Improvements on Carbon Nanotube Structures in High-Energy Density Ultracapacitor Electrode Design

by

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Abstract

Ultracapacitors are a class of electrochemical energy storage device that is gaining significant industrial traction due to their high charging rate and cycle life compared to rechargeable batteries; however, they store significantly less energy on a per-volume basis. The quest to find an electrode material that could bridge the gap between energy and power density in electrochemical storage devices has been the object of significant industrial and academic research efforts over the past two decades. One promising material, and the focus of this research, is a dense forest of vertically-aligned carbon nanotubes (CNTs). Previous work at MIT has projected that such structures could augment the energy density of ultracapacitors by a factor of five over existing packaged devices. This thesis is an investigation into the electrode fabrication techniques that approach this goal.

Carbon nanotube forests are synthesized on thin tungsten substrates by chemical vapor deposition (CVD) to form porous, high-surface area electrodes. We demonstrate that the capacitance of CNT electrodes is very highly correlated to the morphological and geometrical features of the CNT forest. These features, such as areal density, mean nanotube diameter, and nanotube length, are shown to be tunable and a series of pre- and post-treatment steps are examined to achieve two specific goals: an increased electrode specific surface area (m²/cm³) and an improved differential capacitance (µF/cm² of CNT surface).

Substrates are prepared for CVD by depositing a thin sub-nanometer film of catalytically active material via magnetron sputtering. Electrodes we fabricated using this conventional technique did not exhibit a specific surface area large enough to provide the high capacitance required for energy-dense electrodes. Numerous enhancements to this “standard” procedure are explored, such as varying the material deposition rate and substrate temperature, adding reactive gases during deposition, and depositing multiple catalyst layers. A nearly 5× increase in specific surface area is achieved. Furthermore, the surface properties of as-grown CNTs are modified by exposure to reactive plasmas and other high-energy environments; these treatments result in over a 2× increase in differential capacitance. Compounded, the fabrication methods explored in this thesis provide a nearly 10× performance increase over conventional CNT electrodes, with a demonstrated cell capacitance of 56 mF using two 1 cm² electrodes. Finally, some key arguments are presented that assess the commercial viability of CNT-based ultracapacitors.

Thesis supervisor: John G. Kassakian
Title: Professor of Electrical Engineering
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The completion of this thesis represents the culmination of a 4-year effort – a truly turbulent journey filled with moments of exhilaration as well as self-doubt, an intellectual, psychological, and emotional roller coaster promising little more than an opportunity to make a modest advancement in an exciting field – which I ultimately consider to be a profoundly meaningful and rewarding research experience. I am humbled by the guidance and support that was made available to me throughout the duration of this project and would like to formally recognize individuals whose scholarliness, patience, and generosity helped me get to this point and shape my personal and professional goals:

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Introduction

The past decade has seen a notable increase in the manufacturing and sale of ultracapacitors, with some studies predicting a yearly market growth of 25 - 30% in the foreseeable future [1, 2]. Even though the revenue from ultracapacitor sales ($500 million in 2013 [1]) is completely dwarfed by that of lithium ion batteries ($11.7 billion in 2012 [3]), ultracapacitors are beginning to cause some paradigm shifts in the world of electrochemical energy storage. This chapter introduces the reader to the fundamental characteristics of an ultracapacitor, describes how they compete with or complement battery-based systems, provides a brief description of carbon nanotubes, and outlines the motivation to investigate carbon nanotube forests as an alternate material in their electrodes.

1.1 What is an Ultracapacitor?

Ultracapacitors, more formally known as electrochemical double-layer capacitors (EDLCs), are devices that store energy in the electric field that forms on the solid/liquid interface between the electrodes and an electrolyte. They are given their name because impressively high capacitances can be achieved ($10^4 \text{ F}$) relative to conventional capacitors that are typically used for filtering purposes ($10^{-15} - 10^{-2} \text{ F}$). Such high capacities are possible because the electrodes used in these devices possess an enormous surface area - usually over $10^3 \text{ m}^2/\text{g}$ - and electrolyte ions distribute themselves across much of this area that is made available to them. A high surface area coupled with a low separation of approximately 1 nm between opposite charges on the electrode/electrolyte interface (the double-
layer) results in the kilo-Farad capacitances observed in devices sold today by Maxwell Technologies, NessCap, and other manufacturers. The electrode material these manufacturers typically employ is activated carbon, a highly granular and porous form of carbon that is held together with a polymeric binder such as PTFE. The activated carbon electrode is attached to a current collector, usually aluminum foil, with the help of the same binder and other additives [4].

Ultracapacitors have two key advantages over batteries for energy storage applications. Unlike batteries, which rely on differences in chemical potential between two different materials to store energy in a chemical reaction that involves mass and charge transfer, ultracapacitors can be designed so that their electrodes do not experience any charge transfer: the electrodes are inert, and can therefore be fully charged and discharged many hundreds of thousands of times before any significant degradation occurs. Comparatively, a battery’s lifespan is much shorter; in fact, charge-monitoring mechanisms frequently limit a battery’s state of charge to a window between 15 and 85% of its capacity so as to prolong its cycleability. Second, ultracapacitors have the ability to charge or discharge approximately ten times faster than batteries; they have a higher power density. This trait is highly desirable in applications like hybrid or electric vehicles, for example, which require significant bursts of energy to be available when accelerating or to be stored when braking.

Compared to batteries, however, ultracapacitors come up short on the key metric of energy density: modern devices store only about 5% of the energy per unit weight of lithium-ion batteries on the market today. Largely, this deficiency is due to practical considerations that limit activated carbon-based ultracapacitor voltages to about 2.7 V per cell. Higher potentials result in significantly increased leakage currents that arise from impurities at the electrodes, secondary electrochemical reactions, and the stability of the PTFE binder. The resulting challenge is to find or design an electrode material whose surface area exceeds that of modern materials or can allow an ultracapacitor cell to operate at a higher voltage.

1.2 Carbon Nanotubes as an Alternate Electrode Material

Carbon nanotubes (CNTs) are a graphitic allotrope of carbon with cylindrical symmetry and are usually less than 30 nm in diameter but can be more than a millimeter in length. They are
excellent electrical and thermal conductors, and can grow on a variety of both metallic and non-metallic surfaces. Most importantly, aligned CNTs in dense forests can be made extremely pure and do not require a polymeric binder for rigidity, which implies that higher working voltages are possible – a key requirement to increase the energy density of ultracapacitors. Figure 1.1 provides a schematic and some images of CNTs.

![Figure 1.1: (a) Conceptual schematic of a single and multi-walled carbon nanotube with typical dimensions (adapted from [5]). (b) Photograph of vertically-aligned CNT forest on a metallic substrate. (c) SEM image of vertically-aligned CNT forest.](image)

The earliest reference to the use of CNT arrays as electrodes in ultracapacitors appeared in 1997 [6]. However, the material as prepared by the authors was not competitive with existing electrodes made from activated carbon, which exhibit a cell capacitance of 350 mF/cm² (areal, or Euclidean area) for a 100 μm-thick film. In the last decade, there has been a tremendous effort in both academic and industrial settings to understand the synthesis mechanisms and properties of CNTs. Furthermore, high-purity forms of CNTs have become commercially available and are sold by companies such as Hyperion Catalysis International (USA), Arkema (France), Bayer Material Science AG (Germany), and Showa Denko (Japan). In 2009, Riccardo Signorelli completed his Ph.D. thesis after researching the viability of carbon nanotubes as the active electrode material with the goal to commercialize a CNT-based product [7]. He designed and built a CNT growth chamber, devised a method to grow tall forests of aligned CNTs on thin, conductive substrates, and drew the following conclusions based on their electrode characterizations:
Chapter 1. Introduction

1. Compared to activated carbon electrodes, CNT electrodes offer a 5 – 10× higher power density (charge/discharge rate).

2. The specific surface area – the amount of wettable surface area per unit mass or volume of material – of aligned CNT forests is significantly lower than that of activated carbon, but a higher percentage thereof participates in storing energy.

3. The group’s best working cell demonstrated a capacitance of 6 mF with two 1 cm² electrodes, a factor of 60 below a similarly-sized cell made with activated carbon electrodes.

4. There are two important challenges in order to make CNT-based electrodes competitive
   - The specific surface area of the material needs to be increased by a factor of at least 10. This could be achieved by augmenting the areal density of nanotubes (CNTs/cm²) on the substrate.
   - The differential capacitance, which is the capacitance offered per unit nanotube surface area, needs to be increased by modifying certain surface characteristics of the nanotubes themselves.

5. Electrodes made from high-purity CNTs are electrochemically compatible with common electrolytes (such as propylene carbonate), even at an elevated voltage of 3.5 – 4.0 V.

6. A CNT-based electrode with a specific capacitance (F/g or F/cm³) equal to that of activated carbon electrodes could offer up to a sevenfold increase in energy density compared to conventional ultracapacitors thanks to the higher working voltage.
1.3 Thesis Motivation

The scope of this thesis is defined by the challenges identified in Signorelli's work: we seek to improve the capacitance of CNT arrays by investigating fabrication techniques that would augment the electrodes' specific surface area and differential capacitance. The experimental motivation is twofold:

1. The specific surface area of a CNT forest can be controlled by modifying the areal density of nanotubes and their average diameter. A forest with smaller but more numerous CNTs will have a higher surface area than one with larger and less numerous CNTs.

2. The surface characteristics of CNTs can be modified in a way to increase their differential capacitance.

The experimental goal of this work is to use the compound effect of "densified" and surface-treated CNT forests to demonstrate that the total capacitance of a CNT-based electrode can be augmented to the same level as that of activated carbon electrodes. Based on Signorelli's calculations, this would imply a five- to seven-fold increase in the energy density of a packaged capacitor due to the feasibility of a higher operating voltage. Although the resulting device would still pack less energy than a similarly-sized lithium ion battery, it would be competitive in applications that require frequent charge cycling such as electric vehicles, buffers for intermittent electricity generation, and low-frequency (< 1 Hz) filtering.
1.4 Thesis Outline

This document presents the findings of a four-year investigation into the tailoring and modification of various fabrication techniques to improve the material characteristics of carbon nanotube forests in high-energy density ultracapacitors, and is organized according to the following chapters:

Chapter 2 provides an overview of the two principal forms of electrochemical energy storage: rechargeable batteries and ultracapacitors. The reader is familiarized with some high-level mechanics of both technologies and presented with examples of how ultracapacitors compete with or complement battery-based systems. Lastly, this chapter presents a comprehensive review of prior research in the use of carbon nanotubes as the primary electrode material in ultracapacitors and summarizes the key findings that led to the motivation for this thesis.

Chapter 3 describes existing methods for synthesizing carbon nanotubes and then focuses on the fabrication steps used to produce uniform, aligned CNT structures on metallic substrates. It describes the essential components in an ultracapacitor test cell and details how the as-prepared electrodes were assembled. Lastly, this chapter presents the different approaches that were used to characterize CNT-based electrodes, including various imaging techniques and electrochemical methods.

Chapter 4 explores experimental investigations on electrodes that were prepared using the techniques described in Chapter 3.

Chapter 5 introduces the reader to the different pre- and post-treatment methods that were investigated to enhance the meta-material properties of CNT structures in ultracapacitor electrodes. It provides a thorough description of both failed and successful attempts at increasing the CNT areal density, as well as the methods explored to treat the surfaces of as-grown CNTs.

Chapter 6 describes the evolution of the scientific community's understanding of the electrochemi-
cal double layer, provides a technical description of the mechanics of porous structures in electrochemical systems, and demonstrates how relatively simple models of the double-layer explain the experimental results obtained in this investigation.

Chapter 7 summarizes the findings of the work presented in this thesis and presents some of the remaining challenges that need to be addressed before CNT-based materials can be employed at scale in high-energy density ultracapacitors.
Chapter 2

Background

This chapter introduces the reader to the energy storage mechanisms in secondary (rechargeable) batteries and capacitors, describes the structure, properties, and synthesis of carbon nanotubes, and provides a review of prior and current work relating to the use of carbon nanotubes in ultra-capacitors.

2.1 Overview of Electrochemical Energy Storage

"Electrochemistry" refers to the study of the reactions that take place on the solid-liquid interface between an electrode and an electrolyte. An electrochemical cell produces an electric current from the energy released due to the presence of a spontaneous reduction/oxidation (redox) reaction. Proton-exchange membrane fuel cells, microbial fuel cells, flow batteries, and alkaline batteries are all examples of different systems that store energy electrochemically. The focus in this chapter is on two other forms of electrochemical energy storage: secondary batteries (specifically, lead acid and lithium ion) and ultracapacitors, formally referred to as electrochemical double-layer capacitors (EDLCs). Strictly speaking, the EDLCs investigated in this work do not undergo electrochemical reactions at their electrodes, but are nevertheless classified as electrochemical devices.

When comparing different forms of electrochemical energy storage, the four primary metrics of interests are energy density, power density, cycleability, and cost. One must be exceedingly careful when reading or citing published figures relating to the performance of energy storage devices.
Sometimes, density figures account only for the mass of the active material; sometimes they include the electrolyte but not the packaging; and most often, the normalization is ambiguous. Unless stated otherwise, any performance figures cited in this section relate to fully packaged products – which is why some energy and power densities listed throughout may seem low compared to claims made in other documents.

2.1.1 Secondary Batteries

Unlike primary cells such as standard alkaline batteries, secondary batteries undergo reversible chemical reactions and can therefore be recharged hundreds, often thousands of times before permanent degradation occurs. Common chemistries include nickel cadmium (NiCd), nickel metal hydride (NiMH), lead-acid, and lithium ion. This section briefly describes the mechanics of the latter two.

Lead-acid Batteries

Invented in 1859 by Gaston Planté, the lead-acid battery may be the oldest type of rechargeable battery but still has the highest market share (nearly two thirds) of all electrochemical storage devices today, with global revenues exceeding $35 billion in 2010 [8]. Over 50% of lead-acid batteries are used as starter batteries in automobiles and motorcycles. Typical devices have energy and power densities of approximately 30 Wh/kg and 0.2 kW/kg, and can usually be cycled fewer than 1000 times. The reason lead-acid batteries are so widespread is because they are cheap to manufacture, with a per-energy cost of $100/kWh.

When charged, the electrodes in a lead-acid battery are lead and lead oxide. The electrolyte is concentrated sulfuric acid. As the battery discharges, both the negative and positive plates become lead sulfate and the electrolyte becomes more dilute. During the charging process, the negative and positive plates get reduced and oxidized to lead and lead oxide, respectively. The electrolyte becomes concentrated again. The half-cell reaction equations are provided below (the forward reaction represents the charging process):
Negative plate reaction
\[
PbSO_4(s) + H^+_\text{(aq)} + 2e^- \rightleftharpoons Pb(s) + HSO^-_4(\text{aq})
\]

Positive plate reaction
\[
PbSO_4(s) + 2H_2O(\text{l}) \rightleftharpoons PbO_2(s) + HSO^-_4(\text{aq}) + 3H^+_\text{(aq)} + 2e^-\]

Lead-acid batteries can operate effectively at temperatures between −20 and 40 °C. Performance degrades rapidly outside this temperature window, especially in colder environments. Temperatures below −20 °C are not uncommon, and vehicles that operate in such environments are typically equipped with heating systems that quickly warm up the battery before the engine starter is engaged. There are a number of safety, health, and environmental concerns related to the use of lead-acid batteries. Sulfuric acid is inherently hazardous. Overcharging results in the electrolysis of the water in the electrolyte, which in rare cases can result in an explosion. Accidental shorting can be catastrophic for the same reason. Disposal is difficult from an environmental point of view due to the high toxicity of the materials involved, and although the United States recycles a large portion of the lead used in automotive batteries, many regions of the world do not have similar programs and often suffer from improper disposal practices. Despite these setbacks, lead-acid batteries remain as one of the most reliable, ubiquitous, and inexpensive forms of electrochemical energy storage.

**Lithium Ion Batteries**

Lithium ion batteries are the most commonly used type of rechargeable battery in portable electronics, and are becoming increasingly popular in electric vehicle applications. The industry is currently experiencing a 15% annual growth rate, with global revenues of over $11 billion in 2012 [3]. As a result, the performance of emerging battery and other storage technologies is often compared to that of lithium ion batteries. Typical packaged devices have energy and power densities of 150 – 200 Wh/kg and 0.3 kW/kg, and a per-energy cost of $500 – $1000/kWh [9, 10]. This last figure adjusts for manufacturing yield, which can be as low as 50% [10]. One must note, however, that these manufacturing technologies are moving rapidly and that the costs of lithium ion battery production are expected to drop quickly in the next decade.
Lithium ion batteries are composed of a lithium-containing compound such as lithium cobalt oxide (LiCoO$_2$) or lithium iron phosphate (LiFePO$_4$) at the positive electrode and graphite at the negative electrode.$^1$ The electrolyte is a solution of a lithium-containing salt, typically lithium hexafluorophosphate (LiPF$_6$) or lithium tetrafluoroborate (LiBF$_4$), dissolved in an organic solvent such as ethylene carbonate. Lithium ions migrate from one electrode to the other during both the charging and discharging process, which is why lithium ions must be present in the electrolyte. When charging, ions are extracted from the lithium compound (anode) and intercalate into the graphite electrode (cathode) by inserting themselves in between individual graphite layers. During discharge, lithium ions de-intercalate from the graphite (anode) and insert themselves in the compound (cathode). These processes are shown schematically in Figure 2.1.

![Figure 2.1: Schematic showing the electrochemical processes in a lithium ion battery (adapted from [11]).](image)

$^1$The terms “cathode” and “anode material” are used in the industry to designate the lithium compound and graphite electrodes, respectively; however, these terms are not strictly correct because a given electrode can behave as either the cathode or anode depending on whether the device is charging or discharging.
The electrochemical half-cell reactions are as follows (the forward reaction represents the charging process):

**Positive electrode**

\[
\text{LiCoO}_2(s) \rightleftharpoons \text{Li}_{1-n}\text{CoO}_2(s) + n\text{Li}^+(aq) + ne^-
\]

**Negative electrode**

\[
n\text{Li}^+(aq) + ne^- + C(s) \rightleftharpoons \text{Li}_nC(s)
\]

The performance of lithium ion batteries is very sensitive to temperature and state of charge (SOC). Frequently, a significant portion of the volume used to package a battery is dedicated to a variety of complex monitoring circuitry that prevents overcharging (a typical SOC window is between 15 and 85% of the battery’s capacity) and has the ability to shut off the battery completely in case temperatures get too high. In addition to heating up, the battery expands and contracts slightly during the charging and discharging processes, preventing compact designs. Over time, the electrodes degrade as a result of these stresses. Under good conditions, lithium ion batteries can be cycled several thousand times. Figure 2.2 shows a disassembled laptop battery and highlights the different components.

![Disassembled lithium ion battery](image)

**Figure 2.2:** Disassembled lithium ion battery from a laptop computer (adapted from [12]).
2.1.2 Capacitors

Capacitance is a measure of the ability to hold charge at a given voltage. In its simplest form, a capacitor consists of two parallel conducting plates separated by an insulator. When a voltage is applied, charges accumulate at the electrodes and an electric field forms across the insulator. For a structure consisting of two plates with area \( A \), separation \( d \), and an insulator material with permittivity \( \varepsilon \), its capacitance \( C \) is computed according to: \( C = \frac{\varepsilon A}{d} \).

Capacitors are common passive circuit components that store energy electrostatically in the electric field that forms between two opposing electrodes as charge accumulates. They come in many different sizes and shapes, and are broadly categorized into three groups: non-electrolytic, electrolytic, and electrochemical.

Non-electrolytic capacitors are typically used for filtering purposes in electronic circuits, and have capacitances between \( 10^{-15} \) and \( 10^{-5} \) F. Their electrodes are usually copper or aluminum, and various dielectrics such as polymer film, ceramic, or air are used. The energy density of packaged devices is on the order of \( 10^{-3} \) Wh/kg.

Electrolytic capacitors are polar devices with an aluminum anode and a liquid electrolyte (aqueous solution of sodium borate) as the cathode. A thin, usually micron-thick layer of aluminum oxide (formed by anodizing the anode) separates the two. A second piece of aluminum foil is used as the cathode current collector. The thinness of the oxide layer allows these devices to have a significantly higher specific capacitance: typical device capacities range between \( 10^{-7} \) to \( 10^{-2} \) F with energy densities between \( 10^{-2} \) and \( 10^{-1} \) Wh/kg and an operating voltage of up to several hundred volts.

Electrochemical capacitors are composed of two high-surface area electrodes immersed in an electrolyte and are the only type of capacitor suitable for bulk energy storage. Packaged products can have capacities in the kilo-farad range, and exhibit an energy density between 5 and 10 Wh/kg. In 2013, sales from electrochemical capacitors accounted for approximately $500 million, but the
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market is experiencing high growth rates of over 25% per year and is expected to be worth $11 billion in 2024 [1]. There are two energy storage principles:

1. Double-layer capacitance, which arises from the distributed electric field that forms on the solid/liquid interface between each electrode and the electrolyte;

2. Pseudocapacitance, which relies on charge transfer through redox reactions or intercalation at the electrodes. In order to make use of pseudocapacitance, high-surface area materials are coated with electrochemically active substances such as manganese oxide, ruthenium oxide, or vanadium oxide [4]. Although pseudocapacitance offers a typically superior energy storage capability, the presence of the chemical reactions causes many of the problems that affect batteries: low cycleability, inferior power density, and a higher temperature sensitivity.

Symmetric electrochemical capacitors comprise two identical electrodes, and can be either double-layer capacitors or pseudocapacitors. Asymmetric electrochemical capacitors, sometimes humorously referred to as “supercabatteries,” are hybrid devices that have one electrochemically active and one inert electrode. Recently, a lithium-based asymmetric capacitor has been developed with a packaged energy density of 22 Wh/kg [13].

2.2 Symmetric Electrochemical Double-Layer Capacitors

The carbon nanotube-based devices investigated in this thesis belong to the class of symmetric electrochemical double-layer capacitors (EDLCs). Although the terms “super-” and “ultracapacitor” can refer to any type of electrochemical capacitor, they refer exclusively to symmetric EDLCs in this thesis. This section provides a high-level description of how these devices work and how they’re fabricated.

2.2.1 Description of Modern Ultracapacitors

As mentioned in previous paragraphs, the kilo-farad capacities of modern ultracapacitors are possible because electrodes possess an enormous surface area and the separation between opposite charges at the solid/liquid interface is typically under a nanometer. Currently, the material of
choice for the electrodes is activated carbon, which is fabricated by impregnating the source material (wood, nutshells, coconut husk) with a variety of chemicals (strong acids or bases and high-pressure steam) and then carbonizing it via pyrolysis. The resulting product is highly porous and granular, with a specific surface area that can exceed 1000 m$^2$/g, and a polymeric binder is added to give it structural rigidity. The electrode is bound to a metallic current collector with the help of the same binder, and is usually on the order of 10 – 50 $\mu$m thick. A permeable separator is sandwiched between two such electrodes to prevent accidental shorting, and the structure is rolled or otherwise compacted into its final shape. Lastly, the entire assembly is impregnated with an electrolyte before being packaged in an aluminum can. Figure 2.3(a) depicts the sandwich structure in a conventional ultracapacitor, with charges and electrolyte ions shown in blue and orange. A schematic for a packaged device is provided in Figure 2.3(b).

The choice of electrolyte plays an important role in designing high-energy density ultracapacitors. Since the energy stored in a capacitor is proportional to the square of the voltage across its electrodes, a high voltage is desired. Unlike in conventional electrolytic capacitors, however, the electrolyte shares an interface with conductive surfaces of both electrodes. This means that the electrolyte’s voltage stability window, which describes the range of voltages that it can withstand before the onset of electrochemical decomposition, becomes an important limitation in an ultracapacitor’s operating voltage. Under such conditions, aqueous solutions are limited to a voltage

Figure 2.3: (a) Ultracapacitor sandwich structure [14]. (b) Structure of a packaged device with activated carbon electrodes (adapted from [15]).
window of 1.23 V, at which point electrolysis of water occurs and hydrogen/oxygen evolution reactions begin. Organic solvents (without dissolved salts) such as acetonitrile and propylene carbonate have electrochemical stability windows in excess of 4 V. Ionic liquids are a class of electrolyte that consists solely of ions: they are room-temperature molten salts with no solvent molecules and boast stability windows over 5 V.

Other desirable properties for the electrolyte are chemical compatibility at both the anode and cathode over the entire voltage window and a high ionic mobility. Tetraalkylammonium salts such as tetraethylammonium tetrafluoroborate (TEA-BF$_4$ or Et$_4$NBF$_4$) are typically used as the electrolyte solute due to their low chemical reactivity and high solubility in organic solvents. Salts such as the ones used in lithium ion batteries (LiBF$_4$ and LiPF$_6$) also have good characteristics, but can only be used over a voltage range of 3.04 V, the cathodic limit for lithium. Ionic liquids, while promising in terms of voltage stability, generally suffer from low viscosity and tend to be much more expensive.

### 2.2.2 Current Applications for Ultracapacitors

Ultracapacitors are becoming increasingly popular storage devices because they operate safely at a much wider temperature range, can charge and discharge much faster when bursts of energy are required (and are therefore used as transient buffers in hybrid battery/capacitor systems), are composed of non-toxic and abundant materials, and most importantly, can be cycled orders of magnitude more times than rechargeable batteries. This last trait is particularly important in electric vehicle and grid storage applications, where system costs are not looked at in terms of $/kWh or $/W, but rather on a per cycle basis in order to capture costs of ownership and replacement.

The consumer appeal to fast charge times is fairly high, and there exist a number of devices that make use of ultracapacitors for that purpose. In 2007, Coleman produced a capacitor-powered cordless screwdriver that has about half the energy capacity of a similarly-sized battery-based device, but could be fully recharged in 90 seconds [16]. There is natural interest to have similar functionality for portable consumer electronics, but the energy density required for a storage device in, say, a mobile phone with moderate use over a 12-hour period is greater than what ultracapacitors
The majority of applications for ultracapacitors are in the industrial sector. For example, they are commonly used as emergency backup power sources for large memory modules in computer and server systems. In 2006, commercial bus routes in Shanghai utilized entirely ultracapacitor-powered vehicles that had the ability to partially charge at bus stops along the route and fully charge at the terminus, in addition to capturing energy from regenerative braking. Over their lifetime, these buses are about 40% cheaper than similarly-sized lithium ion-based vehicles and can achieve cumulative fuel savings of $200,000 based on prices in 2009 [17]. In 2012, Zhouzhou Electric Locomotive demonstrated a light metro-like train equipped with ultracapacitors that had a range of 2 km and could be charged in 30 seconds. In between stops, it is able to carry 320 passengers at a speed of 80 km/h. The company sees this technology as a viable means of urban transportation in smaller cities [18].

Frequently, ultracapacitors are used to complement battery-based systems. A powerful example that demonstrates how compatible these two storage technologies can be is a product recently developed by Maxwell that addresses the problems with cold-starting diesel engines in large commercial vehicles. Standard starter banks in trucks comprise three or four lead-acid batteries; in 2012, Maxwell introduced a drop-in ultracapacitor module that simply takes the place of one of these lead-acid batteries and permits engine starts without any preconditioning over a temperature range between -40 and +60 °C. At a packaged weight of 9.5 kg, it can deliver a peak power of 32.8 kW, can be fully charged in 15 minutes, and stores a total energy of 40 Wh.² A photograph of this drop-in configuration is provided in Figure 2.4.

²The Interstate 31-MHD Truck & Van Battery, which has identical dimensions, weighs 27 kg, delivers a peak power of 11.4 kW, stores 1400 Wh, and has a suggested retail price of $180 [19].
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PLASTIC LID
Thermal Weld (Heat Plate) to Case

ELECTRONICS ASSEMBLY
With DC-DC Converter and Controller Electronics

LASER-WELDED CELL PACK
(12 each 3000-Farad Maxwell Ultracapacitor Cells) with Plastic Spacers and Terminals

POLYPROPYLENE PLASTIC CASE

ESM INSTALLATION IN 3 AND 4 BATTERY BANKS.

Figure 2.4: Schematic and photographs of Maxwell’s Engine Start Module (ESM) adapted to 3- or 4-battery systems. Courtesy of Maxwell Technologies.

2.2.3 Limitations of Activated Carbon in Modern Ultracapacitor Electrodes

High-performance devices sold today by Maxwell, Nesscap, and other companies are rated to 2.7 V (absolute maximum of 2.8 V) and have an energy density of about 7 Wh/kg. From first principles, increasing the working voltage to 4.0 V per cell would result in over a 2× increase in energy density. The limitation in this endeavor is often attributed to the electrochemical stability window of the electrolyte [20], but that is incorrect. Both acetonitrile and propylene carbonate-based electrolytes, which are usually employed in commercial products, can operate sustainably at higher voltages [4, 21, 22]. In addition, lithium ion batteries – which also require a stable electrolyte to function – operate at voltages of around 3.7 V.

The true bottleneck comes from constituents in the activated carbon electrode. During the activation process which is necessary to augment specific surface area, the carbonized source material is exposed to a variety of acids, high-pressure steam, and/or other chemicals that leave behind impurities, surface functional groups, and dangling bonds which reduce electrochemical stability. Additionally, the polymeric binder which is added to give the electrode structural rigidity (usually PTFE) accounts for up to 15% of the total electrode mass and is not chemically inert. For
these reasons, activated carbon electrodes degrade rapidly at voltages even slightly above the rated amount. In a study on the aging mechanisms in EDLC electrodes, Ruch et al. observed multiple degradatory processes at voltages above ~3 V, including the defluorination of PTFE, loss of electrode porosity, and electrochemical modification of the activated carbon, all of which can be attributed to the presence of non-carbonaceous products in the electrode [23].

Activated carbon also poses limitations in the power density of packaged devices. The high specific surface area these electrodes offer is due to pores of different sizes, ranging from less than a nanometer to tens of microns wide. This inhomogeneous structure results in a range of ion diffusion characteristics which manifests itself as reduced overall ionic mobility (increased resistance). Furthermore, the electrical conductivity of the carbon is reduced by the presence of the afore-mentioned impurities and the polymeric binder, reducing the ability to deliver high power.

The resulting challenge is to find an alternate high-surface area electrode material that is compatible with the other constituents at higher working voltages. Some materials that are receiving notable attention are graphene and graphene composites, lithium/carbon compounds in asymmetric devices, and carbon aerogels. Carbon nanotubes are an attractive possibility for multiple reasons: they are excellent electrical conductors, can be shape-engineered into dense forests, can be extremely pure, and do not require a binder for rigidity – all of which are necessary properties in the quest to develop high-energy density electrodes.
2.3 Overview of Carbon Nanotubes

Carbon nanotubes are an allotrope of carbon with cylindrical symmetry. They are long, continuous molecules with either one or multiple concentric graphitic walls (referred to as single- or multi-wall nanotubes: SWNT and MWNT, respectively). This arrangement of carbon atoms results in exceptional material properties, among which are a thermal conductivity higher than that of copper, a tensile strength superior to that of stainless steel wire, and a high theoretical specific surface area of 1,300 m$^2$/g. Furthermore, the span of material properties can be broadened by chemically functionalizing the carbon surface or by mixing CNTs with a variety of composite host materials (polymers, alloys, etc.) Figure 2.5 provides some schematic illustrations of SWNTs and MWNTs.

![Schematic of SWNTs and MWNTs](image)

Figure 2.5: Left: schematic of single- and multi-wall CNTs, adapted from [24]. Right: TEM images of double-wall and multi-wall CNT, adapted from [25].

CNTs also have unique electronic properties. Depending on their chirality, they can be metallic (electrically conducting, with a conductivity superior to that of copper) or semi-conducting. The notion of chirality was investigated by Dresselhans [26] and describes the different arrangements of atoms in the individual graphene sheets that comprise a nanotube. If one were to create a CNT by taking a two-dimensional sheet of graphene and wrapping it around a central axis, the “seam” that would form by connecting the two edges could either appear perfectly symmetrical – seamless – or it could be offset by one or more carbon atoms. In the case of a seamless geometry,
the structure exhibits metallic behavior; otherwise, it is semi-conducting. However, a nanotube’s bandgap decreases as its diameter increases: at a diameter of approximately 3 nm, the band gap energy is less than the thermal energy at room temperature. Thus, while SWNTs with small diameters can be either metallic or semi-conducting, MWNTs are usually metallic. The growth of chirality-selective CNTs is a matter of current research [27].

2.3.1 A Brief History of CNT Research

The discovery of carbon nanotubes is often attributed to Iijima in his landmark 1991 publication [25]; however, filamentous carbon has been studied for well over a century. Thomas Edison invented a method for carbonizing natural fibers from hemp or bamboo as early as 1892 [28], and these filaments were then used in his incandescent bulbs. Perhaps the least-recognized engineering feat in the history of carbon engineering is the first reported catalytic chemical vapor deposition (CVD) of carbon by Radushkevich in 1952 [29]. He and his team successfully synthesized what, in hindsight, were multi-wall carbon nanotubes by flowing carbon monoxide over iron “contacts” at temperatures of between 400 and 700 ºC. Published in Russian in the Soviet journal Zhurnal Fizicheskoi Khimii (Journal of Physical Chemistry), it received absolutely no international attention.

In 1976, carbon fibers consisting of “turbostratic stacks of carbon layers, parallel to the fiber axis, and arranged in concentric sheets like the ‘annual ring structure of a tree’” were observed by catalytically decomposing benzene at elevated temperatures, and the catalytic role of iron in the formation of these cylindrical cores – in hindsight, also multi-wall carbon nanotubes – was confirmed [30]. Iijima’s paper in 1991 sparked CNT science worldwide with the observation that “engineering of carbon structures should be possible on scales considerably greater than those relevant to the fullerenes” [25]. This statement was particularly relevant due to widespread industrial efforts to develop lightweight carbon-based structural materials. By 2005, Hyperion (a US-based company) produced around 100 tons of CNTs per year.³ In 2011, worldwide CNT production capacity reached 4.6 kilotons per year [32,33]. Figure 2.6 displays some of the trends in the past

³Much of the information presented here, and additional details about the early history of CNTs, can be found in [31].
decade relating to the research and commercialization of carbon nanotubes – as is clearly shown, both the number of annual publications and production capacity are experiencing significant yearly growth.

![Graph showing yearly trends in the research and commercialization of CNTs.]

Figure 2.6: Yearly trends in the research and commercialization of CNTs [32].

### 2.3.2 Applications

Perhaps the earliest example of an application utilizing the properties of carbon nanotubes – though it was obviously not known at the time – is the forging of Damascus steel blades, known for their legendary sharpness, in the mid-seventeenth century. Toward the end of the manufacturing process, blacksmiths would etch the blades with acid. While some of the steel would dissolve, it is theorized that individual steel “nanowires,” encapsulated in CNTs, were protected from this treatment. After etching, these nanotube/nanowire structures stuck out from the blade’s edge, giving it tiny saw-like teeth [34,35].

Today, CNTs are used on a commercial level as additives in conductive inks, plastics, and alloys to improve the mechanical, thermal, and/or electrical properties of the bulk product. Examples include tennis racquets, golf clubs, and bicycle frames.\(^4\) Continuous sheets containing large amounts of CNTs are used as EMI\(^5\)-shields in certain aircraft and are expected to replace copper for that purpose [37]. On a smaller scale, CNTs are used as tips for atomic force microscopy probes (sold, for

---

\(^4\)The winning bicycle of the 2006 Tour de France had nanotubes swirled into its frame; as a result, this frame weighed less than 1 kg, approximately 20% lighter than others made by the Swiss manufacturer, BMC [36].

\(^5\)Electromagnetic interference.
example, by NanoScience Instruments), mechanical resonators, field emitters in high-performance X-ray tubes, and the anode material in specialty batteries. In 2012, the global market for CNTs was on the order of $250 million with a projected CAGR\(^6\) of over 20\% [38].

One must note that CNT-based materials are still very far from achieving the thermal, mechanical, and electronic properties of individual CNTs. Massively aggregating individual nanotubes and obtaining long-range continuity is a difficult materials challenge. However, recent research has identified CNTs as the key components in a multitude of potential applications that are in their early development stages:

- **Thermal**: CNT bundles are demonstrated as effective materials in vias and interconnects in integrated circuits and thermal interface materials [39];

- **Structural**: CNT-infused fabric is used to design a professional-looking high-end men's suit capable of blocking a 9 mm bullet [40]. The material is 50\% lighter and 30 times stronger than Kevlar, highly flexible, and intensely researched by DARPA\(^7\) in the pursuit of lightweight body armor for military applications.

- **Electronic**: The first CNT field-effect transistor was demonstrated in 1998 [41]; in 2013, researchers demonstrated a computer built entirely using CNT transistors [42];

- **Chemical**: An ammonia gas sensor is designed using CNTs that were chemically functionalized with polyaniline [43].

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\(^6\) Compound annual growth rate.

\(^7\) Defense Advanced Research Projects Agency.
2.4 Review of Carbon Nanotube Electrodes in Ultracapacitors

This section reviews prior use of carbon nanotubes as an electrode material in ultracapacitors. Much of the cited literature from before 2005 frames the work initiated in Signorelli's thesis, and a detailed description of his experiments and analysis is provided to establish the experimental context that motivated this thesis.

2.4.1 Early Work

Due to their excellent mechanical, thermal, and electrical properties and their ability to grow on a variety of metallic and nonmetallic substrates, carbon nanotubes have been identified as a possible electrode material in high-energy density ultracapacitors ever since their propagation by Iijima et al. in 1991 [25]. The first embodiment of such an electrode was put forth by Niu et al. in 1997 [6]. Randomly entangled CNTs were acquired externally and treated with nitric acid to disassemble them. After being filtered and dried, they were annealed on a nickel foil current collector to form an electrode. This contribution was significant because it demonstrated that an appreciably higher power density was obtainable with CNT-based electrodes: at 8 kW/kg, Niu's electrodes outperformed existing materials by a factor of five. Despite these advantages, the energy density of Niu's devices fell far below that of existing ultracapacitors, at about 0.5 Wh/kg.

Uniform films of vertically aligned CNTs were first demonstrated in 1995 [44] but it wasn't until four years later that such structures were first synthesized by a much more simple chemical vapor deposition (CVD) process [45]. Yoon et al. [46] adapted this synthesis process to produce the first vertically-aligned CNT-based ultracapacitor electrodes in 2004. In a novel catalyst-free method, uniform films of aligned CNTs were grown directly on a nickel foil current collector, and two such electrodes were successfully tested in an assembled coin cell as shown in Figure 2.7. The group also demonstrated that briefly exposing as-prepared CNT films to an ammonia plasma increased the material's specific surface area, likely due to the removal of amorphous carbon residue that formed during the CNT growth process. They report a capacitance increase by a factor of five as a result of this treatment.
Early explorations of CNTs and their properties led many researchers to attempt coating, treating, or otherwise modifying the surfaces of individual nanotubes so as to improve certain material characteristics. Specifically for the purposes of energy storage, a higher specific surface area and differential capacitance are desired. An et al. [47] demonstrated that the specific surface area and pore size distribution in a composite formed of tangled CNTs and a PVDC binder could be altered by exposure to high temperatures in an inert, argon atmosphere. The specific capacitance of an electrode treated at 1000 °C was 50% higher than one treated at 500 °C, with an estimated differential capacitance at the double layer of 50 μF/cm². Comparatively, the typical differential capacitance of activated carbon structures is less than 10 μF/cm².

Other investigations explored the possibility of coating CNTs with an enhancing material. It was already well known that various metal oxides (RuO₂, MnO₂, V₂O₅, and others) exhibited pseudocapacitance. In order to take advantage of this effect as well as double-layer capacitance, Qin et al. developed a composite hydrous ruthenium oxide/CNT electrode that exhibited a 10× increase in specific capacitance when compared to pristine nanotubes [48]. These nanotubes were, strictly speaking, deposited by coating the surface of an anodized aluminum oxide template with carbon and then using an acid bath to dissolve the template, rather than grown using the more conventional technique of decomposing a carbon-containing gas over catalytic nanoparticles.

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8Differential capacitance is a microscopic property and pertains to the amount of capacitance that is offered by a differentially small amount of material surface area (μF/cm²). This is in contrast to specific capacitance, which is a macroscopic property that describes the amount of capacitance that a material offers per unit mass or volume (μF/cm³).

9Poly(vinylidene chloride).
The idea to coat nanotube structures with ruthenium oxide was further explored by Ye et al., who grew films of vertically aligned CNTs and proceeded to deposit a thin layer of ruthenium oxide on top via reactive sputtering of ruthenium metal in a 3:1 oxygen/argon atmosphere [49]. They report area-specific capacitances of 0.35 and 16.9 mF/cm² for bare and RuO₂-coated electrodes, respectively (a 50× increase). Other research groups explored the coating of CNTs with various polymers. In particular, polyaniline [50] and polypyrrole [51] nanocomposites both demonstrated superior performance when compared to "naked" CNTs. Ultimately, however, these enhancing procedures come at the high cost of complexity in the fabrication process. Furthermore, the presence of pseudocapacitive reactions – the principal effect that improved the performance of CNT-based materials in these researchers' investigations – implies that, like batteries, the electrodes would degrade faster, the range of operating temperatures would become narrower, and the power density would be lower than in a device which relied purely on double-layer capacitance.

2.4.2 Prior CNT-Ultracapacitor Work at MIT

Ph.D. candidate Riccardo Signorelli, working under the supervision and guidance of Professors John Kassakian and Joel Schindall with support from the MIT LEES Auto Consortium, the Ford-MIT Alliance, and the MIT Energy Initiative, began exploring carbon nanotubes and the role they may have as an electrode material in 2004. The goal was to grow tall vertically aligned forests directly on metal foil and assemble a purely double-layer-based ultracapacitor by incorporating two such electrodes in a cell [7]. In his thesis, Signorelli describes the use of a reaction chamber based on the design by van Laake, Hart, and Slocum [52] which could ramp to the target CVD temperature in a matter of seconds, compared to conventional methods which utilize a tube furnace and take almost an hour to heat up. The group investigated different current-collecting substrate materials (tantalum, tungsten, aluminum) and was able to bring the CVD temperature low enough to grow uniform forests of CNTs directly on aluminum foil. Although these growths were typically under 100 μm tall, electrochemical characterization of the cells allowed Signorelli to devise and validate a model for the behavior of the electrodes, and he subsequently utilized this model to make certain extrapolations and predict the performance of CNT-based ultracapacitors. These extrapolations were based on the microscopic properties of the CNT forests he grew, such as the areal density
(CNTs/cm²), average CNT diameter, and differential capacitance.

Signorelli’s best demonstrated cell had the following characteristics:

- Two tungsten electrodes, both 1 × 1 cm squares.
- Vertically-aligned CNT forests 75 μm tall.
- A 1 M solution of TEA-BF₄ in acetonitrile.
- CNT areal density of 7.5×10¹⁰ cm⁻².
- Average CNT diameter of 6.5 nm.
- Cell capacitance of 5.7 mF using two 1 × 1 cm electrodes.
- Differential capacitance of 12 μF/cm².

This cell and others were used to validate Signorelli’s electrochemical model for the performance of CNT-based electrodes. The projection described in his thesis calls for:

- CNT forests over 100 μm tall.
- A differential capacitance of 50 μF/cm² (as demonstrated by An et al. [47]).
- A CNT areal density of 10¹² cm⁻² with an average diameter of 6.5 nm.

A packaged D-sized cell with electrodes exhibiting these properties and a voltage of 3.5 V would exhibit an energy density of 30 Wh/kg. A detailed analysis of Signorelli’s methods and projections was published by the IEEE in 2009 [53]. The paper compares the material properties of CNTs to those of activated carbon and describes the different performance metrics and characterization methods that were used to arrive at the final projection.

2.4.3 Recent Advances in CNT-Based Ultracapacitors
(2009 – present)

As a routine Internet search shows, claims that CNTs will drastically improve the performance of ultracapacitors are fairly widespread. However, the use of CNTs in ultracapcitors, and electro-
chemical energy storage devices in general, is still in fairly early stages of development and there are relatively few established entities that are actively pursuing the development of a commercial product.

Over the past five years, much of the academic work relating to CNT electrodes has focused on designing carbon composite materials by combining CNTs with graphene,\textsuperscript{10} different forms of carbon paper, or activated carbon [55–58]. Kim et al. report the out-of-plane growth of CNTs on individual graphene sheets and suggest that such a hybrid carbon material will facilitate electron transport throughout the structure during the charge-discharge process [59]. A compositional dual of this material is a structure consisting of graphene foliates grown along the length of a CNT: Parker et al. demonstrated that these “graphenated CNTs” demonstrated a weight-specific capacitance that was 5.4× that of similar CNTs without the foliates [60,61]. SEM images of this material is provided in Figure 2.8. The weight-specific capacitances reported for these carbon/carbon materials — approximately 100 F/g — are higher than the purely CNT-based forests grown by Signorelli (28 F/g); however, the researchers have not been able to accumulate enough of either material on an electrode and the total capacitance is, in fact, lower.

With the development of novel printed materials and printed electronics, some research groups have been investigating the development of CNT-based thin-film storage devices that can be printable, transparent, flexible or shape-conforming [62–64]. Typically, such miniature ultracapacitors would complement battery systems in consumer electronics and improve behavior during peak power loading. The techniques used to fabricate these devices, however, are incompatible for bulk energy storage purposes.

There has also been notable effort in the development of new coating materials or coating processes that enable or improve the pseudocapacitive capabilities of CNTs. Tang et al. describe the fabrication of a nickel hydroxide-enhanced CNT electrode (Ni(OH)\textsubscript{2}/CNT) wherein forests of CNTs, grown directly on a nickel foam current collector, are coated in Ni(OH)\textsubscript{2} via a novel chemical bath deposition process [65]. One such electrode is combined with a traditional activated

\textsuperscript{10}Graphene is a two-dimensional form of carbon and can be thought of as a one-atom thick layer of graphite. It was first isolated in 2004 and has received a lot of attention as the century’s \textit{Wundermaterial}, or “wonder material.” In fact, purely graphene-based electrodes are also being researched with the goal of fabricating high energy-density ultracapacitors [54].
carbon counter-electrode to form an asymmetric cell at a voltage of up to 1.8 V. Its performance is impressive: the authors report an areal capacitance of 16 F/cm$^2$, which is far greater than what can be achieved with activated carbon alone (approximately 0.7 F/cm$^2$). However, the device exhibited poor cycling stability, losing 17% capacity after only 3000 cycles.$^{11}$

The crux of this thesis is to develop a fabrication recipe that would bring the areal capacitance of CNT-based electrodes to the same level as that of activated carbon electrodes. As described in previous sections, the feasibility of a higher working voltage would imply an increased energy density over existing packaged devices. The premise that CNTs are indeed capable of maintaining their performance at an elevated voltage is substantiated in published literature. Although multiple groups report the compatibility of CNTs at elevated voltages with ionic liquids as electrolytes [66-68], the key to commercializing a CNT-based ultracapacitor is operating at a high voltage while utilizing a conventional organic electrolyte. In 2010, Izadi-Najafabadi et al. demonstrated that an electrode made of highly pure SWNTs (0.013 weight-% of noncarbon content) had an operating voltage range of 4 V, the highest-reported voltage range for any single-cell ultracapacitor using a

$^{11}$The authors actually laud this result, claiming that their cell exhibited "excellent cycling stability;" it is, however, wholly inadequate for the purposes of highly cycleable bulk energy storage.
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1 M solution of Et₄NBF₄ in propylene carbonate [22]. The cycleability tests produced encouraging results: after 1000 cycles, performance declined by only 3% at 4 V, compared to an activated carbon-based cell which degraded by 46% operated at 3.5 V (one must note, though, that any device would need to be tested to millions of cycles before having real commercial value). The negative influence of impurities on the electrochemistry of carbon nanotubes had been reported previously [69], and the results here corroborate the notion that a high purity electrode material is required to achieve stable performance at a voltage of up to 4 V. Zheng et al. report similar successes with CNT-based cells at voltages of 3.5 and 4.0 V, and additionally suggest that exposing CNT forests to a mild carbon dioxide plasma environment helps remove impurities [70].

The impact of Izadi-Najafabadi’s results on this thesis is significant because the electrochemical tests required to characterize ultracapacitor electrodes are highly sensitive to environmental contamination if performed at elevated voltages. The demonstrated compatibility of CNT-based electrodes in an organic electrolyte at a working voltage of 4 V legitimizes our group’s focus on specific capacitance as opposed to other characteristics such as working voltage and energy density, and allows us to legitimately extrapolate our results (which are typically reported up to a voltage of less than 2 V) in the context of a 4 V cell without requiring the same type of rigorously controlled working environment to avoid contamination.

2.5 A Summary of Electrochemical Storage Device Performance

This section concludes the chapter by providing an at-a-glance comprehensive comparison of the various forms of electrochemical storage described above: lead-acid batteries, lithium ion batteries, ultracapacitors with activated carbon electrodes, and ultracapacitors with CNT-based electrodes (experimental results before, as well as projections set by, Signorelli’s work).
Table 2.1: Comparison of different electrochemical storage technologies.

<table>
<thead>
<tr>
<th></th>
<th>Lead-acid</th>
<th>Lithium ion</th>
<th>Ultracapacitors (activated carbon)</th>
<th>Ultracapacitors (CNTs, experimental)</th>
<th>Ultracapacitors (CNTs, projected [53])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy density (Wh/kg)</td>
<td>30</td>
<td>150</td>
<td>7</td>
<td>0.5</td>
<td>30</td>
</tr>
<tr>
<td>Power density (kWh/kg)</td>
<td>0.2</td>
<td>1</td>
<td>10</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>Rated voltage (per cell, V)</td>
<td>2.1</td>
<td>3.7</td>
<td>2.7</td>
<td>2.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Longevity (cycles)</td>
<td>&lt; 10³</td>
<td>10³ – 10⁴</td>
<td>10⁵ – 10⁶</td>
<td>10⁵ – 10⁶</td>
<td>10⁵ – 10⁶</td>
</tr>
<tr>
<td>Temperature window (°C)</td>
<td>-20 – 40</td>
<td>0 – 45</td>
<td>-40 – 65</td>
<td>-40 – 65</td>
<td>-40 – 65</td>
</tr>
</tbody>
</table>

2.6 Chapter Summary

This chapter provided a condensed overview of the most prevalent forms of electrochemical energy storage – lead-acid batteries, lithium ion batteries, and ultracapacitors – including details about how the different technologies work, what significance they have in the energy storage market today, and what the technological or market impacts will be in the foreseeable future. It proceeds by outlining the structure and properties of carbon nanotubes, describing various applications and detailing some relevant market information. Our investigation of CNT-based electrodes is then fully motivated by explaining the limitations of current technologies and how CNTs could improve the performance of modern ultracapacitors. The chapter then provides an overview of prior work in this field, outlining many different ways researchers have engineered carbon- and/or CNT-based materials to improve the energy capacity of ultracapacitor electrodes. It summarizes the key findings that resulted from Signorelli’s prior work, and presents a summary of various research results that have been published since. Finally, the chapter ends with a compare-and-contrast summary of the technical specifications for the different energy storage technologies explored here.
Chapter 3

Electrode Fabrication, Assembly, and Characterization

This chapter provides background information on how carbon nanotubes are synthesized, with some details on the prevalent methods used to produce industrial quantities today. Thereafter, it describes the standard electrode preparation technique and experimental setup used in our laboratory to grow nearly millimeter-tall, uniform forests of vertically aligned CNTs (VACNTs) on small $0.75 \times 0.75$ cm tungsten foil substrates. Details are provided on how the surfaces of these electrodes are characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM), how ultracapacitor test cells are assembled using two as-prepared electrodes, and how the test cells are evaluated using electrochemical techniques such as cyclic voltammetry and impedance spectroscopy. Finally, the chapter introduces the notion of the $\rho d$ product, a useful geometrical tool used to evaluate the quality of a VACNT forest and predict its specific capacitance.

3.1 CNT Synthesis Methods

Appreciable quantities of CNTs today can be produced using a variety of different synthesis procedures. Various factors dictate their industrial widespreadness, such as the physical or chemical characteristics and homogeneity of the resulting CNTs, the level of impurities, and economies of scale. This section briefly describes the most common methods in use today; a highly detailed and
comprehensive review can be found in [71].

3.1.1 Arc-Discharge

The "helical microtubules" described by Iijima in his 1991 paper were a product of dc arc-discharge between two graphite electrodes in a low-pressure helium atmosphere. The electrodes are brought close together and an arc (plasma) is struck. CNTs, as well as other forms of crystalline and amorphous carbon, are deposited on the cathode as a result of the high-energy environment. Some parameters that affect the yield and quality of the resulting CNTs are the atmosphere constituents (which can be an inert gas or a dilute mixture of methane or other carbonaceous gas), distance between electrodes, and presence of a metal catalyst at the anode [72,73]. A schematic diagram of the arc-discharge apparatus is provided in Figure 3.1.

![Schematic diagram of a simplified arc-discharge apparatus, as shown in [73].](image)

3.1.2 Laser Ablation

First developed by Guo et al. in 1995 [74], the laser ablation method (also known as "laser vaporization") has been shown to be a high-yield method of producing both single- and multi-walled CNTs with relatively low amounts of contaminants or defects. The synthesis system consists of a laser beam source, a graphite rod, and copper collector plates in an argon-filled furnace. The laser vaporizes the surface of the graphite rod, the vapor is swept by the argon flow, and deposits form on the collector plates located just downstream of the furnace. Some tunable parameters are the
furnace temperature, gas flow rate, and composition of the graphite rod (which can be mixed with catalytic material such as iron, cobalt, or nickel).

3.1.3 Catalytic Chemical Vapor Deposition (CVD)

Today, CVD is the most prevalent method of CNT synthesis due to its simplicity, flexibility, scalability, low cost, and low temperature requirements compared to laser ablation and arc-discharge; interestingly, it was also the process by which Radushkevich produced his “nanotubes” in 1954 by flowing carbon monoxide over hot iron “contacts.” The process was promulgated among the academic community in the mid 1990s. The following section provides details on some of the key factors involved.

3.2 Synthesis of CNTs via CVD

Although there are a vast number of tunable parameters in the various adopted CVD methods, the general mechanism for CNT growth is the decomposition of a carbon-containing gas over heated nano-sized catalytic particles. The catalyst can either “float” as a result of being incorporated into the gas flow [75], or, as is the case for our electrodes, it can be substrate-bound. When the density of catalytic sites is high enough, initial crowding at the onset of growth causes the CNTs to orient themselves perpendicular to the substrate surface, forming what is referred to as “vertically aligned CNTs,” or VACNTs. This is the growth mode of interest in our investigation: we desire a very high density of active catalytic sites so that dense VACNT forests with a high specific surface area can be grown.

3.2.1 CVD Process Fundamentals

When a carbon-carrying gas such as methane, ethylene, or acetylene is passed over heated catalytic nanoparticles (typically transition metals such as iron, nickel, or cobalt), it readily decomposes and carbon diffuses into the particles. They quickly become saturated and a graphitic layer forms around their surface. As more feedstock gas flows in, the particles continue to discharge carbon and a CNT begins to grow. Eventually, growth terminates when the particle becomes completely
encapsulated or some other deactivation effect takes place [76].

The physical properties of CNTs that grow via CVD are largely dependent on the arrangement, dimension, and activity of the catalytic sites, combined with the surface interactions that take place between the catalyst particles, the base substrate, and the decomposing carbonaceous gas. Other important factors include the choice of substrate and catalyst materials, the components in the gas flow, chamber pressure, and growth temperature.

3.2.2 Process Parameters

The principal process parameters and their role in CVD are described below:

- **Catalyst material**: Iron, nickel, and cobalt are the most common catalyst materials used to synthesize CNTs. Iron tends to be the most popular one. There are conflicting reports on the effectiveness of nickel: some claim it results in a faster CNT growth rate [77,78], while others claim iron is superior [79]. A review on the behavior of different catalysts in CVD systems can be found in [80].

- **Catalyst support layer**: At temperatures above ~500 °C, the diffusivity of materials into silicon and many metals is greatly elevated. The purpose of adding a support layer between the base substrate and the catalyst is to mitigate this effect. Typically, this layer is a ceramic whose surface properties force a non-wetting contact angle with the catalyst upon heating. The result is a highly uniform distribution of evenly-sized catalyst particles over the support-layer surface. Aluminum oxide is widely reported as an effective material for this purpose, even when electrical conductivity between CNTs and substrate are desired. The layer can be made sufficiently thin, and CNTs root themselves strongly enough, that Ohmic contact between CNT forest and base substrate remains excellent. The use of conductive ceramics such as titanium nitride has also been reported to support CNT growth [81].

- **Base substrate**: The most ubiquitously used base substrate is crystalline silicon. It easily withstands CVD reaction temperatures and is atomically smooth, which plays a role in the uniformity of CNT distribution. CNTs are frequently grown on metallic and ceramic
substrates, including aluminum, tantalum, tungsten, titanium nitride, and others. Not all materials prove as effective: copper and platinum, for example, fail to produce aligned CNT structures under the same conditions as other substrates [82].

- **Reactive gas:** Methane, ethanol, ethylene, and acetylene have all been reported to effectively decompose into CNTs. However, Zhong et al. report that acetylene is the actual precursor to CNT growth [83]. When a different feedstock gas such as methane is used, it chemically alters to form acetylene prior to the CVD reaction.

- **Temperature and pressure:** Appreciably good CNT growth conditions can be obtained in both low- and atmospheric-pressure environments [31]. Temperature is a critical factor. Generally, the CNT growth rate is accelerated by higher temperatures. If overly excessive, however, the feedstock gas could self-pyrolize and not decompose as needed to form CNTs. Furthermore, the catalytic nanoparticles' surface mobility is greatly enhanced at higher temperatures, causing many of them to coarsen together via Ostwald ripening or surface diffusion [84-86]. Under most conditions, particles over 20 nm do not nucleate CNTs.

The benchmark procedure calls for the deposition onto a silicon substrate of a ~10 nm thick bi-layer film of aluminum oxide and iron via sputtering or e-beam evaporation. The aluminum oxide “support layer” mitigates diffusion of iron into the bulk substrate. Upon heating, usually in a tube furnace, the initially uniform layer of iron dewets and coalesces into well-distributed nanoparticles, each of which has the ability to catalyze the growth of a single CNT. Figure 3.2 schematically depicts this growth process.


3.3 Electrode Preparation

The electrodes used throughout this investigation were prepared by catalytic chemical vapor deposition on 50 μm-thick tungsten foil, which served as the current collector. Tungsten was selected due to its known ability to support the growth of CNTs [7], high melting point, and good electrical conductivity. A nominally ~10 nm thick bi-layer of aluminum oxide and iron is deposited using a magnetron sputterer. The substrate is then removed from the sputterer and cut into adequately-sized pieces. Lastly, we place one of these pieces in the CVD chamber, whereupon it is heated and subjected to a dilute acetylene flow with argon as the carrier gas; a uniform forest of VACNTs then proceeds to grow on the tungsten foil. This section describes the details about the electrode preparation procedure, the growth apparatus used, and the process parameters that were controlled to obtain high quality and repeatable results.

3.3.1 Nominal Method for Catalyst Deposition

As will be discussed in future sections, the morphological quality of CNT forests is highly sensitive to the catalyst deposition process prior to initiating the CVD reaction. Described here is the general recipe which was inherited from Signorelli’s research. Chapter 5 describes the many modifications to this “conventional” process that were explored subsequent to our own investigations of the basic tunable parameters.
Chapter 3. Electrode Fabrication, Assembly, and Characterization

The tungsten substrate is first thoroughly cleaned by flushing with excess acetone to remove organic residues, isopropyl alcohol (which dissolves any remaining acetone), and de-ionized water. Prior to catalyst deposition, the substrate is inspected visually to ensure a clean and dry working surface. Both the aluminum oxide support layer and iron are deposited using a multi-target magnetron sputterer. A photograph of the machine is provided in Figure 3.3.

![Figure 3.3: Photograph of AJA sputterer.](image)

The source material targets are secured in separate compartments and the substrate is placed on a rotating chuck (the rotation ensures uniformity during the deposition process). After purging the sputterer chamber with argon and evacuating it to a base pressure of approximately $5 \times 10^{-5}$ Torr, argon is reintroduced into the chamber at a controlled pressure of 30 milli-Torr. A plasma is struck at each of the two targets, and individual molecules or atoms from the targets are ejected as a result of high-energy collisions with argon ions in the plasma. The intensity of the plasma can be adjusted to produce a slower or faster deposition rate. A shutter in front of the target can be actuated to allow the sputtered material to reach the substrate. The material deposition rate is also affected.

$1$ Torr = $1$ mm Hg.
by the chamber pressure: at higher values, the path of sputtered material is impeded, resulting in a slower accumulation at the target. Conversely, low pressures increase the deposition rate; however, the plasma cannot be sustained below a threshold value. Our depositions were nominally performed at a chamber pressure of 3 milli-Torr.

The material deposition rate is measured by an in-situ quartz crystal monitor (QCM). Based on previous work by Signorelli and others [7, 85, 87, 88], nominally 10 nm of aluminum oxide and 1 nm of iron are deposited sequentially, forming a thin uniform bi-layer on the tungsten substrate. Figure 3.4 depicts this structure. At a power of 250 W, the aluminum oxide deposition takes approximately 9 minutes, whereas at 35 W, the iron deposition takes approximately 1 minute. For the catalyst layer thicknesses we explored, it was important to deposit the iron slowly, as using a higher plasma power would results in a non-uniform deposition thickness across the substrate due to the limited rotation speed of the chuck.

![Figure 3.4: Schematic of the catalyst/support bi-layer on tungsten substrate.](image)

The performance limits we observed from CNT forests grown on substrates prepared using this preparation technique are discussed in Chapter 4. Numerous enhancements to this “standard” procedure are explored in Chapter 5, such as varying the material deposition rate and substrate temperature, adding reactive gases to the sputterer chamber during deposition, using plasmas to help structure the catalyst as it deposits, and depositing multiple catalyst layers.

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2 As material falls onto the vibrating crystal, its resonant frequency decreases due to a mass increase. The sputterer monitors this frequency change and calculates a deposition rate based on the material’s density.
3.3.2 CVD Setup and CNT Growth

Conventional CVD systems use a tube furnace to bring the substrate up to reaction temperature. Such setups take about an hour to heat up, which is prohibitive for prototyping purposes. Based on a design by van Laake [52], Signorelli built a reaction chamber using a piece of mildly conductive silicon which would heat up when passing an electrical current through it. Our own group utilized this setup to synthesize CNT forests. The reaction chamber is easily accessed by sliding an outer quartz tube and revealing the heater, and a sample is placed directly on it. A schematic and photograph of the chamber are shown in Figure 3.5, and a detailed description of the experimental setup is provided in Appendix A.

First, the chamber is purged with argon for 3 minutes and evacuated to a pressure below 10 milli-Torr. The CNT growth process is then initiated by introducing acetylene (5% by volume) and hydrogen (10% by volume) diluted in argon at a total pressure of about 15 Torr, and passing an electrical current through the silicon heater which quickly heats up to the growth temperature of approximately 750 °C.3 An infrared thermometer monitors the temperature and a closed-loop feedback system controls the current through the heater to keep it at its setpoint value.4 The initially uniform layer of iron dewets and disaggregates into well-distributed nanoparticles, each of which catalyzes the growth of a single nanotube. After ten minutes, the CNTs usually reach a height of approximately 600 μm, which is similar to the fast growth rate reported in [89].

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3 Much of this recipe was inherited from prior work completed by Signorelli using the same CVD chamber. Fine-tuning of parameters was done empirically.

4 This system was designed and built by David Otten, to whom we are very grateful.
growth is terminated by cutting off the acetylene flow. The heater is turned off, and after purging the chamber with argon for several minutes, the chamber is opened and the sample removed.\footnote{CNTs were also successfully grown on an aluminum substrate by following the same procedure. The CVD reaction temperature, however, had to be brought down to approximately 600 °C in order to prevent the substrate from melting. The resulting growth rate was significantly slower and the final height of the CNTs only about 100 μm tall. We therefore decided to continue using tungsten for all further growths.}

Figure 3.6 shows several photographs of the resulting forests.

Figure 3.6: Photographs of VACNT forests grown on 0.75 × 0.75 cm tungsten substrates. The CNTs were removed with a razor in one corner to reveal the base substrate.
3.4 Ultracapacitor Test Cell Preparation

The ultracapacitor schematics and photographs in the introductory chapters to this thesis show how some commercial products on the market today are put together. Much thought goes into the packaging design to maximize volumetric efficiency. In the laboratory, however, the enclosure must be easily opened, refilled, and fitted with new electrodes; furthermore, it must be corrosion resistant and chemically compatible with a variety of electrolytes. This section describes the ultracapacitor “test cell” that was used to conduct electrochemical characterization of different electrodes.

3.4.1 Anatomy of a Test Cell

The active components in the ultracapacitor test cell are the two porous electrodes, the electrolyte, and a porous separator. The electrodes provide a high surface area over which ions in the electrolyte distribute themselves when a potential is applied across them. The separator ensures that the two electrodes don’t accidentally come into electrical contact and form a short; it is electrically insulating but must be sufficiently permeable to allow solvated electrolyte ions to pass through. Our setup utilized circular Whatman® glass microfiber filters 13 mm in diameter, sold by Sigma Aldrich, for this purpose. The passive components in our cell are a teflon side wall, a spring, an electrode contact, and the enclosure itself. An exploded view of our test cell is provided in Figure 3.7. The teflon sidewall helps align the electrodes, and the spring/contact combination ensures good electrical contact between the top electrode and the top half of the cell enclosure. Figure 3.8 shows a photograph of a sealed test cell.
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Figure 3.7: Schematic of ultracapacitor test cell with labeled components.

Figure 3.8: Photograph of sealed test cell.

The test cell measures approximately 5 cm in diameter and is assembled by first adding a small amount of electrolyte inside the void of the bottom enclosure half, placing all the inner components, and then topping off the remaining space with additional electrolyte before sealing the cell with the top enclosure half. In the case of CNT electrodes, we found that adding electrolyte to the cell after the first electrode is already inside causes some of the CNTs to de-root themselves from the base substrate and partially agglomerate, revealing portions of the tungsten substrate. This is likely due to unbalanced surface forces during the gradual wetting action of the electrolyte as it spreads.
through the porous structure. The effects of this phenomenon on the resulting cell capacitance were not conclusive; however, we found that quickly submersing a CNT electrode into an existing pool of electrolyte leaves the CNT forest intact.

3.4.2 Electrolytes in Ultracapacitors

As outlined in the introductory chapters to this thesis, the choice of electrolyte plays an important role in the performance of ultracapacitors. Aqueous electrolytes are unsuitable for high energy-density devices because of water's narrow electrochemical stability window of 1.23 V. Organic solvents, such as acetonitrile, propylene carbonate, and ethylene carbonate, have a wider window—sometimes exceeding 4 V—but are extremely sensitive to contaminants which complicates manufacturing and requires strict process control during device assembly. Toxicity is also a concern: acetonitrile is metabolized as hydrogen cyanide in many living organisms, including humans. Ionic liquids, also known as room-temperature molten salts, are capable of withstanding voltages over 5 V at room temperature but are generally viscous and have relatively poor wetting capabilities as well as a higher equivalent series resistance; they too are sensitive to contamination.

During our investigation, we explored a variety of electrolytes:

1. A 1 molar solution of sulfuric acid (H₂SO₄), which has a very high conductivity and ion mobility. This solution destroyed our electrodes due to a combination of reactions with the CNTs and tungsten electrode.

2. A 1 molar solution sodium sulfate (Na₂SO₄) in water, which may not have as high a conductivity as sulfuric acid but is pH-neutral and does not react with the electrodes. One of our goals was to perform electrochemical tests in aqueous solutions before moving to organic solvents; sodium sulfate was selected based on investigations in [90].

3. A 1 molar solution of tetraethylammonium tetrafluoroborate (Et₄NBF₄) in acetonitrile, graciously provided by FastCap Systems, which is a standard electrolyte used in commercial ultracapacitors today.

4. A 1 molar solution of lithium tetrafluoroborate (LiBF₄) in propylene carbonate (PC). Al-
though PC is slightly more viscous than acetonitrile and has a lower saturation concentration,\textsuperscript{6} it is being used increasingly in various applications due to lower environmental and health hazards. Lithium ion battery manufacturers readily use lithium-based salts such as LiBF\textsubscript{4} and LiPF\textsubscript{6} in solvents such as propylene carbonate and ethylene carbonate. Over a voltage window between \(-1.5\) and \(1.5\) V, this electrolyte performed almost identically to Et\textsubscript{4}NBF\textsubscript{4} in acetonitrile, and we used it for the vast majority of our experiments.

5. 1-butyl-1-methylpyrrolidinium tetracyanoborate, an ionic liquid developed by the German company Merck (doing business as EMD Millipore in the United States and Canada), graciously provided by their laboratory in Waltham, MA. We abandoned this electrolyte fairly quickly because the solution would crystallize when coming into contact with our test cell.

\textsuperscript{6}We were able to make a 1 M solution by gently heating the solution while stirring the salt into it.
Chapter 3. Electrode Fabrication, Assembly, and Characterization

3.5 Electrode Characterization

One of the primary goals of this thesis was to investigate the links between the morphological quality of VACNT forests and their specific capacitance. In order to achieve a good understanding between these two material properties, CNT forests had to be qualitatively and quantitatively characterized. This section describes the different imaging and electrochemical techniques used to do so, as well as how the performance metrics are defined.

3.5.1 Morphological Characterization

"Morphological characterization" of CNT structures refers to the study of the size, shape, and distribution of individual CNTs which, when assembled into dense forests, give an electrode its macroscopic characteristics. The physical properties of interest are:

- The **electrode area** $A_E$, which is the Euclidean area of the substrate onto which nanotubes are grown and has units of cm$^2$. Unless indicated otherwise, this value is measured using a ruler with millimeter precision.

- The **electrode surface area** $A_{TOT}$, which refers to the cumulative surface area made available for electrolyte wetting by the electrode's porous structure and has units of m$^2$.

- The electrode’s **specific surface area** (SSA), which is the normalization of its total surface area with respect to its volume and has units of m$^2$/cm$^3$.

- The **areal density** of nanotubes $\rho$, which refers to the number of nanotubes grown on the substrate normalized by its Euclidean area and has units of CNTs/cm$^2$ (or cm$^{-2}$).

- The **nanotube diameter** $d$, which refers to the outer diameter of the nanotubes grown on the electrode and has units of nm.

The central conjecture of this thesis is that a CNT electrode’s capacitance scales with its total surface area, and that the engineering efforts should be focused on increasing this surface area. Measuring it, however, is non-obvious. It can be done using the Brunauer-Emmett-Teller (BET) technique, by which a monolayer of gaseous molecules adsorbs to the porous surface and the ratio
Chapter 3. Electrode Fabrication, Assembly, and Characterization

of equilibrium and saturation pressures is measured to calculate the cumulative surface area [91]. Many machines that perform this measurement, however, require a sufficiently large total surface area (on the order of 10 m²) in order to provide accurate information; this limitation proved prohibitive for the small ~1 cm² samples we grew one at a time.

Instead of measuring surface area directly, we consider two of the other geometrical features: areal density of nanotubes $\rho$ and mean nanotube diameter $d$. For a given CNT forest height and electrode (Euclidean) area, the total electrode surface area is a function of the product of these two quantities. The electrode’s specific surface area (SSA) is proportional to this product. If each nanotube were a rigid cylinder, the SSA of an electrode with total surface area $A_{TOT}$, an electrode (Euclidean) area $A_E$, volume $V$, an array of $n$ CNTs of height $h$ and diameter $d$ evaluates to:

$$\text{SSA} = \frac{A_{TOT}}{V} = \frac{n}{A_E} \cdot \frac{\pi dh}{h} = \pi \rho d$$ \hspace{1cm} (3.1)

However, the CNTs do not grow as perfect cylinders and there is significant entanglement among nanotubes. The true SSA is still proportional to the areal density and mean CNT diameter, but the constant of proportionality is not known a priori:

$$\text{SSA} = \frac{A_{TOT}}{V} \propto \frac{ndh}{A_E h} = \rho d$$ \hspace{1cm} (3.2)

We assume that the degree of CNT entanglement is constant across samples. This leads us to define the relative SSA (rSSA) between differently-prepared CNT electrodes as the $\rho d$ product according to Equation 3.2. An electrode’s rSSA – its $\rho d$ product – becomes the metric against which its capacitance is evaluated, allowing for the quantitative assessment of the relationship between its morphological and electrochemical characteristics.

Finding accurate values of a CNT forest’s areal density is also non-trivial. It has been indirectly measured or estimated by other research groups using the weight-gain method\textsuperscript{7} [92], percent of areal

\textsuperscript{7}By measuring the electrode mass before and after CNT growth, an approximation for the areal CNT density can be made by estimating an average number of walls per nanotube and knowing the density of graphite, the CNT forest height, and mean nanotube diameter.
shrinkage after liquid-induced collapse\(^8\) [93], and direct imaging of the substrate surface prior to CNT nucleation by annealing the substrate in an inert atmosphere and counting nanoparticles [94]. By themselves, we found each of these methods to be unreliable for the following reasons:

- A 1 cm\(^2\) electrode experiences a typical weight gain of several hundreds of micrograms, which cannot be reliably measured by observing changes to the last decimal of a 0.1 mg balance. True microgram-resolution balances do exist, but need to be used in very controlled conditions to account for day-to-day variability in environmental humidity. In our setup, CNT forests were frequently transported in air from one laboratory to another, so this method was impractical. Furthermore, the extrapolation from weight gain to CNT density takes into account only an estimate of the average number of CNT walls.

- Differences in a CNT forest's areal shrinkage after liquid-induced collapse only provide proportional information about CNT areal density (i.e., forest A is 25% more compact than forest B). The true CNT count cannot be obtained using this method alone.

- While nanoparticle density before CNT growth is certainly correlated with the CNT density after growth, we found that the annealing process produces a higher count of catalyst nanoparticles as the thin film disaggregates than the number of CNTs that ultimately grow, sometimes by a factor of almost 10. We suggest that the surface mobility of the catalyst NPs during CVD is still high enough that additional coarsening occurs after acetylene is introduced into the reaction chamber, as discussed in [95].

Instead of resorting to an indirect method to estimate the CNT count, we image the substrate surface after the growth has been carried out and the CNTs excised with a razor.\(^9\) Individual “craters” left behind are then observed and counted using high-resolution scanning electron mi-

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\(^8\)After immersing a CNT forest in a solution of isopropyl alcohol, the electrode is heated. As the solution evaporates, surface tension forces cause the partially-dewetted CNTs to bundle together. This effect is strong enough to de-root individual nanotubes from the surface and expose the metal substrate. An estimate for the (relative) CNT areal density is then made by comparing the severity of this compaction effect.

\(^9\)We also attempted to remove CNTs by sonication the electrodes in a heated solution of isopropyl alcohol. However, many CNTs remain rooted in the substrates even after aggressive sonication for five minutes. We found the razor technique to be much more effective.
 microscopy (HR-SEM). By sampling the electrode surface in a number of well-separated locations, a direct estimate can be made not only of the CNT areal density, but also of their average diameter – allowing for a fully quantitative measurement of the relative total surface areas (\( \rho d \) products) of differently-prepared electrodes. Transmission electron microscopy (TEM), which produces higher-resolution scans, could provide increased accuracy in measuring CNT diameters but would be prohibitively slow for scanning large surface areas with hundreds of CNTs. We find that imaging these craters via SEM allows for a rapid and reliable evaluation of the distribution of CNT diameters. An example image is provided in Figure 3.9; additional scans with substantial commentary are shown in the next chapter.

![SEM Image of CNT Forest](image-url)

Figure 3.9: Scanning electron microscope image of a tungsten electrode surface after CNTs are grown and removed by a razor. Removing the CNTs in this manner exposes craters whose size and distribution provide insight into the morphological quality of the overall CNT forest.

Throughout our investigation, we often found it useful to analyze the surface of a substrate after the catalyst has been deposited but before CNTs are grown, specifically to observe the size and distribution of any catalytic nanoparticles that may be present. In addition to HR-SEM, a useful imaging technique is tapping-mode atomic force microscopy (AFM), which can provide information

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10This technique is mentioned in Signorelli’s thesis [7] but not extensively explored. To the best of our knowledge, our report [96] is the first academic publication to make practical use of it.
about the topography of a surface with angstrom resolution. A sharp cantilevered probe tip is mechanically excited at its resonant frequency and brought close to the sample surface. As it gets closer and eventually contacts the surface, the resonance is disturbed and a highly sensitive piezoelectric z-stage brings the probe back up just the right amount to maintain resonance. The probe is swept in a raster-scanning pattern over typically a $1 \times 1 \ \mu m$ area, and a topological image of the surface is produced by measuring the displacement of the z-stage. Imaging via AFM is quite slow: scanning a $1 \times 1 \ \mu m$ area takes several minutes as opposed to a few seconds with SEM. Furthermore, unlike SEM, one cannot make rapid crude scans across the surface until a specific location or feature is found and focused on; atomic force microscopists are completely blind except for the spot they choose to analyze. The single advantage of AFM over SEM is that it provides higher-resolution height information about features on a substrate surface (SEM provides no height information). Since the only features of interest in our scans were the size and distribution of relatively spherical nanoparticles, we abandoned the technique altogether and resorted only to SEM.

Figure 3.10 shows both an AFM and SEM image of an example substrate surface after iron nanoparticles have formed (before any CNTs are grown). The relationship between catalytic nanoparticle distribution and the morphological quality of subsequently-grown CNT forests is discussed in the next chapter.

Figure 3.10: Substrate surface revealing the presence of catalytic nanoparticles, imaged using (left) HR-SEM and (right) AFM.
3.5.2 Electrochemical Characterization

Each ultracapacitor cell we assemble as outlined in section 3.4.1 comprises two identically-prepared CNT electrodes to ensure symmetry between the cathode and anode. Its electrical performance is then evaluated using the electrochemical methods described below.

Cyclic Voltammetry

During cyclic voltammetry (CV), a test cell is subjected to a triangle voltage waveform with a defined ramp rate, and its current response is measured. Cyclic voltammograms are plots of the response current versus applied voltage, and time is a parametric variable. This test is typically used to study the electrochemical properties of an analyte in solution: anodic (or cathodic) current peaks identify the presence of reduction (or oxidation) reactions, and oftentimes, electrochemical systems produce multiple such peaks per voltage sweep. Most CV tests apply a voltage sweep rate between 10 and 1000 mV/s, cycle 3 – 5 times, and take tens of seconds to several minutes to complete.

An ideal capacitor, whose current response to a linear sweep is proportional to the voltage ramp rate, produces perfectly rectangular CVs. Adding series resistance makes more rounded corners, while leakage (parallel) resistance slants the entire rectangle. The figures below show some example circuits and their simulated CVs, as well as plots of terminal current versus time, to familiarize the reader with this electrochemical technique. In each case, a simulated triangle waveform from -1 to 1 V with a ramp rate of 2 V/s is applied to the mini-circuit terminals.
Chapter 3. Electrode Fabrication, Assembly, and Characterization

\[ R = 1 \text{ k}\Omega \]

Figure 3.11: Simulated current-vs-time plot and cyclic voltammogram for an ideal resistor.

\[ C = 20 \text{ mF} \]

Figure 3.12: Simulated current-vs-time plot and cyclic voltammogram for an ideal capacitor.
Figure 3.13: Simulated current-vs-time plot and cyclic voltammogram for series resistor/capacitor combination.

Figure 3.14: Simulated current-vs-time plot and cyclic voltammogram for a parallel resistor/capacitor combination.
The main benefit of CV when studying ultracapacitors is that the test allows for instant evaluation of the test cell's capacitance. Referring to a capacitor's voltage-current constitutive relationship, the ratio of capacitive current $I$ (measured) to voltage sweep rate $\frac{\partial V}{\partial t}$ across the device (known) is equal to its capacitance $C$ (unknown):

$$I = C \frac{\partial V}{\partial t} \implies C = \frac{I}{\frac{\partial V}{\partial t}}$$

To ensure that only capacitive current is included in the calculation (as opposed to any leakage current from parallel paths), $I$ is evaluated when the voltage across the test cell is zero. Necessarily, the measurements therefore include the effects of any series resistance. But these were generally small enough (very little roundedness in the voltammogram corners) and were neglected. Cyclic voltammetry was used extensively throughout the investigations in this thesis to evaluate the capacitance of different CNT electrodes.
Electrochemical Impedance Spectroscopy

Cyclic voltammetry is often limited by slow voltage sweep rates (fundamental frequency < 1 Hz) and cannot provide information about a device’s response at elevated frequencies. Electrochemical impedance spectroscopy (EIS) is a test whereby a small-signal sinusoidal voltage is applied on the device terminals over a wide range of frequencies ($10^{-3} - 10^6$ Hz) and the complex impedance is recorded. Typically, three to five frequencies are tested per decade. A test spanning 0.1 – 10,000 Hz with five test points per decade lasts approximately ten to fifteen minutes. The collected information can be used to make a Bode plot but electrochemists find it more useful to graph the imaginary versus real parts of the impedance in what is known as a Nyquist plot. EIS is useful for extracting information about any stray series or parallel resistances and capacitances that may exist, and at what frequencies they manifest themselves.

3.5.3 Electrode Capacitance

The capacitive performance of ultracapacitor electrodes is evaluated in three ways:

- **Area-specific capacitance** $C_A$ refers to the capacitance of the test cell as evaluated using cyclic voltammetry, normalized by the (Euclidean) area $A_E$ of one electrode and has units of mF/cm$^2$. A 10 mF test cell comprising two 1 cm$^2$ CNT electrodes has an area-specific capacitance of 10 mF/cm$^2$.

- **Differential capacitance** $C_d$ is a microscopic property of the CNTs themselves that describes how much capacitance is offered by a differentially small amount of surface area provided by a CNT and has units of μF/cm$^2$. This value cannot be measured directly.

- **Volume-specific capacitance** $C_V$ is the capacitance of the test cell normalized by the volume of one of its electrodes and has units of mF/cm$^3$. A 10 mF test cell comprising two 1 cm$^2$ electrodes with a CNT forest height of 500 μm has a specific capacitance of 200 mF/cm$^3$.

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11 Strictly speaking, the instrument measures the response current magnitude and phase relative to the applied voltage.

12 Bode plots are two-part graphs that plot the magnitude and phase of a system's response against the applied actuating frequency.
Chapter 3. Electrode Fabrication, Assembly, and Characterization

The explicitness of these definitions is important because authors of frustratingly many academic papers provide data, for example, in the form of cyclic voltammograms where the vertical axis has units of current, but the normalization with respect to electrode area or volume is either ambiguous or omitted and effective performance comparisons cannot be made. The engineering focus of this work is to enhance the specific capacitance of CNT electrodes by (1) developing recipes for CNT forests with a higher specific surface area and (2) simultaneously exploring various ways to increase the CNTs' differential capacitance by modifying the surface characteristics of as-grown forests.

3.6 Chapter Summary

This chapter presented the industry-dominant methods of producing CNTs and described the steps involved in making our own electrodes and ultracapacitor test cells. Two sets of characterizing techniques were discussed: morphological characterization, which uses imaging techniques to obtain information about a CNT forest's geometrical features, and electrochemical characterization, which makes use of electrochemical techniques to quantify a test cell's capacitance and understand its frequency response. The next chapter discusses how these tools were used to assess the performance of CNT forests grown by the as yet unenhanced methods described here.
Chapter 4

Performance of
Conventionally-Prepared CNT Electrodes

This chapter describes our initial investigations which explored how the amount of iron catalyst deposited during the electrode preparation stage affects the specific capacitance of the resulting CNT forests. Our fundamental experimental objectives were to vary the deposition/growth procedure, demonstrate that these different procedures led to CNT structures of differing quality, and observe the effects that these structures had on the cell’s capacitance. The catalyst deposition thickness was varied between 0.6 and 1.0 nm and a capacitance maximum was observed at 0.8 nm. The CNTs’ differential capacitance was independent of their areal density, mean diameter, length, and the amount of catalyst initially deposited. Specific capacitance and specific surface area were shown to be linearly related. However, with a peak electrode capacitance of under 15 mF/cm², the CNT forests we developed using the methods explored in this chapter lag far behind in performance compared to conventional activated carbon electrodes, which typically offer around 300 mF/cm².
4.1 Evaluation of CNT Morphology

The previous chapter discusses how a CNT forest’s specific surface area can be quantitatively assessed (at least in a relative sense) by sampling the substrate’s surface and examining the diameters and distribution of “craters” left behind after CNT removal. Figure 4.1 shows representative surface images of CNT growths prepared with catalyst deposition thicknesses of 0.6, 0.8, and 1.0 nm.

![Figure 4.1: High-resolution SEM images of substrate surfaces after CNT removal; corresponding histograms of CNT diameters. (a) 0.6 nm deposition, showing a CNT density of $1.4 \times 10^{11}$ cm$^{-2}$ and (d:i) mean CNT diameter of 4.6 nm. (b) 0.8 nm deposition, showing a CNT density of $1.2 \times 10^{11}$ cm$^{-2}$ and (d:ii) mean CNT diameter of 6.3 nm. (c) 1.0 nm deposition, showing a CNT density of $5.8 \times 10^{10}$ cm$^{-2}$ and (d:iii) mean CNT diameter of 10.1 nm.](image-url)
Chapter 4. Performance of Conventionally-Prepared CNT Electrodes

As discussed in the previous chapter, the total electrode surface area is a function of the product of the CNT areal density $\rho$ and the mean nanotube diameter $d$. We observe the following important trend (which was independently observed and explained in [97] and [98]): the thinner the iron deposition, the smaller and more numerous the resulting CNTs.

Substrate surfaces were sampled in five locations to gather sufficient information about CNT density and mean diameter across the sample. The results are compiled in Figure 4.2, which shows how the mean CNT diameter and areal density varied for differently-prepared electrodes (measurements from the SEM images in Figure 4.1 are incorporated therein).

![Figure 4.2: Distribution of CNT densities and mean diameters for different catalyst film thicknesses.](image)

The 1.0 nm deposition showed significant variability in both CNT density and diameter – unlike results typically obtained when using crystalline silicon substrates [94]. We attribute this variability to the fact that our metallic substrate is not atomically smooth and that the dewetting action, driven by the minimization of surface energy, can become highly localized. We believe that slight topographic variations on the substrate surface can favor the formation of smaller or larger nanoparticles. However, the variability in CNT size and distribution is smaller for thinner catalyst depositions.

Additional iron deposition thicknesses of 0.5 and 1.3 nm were attempted. However, the resulting CNT growths were poor. Although other authors have successfully grown CNTs following iron
depositions as thin as 0.2 nm on silicon substrates [99], it is our belief based on the studies performed in [100] that depositions thinner than 0.5 nm on tungsten result in severe iron diffusion despite the presence of the aluminum oxide buffer layer. CVD reaction of 1.3 nm-thick iron depositions produced non-uniform, scattered CNT growth instead of the vertically aligned structures observed with thinner depositions. Images of these growths showed a large number of nanoparticles that did not nucleate CNTs. Many of these particles had diameters over 18 nm, which is presumably unsuitable for CNT growth in the CVD conditions explored here.

### 4.2 Capacitance Measurements

Three sets of substrates were prepared. The first was prepared with an iron deposition thickness of 0.6 nm, the second with 0.8 nm, and the third with 1.0 nm. For each set of substrates, three pairs of electrodes were prepared by placing them in the CVD chamber for 2, 6, and 10 minutes to produce CNT forests of increasing heights. There was a total of 27 electrode pairs (three different iron deposition thicknesses, each of which had three different CNT forest heights grown). Each pair of electrodes was subjected to cyclic voltammetry to determine their capacitance. The voltage waveforms were symmetrically swept between $-1$ and $1$ V at rates of $50$, $150$, and $300$ mV/s. The voltammograms are shown in Appendix B.

The compiled results are presented in Figure 4.3. Two-minute growths were about $100$ µm tall for all three substrate sets; six- and ten-minute growths produced CNT heights of about 450 and 550 µm, respectively. Each cluster of three like-colored points in the figure represents the capacitance measured for a given cell at the different voltammetry scan rates (50, 150, and 300 mV/s). The values reported here represent only the capacitance due to the active CNT forest surface area; any additional capacitance that arose from the stainless steel enclosure or the tungsten foil was accounted for by comparing the cyclic voltammograms of a loaded versus an unloaded enclosure and taking the difference.

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1The exact height is found by scraping a small amount of CNTs off the substrate and placing the sample under an optical microscope. A z-stage on the microscope is used to measure the distance between two planes of focus: the top of the CNT forest (light intensity must be set to maximum setting in order to catch it) and the metal substrate.
Chapter 4. Performance of Conventionally-Prepared CNT Electrodes

Figure 4.3: Compiled results for the 27 ultracapacitor cells comprising electrodes of different iron deposition thicknesses and CNT forest heights.

For all CNT heights, we see that the 0.8 nm deposition produced the highest cell capacitance. An important feature of this plot is that the linear fits are excellent; we do not observe a tapering-off in capacitance as the CNT forest height increases, indicating that the electrolyte penetrates fully and wets the electrodes uniformly. The slope of each line indicates the corresponding electrode’s specific capacitance (i.e., how capacitance increases per unit electrode volume). This is the figure of interest for the ensuing analysis: it allows for the comparison of electrode capacitance as a meta-material property of the CNT arrays grown on substrates with different amounts of deposited catalyst, with other parameters (growth temperature, gas composition, etc.) fixed.

4.3 Discussion and Analysis

What isn’t immediately obvious is why the 0.8 nm deposition produces a higher cell capacitance than the other two (i.e., why there is a local maximum). We explain these results by demonstrating that a strong correlation exists between the electrode’s morphological/geometric structure and the resulting cell capacitances. The key metric in our analysis is the total electrode surface area. As described in earlier sections, two geometrical features were analyzed by SEM: the CNT areal density $\rho$ and the distribution of CNT diameters $d$. An electrode’s relative specific surface area (rSSA) is the product of these quantities.
As exhibited by the data in Figure 4.2, there is some variability in the measurements of both CNT density and diameter for each of the three different electrodes. However, the $\rho d$ product (the rSSA) is approximately constant for a given electrode. With this variability taken into account, we can calculate the mean of each electrode’s rSSA. These values are provided in Table 4.1 along with the specific capacitance computed from the slope of the lines in Figure 4.3.

Table 4.1: Comparison of electrode SSA and specific capacitance.

<table>
<thead>
<tr>
<th>Deposition thickness (nm)</th>
<th>Mean relative SSA</th>
<th>Specific capacitance (mF/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>63</td>
<td>186</td>
</tr>
<tr>
<td>0.8</td>
<td>77</td>
<td>280</td>
</tr>
<tr>
<td>1.0</td>
<td>51</td>
<td>150</td>
</tr>
</tbody>
</table>

Consistently, the 0.8 nm deposition produced CNT structures that yielded the highest rSSA. This result emphasizes the importance of both areal density and mean diameter. The higher rSSA of the 0.8 nm deposition is a result from the compounded effect of $\rho$ and $d$. Although the 0.6 nm deposition had a larger $\rho$, its $\rho d$ product was smaller. Figure 4.4 plots the specific capacitance of the cells against the electrodes’ rSSA.

![Figure 4.4: Plot showing correlation between specific capacitance and electrode SSA.](image)

Our analysis treats specific capacitance and SSA as meta-material, *macroscopic* properties of CNT forests, allowing to distinguish between differently-prepared substrates. A significant feature in the graph is that there exists an excellent ($R^2 = 0.95$) linear fit that goes through the three points
and the origin. Intuitively, this corroborates the notion that capacitance is proportional to the electrode's total surface area. Furthermore, these results imply that a CNT height of ~500 μm does not present electrolyte diffusion limitations even for the densest CNT structures (~1×10^{11} CNTs/cm^2). Lastly, the linear relationship between SSA and specific capacitance offers insight into the CNTs' differential capacitance (a microscopic property that describes how much capacitance is offered by a differentially small amount of surface area provided by a CNT), which is the slope of the line in Figure 4.4. Although it may still be a function of other fabrication parameters, such as the composition and molarity of the electrolyte or any surface treatments on the CNTs, our results show that the differential capacitance does not vary with geometrical parameters, such as areal density, mean diameter, and length, or the amount of catalyst used to grow the forests. However, we do not yet know its true value because the claims made here are based only on the relative specific surface area. Chapter 6 revisits this notion and discusses how the horizontal axis of the graph can be accurately scaled, allowing to quantify both the total surface area and true SSA of differently-prepared electrodes and ultimately reveal the true differential capacitance of our CNT structures.

### 4.4 Observed Capacitance Limits of Conventionally-Prepared CNT Electrodes

The results from the experiments explored in this chapter were encouraging because they confirmed the linear relationship between specific capacitance and specific surface area – one of the early conjectures – and demonstrated that CNT differential capacitance is independent of a forest's geometric and morphological qualities. This outcome may seem fairly intuitive, but it highlighted the reality that a material limit had not been reached and validated subsequent engineering focus on increasing electrode SSA.

In the broader picture, however, these experiments also showed that the specific capacitances of the best and worst CNT electrodes we prepared were barely within a factor of two from each other whereas a factor-of-twenty increase is required to rival that of activated carbon. Although the areal density of a CNT forest is clearly sensitive to the amount of deposited catalyst, the observed
variability, at least as shown here and as reported in literature, is insufficient to meet the energy density targets outlined in the introduction to this thesis and motivates fundamental changes to the process of preparing substrates for CVD; these are revealed in the next chapter.

4.5 Chapter Summary

This chapter described a set of experiments whereby the specific surface area of CNT electrodes was altered by varying the amount of catalyst deposited prior to CNT growth. The 0.8 nm-thick layer of iron produced electrodes with the highest capacitance of approximately 15 mF/cm² for electrodes ~500 µm thick. Other depositions, both thicker and thinner, produced less capacitive electrodes; this result was explained using geometrical arguments based on the relative specific surface area of the different electrodes. In the quest to approach the performance of activated carbon (approximately 300 mF/cm²), the electrode preparation techniques described here are insufficient.
Chapter 5

Performance Enhancement

Techniques for CNT Electrodes

The previous chapter described the effects of deposited catalyst thickness on the morphology of subsequent CNT growth. The electrodes’ specific capacitance was shown to be proportional to their relative specific surface area, which for catalyst depositions between 0.6 and 1.0 nm varied by a factor of about two. From our work, it appears that the conventional method of producing CNT forests by directly depositing a single layer of catalytic material is insufficient to synthesize electrodes with a comparable energy density to activated carbon. This chapter describes a variety of different approaches that were taken to enhance the performance of CNT electrodes. We were motivated by a simple fact: scans of the different substrate surfaces after CNT removal clearly showed that there was much unused space capable of fitting many additional nanotubes. There were two fundamental goals: (1) increase the forests’ specific surface area and (2) improve the CNTs’ differential capacitance; the effects of these two enhancements on total electrode capacitance is multiplicative. The best demonstrated test cell exhibited area-specific and volume-specific capacitances of 56.3 mF/cm² and 1,410 mF/cm³, respectively, representing an increase by a factor of six over previous electrodes.
Chapter 5. Performance Enhancement Techniques for CNT Electrodes

5.1 Decoupling Nanoparticle Formation from the CVD Process

As it stood, our method for growing CNT forests did not allow for independent control of the formation of distributed iron nanoparticles (NPs). After a uniform layer of catalyst was deposited, samples would be placed in the CVD chamber and brought to reaction temperature in an acetylene-containing atmosphere. Catalytic activity would begin right as the iron layer coalesced into particles, with the distribution and size of said particles *de facto* predetermined by equilibrium surface forces resulting from external parameters such as reactor temperature and quantity of initially deposited catalyst. The particles' surface mobility was presumably hindered by the onset of CNT growth. It was necessary early on to correlate nanoparticle density and CNT density, and three methods were explored to decouple the NP formation process from subsequent CVD: annealing the substrate before adding reactive gases to the CVD mix, structuring the catalyst film by exposure to a plasma before CVD, and depositing the catalyst on a pre-heated substrate. A detailed description of these processes and additional results are available in [101].

5.1.1 Substrate Annealing Prior to CVD

A reasonably simple way to see what the substrate surface looks like before CNTs start to grow is to simply delay the introduction of acetylene into the gas flow, effectively annealing the substrate in an inert atmosphere. The sample is placed on the heater and the identical growth procedure followed, but the heater is turned on for a certain amount of time in pure argon or dilute hydrogen before allowing the reactive gas to flow. Nessim et al. conducted a study whereby hydrogen gas was introduced into the gas flow mix at a variety of interval delays relative to the carbon feedstock gas [102] (hydrogen flow started five, ten, or fifteen minutes before, at the same time, and five or ten minutes after starting the flow of reactive gas). Their reasoning was that the initially deposited iron film is sufficiently oxidized to iron oxide while transferring (in air) the sample from the sputterer to their CVD reactor and that a reducing step was necessary to bring the catalyst to its active (metallic) state. Exposing the film to a reducing atmosphere at elevated temperatures would allow NPs to form, whose size and distribution depended on the annealing time. As shown in Figure 5.1, their results indicate that some hydrogen treatment increases the number of particles formed, but
too much exposure causes NPs to overcoarsen.

Figure 5.1: Left: Effect of hydrogen exposure time on surface roughness (i.e., NP size and distribution density) as measured by AFM. Right: schematic of proposed model. (a) The initially oxidized film is (b) reduced, and (c) – (d) the particles coarsen with increased exposure time. Adapted from [102].

In our setup, we did not obtain the same level of control over NP formation using this method. In fact, running CVD without any hydrogen at all produced CNT forests that were morphologically identical to those grown by introducing hydrogen and acetylene at the same time.\(^1\) We surmise that the choice of carbon feedstock gas plays a role here. Whereas Nessim used ethylene, our setup used acetylene which is known to have slight reductive properties by itself [103] and was likely able to structure the uniform catalyst layer into particles without the assistance of hydrogen. However, waiting even just a minute at high temperature before introducing acetylene resulted in either very poor or no growth. SEM and AFM probing of the surface revealed that after one minute of annealing in pure argon or dilute hydrogen, the catalyst layer had severely agglomerated into few but very large (> 50 nm) particles, which are unsuitable for CNT growth.

Another explanation is that the catalyst layer may not be so immobile to begin with. We attempted to capture the dewetting action by very briefly (approximately 1 second) bringing the silicon heater in our setup to CVD temperature and then immediately turning it off. SEM analysis showed the formation of relatively large nanoparticles (> 10 nm) with an areal density of under \(2\times10^{10} \text{ cm}^{-2}\), as shown in Figure 5.2. This distribution of size and density is sparser than our

\(^1\)That said, the presence of hydrogen did prolong catalyst activity and CNTs grew for a longer time.
sparsest CNT forest, indicating that even the brief amount of time at high temperature was sufficient to over-coarsen the NPs and that this method is ineffective in estimating the distribution of NPs at the onset of CNT growth.

Figure 5.2: SEM images of substrate surface after brief annealing. NPs are visible, but are sparser than even the sparsest CNT forest we have grown, suggesting that even the brief anneal time was sufficient to over-coarsen the particles.

5.1.2 Plasma Structuring of Catalyst Layer

Based on the procedures suggested in [104], we attempted to restructure the initially uniform catalyst layer by exposing it to different plasmas in order to form catalytically active NPs. Exposure to such high-energy environments is unique in the sense that individual molecular collisions with ionized gases occur at very high temperatures, but with so little mass involved, the amount of energy transferred is actually quite low and the surface mobility of any particles remains low. Presumably, one could study the evolution of catalyst coarsening by observing the substrate surface after increasing plasma exposure times. Both physical and chemical alterations are possible; in fact, plasma-assisted or plasma-enhanced CVD is an oft-cited procedure for growing CNTs and has been shown to permit CNT growth at a reaction temperature below 150 °C [105].

The gases we investigated were air and a 5% hydrogen 95% nitrogen mixture using a plasma asher (a tool commonly used in lithography processes to etch or remove photoresist from wafers).
However, neither successfully restructured the uniform catalyst layer into NPs. Treatment with mild plasma settings had no effect on the quality of subsequent CNT growths. As treatment settings were made more aggressive, however, the resulting growths became poorer. This effect was likely due to the back-sputtering of the catalyst layer: just like a sputterer, the plasma settings were strong enough to knock catalyst atoms away from the substrate. Presumably, using pure hydrogen may have been more suitable due its highly reductive properties, but was not available in our facilities.

5.1.3 Catalyst Deposition on Heated Substrates

One of the more successful insights during our investigation was to make use of the heated stage inside the sputterer and deposit the catalyst on a hot substrate ("hot depositions"). The presumption was that catalytic nanoparticles would form spontaneously as the material made contact with the substrate. As the deposition continued, more NPs would form, until eventually, surface forces and mobility would cause them to coarsen. To our knowledge, this method of forming NPs is unreported in literature.

The melting point of bulk iron is 1538 °C, but nano-sized particles of many materials adopt liquid-like properties and catalytic mobility at much lower temperatures. Semi-empirical set points known as the Hüttig and Tammann temperatures have been defined as $T_H = 0.3 \cdot T_m$ and $T_T = 0.5 \cdot T_m$ respectively, where $T_m$ is the melting point of the bulk material in absolute units (Kelvin). At $T_H$, atoms at defects become mobile; at $T_T$, atoms in the bulk will exhibit mobility [76]. In a study on the mobility of particles approximately 10 nm in diameter, the Tammann temperature of many different materials, including iron,\(^2\) is reported to be an accurate transition point for when the particles gain full mobility over a non-wetting surface [106].

The target nanoparticle size for our purposes was significantly smaller than 10 nm, and hot depositions were attempted at temperatures ranging from 200 to 500 °C based on the assumption that the smaller NPs would become mobile even before reaching the Tammann temperature. Figure 5.3 shows the remarkable effects that temperature has on the surface mobility of particles.

\(^2\)For iron, $T_T = 630 \degree C$. 

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In each case, an identical amount of iron is deposited (QCM\textsuperscript{3} reading of 0.6 nm), but the surface distribution of particles differs hugely. Every 50 °C increase in substrate temperature causes a notable increase in the average NP diameter and decrease in areal density. The SEM of the hot deposition at 450 °C is particularly interesting: upon careful observation, one can clearly notice individual crystal planes on the different particles. The magnification is much lower, emphasizing that at some point between 400 and 450 °C, the level of coarsening spikes; the resulting particles are significantly larger, around 100 nm, and are unsuitable for CNT growth. Based on these results, we selected a nominal substrate temperature of 200 °C for our hot depositions.

\textsuperscript{3}Quartz crystal monitor. See Chapter 3 for additional details.
Figure 5.3: SEM of substrate surfaces after depositing 0.6 nm iron at different temperatures.
5.1.4 Modification of Aluminum Oxide Support Layer

Although the diffusion of the iron catalyst into the base tungsten substrate is well mitigated by the presence of the aluminum oxide support layer, catalyst depositions 0.5 nm or thinner did not nucleate CNTs, presumably because such thin layers still exhibit sufficient diffusion. Zhong et al. attribute the inability of aluminum oxide to hold ultrathin iron layers to the fact that the support layer is itself a porous matrix; they propose a simple procedure to prepare a more diffusion-resistant support by exposure to a mild oxygen plasma *before* depositing the iron catalyst [92]. The result is a denser and more fully-oxidized underlayer of aluminum oxide, as verified by secondary ion mass spectrometry (SIMS). These findings are further confirmed in [107].

Our attempts at increasing NP density by adopting this modification proved successful. Whereas depositions of 0.6 nm had priorly resulted in a density of roughly $6 \times 10^{11}$ cm$^{-2}$, this number was improved to approximately $1 \times 10^{12}$ cm$^{-2}$ as displayed in Figure 5.4.

![Figure 5.4: Substrate surface after hot depositions of 0.6 nm iron. Left: no plasma treatment prior to Fe deposition; right: with O$_2$-treated aluminum oxide support layer.](image)
5.2 Cyclic Catalyst Deposition

Although the physical properties of individual carbon nanotubes are truly phenomenal, it remains a grand challenge to demonstrate these properties on a bulk level. One step in that direction would be to fabricate sufficiently dense forests of VACNTs. Prof. Robertson’s group at the University of Cambridge, UK, was focusing on the use of CNTs as interconnects in integrated circuit and thermal interface materials, and struggled with the fact that conventional arrays of CNTs contained too much void for the forests’ macroscopic properties to exceed those of standard materials such as copper. Much like our own observations in Chapter 4, they noted that thinner catalyst depositions result in a higher number of smaller particles, whereas thicker depositions form fewer and larger ones. A catalyst layer that is too thin, however, results in no CNT growth. The materials challenge is to surpass this limitation somehow. In 2010, Robertson’s group devised a novel – and now much-cited – method of growing aligned CNT forests with a significantly higher areal density than had previously been reported referred to as “cyclic catalyst deposition,” and they foresee the adaptation of this method for a variety of applications [94,98,99]. This section describes their method and our efforts at reproducing their results.

5.2.1 Method Description

In their paper [94], Robertson’s group describes the dewetting limits (maximum areal density of discrete particles) for a thin iron layer on an aluminum oxide support based on the surface forces experienced by individual NPs as the initially uniform film disaggregates. They surpass this limit by preparing their substrates via cyclic catalyst deposition. A layer of iron is deposited as usual. After annealing it (in argon) and forming one set of NPs, they introduce oxygen into the gas flow mix to oxidize their outer shell. A second layer of iron is then deposited, of identical nominal thickness as the first, and the substrate is subsequently annealed again. The key innovation is that a new set of NPs forms in the spaces between the old ones, rather than existing NPs from the previous deposition becoming larger. This phenomenon occurs because of the surface interactions between the new iron layer, the oxidized iron NPs, and the aluminum oxide support: it is energetically more favorable to fill in empty spaces on the support layer. Had the original set of NPs not been oxidized, they
would have maintained their mobility, and the second deposition would have made these existing particles larger rather than creating a new set. The following immobilization procedures are listed (taken directly from [94]):

1. Deposit an Fe layer, anneal the metal into droplets, allow it to oxidize, cool. Deposit the next Fe layer, anneal it, oxidize it, and so on. Oxidation can happen by exposure to either air or water vapor in a low vacuum.

2. Deposit Fe, deposit a 0.2 nm discontinuous Al layer on the Fe, anneal, allow Al to oxidize into discontinuous Al$_2$O$_3$ layer, cool, deposit more Fe and Al, anneal, and so on.

3. Deposit Fe, anneal, plasma oxidize or nitride, cool, deposit more Fe, etc.

Finally, to form a forest of VACNTs, the oxidized NPs are subjected to a dilute hydrogen flow for five minutes before introducing acetylene into the CVD reactor. CNTs nucleate with a reported density of $10^{13}$ cm$^{-2}$ as a result. This process is described schematically in Figure 5.5.

Figure 5.5: Schematic of the cyclic catalyst deposition process, as shown in [108].

The authors' method of counting CNTs, which is a combination of the weight-gain and liquid-induced compaction techniques, is much less rigorous than our method of imaging the substrate surface by SEM after removing CNTs and counting craters. Based on SEMs that the authors do provide and our own empirical observations, the cited figure is likely an overestimate.
5.2.2 Immobilization of Catalyst Layers

The key to increasing the number of catalyst particles with additional iron depositions, as opposed to making existing ones bigger, is to immobilize them immediately after the uniform layer initially dewets. Methods for immobilization can be broadly classified into three categories: (1) explicit oxidation via direct exposure to oxygen gas or oxygen plasma; (2) passive oxidation, during which iron NPs interact with non-gaseous oxygen that is present in the support layer [109]; and (3) addition of a “buffer layer,” which is a thin deposition of a tertiary material that coats the NPs and inhibits their mobility.

Immobilization via Explicit Oxidation

Significant efforts were put into reproducing the results reported by Robertson’s group using their first technique. It proved extraordinarily cumbersome, however, to carry substrates from the sputterer to our CVD chamber and back to the sputterer as required for cyclic catalyst deposition. Fairly quickly, we resorted to our method of forming NPs by depositing iron on heated substrates. NP immobilization was carried out directly in the sputterer, which allowed us to deposit multiple catalyst layers without having to move the substrate.

Over a period spanning almost six months, however, we had a lot of trouble obtaining reproducible results. Early on, we wanted to demonstrate high-quality CNT growth on substrates prepared with a single run of Robertson’s cyclic catalyst deposition procedure using a nominal iron thickness between 0.6 and 1.0 nm. Explicit oxidation via exposure to either oxygen gas or oxygen plasma was carried out inside the sputterer. For reduction of immobilized NPs to catalytically active ones, we subjected the substrate either to a mild 5% hydrogen / 95% nitrogen plasma in the asher or to dilute hydrogen flow in our CVD chamber. Approximately half of the substrates prepared in these ways grew uniform forests of CNTs as desired; the others either produced sparse forests, tangled (unaligned) and short CNTs, or no CNTs at all. It took many repeat runs to determine if there was a critical parameter that presented these troubles. Ultimately, we surmised that despite our attempts, the chemical composition of the catalyst NPs could not be controlled.

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5 In their original paper, they mention the other two methods as possible alternatives to the first, but do not investigate them experimentally.
well enough in the available facilities. Samples had to be carried around in air and were often stored (in air) for varying amounts of time. The moisture content in the CVD reactor was not controlled and may also have had an effect on the ability for NPs to nucleate CNTs. In a procedure as delicate and parameter-rich as the one described here, it becomes exceedingly important to pay much attention to process control: ideally, every step would have been carried out in the sputterer, including CVD.6

**Immobilization via Passive Oxidation**

In an extensive study on the chemical composition of the different components during the formation of CNTs, de los Arcos et al. note that iron NPs can be oxidized by the underlying aluminum oxide support layer [109]. After relatively few attempts, we determined that this effect was strong enough to allow a new set of NPs to form with a second iron deposition. CNTs grew in uniform forests, but their areal density was significantly lower than that of the preceding nanoparticles. Presumably, the passive oxidation step immobilized NPs just enough to prevent coarsening during the cyclic deposition process but did not hold at the higher CVD temperatures, causing many NPs to agglomerate before the onset of CNT growth (as supported by the SEM image in Figure 5.6).

**Immobilization via Deposition of Buffer Layer**

There are several requirements for a “buffer layer” in between sequential catalyst depositions. It must:

1. inhibit the surface mobility of NPs at the deposition temperature;

2. be non-wetting and allow new NPs to form during subsequent depositions;

3. withstand the high temperature during CVD; and

4. allow individual NPs to nucleate the growth of CNTs during CVD (i.e., it cannot completely block access to the acetylene flow).

---

6The sputterer in our facility is designed for multi-user use and reactive gases such as acetylene are not allowed.
Our first attempts at buffer layer immobilization were with aluminum, as suggested in [94]. However, because the quantities of aluminum deposited were so small (typically 0.2 – 0.5 nm), the aluminum itself beaded up and formed islands of its own rather than remaining as a single continuous layer. This phenomenon likely occurred because the deposition temperature of 200 °C is above aluminum’s Tammann temperature.

Next, we tried aluminum oxide due to its known compatibility with iron NPs. We deposited 0.2 nm on a single set of NPs before attempting multiple catalyst layers; however, no CNTs grew during CVD. Presumably, aluminum oxide blocks the NPs’ access to acetylene, and is therefore unsuitable as a buffer layer.

Yamazaki et al. report the formation of closely packed CNT forests by separating the CVD process into three steps. First, a uniform layer of catalyst (in their case, cobalt) is heated in dilute hydrogen plasma to form NPs. In a novel second step, they introduce methane at a low temperature (< 200 °C) with the plasma still on, which coats the NPs with a thin layer of graphite. CNTs don’t grow, however, until the temperature is elevated above 500 °C. NPs would normally coalesce at that
temperature but actually remained immobile due to the presence of the thin graphite layer [110].

Inspired by this account, we explicitly deposited carbon as a buffer layer. This insight proved largely effective: the carbon successfully immobilized particles resulting from the hot deposition of a single 0.6 nm layer of iron without hindering subsequent growth; and furthermore, we were able to show a CNT density increase when two layers of iron were used.

5.3 Modified Cyclic Deposition Procedure

The previous section discussed the many procedures that were explored to improve upon the conventional CNT electrode fabrication procedure and form higher-density forests; here, step-by-step descriptions of the techniques are provided.

5.3.1 Substrate Preparation and Al₂O₃ Deposition

A 50 × 10 mm strip of tungsten is cleaned in excess acetone, isopropyl alcohol, and de-ionized water before placing it onto the sputterer chuck. The strips had a tendency to coil up a little, and so two clamps were used to ensure good contact (see Figure 5.7). The chuck is then inserted into the sputterer which, like before, is evacuated to a base pressure below $5 \times 10^{-5}$ Torr before introducing argon at a pressure of 30 milli-Torr.

The aluminum oxide gun is ignited, the chamber pressure is reduced to 3 milli-Torr, and the plasma pressure is brought up to the deposition setting of 250 W. After the material deposition reaches steady state, the aluminum oxide shutter is opened until 10 nm of material have deposited (so far, these steps are identical to the procedure described in Chapter 3).

The next step is to expose the support layer to oxygen plasma to improve its diffusion-barrier characteristics. After the aluminum oxide deposition is complete, the gun is turned off and the argon flow is replaced by pure oxygen at 30 milli-Torr. A substrate bias is applied and a 50 W plasma is

---

The reported CNT areal density is $10^{12}$ cm$^2$. They arrive at this number by first estimating a fill factor from low-magnification SEM, then measuring mean CNT diameter using TEM, and lastly carrying out geometric analysis to arrive at an areal density. This method is less rigorous than even the weight-gain method, and certainly far less accurate than our method of counting craters after CNT removal. However, it seems plausible for their figure to be correct within a factor of two.
struck in the sputterer chamber and maintained for 10 minutes. An important parameter here is the oxygen pressure at which the plasma is kept: while 30 milli-Torr would modify the aluminum oxide support layer in the desired manner, a lower pressure of 3 milli-Torr (the standard material deposition pressure) would cause back-sputtering of the material that had just been deposited onto the tungsten substrate.

5.3.2 Iron Deposition and Nanoparticle Immobilization

After oxygen treatment of the support layer is complete, the gas flow is replaced by argon at 30 milli-Torr. The chuck heater is set to 200 °C, and it takes approximately 10 minutes to reach that temperature. During that time, the sputterer guns on the iron and carbon targets are ignited and brought to their setpoint values. Carbon deposits very slowly, so using a dc rather than an RF plasma is better (faster deposition rate). Even with a dc gun, it is difficult to get a stable deposition rate for carbon. The plasma needs to start out at a high setting (190 – 200 W) and be gradually brought down to the eventual deposition power, typically around 165 W for a rate of 0.1 nm/s. Throughout this setup phase, a screen covers the substrate to protect it from undesired depositions and an in situ QCM measures the deposition rate until the correct settings are obtained.

With the chuck at 200 °C, the iron deposition begins (chamber pressure at 3 milli-Torr). Once
complete, the iron shutter is closed, and the carbon shutter is opened until the immobilization “buffer layer” has finished depositing. This process is repeated until the desired number of cycles has been completed. After the last carbon deposition, the guns and heater are turned off, the chuck is left to cool in argon for approximately 5 minutes, and the chamber is vented.

By themselves, the explicit and passive oxidation technique for immobilizing NPs were shown to be less effective than using carbon. However, we obtained very good results by sputtering a single thin layer of carbon in a final step, after multiple layers of iron had been deposited and oxidized (either by direct exposure to oxygen or by interaction with the aluminum oxide support layer). The sputtering procedure is largely the same but, in the case of explicit oxidation, the plasmas are turned off while oxygen is passed through the chamber.
5.4 Specific Capacitance vs. rSSA for Different CNT Forests

This section documents the experimental results relating the specific capacitance of various CNT electrodes and their relative specific surface area. As outlined in the previous section, many different recipes were explored. Particular attention was paid to how surface-bound NPs were immobilized. Table 5.1 describes the properties of all the different CNT electrodes we successfully fabricated and tested. Below are explanations for the terms and abbreviations in the “deposition recipes” column:

- Conventional \( x \): \( x \) nm of iron catalyst is deposited on a cold substrate in a single layer, as per the procedures described in Chapter 3.

- SLHD, \( x/y \): Single-layer hot deposition. \( x \) nm of iron and \( y \) nm of carbon are deposited sequentially on a hot substrate.

- DLHD, \( x/y \): Double-layer\(^8\) hot deposition. \( x \) nm of iron and \( y \) nm of carbon are deposited sequentially on a hot substrate, twice. The final structure is Fe/C/Fe/C.

- Exp. ox., \((z \times x)/y\): Immobilization achieved by explicit oxidation. A layer of iron \( x \) nm thick is deposited on a hot substrate and exposed to oxygen gas for 30 s. Additional layers of iron of identical thickness, for a total of \( z \) layers, are added, with an oxidation step in between each. After the last oxidation step but before venting the sputterer, a \( y \) nm-thick layer of carbon is deposited.

- Pass. ox., \((z \times x)/y\): Immobilization achieved by passive oxidation. A layer of iron \( x \) nm thick is deposited on a hot substrate and left to sit (in ambient argon) on the aluminum oxide support layer for approximately 3 minutes. Additional layers of iron of identical thickness, for a total of \( z \) layers, are added, with an oxidation step between each. After the last passive oxidation step but before venting the sputterer, a \( y \) nm-thick layer of carbon is deposited.

Figure 5.8 plots specific capacitance vs. rSSA for all the electrodes in the table above. The three points in Figure 4.4 (from Chapter 4, “Performance of Conventionally-Prepared CNT Electrodes”),

\(^8\)“Double-layer” here refers not to double-layer capacitance, but the number of catalyst deposition cycles.
which relate the electrode characteristics for CNT forests prepared using the conventional single-layer deposition technique, are included in this figure. The fit is less good ($R^2 = 0.84$) but the new points add remarkably well to the already-existing linear trend. Recall that the horizontal axis is a relative measure of the electrodes’ SSA, and the constant of proportionality is not yet know. The slope of the line represents the differential capacitance of the CNT surface, and the next chapter is dedicated to a series of experiments and modeling efforts to determine its absolute value.

Table 5.1: Properties of CNT electrodes prepared by different recipes.

<table>
<thead>
<tr>
<th>Deposition recipe</th>
<th>$\rho$ (cm$^{-2}$)</th>
<th>$d$ (nm)</th>
<th>$\rho d$ ($\times$ m$^2$/cm$^3$)</th>
<th>$h^0$ (mm)</th>
<th>$C_A$ (mF/cm$^2$)</th>
<th>$C_V$ (mF/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional 0.6</td>
<td>$1.6\times 10^{11}$</td>
<td>4.0</td>
<td>64</td>
<td>0.55</td>
<td>11</td>
<td>200</td>
</tr>
<tr>
<td>Conventional 0.8</td>
<td>$1.1\times 10^{11}$</td>
<td>7.0</td>
<td>77</td>
<td>0.53</td>
<td>14</td>
<td>264</td>
</tr>
<tr>
<td>Conventional 1.0</td>
<td>$7.0\times 10^{10}$</td>
<td>7.5</td>
<td>53</td>
<td>0.51</td>
<td>7.0</td>
<td>137</td>
</tr>
<tr>
<td>SLHD, 0.6/0.4</td>
<td>$2.0\times 10^{11}$</td>
<td>3.5</td>
<td>70</td>
<td>0.52</td>
<td>13</td>
<td>250</td>
</tr>
<tr>
<td>SLHD, 0.8/0.4</td>
<td>$9.0\times 10^{10}$</td>
<td>8.0</td>
<td>72</td>
<td>0.55</td>
<td>12</td>
<td>218</td>
</tr>
<tr>
<td>DLHD, 0.6/0.4</td>
<td>$3.4\times 10^{11}$</td>
<td>3.5</td>
<td>119</td>
<td>0.50</td>
<td>24</td>
<td>480</td>
</tr>
<tr>
<td>DLHD, 0.6/0.4</td>
<td>$5.4\times 10^{11}$</td>
<td>5.0</td>
<td>150</td>
<td>0.52</td>
<td>25</td>
<td>481</td>
</tr>
<tr>
<td>DLHD, 0.8/1.0</td>
<td>$3.0\times 10^{11}$</td>
<td>5.0</td>
<td>150</td>
<td>0.41</td>
<td>12</td>
<td>293</td>
</tr>
<tr>
<td>DLHD, 0.4/1.0</td>
<td>$1.2\times 10^{12}$</td>
<td>4.5</td>
<td>54</td>
<td>0.62</td>
<td>17</td>
<td>274</td>
</tr>
<tr>
<td>Exp. Ox., 2 × 0.6/0.4</td>
<td>$5.2\times 10^{11}$</td>
<td>4.0</td>
<td>208</td>
<td>0.41</td>
<td>29</td>
<td>707</td>
</tr>
<tr>
<td>Exp. Ox., 3 × 0.4/0.4</td>
<td>$5.4\times 10^{11}$</td>
<td>3.5</td>
<td>189</td>
<td>0.46</td>
<td>25</td>
<td>543</td>
</tr>
<tr>
<td>Pass. Ox., 2 × 0.6/0.4</td>
<td>$5.3\times 10^{11}$</td>
<td>4.0</td>
<td>212</td>
<td>0.40</td>
<td>26</td>
<td>650</td>
</tr>
</tbody>
</table>

Figure 5.8: Specific capacitance vs. rSSA for various CNT electrodes, superimposed with the best linear fit ($R^2 = 0.84$).
Some SEM images of electrode surfaces after CNT removal are shown in Figure 5.9, highlighting how highly tunable the forests' morphological properties (areal density and mean CNT diameter) can be.

![SEM images](image)

Figure 5.9: SEM images of example substrate surfaces after CNT removal. (a) 1 nm cold deposition. (b) Two-cycle hot deposition of (0.4 nm Fe and 0.4 nm C). (c) Single-cycle hot deposition of (0.6 nm Fe and 0.4 nm C). (d) Two-cycle hot deposition of (0.6 nm Fe and 0.4 nm C).
5.5 Post-Growth Treatment of CNTs

Literature abounds with a variety of ways that CNTs can be treated to alter their surface properties, and one of our goals was to see how these methods could be adapted to increase the differential capacitance of already grown CNT forests. The primary motivation was to compound the effects of an increased SSA with a higher differential capacitance, which are multiplicative on specific capacitance. There are two broad categories of treatments: “wet,” during which the CNT forests are immersed in a solution or other liquid (acids, bases, suspensions, etc.), and “dry,” which does not involve any liquid contact (exposure to gases or plasmas, annealing, etc.). Electrodes were prepared via the “control process” (1 nm iron, deposited on a cold substrate as described in Chapter 4), which, with the passage of time, had demonstrated to repeatably produce CNT forests of constant morphological quality. After growth, the forests were exposed to different high-energy environments to see what the impact on capacitance would be compared to untreated electrodes.

There are a variety of mechanisms by which a CNT surface can change to produce additional capacitance. For example, while CNTs grow as crystalline $sp^2$-hybridized structures, introducing defects or kinks can result in an increased concentration of charge at those locations. Amorphous carbon, which may have been deposited as a side-product of CVD and is generally a poorer charge conduit than the underlying graphitic carbon, can be etched away using plasmas or acids. This section recounts our efforts in exploring these effects, the vast majority of which was completed by Berk Öztürk in the summer of 2013.

5.5.1 Wet Treatments

Motivated by a previous report of successfully oxidizing CNTs by chemical means [111], we attempted to follow a similar procedure to see if the same type of defect-engineering could be achieved and if it would lead to an increased differential capacitance. We submersed electrodes in solutions of:

- 1 M sulfuric acid for one minute.
- 1 M potassium hydroxide for two minutes.
• Nitric acid (29 wt%), followed by hydrogen peroxide (30 wt%) for two minutes.

In each case, the CNT array derooted from the substrate and we were unable to put test cells together. Furthermore, both the sulfuric and the nitric acid treatments reacted with the tungsten substrate, causing visible deterioration on the surface. This wasn’t a problem for the authors in [111] because they were looking at dispersed CNTs rather than substrate-bound VACNT arrays.

As a result of these undesired effects, we quickly abandoned further exploration of wet treatments.

5.5.2 Dry Treatments

High energy environments such as plasmas, reactive gases, and high temperatures have the ability to significantly modify the surface features of many materials. In the case of carbon nanotubes, there are numerous reports which explore what modifications are possible with such “dry treatments.”

Oxygen (O₂) Plasma

A threefold increase in specific capacitance over untreated samples has been reported as a result of exposing CNTs to an oxygen plasma [112]. CNTs were grown on silicon substrates, then removed and transferred to a current collector with the help of a binder. The authors explain this effect from the attachment of hydroxyl, carbonyl, and carboxyl groups onto the surface of CNTs, and also describe how their relative distribution can be tuned by the plasma conditions. As shown in Figure 5.10, these functional group are thought to increase the effective wetted surface area of the CNT array. However, excessive exposure to oxygen plasma can result in excessive damage to the crystalline CNT surface [113].

In our own investigation, we varied the plasma power between 5 and 30 W at a base pressure of 100 milli-Torr with an oxygen flow rate of 150 sccm.¹⁰ All treatments lasted five minutes. SEMs of post-treatment CNTs show that functional groups were indeed attached to their surface (see Figure 5.11). Their composition wasn’t identified but could be determined via X-ray photoelectron spectroscopy. We observed a maximum capacitance increase of 48%.

¹⁰Standard cubic centimeter per minute.
Chapter 5. Performance Enhancement Techniques for CNT Electrodes

Figure 5.10: Schematic drawing of VACNT array and how an oxygen plasma can increase the effective wetted area. (a) A screening shell of charge forms around bundles of closely-packed CNTs, preventing a double-layer from forming on some walls. Surface functional groups increase affinity for solvent molecules and (b) the entire surface area is captured. Adapted from [112].

Figure 5.11: SEM image of CNTs after oxygen plasma treatment, with clearly visible surface functional groups.

Ammonia (NH₃) Plasma

Treatment with ammonia plasma can cause the addition of imine, amine, nitrile, and amide groups. Yoon et al. claimed a 5× increase in specific capacitance as a result of mild ammonia treatments [46].
Chapter 5. Performance Enhancement Techniques for CNT Electrodes

We varied plasma conditions between 10 and 50 W, with a gas flow rate of 12 sccm and a treatment duration of 5 minutes. However, we observed a decrease in capacitance in all cases. A likely explanation for Yoon’s result is that an aqueous solution was used as the electrolyte, and that the surface functional groups improved wetting (untreated CNTs are inherently very hydrophobic). Our test cells, which used an organic electrolyte, did not benefit from the treatment in the same manner.

Argon (Ar) Plasma

Argon plasma treatment has been shown to improve CNT capacitance [114]. The authors attribute this effect to the introduction of charged defects into the CNT structure, which allow additional charge to accumulate at those locations. The primary ionic component in argon plasma is Ar$^{2+}$, which is also effective in etching away $sp^3$ carbon impurities.

CNT forests were treated with an argon plasma power between 10 and 70 W at a base pressure of 100 milli-Torr and an argon flow rate of 12 sccm for five minutes. A maximum capacitance increase of 62% was observed at 50 W; treatment at 70 W decreased capacitance.

Argon/Oxygen (Ar/O$_2$) Plasma

Zhao et al. demonstrated that oxygen-containing functional groups form effectively on the surface of CNTs when using a mixed argon/oxygen plasma [115]. Based on their investigations, we treated CNTs with 1:1, 1:2, and 2:1 partial pressure mixtures of the two gases at a base pressure of 100 milli-Torr and total gas flow rate of 30 sccm. A maximum capacitance increase of 115% was observed when the partial pressures of argon and oxygen were equal. The 2:1 mixture resulted in a smaller increase of 45%, while the 1:2 mixture caused a slight decrease.

Carbon Tetrafluoride (CF$_4$) Plasma

The surfaces of CNTs treated by carbon tetrafluoride plasma can undergo two types of changes: chemical and physical. Chemically, various forms of fluorination can occur [113]. Physically,
CNTs can unzip longitudinally to form graphene nanoribbons\(^\text{11}\) due to interactions with the CF\(_4\) plasma [117]. This phenomenon is of particular interest because it exposes additional surface area to the electrolyte.

Our own investigation into reproducing these effects proved successful. At least partial longitudinal unzipping was observed via SEM imaging (see Figure 5.12). The plasma power was varied between 10 and 80 W at a base pressure of 100 milli-Torr and a gas flow rate of 35 sccm, and a maximum capacitance increase of 76% was recorded.

![Figure 5.12: SEM images of CNTs after CF\(_4\) plasma treatment, with partial unzipping of nanotubes noticeable.](image)

**Sequential Plasma Treatments**

Individually, the CF\(_4\) and Ar/O\(_2\) plasma exposures produced the best improvements in capacitance over untreated cells. We surmised that the effects of each treatment could be compounded by exposing CNT forests to the two plasmas sequentially.

- CF\(_4\) followed by Ar/O\(_2\) resulted in a 59% increase.
- Ar/O\(_2\) followed by CF\(_4\) resulted in a 69% increase.

\(^\text{11}\)The first mention of longitudinal unzipping of CNTs was reported in [116], whereby dispersed CNTs are unzipped by a solution-based process.
In both cases, the base pressure was 100 milli-Torr, the Ar/O\textsubscript{2} gas flow rate was 30 sccm (at 1:1 partial pressures) at 30 W, and the CF\textsubscript{4} gas glow rate was 35 sccm at 60 W.

5.5.3 Summary of Performance Changes after Plasma Treatments

The bar graph in Figure 5.13 provides a compilation of the results obtained from the different plasma treatments we explored.

![Bar graph showing % change in capacitance (vs. untreated samples) after plasma treatments using different gases.](image)

Figure 5.13: Compiled results from plasma treatments using different gases.
5.5.4 Post-Growth Treatments on Enhanced Electrodes

The final step in our investigation is to combine the capacitance improvements demonstrated via surface-treatment of nanotubes (this chapter) with the high-density CNT forests grown by the modified catalyst deposition technique (Chapter 5). We treated electrodes in both CF$_4$ and 1:1 Ar/O$_2$ plasmas. The list below summarizes the properties of our best-performing electrodes.

- CNT areal density: 5.2x10$^{11}$ cm$^{-2}$
- Mean CNT diameter: 4.0 nm
- Forest height: 410 µm

<table>
<thead>
<tr>
<th></th>
<th>Area-specific capacitance (mF/cm$^2$)</th>
<th>Volume-specific capacitance (mF/cm$^3$)</th>
<th>% increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>29</td>
<td>725</td>
<td></td>
</tr>
<tr>
<td>CF$_4$-treated</td>
<td>49</td>
<td>1230</td>
<td>70</td>
</tr>
<tr>
<td>Ar/O$_2$-treated</td>
<td>56</td>
<td>1410</td>
<td>94</td>
</tr>
</tbody>
</table>

Both the CF$_4$ and the Ar/O$_2$ treatments resulted in slightly smaller capacitance increases than those reported in the previous section but nevertheless provide an almost 2× improvement over untreated electrodes. Such plasma treatments are an inexpensive and easily-scalable method of increasing differential capacitance in would-be commercial processes.

Our best-performing electrode represents a nearly 10× increase in capacitance over Signorelli’s prior work. Ultimately, however, we were unable to achieve the improvements necessary to approach the target value of 350 mF/cm$^2$, which is still a factor of six away. The concluding chapter to this thesis makes suggestions for future explorations that could close the gap.
5.6 Chapter Summary

This chapter described the multitude of ways we attempted to enhance CNT areal density and differential capacitance. Combined, their effects on specific capacitance are multiplicative. In the beginning, the focus was on preparing the correct distribution of catalytically active iron NPs. One of our most successful endeavors was depositing iron on a heated substrate, which produced a far greater number of particles than conventional deposit/anneal procedures. Then, based on research performed in Prof. Robertson's group at the University of Cambridge, UK, we adopted a cyclic catalyst deposition technique whereby multiple layers of catalyst are deposited sequentially to form a cumulatively increasing number of NPs. We modified their procedure somewhat because we were not as successful at immobilizing NPs using oxygen gas or plasma. Instead, we showed that a thin layer of carbon in between iron depositions has the intended effect, and we observed a maximum CNT areal density of $5.4 \times 10^{11}$ cm$^{-2}$.

The thicknesses of the catalyst and immobilization layer were parametrically varied to see if a maximum CNT density could be reached. For each recipe that produced good CNT growths, the electrode's specific capacitance and relative specific surface area were measured and plotted. Although the horizontal axis of the resulting graph is scaled by an unknown amount, there is a clear linear relationship between these two electrode properties which corroborates the intuitive notion that capacitance scales with surface area.

Lastly, we explored a variety of surface treatments on as-grown CNTs to improve their differential capacitance. Exposure to carbon tetrafluoride and argon/oxygen plasmas resulted in 76% and 115% increases in the electrodes' capacitance, respectively. Both structural and chemical modifications to the surfaces were observed with high-resolution SEM. Electrodes grown using the modified cyclic deposition technique and then treated by exposure to an argon/oxygen plasma resulted in an area- and volume-specific capacitance of 56 mF/cm$^2$ and 1,410 mF/cm$^3$, respectively.
Chapter 6

Electrochemical Modeling and Theoretical Corroboration of Experimental Results

The previous chapters described the fabrication procedures and performance of a variety of CNT-based ultracapacitor cells. We saw that substrate preparation by conventional techniques produced insufficiently capacitive electrodes, and a series of enhancements was explored to improve both the areal density and differential capacitance of CNT structures. However, because the data could only be analyzed in a relative sense, true values for total surface area, specific surface area, and differential capacitance have not yet been calculated.

Double-layer capacitance is a result of the interactions that occur on the interface between a charged solid and an enveloping fluid of mobile charged particles – the electrolyte. The following sections describe the mechanics of what occurs on this interface under different conditions, with a particular emphasis on the different electrochemical models that have been proposed over the last two centuries as scientists’ understanding of these phenomena have evolved. Lastly, this chapter demonstrates how relatively simple models of the double-layer predict the experimental results shown in the previous chapter.
6.1 Modeling of the Electrochemical Double-Layer

6.1.1 The Helmholtz Model

The earliest realization that charged surfaces immersed in solutions have an effect on charge distributions is attributed to Hermann von Helmholtz in 1853, when he suggested that two charged layers of opposite polarity form on the solid/liquid interface [118]. It is an intuitively simple theory whereby the surface charge on an immersed conductor is perfectly screened by a monolayer of adsorbed solvated counterions in the electrolyte. The resulting structure is analogous to that of a parallel-plate capacitor with a separation equal to the solvated ion radius \( r \) and a dielectric constant \( \epsilon \) equal to the permittivity of the solvent. A schematic representation of this model is shown in Figure 6.1; also shown in the figure is a plot of the space-varying electric potential \( \psi \) (in red) which results from the suggested charge distributions.

![Figure 6.1: Schematic representation of the solid-liquid interface according to the Helmholtz model. Negative counterions (solvated) screen the electrode's positive charge. Note that the figure includes a plot of the electric potential \( \psi \) as a function of the distance away from the electrode (in red). \( \psi_s \) and \( \psi_b \) are the potentials at the electrode surface and in the infinite bulk, respectively. Adapted from [119].](image)

When normalized for total electrode surface area, the differential capacitance \( C_d^H \) according to the Helmholtz theory equates to:

\[
C_d^H = \frac{\epsilon}{r}
\]  

(6.1)
Using values of 64 for the relative permittivity of propylene carbonate and 0.3 nm for the radius of a solvated lithium ion [4,120], the Helmholtz differential capacitance equates to 190 μF/cm².

6.1.2 The Gouy-Chapman Model

Louis Gouy in 1910 [121] and David Chapman in 1913 [122] independently developed what is now referred to as the Gouy-Chapman theory of the double-layer by accounting for the fact that ions in solution are mobile and that they are subject to both electrostatic and diffusion forces. As such, ions do not perfectly screen the electrode in a single layer as posited by Helmholtz; rather, the equilibrium ion concentration \( c_i(\psi) \) for a binary 1:1 solution\(^1\) with bulk concentration \( c_\infty \) follows a Boltzmann distribution:

\[
c_i(\psi) = z_i c_\infty \exp\left(-\frac{z_i \psi}{V_{TH}}\right)
\]

where \( c_\infty \) is the concentration of the species in the bulk solution, \( \psi \) is the local (spatially varying) electric potential, \( z_i \) is the charge of species \( i \) (in our case, there are two species – the cation and the anion – and the charge \( z_i = \pm 1 \)), and \( V_{TH} \) is the thermal voltage \( \left(\frac{kT}{e}\right) \approx 25 \text{ mV at room temperature} \). \( \psi \) is determined by Poisson’s relation in electrostatics (Gauss’s law):

\[
-\nabla \cdot (\varepsilon \nabla \psi) = \rho(\psi)
\]

where \( \rho(\psi) \) refers to free charge, which is itself a function of the spatially-varying electric potential. For a binary 1:1 electrolyte, \( \rho(\psi) \) is related to \( c_i(\psi) \) according to:

\[
\rho(\psi) = F \sum \limits_i z_i c_\infty \exp\left(-\frac{z_i \psi}{V_{TH}}\right)
\]

\[
= F c_\infty \left[ \exp\left(-\frac{\psi}{V_{TH}}\right) - \exp\left(\frac{\psi}{V_{TH}}\right) \right]
\]

\[
= -2 F c_\infty \sinh\left(\frac{\psi}{V_{TH}}\right)
\]

\(^1\)A “binary 1:1” solution is one in which there exist only two species of solvated ions and they have a charge of \( \pm 1 \). This is the case for all electrolytes used in this thesis. The Gouy-Chapman model can be generalized for asymmetric electrolytes but the expressions are needlessly messy for the purposes of this study.
where \( F \) is Faraday's constant (equal to the Coulombic charge value of a mole of electrons, approximately 96,500 C/mol). Figure 6.2 is a schematic representation of the charge distributions according to the Gouy-Chapman theory and is overlaid with a plot of the spatially-varying potential \( \psi \).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{schematic_representation_of_the_solid-liquid_interface_according_to_Gouy-Chapman_theory.png}
\caption{Schematic representation of the solid-liquid interface according to Gouy-Chapman theory. Adapted from [119].}
\end{figure}

Combining Poisson’s equation for electrostatics (Equation 6.3) with a charge density function that follows Boltzmann’s distribution (Equation 6.6) yields the Poisson-Boltzmann equation, which is used frequently in contexts of polymer science, semiconductor physics, and electrochemistry:

\[
\nabla \cdot (\epsilon \nabla \psi) = 2F \epsilon_\infty \sinh \left( \frac{\psi}{V_{TH}} \right)
\]  \hspace{1cm} (6.7)

Gouy and Chapman solved for \( \psi \) explicitly and arrived at the following expression for what is known as the Gouy-Chapman differential capacitance \( C_d^{GC} \):

\[
C_d^{GC} = \frac{\epsilon}{\lambda_D} \cosh \left( \frac{\psi_s}{2V_{TH}} \right) ; \lambda_D = \sqrt{\frac{\epsilon RT}{2F^2 \epsilon_\infty}}
\]  \hspace{1cm} (6.8)

where \( R \) is the modified gas constant, \( T \) is temperature, and \( \psi_s \) is the potential on the electrode surface (a boundary condition). Today, the term \( \lambda_D \) is referred to as the Debye screening length, and it plays an important role in colloid science, plasma physics, and electrochemistry. Measurements of surface charge on mercury drop electrodes submerged in an electrolyte published by David Grahame in 1947 [123] significantly corroborated the Gouy-Chapman theory that capacitance is exponentially...
dependent on potential, but this was only true for sufficiently dilute electrolytes (under 0.1 M) and small surface potential (several thermal voltages).

6.1.3 Debye-Huckel Theory

In 1923, Peter Debye and Erich Huckel also examined solutions to Equation 6.7 [124] and suggested that the potential $\psi$ was small compared to the thermal voltage in a variety phenomena and experimental observations. Consequently, they derived what is known today as the “Debye-Huckel” linearization of the Poisson-Boltzmann equation by approximating $\sinh(x) \approx x, x \ll 1$:

$$-\nabla \cdot (\varepsilon \nabla \psi) = \rho(\psi) = -2F \varepsilon_{\infty} \sinh \left( \frac{\psi}{V_{TH}} \right) \rightarrow \nabla \cdot (\varepsilon \nabla \psi) \approx 2F \varepsilon_{\infty} \frac{\psi}{V_{TH}}$$

(6.9)

The resulting Debye-Huckel differential capacitance $C_{d}^{DH}$ is

$$C_{d}^{DH} = \frac{\varepsilon}{\lambda_D} ; \lambda_D = \sqrt{\frac{\varepsilon RT}{2F^2\varepsilon_{\infty}}}$$

(6.10)

which includes the same term $\lambda_D$ and, unsurprisingly, is equal to $C_{d}^{GC}$ at zero potential. Even though this result is less rigorous than the Gouy-Chapman solution, Debye’s work gave very successful predictions of phenomena in contexts of electrochemistry and plasma science and earned him the Nobel Prize in Chemistry in 1936.

6.2 Gouy-Chapman-Stern Theory of the Double Layer

A limitation of both the Gouy-Chapman and Debye-Huckel expressions for differential capacitance is that there is a dependence on bulk concentration $\varepsilon_{\infty}$ which causes the terms $C_{d}^{GC}$ and $C_{d}^{DH}$ to grow without bound for ever-increasing ionic strengths. In 1924, Otto Stern proposed a modification to the model that resolved this issue by combining the Helmholtz and Gouy-Chapman models. Positing that the electric double-layer is composed of two layers – a compact layer of strongly
adsorbed and immobile ions close to the electrode surface, and a diffuse layer where the ions are mobile and follow the Gouy-Chapman model – Stern modeled the total electrode capacitance as the combination of two capacitors in series. The smaller of the two dominates the expression for total capacitance. Figure 6.3 schematically depicts this modification and shows the potential varying linearly across the Stern layer and exponentially in the diffuse layer.

Figure 6.3: Schematic representation of the solid-liquid interface according to the Gouy-Chapman-Stern model. Adapted from [119].

All of the theories described above assume a dilute electrolyte ($\ll 1$ M) but are surprisingly good at predicting a wide variety of experimental results with concentrated solutions [125–127]. More complex theories that account for finite ion size in concentrated solutions have been developed by Stern himself as early as 1924 [128] and were periodically re-derived a number of times over the past century [125], but often end up being less accurate than the simple models. To date, a unifying theory that describes the double-layer structure over vast parameter ranges ($10^{-3}$ to 10 V in voltage, $10^{-6}$ to 1 M in ionic strength) remains elusive.
Chapter 6. Electrochemical Modeling and Theoretical Corroboration of Experimental Results

6.3 Validating a Model

6.3.1 Experimental Setup

Cyclic voltammetry of our CNT electrodes shows that, unlike predictions by Gouy-Chapman, current (and, therefore, differential capacitance) is relatively constant over the full 1 V voltage sweep range for electrodes immersed in a 1 M solution of LiBF$_4$ in propylene carbonate. We therefore wish to simplify the Stern model by purposefully ignoring the implied exponential dependence of differential capacitance on voltage, and utilize the Debye-Huckel relation for the diffuse layer capacitance.

To justify this step, a series of experiments had to be carried out in order to evaluate just how well the Debye-Huckel theory applied to our CNT electrodes. The notable aspect of the differential capacitance is its dependence on bulk concentration; namely, $C_d^{DH} \propto \sqrt{c_\infty}$. We therefore performed cyclic voltammetry on a given set of electrodes at a set CV scan rate while varying the electrolyte molarity from $10^{-4}$ to 1 M. The expectation was to observe, on a log-log plot of capacitance vs. concentration, a line with a slope of 0.5 at low ionic strengths. As the concentration increases above ~0.1 M, capacitance is expected to taper off according to the Stern theory. The higher-level goal with this study is to predict the slope of the line in Figure 5.8, reproduced below for convenience. The implications of doing so are powerful:

- The horizontal axis, emphasized numerous times to show the relative SSA of the various CNT forests, can be correctly scaled by the as of yet unknown proportionality constant and finally have true units of m$^2$/cm$^3$.
- An indirect measurement of the total electrode surface area can subsequently be deduced.
- With the axis scaled, the slope of the line will reveal the differential capacitance of our CNT forests.

The experiment described above was carried out for three different sets of electrodes: (i) a low-density CNT forest, synthesized via the "conventional" techniques from Chapter 4; (ii) a high-density forest following the cyclic deposition technique from Chapter 5; and (iii) a pair of activated
carbon electrodes. We only considered CNT forests that were not plasma-treated. Figures plotting current-vs-time and the corresponding cyclic voltammograms are provided in Appendix C. In all cases, the electrolyte was a 1 M solution of LiBF₄ in propylene carbonate, and the voltage sweep rate was 50 mV/s. Initially, sweep rates of 150 mV/s were also attempted, but yielded poor results at the lower electrolyte concentrations.
6.3.2 Analytical Evaluation

We first consider the low-density CNT forests to see if the relation between capacitance and concentration follows the Debye-Huckel and/or Stern models. According to Stern, the total capacitance is the series combination of the compact and diffuse layer capacitances, so

$$C_{d}^{TOT} = \left( \frac{1}{C_{d}^{DH}} + \frac{1}{C_{d}^{S}} \right)^{-1} = \left( \frac{\lambda_{D}}{\epsilon_{DH}} + \frac{r}{\epsilon_{S}} \right)^{-1}$$  \hspace{1cm} (6.11)

Figure 6.5 plots the low-density CNT forest capacitance data points (y-axis is shown in mF for the test cell comprising two 1-cm$^2$ electrodes) and a scaled value$^2$ of $C_{d}^{TOT}$ using the following parameters:

$$\lambda_{D} = \sqrt{\frac{\epsilon_{DH} RT}{2F^{2}\epsilon_{\infty}}}$$
$$\epsilon_{DH} = \epsilon_{S} = 64\epsilon_{0}$$
$$r = 3 \text{ nm}$$

Figure 6.5: Plot of capacitance vs. electrolyte concentration for the low-density CNT forest. The modeled curve assumes $\epsilon_{DH} = \epsilon_{S} = 64\epsilon_{0}$.

$^2$The SI units of $C_{d}$ are F/m$^2$, whereas the collected data are in F. Here, “scaling” the model refers to finding the best fit parameter $\alpha$ such that $\alpha \cdot C_{d}$ overlays the measured data.
Chapter 6. Electrochemical Modeling and Theoretical Corroboration of Experimental Results

Observations:

- At low concentration, the data follow the theoretical $1/2$ slope very well.
- Toward the 1 M concentration, the measured capacitance tapers off faster than predicted by the model.

An important consideration was left out when plotting the model above. The permittivity of polarizable media, including solvents, is known to significantly decrease in the presence of large electric fields on the order of 1 V/nm [119,129] (this is easily the case here). The physical phenomenon at play is that the electrolyte molecules become highly aligned at high fields, and any additional orientation of the molecules does not provide additional polarization; hence, the effective permittivity is reduced. What researchers commonly do is treat the Stern permittivity as a fitting parameter. Reported values for the relative permittivity of propylene carbonate under high-field conditions vary between 5 and 15 [130]. These fall right in line with the commonly used Booth model [131–133], which relates a material’s relative permittivity to the applied electric field:

$$
\varepsilon_r(E) = n^2 + (\varepsilon_r(E = 0) - n^2) \cdot \frac{3}{\beta E} \left[ \coth(\beta E) - \frac{1}{\beta E} \right]; \beta = \frac{5\mu}{2kT} (n^2 + 2) \quad (6.12)
$$

where $n$ is the material’s index of refraction, $\varepsilon_r(E = 0)$ is its relative permittivity at zero field, and $\mu$ is its electric dipole moment. Results of molecular dynamics simulations for different electrolytes have verified that the Booth model accurately predicts the electrolyte permittivity of propylene carbonate ($\varepsilon_r = 64$, $\mu = 1.63 \times 10^{-29}$ C-m, $n = 1.42$) varies with field strength according to the Booth model [134]. Figure 6.6 is a plot of Equation 6.12 for propylene carbonate. Note that the purpose of this exercise is not to validate the Booth model; rather, we use it simply to corroborate the different electrolyte permittivities reported in literature.
Chapter 6. Electrochemical Modeling and Theoretical Corroboration of Experimental Results

Figure 6.6: Dependence of the relative permittivity of propylene carbonate on electric field, according to the Booth model.

Although Booth’s model does not include the effects of finite ion size, it clearly indicates that the Stern layer permittivity, where the electric field strength is on the order of 0.5 – 1.0 V/nm, is expected to fall far below its bulk value. Figure 6.7 is a plot of equation 6.11 accounting for non-uniform permittivity by substituting $\epsilon_r^S = 10$.

![Figure 6.7: Plot of differential capacitance $C_d^{TOT}$ according to the Stern model (equation 6.11) accounting for nonuniform electrolyte permittivity. Here, $\epsilon^S = 10\epsilon_0$ and $\epsilon^{DH} = 64\epsilon_0$. Note that 1 F/m$^2$ = 100 μm/cm$^2$.](image-url)
Rescaling the graph of differential capacitance and overlaying with collected data gives the plot in Figure 6.8.

![Figure 6.8: Capacitance vs. concentration for low-density CNT forest, overlaid with Booth model which accounts for the reduced permittivity of propylene carbonate in the Stern layer.](image)

Applying the same method to the high-density CNT electrodes, we obtain the plot shown in Figure 6.9.

![Figure 6.9: Capacitance vs. concentration for high-density CNT forest.](image)
Observations:

- Decreasing the value of the Stern permittivity according to Booth’s equation makes the model fit the collected data very nicely, in both the low and high-density case.

- The scaling factor used to align the model (units of F/m²) with the collected data (units of F) has units of m² and is an indirect measurement of the total electrode surface area.

The last step in our quest to quantitatively determine the value of the CNTs’ differential capacitance is to reconcile the scaling factors used to align the modeled capacitance $C_{d}^{TOT}$ in Figures 6.8 and 6.9 with the electrodes’ $\rho d$ product and the scaling of the horizontal axis in Figure 6.4. The step-by-step procedure is as follows:

1. Assume that the capacitance model in Equation 6.11 is correct. At a concentration of 1 M, it yields a differential capacitance $C_{d}^{TOT} = 0.26$ F/m², as can be verified in Figure 6.7.

2. $C_{d}^{TOT}$ is scaled by a fitting parameter $\alpha$ so as to overlay the collected data. Two values of $\alpha$ are found: one for each of the low- and high-density CNT electrodes.

3. $\alpha$ has units of m² and represents the electrodes’ total surface area.

4. The electrode’s true (not relative) specific surface area is $\alpha$ divided by the electrode volume.

5. The electrode’s true surface area is also proportional to its $\rho d$ product. Mathematically:

$$K \rho d = \frac{\alpha}{V} \implies K = \frac{\alpha}{\rho d \cdot V}$$

6. Now that we have the value for $K$, we know by how much to scale the horizontal axis in Figure 6.4, and can infer the measured differential capacitance by evaluating the slope of the line (which now has true units of F/m²). The calculations are performed in Table 6.1 below.
Table 6.1: Comparison of electrode SSA and specific capacitance.

<table>
<thead>
<tr>
<th>CNT Density</th>
<th>$\rho$ (CNTs/cm²)</th>
<th>d (nm)</th>
<th>CNT height (mm)</th>
<th>Relative SSA $\rho d \propto$ m²/m³</th>
<th>CNT electrode volume (m³)</th>
<th>$\alpha$ (m²)</th>
<th>K</th>
<th>Measured $C_{\text{TOT}}^F$ (F/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>$6.5 \times 10^{10}$</td>
<td>8.0</td>
<td>0.43</td>
<td>$5.2 \times 10^6$</td>
<td>$4.3 \times 10^{-8}$</td>
<td>0.020</td>
<td>0.089</td>
<td>0.36</td>
</tr>
<tr>
<td>High</td>
<td>$3.4 \times 10^{11}$</td>
<td>4.0</td>
<td>0.35</td>
<td>$1.36 \times 10^7$</td>
<td>$3.5 \times 10^{-8}$</td>
<td>0.095</td>
<td>0.20</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Observations:

- Once scaled for height, the SSA of the high-density CNT forest is a factor of $5.8 \times$ higher than that of the low-density one.

- The values of $K$ (horizontal axis scaling factor) are spread by a factor of about 2.

- The inferred differential capacitance, calculated by dividing the slope of the line in Figure 6.4 (unscaled slope = 0.032) by the corresponding value of $K$, in both cases comes close to the modeled valued of 0.26 F/m².
6.4 Chapter Summary

Early sections in this chapter described the evolution of the scientific community's understanding of the electrochemical double-layer. One of the simpler, yet sufficiently rigorous interpretations thereof is Stern’s model, which accounts for capacitance contributions of both a compact and a diffuse charge layer. The total capacitance is the series combination of the two. In order to validate the model, the capacitance of two sets of CNT electrodes (one high- and the other low-density) was measured over a wide range (10^{-4} to 1 M) of electrolyte concentrations. Initially, the data did not quite land on top of what the Stern model predicted. This discrepancy was corrected by devaluing the electrolyte permittivity in the compact layer according to Booth’s model.

In order to “come full circle,” the inferred electrode surface area (equal to the scaling factor that was used to fit the plot of the modeled Stern differential capacitance to the measured capacitance data) was compared to its \( \rho d \) product so as to correctly scale the horizontal axis in the original graph of specific capacitance vs relative specific surface area. Ultimately, the two values deduced for the measured differential capacitance, 0.36 and 0.16 F/m^2, come very close to the modeled value of 0.26 F/m^2. Additionally, they are in strong agreement with values reported in literature [4,47,53]. This result emphasizes the legitimacy of our initial assumptions and supports the analysis which followed.
Chapter 7

Conclusions and Recommendations for Future Research

This thesis explores the use of carbon nanotubes (CNTs) as an alternate material to activated carbon in ultracapacitors and the various enhancements that can be made to CNT structures to augment their capacitance. The fundamental motivation is that, unlike activated carbon, CNT forests can be made extremely pure and are electrochemically compatible with standard electrolytes even at high voltages of 4.0 V, but have not yet been engineered or aggregated in a way that exhibits sufficient surface area to compete on energy density with existing devices.

7.1 Contributions of This Work

The principal contributions of this work include:

- A rigorous analysis of the current state and trends of electrochemical energy storage technologies on the market today, with a focus on lead-acid batteries, lithium ion batteries, and ultracapacitors.

- A description and parametric study of the performance of CNT-based electrodes prepared using conventional methods.

- A novel and hitherto unreported method of forming iron nanoparticles on a non-wetting
surface by sputtering material on a heated substrate.

- A multi-dimensional study of various immobilization techniques that prevent as-formed nanoparticles from coarsening, the intended result of which is to nucleate the growth of a CNT forest with an augmented areal density.

- The adaptation of the cyclic catalyst deposition process to metallic substrates. After making a number of modifications, an increase in CNT areal density by a factor of nearly ten was achieved over conventional procedures.

- The demonstration of a good linear relationship between the specific surface area and specific capacitance of highly-porous CNT structures, regardless of the deposition recipe, over a wide range of values.

- A thorough study of existing accounts relating to the surface treatment of CNTs, especially by exposure to different plasmas, and a broad experimental investigation seeking how to best improve the differential capacitance of as-prepared CNT electrodes. Appropriate plasma treatment resulted in doubling the specific capacitance of our electrodes.

- A description of the scientific community’s understanding of the electrochemical double-layer as different theories have evolved over the last 200 years, as well as an adaptation of the Gouy-Chapman-Stern theory to predict the measured electrode differential capacitance of our CNT structures.

### 7.2 Recommendations for Future Research

Despite the various ways in which we enhanced the performance of CNT electrodes, the early goal of demonstrating an area-specific capacitance of 350 mF/cm², equivalent to the area-specific capacitance of activated carbon and projected by Signorelli to be within reach, was not achieved. As before, the fundamental limitation is the electrodes’ specific surface area, which still falls short by a factor of about five. However, we know more about various crucial factors in the CNT synthesis.
process as a result of our experimental investigations, and can make the following recommendations for future explorations on the subject:

- From start to finish, the process of synthesizing arrays of CNTs is extraordinarily parameter-rich and highly sensitive to ambient environment. Rigorous attention must be paid to the control of many seemingly innocuous variables such as humidity, air exposure, and contamination. The ideal research setup would use a single tool for both catalyst deposition and CVD, such as a plasma-enabled multi-target sputterer compatible with acetylene or other carbon-containing gas.

- The areal density and diameter distribution of CNT arrays has been clearly shown to be highly tunable. The methods for quantifying these morphological qualities are not always very rigorous, and new ways to accurately estimate CNT density would hugely benefit this branch of research.

- With these precautions in mind, there is strong evidence that the cyclic deposition technique has many more fruits to bear. The parameter space, which includes the composition of the catalyst, type of support layer, temperature during deposition, and immobilization steps, has not yet been fully explored.

- Most importantly, if CNTs are indeed to find their way into massively-deployed electrochemical storage products, significant research is necessary into the scaling of the processes explored in this thesis and in the cited academic articles.
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Appendix A

Description of Experimental Setup

Our custom CVD setup is designed to attain CVD growth temperatures, typically between 700 and 800 °C, in a matter of seconds. This is achieved by using a mildly conductive piece of silicon as a heater and passing a controlled amount of current through it. Substrates onto which catalyst layers have been deposited are placed directly on the heater. An infrared thermometer measures the heater’s temperature. With the exception of the quartz tube (which slides out to grant access to the heater), all piping components are stainless steel. A cabinet holds the argon, hydrogen and acetylene gas cylinders, each of which is connected to a calibrated mass flow meter that is controlled by a custom-made Labview program. Photographs of the setup are provided below.

Figure A.1: Photograph of CVD setup. The gas flow mixture flows in from the right. A high-volume vacuum pump is placed downstream and can be seen on the far left of the image.
Appendix A. Description of Experimental Setup

Figure A.2: Zoom-in on the chamber itself, showing the silicon heater suspended inside the quartz tube. Below the tube, an infrared thermometer measure the heater temperature. The instrument on the left measures chamber pressure.

Figure A.3: Photograph of CVD chamber with heater turned on with sample on top.
Appendix B

Cyclic Voltammograms of Conventional Electrodes

Figure B.1 shows three sets of cyclic voltammograms (sweep rate 150 mV/s), each of which depicts the current-vs-voltage response of ultracapacitor test cells prepared with a given amount of catalyst (0.6, 0.8, or 1.0 nm depositions) for CNT growth durations of 2, 6, and 10 minutes.

Observations:

- The capacitance of a cell is measured by taking the current at zero volts and dividing by the sweep rate.

- In agreement with Figure 4.3, the 0.8 nm deposition produces test cells with the highest capacitance, capable of drawing the most current.

- There is very little slant in the CVs, indicating a low series-conductance path (this is a desired characteristic).
Figure B.1: Cyclic voltammograms of conventionally-prepared electrodes with increasing forest growth time. Top-left: 0.6 nm deposition. Top-right: 0.8 nm deposition. Bottom: 1.0 nm deposition. In all cases, CV scan rate is 150 mV/s.
Appendix C

Cyclic Voltammograms of Low- vs. High-Density CNT Electrodes

Figure C.1 shows current-vs-time plots and the corresponding cyclic voltammograms as a function of electrolyte concentration for three different electrode types: low-density CNT forest, high-density CNT forest, and activated carbon. The results shown here were used to make the log-log plots of capacitance vs. electrolyte concentration in Chapter 6.

Observations

- At low concentrations, all CVs are less “rectangular” and the current-vs-time waveforms less square. This is due to the increased ESR that arises from a low-concentration electrolyte.

- The high-density forest consistently displays a capacitive current that is approximately 4-5× greater than that of the low-density forest. This is in line with other observations.

- The activated carbon electrodes produced much less ideal-looking waveforms, though they drew approximately three times more current. This is due to an innately higher ESR from the structure of the AC electrode; furthermore, no explicit current collector was used in the test cell (the AC film was simply cut into 0.75×0.75 cm squares and placed in direct contact with the stainless steel test cell enclosure), so there may be additional contact resistance.

- The low-density CNT electrodes appear more “leaky” than the high-density electrodes, but that is just a visual effect due to the scaling of the axes. Both sets of electrodes conduct approximately 0.2 mA more current toward the end of each voltage sweep than at the start.
Figure C.1: Plots of current vs. time and corresponding cyclic voltammograms as a function of varying electrolyte molarity ($10^{-4} - 1$ M). (a) & (b) low-density CNT forest, (c) & (d) high-density CNT forest, (e) & (f) activated carbon electrodes.
Appendix D

Various Photographs of Equipment

Figure D.1: Photograph of Helios microscope, used to make HR-SEM images with up to 1,000,000× magnification.
Figure D.2: Matthew D'Asaro filling the test cell with electrolyte inside the glovebox.

Figure D.3: Photograph of reactive ion etcher used for plasma treatments of CNT forests.