layer on a Si substrate.

A.2 Porous Si synthesis

Porous Si electrodes used in chapter 4 were synthesized by hydrofluoric acid (HF) anodization using a p-type Si substrate. The substrate was placed between two electrodes in an aqueous HF-ethanol solution (10% HF, 20% ethanol) in a Teflon container. A current of 6–12 mA/cm\textsuperscript{2} was applied between both sides of the substrate according to the constant current anodization method. Fluorine ions react with the Si to form pores; once the first pores form, the HF attack occurs preferentially at the bottom of the pores leading to porous Si formation.\textsuperscript{171,266}