RICE UNIVERSITY

Two Studies from the Development Cycle of Macroscopic Carbon Nanotube Materials: Rheology of Carbon Nanotubes in Superacids and Characterization of the Electrochemical Circuit Behavior of Carbon Nanotube Fiber Electrodes for Electrophysiology

by

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Abstract

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Carbon nanotubes (CNTs) possess a variety of properties which make them attractive as building blocks for high performance multi-functional materials. The discovery that superacids such as chlorosulfonic acid (ClHSO₃) act as true solvents for CNTs has led to the development of fluid processing techniques by which a variety of macroscopic CNT materials can be fabricated. This work presents two studies which are linked by the common thread of CNT materials development from acid solution precursors. The first study compares the rheology of two different CNT species in ClHSO₃ as a function of concentration and frequency. The development of elastic structure with increasing solution concentration is found to depend strongly on the morphology of the liquid crystalline phase domains in the biphasic regime; physical interactions between non-interpenetrating liquid crystal domains are found to be a significant source of viscoelastic stress. An analysis of the scaling of viscoelastic behavior at short time scales, based on models of semiflexible polymer rheology, reveals that the primary contribution to the stress at short times is longitudinal tension resulting from contour fluctuations of individual CNTs; this tension-dominated stress is the primary viscoelastic stress for low concentration solutions. The second study investigates the electrochemical properties of macroscopic CNT fibers for applications in electrophysiology and cardiac medicine. CNT fibers exhibit much lower interfacial impedance with physiological saline and cardiac tissue than platinum wire of the same geometric surface area. Equivalent circuit modeling demonstrates that the low area-specific impedance of these fibers arises from a large double layer capacitance, which in turn arises from wetting of the internal porous surface area. Aging and storage conditions are shown to affect the wettability of this structure, and an electrowetting treatment is demonstrated which creates a stable increase in CNT fiber electrode performance. The specific circuit behavior of the CNT fiber is used to construct a theoretical model for CNT fiber electrode performance in cardiac tissue *in vivo* and to calculate a transfer function which represents the efficiency with which a cellular action potential may be transmitted through a CNT fiber between two electrically separated regions of cardiac tissue.

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This thesis is the end result of a long process, a long journey, and a large number of hours of my life. Looking back on the time I have spent and the work I have done in the last several years, I am happy to be able to say, with a bit of humility and a great deal of gratitude: all of the hardest parts were of my own making, and all of the best parts were possible because of the people who surrounded me. A great many freinds, family members, and colleagues have helped me along the way to this finish line, and I cannot properly finish the work without first celebrating their kindness and quality.

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Midway through my graduate career, I was lucky enough to be presented with an opportunity

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Chapter 1

Introduction

The most general question for researchers seeking to apply nanoscience to the field of materials engineering is "How can we exploit or manipulate nanoscale structure to create materials with novel properties, i.e., properties that have not previously been achieved?" Each sphere of engineering involves a specific version of this question. For aerospace applications the question might be "How can we create a material that is cheap to produce and that has a specific conductivity greater than copper?" For energy storage the question might be "How can we create a material with high surface area and good conductivity, and that will maintain its structure and properties over many charging cycles?" For ballistic shielding the question might be "How can we produce a flexible material with a modulus and toughness exceeding that of woven PPTA fiber?" In the field of medical electrodes the question might be "How can we create a material with high surface area and good conductivity that will also be non-toxic and highly durable if implanted in living tissue?" Research into carbon nanotubes (CNTs) has attracted considerable attention and many person-hours have been devoted to it because the answer to so many of these questions appears to be: "Create a material which incorporates and exploits the properties of CNTs."

CNTs, which were first identified by Ijima in 1991, are allotropes of carbon that possess a combination of outstanding properties on the molecular scale (Iijima, 1991). They possess a tensile strength greater than that of steel (Peng *et al.*, 2008), thermal conductivity greater

than that of diamond (Pop *et al.*, 2006), and a density lower than that of graphite; some metallic CNTs have a conductivity exceeding that of copper (Park *et al.*, 2004). Many of the unmet needs in modern engineering require that a single tool perform more than one function; hence, although CNT-based materials would be quite useful if any one of these single-molecule properties could be achieved on a macroscopic sale, the greater portion of their potential may lie in their ability to produce multi-functional materials in which more than one of their properties are exploited.

The pursuit of high-performance macroscopic CNT materials leads naturally to a second set of questions: "What are the best ways to create such materials? What properties can be achieved?" Several methods have been used to produce materials either composed of or containing CNTs; these include the formation of composites loaded with CNTs (Biercuk *et al.*, 2002; Cheng *et al.*, 2009; Harris, 2004), continuous dry spinning of CNT fiber directly from a synthesis furnace (Koziol *et al.*, 2007; Li *et al.*, 2004), direct growth of CNT arrays or mats for use as electrodes (Fung *et al.*, 2010; Musa *et al.*, 2012; Minnikanti *et al.*, 2009), and fluid processing techniques such as filtration, roll coating, and wet-spinning of fibers from a solution (Dan *et al.*, 2012; Vigolo *et al.*, 2000; Ma *et al.*, 2013; Mirri *et al.*, 2012; Behabtu *et al.*, 2013). Research on fluid suspensions of CNTs is a field with its own set of questions: "How can CNTs be introduced into and maintained in a fluid state? What CNT microstructures can be achieved in these fluids? What are the rheological properties of these fluids? If the fluids are used as a precursor to a solid material, what is the relationship between starting solution properties, processing steps, and final material properties?"

This thesis presents the results of two studies related to the engineering of CNT materials and devices. The first study focuses on a topic related CNT fluid processing: the rheology of CNT solutions in strong acids. The second study is an investigation into the performance of a specific class of CNT material, continuous aligned CNT fiber, in a specific application: durable and flexible electrochemical electrodes for biological applications.

1.0.1 Rheology of Carbon Nanotubes in Superacids

Davis *et al.* (2009) demonstrated that superacids (solvents with acidity greater than that of 100% sulfuric acid) are an effective solvent for CNTs. The use of superacid solvents has resulted in the creation of a variety of macroscopic articles from neat CNTs, including thin films made of isotropic or partially aligned 2D networks of CNTs (Mirri *et al.*, 2012; Ma *et al.*, 2013), continuous fiber made of highly aligned and densely packed CNT bundles (Ericson *et al.*, 2004; Behabtu *et al.*, 2013), and lightweight porous 3D structures. CNT/superacid solutions may incorporate a wide variety of CNT species (i.e., varying lengths, diameters, numbers of walls, etc) and may take on a wide range of concentrations and phases, ranging from dilute solutions of isotropically oriented CNTs to liquid crystal states in which the CNTs represent 12% or 15% of the solution volume (Davis *et al.*, 2009; Parra-Vasquez *et al.*, 2010). With so many variables to serve as control knobs, research into the creation and optimization of CNT materials from acid has become a broad field of research with many potential applications.

Understanding the rheology of CNT/superacid solutions is important for two reasons. First, optimizing the final properties of a solid material made from a fluid precursor requires an understanding of the microstructure and the flow behavior of that precursor. Different forms of CNT material may be made from CNT solutions with a wide range of starting concentrations, so understanding the evolution of CNT solution rheology over that concentration range is critical. Second, CNT/superacid solutions present an interesting experimental system for the study of semiflexible rods in solution. Rigid and semiflexible rod systems are important in many areas of industry and research beyond material synthesis, and the high aspect ratio and large persistence length of CNTs make them an excellent model system for research in this field.

Chapter 3 presents a study of the viscoelastic properties of CNTs in chlorosulfonic acid (ClHSO₃); it expands on the work reported in Davis *et al.* (2004); Davis (2006); Banzola (2008), and Young (2012). These studies have described the rheology of CNTs of moderate aspect ratio ($\approx 100 - 400$) in weak and strong acid solvents as a function of shear rate, frequency, CNT concentration, and solvent strength. This work compares those results to the results of measurements on CNTs with higher aspect ratio (≈ 4000) in strong acid solvent (ClHSO₃) as a func-

tion of frequency and concentration. The relationship between the development of the liquid crystal phase and the development of elastic network properties is explored, and the primary source of viscoelastic stress in loosely-entangled solutions of both CNT species is identified.

1.0.2 Electrochemical Circuit Behavior of Carbon Nanotube Fibers for Electrophysiology

The design of electrodes for use in implantable medical devices is one of many applications in which optimal performance depends on a combination of material properties. Electrodes which interface with organic tissue must exhibit a low contact impedance with physiological electrolytes; this typically requires a high ratio of surface area to volume. Medical electrodes must also be non-toxic and resistant to chemical and mechanical degradation. CNT fibers possess high conductivity and excellent mechanical properties, and their porous structure and nanometer-scale roughness create a large surface for electrochemical current exchange (Behabtu *et al.*, 2013). CNT fibers have been used effectively as neural electrode implants in rodents, and a chronic *in vivo* trial has demonstrated their biocompatibility (Vitale *et al.*, 2015; McCauley *et al.*, in preparation).

Chapter 4 describes the results of electrochemical measurements on CNT fibers in physiological saline and in mammalian heart tissue *ex vivo*; equivalent circuit modeling is used to describe the physical processes involved in current exchange between CNT fibers and physiological systems, the scaling of CNT fiber electrochemical properties with fiber dimension, and the effects that post-processing and aging may have on these properties. Chapter 5 incorporates the equivalent circuit derived in Chapter 4 into a theoretical model which can be used to describe the performance of CNT fiber electrodes in one particular medical application: treatment of ventricular arrhythmia arising from cellular conduction block.

Chapter 2

Background

2.1 Carbon Nanotubes: Structure and Properties

CNTs were first observed and described in Iijima (1991). They are a class of hollow cylindrical molecules with one or more concentric walls, having an atomic structure similar to that of graphene within the curved plane of each wall and an aspect ratio (ratio of length to diameter) ranging from 100 to over 100,000. This molecular structure grants CNTs significant tensile strength and stiffness; as a result they are often considered a potential building block for the creation of novel, super-strong materials. In addition to mechanical strength, CNTs have a combination of other properties that make them appealing for applications in electronics, materials science, aerospace engineering, and medicine; this broad potential has fueled a considerable research interest in their synthesis, structure, and properties.

CNTs possess outstanding thermal, electrical, and mechanical properties on the singlemolecule scale. Individual CNTs have been measured to have a tensile strength of at least 37 GPa (Walters *et al.*, 1999; Yu *et al.*, 2000), Young's modulus of ~ 1 TPa (Gao *et al.*, 1998; Krishnan *et al.*, 1998; Yu *et al.*, 2000), and thermal conductivity of 3000 W/mK (Hone *et al.*, 1999). CNTs exhibit a range of electrical behavior; they may behave as metals, with electrical resistivity as low as $1 \mu\Omega$ cm and current carrying capacity as high as 10^9 A/cm (Ebbesen *et al.*, 1996; Wei *et al.*, 2001), or as variable band gap semiconductors (Hamada *et al.*, 1992). CNTs also have a low density $(1-2g/cm^3)$ and may be used in the manufacture of lightweight high-performance materials. Assembling CNTs into larger structures which exhibit these single-molecule properties on a macroscopic scale is not trivial, and is a major topic of CNT materials research.

The molecular structure of CNTs can be visualized as one or more sheets of graphene rolled up and joined seamlessly into hollow concentric cylinders. They are composed primarily of sp²-hybridized carbon atoms in a planar hexagonal lattice which is bent into the curvature of the tube; defects which may appear in this lattice include the substitution of sp³-hybridized carbon bonds or missing carbon atoms. Single walled carbon nanotubes (SWNTs) consist of only one graphitic cylinder. Double-walled carbon nanotubes (DWNTs) or multi-walled carbon nanotubes (MWNTs) possess two or more concentric walls; these walls are typically not covalently bonded, and are separated by distances similar to the spacing of graphene layers in graphite.

The variety of structure exhibited by CNTs extends beyond the number of walls. CNTs exhibit a wide range of diameters (ranging from 0.6 nanometers to hundreds of nanometers), and lengths (ranging from tens of nanometers to several centimeters). Additionally, the angle between the carbon-carbon bonds in each CNT wall and the cylinder axis may vary. This angle determines the chirality of that wall; in the case of MWNTs the walls do not typically share the same chirality. The electronic properties of a CNT depend sensitively on the number and chirality of walls it possesses, resulting in the aforementioned range of electronic behavior from metallic conductor to variable band gap semiconductor. The size of the band gap in semiconducting CNTs depends on the CNT diameter (Biercuk *et al.*, 2008).

Due to this extreme variety of structure CNTs must be considered as a broad class of molecules rather than a single type of molecule. The behavior and properties of each species of CNT differ from those of other species, sometimes quite dramatically. Tensile strength and stiffness are determined by diameter and number of walls; electronic properties and chemical reactivity are determined by chirality, diameter, and number of walls. CNT materials research is complicated by the fact that every method of CNT synthesis produces a sample which is polydisperse in one or more of these attributes. Separation or selective purification on a bulk scale is difficult or



Figure 2.1: Models of SWNTs with varying charilities. Also shown are possible sp2-carbon end caps for these SWNTs. Reproduced from Dresselhaus *et al.* (2001) without permission.

impossible with current technologies; as a result, any process or test that involves more than a single CNT molecule will necessarily involve a variety of molecular species with a variety of properties.

2.2 Fabrication of CNT materials

One of the major goals of CNT research is to create macroscopic materials that exhibit a significant fraction of the properties of a single CNT molecule. The essential challenge to be overcome is that the existence of intermolecular junctions tends to lower the properties of the material on the macroscopic scale. The limiting factor for mechanical properties is the strength of adhesion and resistance to relative motion between the constituent CNTs; the limits of thermal or electrical conductivity will be set by the quality of thermal or electrical contact at the interfaces between CNTs and by the number of such interfaces that must be crossed by electrons or phonons as they disperse through a given volume of material. For this reason, the properties of macroscopic articles produced from CNTs depend strongly not only on the properties of the constituent CNTs but also on the geometry of the structure into which they are assembled. For example, a continuous fiber may be composed of closely-packed well-aligned overlapping CNTs to promote long surfaces of contact and efficient stress transfer; this kind of structure may be expected to have good tensile strength and electrical conductivity in the direction in which the CNTs are aligned, but poorer electrical conductivity through its cross-section due to the increased number of CNT-CNT interfaces that must be crossed in that direction. A thin film may be expected to have low mechanical strength due to the small surfaces of contact between perpendicularly crossed CNTs, but to have good in-plane mass-specific electrical or thermal conduction because the large aspect ratio CNTs create a number of long high-conductivity pathways even in a relatively sparse network.

The significant challenge of CNT material processing, therefore, lies in achieving precise control over the micro- and nanometer-scale structure of the CNT assembly while employing a process suitable for scalable production of bulk materials. This is particularly difficult given the challenges of processing and rearranging CNT structure: the large surface areas of CNT molecules give rise to strong attractive van der Waals forces between CNTs that are in parallel contact with one another. Bundles of well-packed and well-aligned CNTs are extremely stable structures, and CNTs tend to arrange themselves into such bundles immediately after synthesis; it is difficult to break or change the structure of these bundles after they are formed.

Methods of fabricating CNT materials can be divided into two categories: solid-state methods and fluid processing methods. Solid-state methods use mechanical working to arrange dry CNT material into a new form, typically without having a large impact on the nanoscale bundle structure (Koziol *et al.*, 2007; Li *et al.*, 2004). Fluid processing methods include blending CNTs into polymer composites or coagulating CNTs from a dispersed state into a solid material that is mostly or entirely composed of CNTs.

Dispersion into a fluid may separate CNTs from their original bundles with varying degrees of success. Methods that have been employed successfully to disperse CNTs include sonication-induced debundling followed by stabilization by polymer or surfactant wrapping (Vigolo *et al.*, 2000), functionalization to increase solvent affinity and prevent close packing (Hudson *et al.*, 2004; Penicaud *et al.*, 2005), and solvation at low concentrations in NMP (Bergin *et al.*, 2008). These methods cannot achieve high concentrations and often fail to completely de-bundle the CNTs; furthermore, sonication and functionalization damage the molecular structure of CNTs, potentially reducing their lengths or changing their electronic properties, and are not therefore not ideal processing methods for applications in which those properties are important.

Two techniques have been demonstrated which allow for the solvation of pristine CNTs without sonication or permanent functionalization. One is the formation of CNT polyelectrolytes in DMSO (Jiang *et al.*, 2013). The second technique is solvation of CNTs in superacids. This technique yields high-concentration solutions of SWNTs and MWNTs, and has been used to create precursor solutions for a variety of solid CNT materials, including films, fibers, and foams (Ma *et al.*, 2013; Mirri *et al.*, 2012; Ericson *et al.*, 2004; Behabtu *et al.*, 2013).

2.3 Carbon Nanotube Solutions in Superacids

True solutions of individually dispersed CNTs can be achieved by using superacid solvents (Ramesh *et al.*, 2004; Davis *et al.*, 2009). The term superacid denotes any acid stronger than 100% sulfuric acid (H_2SO_4); the acids which have been used most extensively as solvents for CNTs are chlorosulfonic acid (ClHSO₃) and mixtures of sulfuric acid with excess sulfer trioxide (SO₃), but other superacids can be used as well (Ramesh *et al.*, 2004). Sufficiently strong acids have the ability to protonate CNTs via a reaction of the form:

$$C_x + yAH \rightarrow \left[C_x^{\delta+} H_y^{(1-k\delta)+}\right] + yA^-$$
(2.1)

This results in a net positive charge on the CNT sidewall (Ramesh *et al.*, 2004). The electrostatic repulsion between positively charged CNTs can partially or completely counterbalance the attraction arising from van der Waals forces, resulting in a solution of CNTs that are only weakly attractive, completely non-interacting, or slightly repulsive at short distances (Green *et al.*, 2009).

The degree of protonation that can be achieved is related to the diameter of the CNT, the density of defects containing sp3 carbon (which is not protonated due to the lack of unbound electrons), and the strength of acid used. 102% H₂SO₄ (H₂SO₄ with 2% excess SO₃ by mass) is an effective solvent for SWNTs with small diameters and relatively short length, although it does not completely counteract the attractive interaction between them. This attractive interaction is compounded in the case of long CNTs which may have very long surfaces of contact, so 102% H₂SO₄ is a poor solvent for long CNTs; also, 102% H₂SO₄ is not able to protonate larger diameter CNTs strongly enough to debundle them (Duque *et al.*, 2010). In contrast, ClHSO₃ has been found to protonate and disperse both SWNTs and multi-walled nanotubes (MWNTs) of any length and diameter, provided that the density of sp3 carbon defects is low (Parra-Vasquez *et al.*, 2010).

Superacids are one of the few solvents in which CNTs are able to form a liquid crystal phase. Solutions of molecules or colloids with anisotropic shapes tend to form such phases at high concentrations (in the case of lyotropic liquid crystals, such as CNTs) or at low temperatures (in the case of thermotropic liquid crystals); this is a thermodynamically driven phase change in which entropy is maximized by sacrificing orientational entropy in order to preserve translational freedom. In order to form a liquid crystal phase, the components of a system must have the freedom to move near each other without being arrested by attractive forces. CNT/superacid solutions, CNT polyelectrolyte solutions, and surfactant stabilized CNT dispersions have also exhibited this phase transition (Davis *et al.*, 2009; Jiang *et al.*, 2013; Song *et al.*, 2003; Islam *et al.*, 2004). A brief discussion of concentration regimes and phase transitions in rigid and semiflexible rod solutions, and of the investigation of CNT solution phases, is provided in Chapter 3.

Solutions of CNTs in ClHSO₃ and 100+% H₂SO₄ have been used in the fabrication of solid CNT materials including transparent conductive films (Ma *et al.*, 2013; Mirri *et al.*, 2012), high strength and high conductivity CNT fiber (Ericson *et al.*, 2004; Behabtu *et al.*, 2013), and lightweight porous sponges. The fabrication of these materials involves either filtration of CNTs out of an acid solution or coagulation of the dissolved CNTs by removal of the acid into a coagulant bath. Suitable coagulant fluids such as water, diethyl ether, or acetone are miscible with the acid but acts as non-solvents for the CNTs). The microstructure and phase of the CNTs in the precursor solution, coupled with the method chosen for acid removal, determine the structure and properties of the resulting solid material.

2.4 Wet-Spun CNT Fibers from Superacids

Polymer fibers, whether made of natural polymers such as cellulose or synthetic polymers such as poly- γ -benzyl-L-glutamate (PBLG) and p-phenylene terephthalamide (PPTA), achieve great strength and flexibility by assembling these highly anisotropic molecular chains into an aligned, well-packed structure. Polymer chains in a fiber share stress efficiently, allowing the large specific mechanical strength of their nano-scale molecular backbones to be expressed on a macroscopic scale. Fibers of this type have been the source of many advances in material science over the last century (Chae and Kumar, 2006). For the same reasons, an aligned and well-packed fiber is one of the most useful structures that can be assembled from CNTs. This structure allows their highly anisotropic properties to be exploited to the fullest effect. In the case of CNTs this applies not only to mechanical strength but also to electrical and thermal conduction; a fiber composed of highly aligned parallel CNTs presents a multitude of parallel low-resistance pathways for electrons and phonons to travel along the fiber axis.

Synthetic fibers are produced in three ways: solid state spinning, wet spinning from a solution state, and melt spinning. Both of the first two methods have been used to fabricate continuous and stable CNT fibers; the third method is not possible for CNTs, which (due to their extreme stiffness) thermally decompose before they form a melt state. Solid state spinning can be accomplished by twisting CNT films or arrays into short lengths of fiber (Jiang *et al.*, 2002). Li *et al.* (2004) reported a method that produces continuous lengths of fiber by collecting and densifying a CNT aerogel as it emerges from the open end of a synthesis furnace. Wet spinning of CNT fiber has been demonstrated using surfactant-stabilized CNTs in an aqueous solution (Vigolo *et al.*, 2000) and CNT/superacid solutions (Ericson *et al.*, 2004; Behabtu *et al.*, 2013).

Wet spinning of CNT fibers from ClHSO₃ has been described in Behabtu *et al.* (2013). Briefly, the process used to create the fiber discussed in Chapters **4** and **5** is as follows: CNTs are mixed with ClHSO₃ to form a spinning dope solution of moderate concentration. The ideal dope concentration will vary depending on several factors, including the aspect ratio of the CNT batch; the best results can be achieved by using a solution which is entirely or predominantly in the liquid crystalline phase regime, but not so high in concentration that the solution cannot flow. This acid dope is loaded into a stainless steel chamber and driven by a piston through a small round aperture (the spinneret) directly into a bath of acetone, which serves as a coagulant fluid. The extruded fluid filament is passed through this bath onto a motor-driven collection drum, which turns with a linear speed greater than the extrusion velocity at the spinneret; the filament is therefore subjected to elongation, promoting alignment of the constituent CNTs along the fiber axis, while it solidifies in the acetone.

The coagulated fiber is washed by submerging the collection drum in heated water (50° C) for 3 hours, then dried in an oven at 115° C overnight. The combination of acetone coagulation and water bath immersion removes the majority of the acid from the solidified fiber structure; small amounts of aqueous acid remains, acting as an electrical dopant (Behabtu *et al.*, 2013).

The structure of wet-spun CNT fibers is hierarchical. The fiber is composed of thin (\approx 100 nm) bundles of CNTs which are well-aligned along the fiber axis and packed closely together. TEM imaging reveals that the constituent CNTs within each bundle are highly aligned and densely packed; in spite of the voids that exist between bundles the overall packing density of the fiber has been measured to be ~ 90% of the theoretical maximum (Behabtu *et al.*, 2013). The fibers are approximately cylindrical, but they take on an irregular shape due to inhomogeneity and instability during coagulation (see Figure 2.2).

CNT fibers produced by wet spinning from ClHSO₃ have achieved specific mechanical strength and thermal conductivity comparable to graphitic carbon fiber and specific electric



Figure 2.2: SEM images depicting the morphology and μ m-scale structure of CNT fibers. The fiber is composed of many aligned bundles of of CNTs, resulting in a structure which is porous on the sub- μ m scale; Image B, a higher magnification view of a portion of the fiber in image A, depicts this fine bundle structure; the bundles range in size from a few nm to ≈ 100 nm. C depicts a fiber end that has been cut and slightly flattened by a razor, illustrating how this laminar bundle structure may lead to easy deformation transverse to the fiber axis. These fibers are representative samples of the Tuball CNT fiber (A & B) and CCNI CNT fiber (C) discussed in Chapter 4.

conductivity comparable to metals (Behabtu *et al.*, 2013). This combination of properties makes them ideal for multi-functional applications.

Chapter 3

Rheology of Carbon Nanotubes in Superacids

3.1 Introduction

(ClHSO₃) is one of the best known solvents for CNTs; it is able to separate CNTs as individuals and achieve uniform fluid mixtures of CNT liquid crystals at concentrations as high as 15% by volume ($\phi = 0.15$), and does so without the addition of surfactants, destructive sonication, or chemical functionalization (Davis *et al.*, 2009; Parra-Vasquez *et al.*, 2010). As a result, processing with ClHSO₃ is a powerful and easily scalable method for the production of neat CNT materials. ClHSO₃ solutions have been used in the fabrication of continuous aligned CNT fiber (Ericson *et al.*, 2004; Behabtu *et al.*, 2013), transparent conductive CNT films (Ma *et al.*, 2013; Mirri *et al.*, 2012), porous CNT sponges, and thick CNT films suitable for use as coaxial cable shielding (Mirri *et al.*, 2016).

This chapter deals with the rheology of CNT solutions in $ClHSO_3$. Rheology is the study of how materials respond to applied stress or strain; the rheological properties of colloidal and polymer fluids, including CNT solutions, varies greatly depending on the size, shape, degree of interaction, and density of packing of the polymers or colloids. Rheological measurement (rheometry) of such a mixture is useful not only because it provides information about how that particular sample will respond to a range of deformations but also because it provides a means of investigating the dimensions, properties, and microstructure of the constituent colloids or polymers (provided that the relationship between these structural details and rheological properties is well-understood).

The rheology of CNT solutions in $ClHSO_3$ is important for two reasons. Firstly, it is important for further development and optimization of CNT materials made using this acid. The microsctructure and properties of a solid material made from a CNT solution precursor (or any other polymer solution precursor, for that matter) will depend on the microstructure present in the solution, the manner in which the solvent is removed, and the flow and shear history of the solution up to that point. Using rheology to investigate mictrostructure and flow behavior is therefore an essential step in achieving better properties in the final material.

Secondly, $CIHSO_3$ is a system which can be compared easily to theoretical models for rigid rod and semiflexible polymer behavior because it one of the few solvents in which CNTs can be dispersed as individuals without attractive interactions. Because $CIHSO_3$ solution rheology can be analyzed using these relatively simple models, it can be used as a tool to measure the properties of the constituent CNTs. Given the large polydispersity of that can be found in any CNT sample it is not easy to measure batch attributes such as average length by direct observation and measurement of individual CNTs; a great number of CNTs need to be examined in order to achieve statistical accuracy, making for a laborious and time-intensive investigation. If the relationship between individual CNT attributions and collective rheological properties is well-understood, then rheometry can serve as an efficient way to measure bulk properties of the entire batch. For example, the length distribution of CNTs in superacid solutions has been deduced from analysis of shear rheology (Parra-Vasquez *et al.*, 2005) and extensional rheology (Tsentalovich *et al.*, 2016).

The earliest investigations into CNT/superacid solution rheology examined solutions of a particular class of CNTs, produced using the high pressure carbon monoxide (HiPco) method, in a relatively weak superacid solvent, 102% H₂SO₄. These studies used shear rheology to map out the rheological behavior of CNTs in this solvent across a broad concentration range and

identified a) the rheological signatures of distinct concentration regimes predicted by rigid rod models, b) the rheological signatures associated with liquid crystal systems, and c) the concentration range in which the CNTs in that solvent appear to form a percolated elastic network (Davis *et al.*, 2004; Davis, 2006) . The first set of rheological measurements on HiPco CNTs in ClHSO₃, reported by Banzola (2008), demonstrated similar hallmarks of liquid crystalline rheology.

Young (2012) extended this body of work by measuring the rheology of HiPco CNTs at lower concentrations and in mixtures of superacids with intermediate solvent strength. This study identified a rheological percolation threshold in $ClHSO_3$ at a higher concentration than the one identified in 102% H₂SO₄; this is consistent with the conclusion drawn in Davis (2006) that rheological percolation in these systems is due to percolation of liquid crystal phase domains rather than percolation of the CNTs themselves. Young (2012) also compared the viscoelasticity of CNT samples below this percolation threshold with the viscoelastic stress that is predicted to arise from orientational Brownian motion in rigid rod solutions, and found that there was poor agreement.

The study presented in this chapter adds to this body of work by reporting rheology as a function of CNT concentration in ClHSO₃ using a second CNT species, obtained from Unidym Inc., with an aspect ratio higher than that of HiPco CNTs. This CNT batch exhibits percolation behavior that is significantly different from that of HiPco CNTs; as with the percolation of HiPco CNTs in ClHSO₃ and 102% H₂SO₄, this behavior is related to liquid crystal domain morphology. The low-concentration viscoelasticity of both HiPco CNTs and Unidym CNTs are in poor agreement with predictions based on orientational Brownian stress in semiflexible rods; an analysis of the scaling of viscoelasticity with frequency and concentration demonstrates that the primary viscoelastic stress in the loosely entangled regime for both systems arises from tension and compression of the individual CNT contours, and is thus inherently related to the slight flexibility possessed by these stiff molecules.

Section 3.2 introduces the theoretical models of rigid and semiflexible rods that are relevant for CNT solution rheology. Section 3.3 describes the methods and apparatus that were used to

mix and perform rheometry on solutions of CNTs in $CIHSO_3$. Section 3.4 presents the results of those measurements. Section 3.5 discusses the physical interpretation of these results as well as prospects and possible direction for future studies of rheology in superacids.

3.2 Background: Rigid Rods and Semiflexible Polymers

In the context of polymer science it is useful to make a distinction between flexible or "coil-like" polymer chains, for which the total length L of the chain is much greater than its persistence length L_p , and stiffer "rod-like" polymer chains, also commonly referred to as "semiflexible" polymers, for which $L \ll L_p$. A semiflexible polymer in solution will maintain an extended, highly anisotropic shape rather than coiling on itself; this greatly enhances both the viscous drag associated with the motion of individual polymers through the solvent and the degree of overlap and entanglement between neighboring polymers, with the result that even small concentrations of semiflexible rods can have a profound effect on solution rheology. Many authors have modeled the behavior of semiflexible rods by considering the limiting case of infinite stiffness, in which case the rods in question may be referred to as rigid rods (Doi and Edwards, 1986).

3.2.1 Concentration regimes and phase transitions

Several distinct concentration regimes may be identified for non-attractive rod-like particles in solution; these regimes are defined not only by the degree of orientational order in the rods (isotropic vs. liquid crystalline) but also by the degree to which the rods interact and entangle with one another. At very low concentrations, well-dispersed rods are separated from one another by distances greater than their own length, and are thus free to translate or rotate without impedance from other rods; this is known as the dilute concentration regime. At higher concentrations the solution enters a so-called semidilute regime, in which the average distance between neighboring rods is less than the rod length L; in this regime the rods are not able to complete a full rotation without encountering one another. In terms of the volume fraction

 ϕ of rods in the solution, rods of diameter d and length L are expected to transition from the dilute to the semidilute regime at a concentration of (Doi and Edwards, 1986)

$$\phi_{\text{dilute}} = \alpha \frac{d^2}{4L^2} \tag{3.1}$$

Here, α is an empirical factor; experiments on rigid rod polymer systems indicate $\alpha \approx 30$ (Teraoka and Hayakawa, 1989; Larson, 1999). As concentration increases so does the degree of entanglement between rods, and their freedom to rotate is increasingly hampered. Above a concentration of

$$\phi_{\rm C} = \frac{\pi d}{4L} \tag{3.2}$$

the rods become so closely packed that the sum of their excluded volumes, defined as the volume near a rod within which a second rod cannot enter if it is perpendicular to the first, becomes comparable to the total volume of the solution. In this regime further packing in the isotropic state is extremely difficult and motion of the rods in any direction other than along their own axes is severely constricted; the formation of an aligned liquid crystalline phase becomes thermodynamically favorable in this concentration regime.

For monodisperse rigid rods, Onsager predicts (Onsager, 1949) that a liquid crystal phase will begin to appear at a volume fraction:

$$\phi_{\rm I} = 3.34 \frac{d}{L} \tag{3.3}$$

At concentrations just above this transition rod solutions exist in a biphasic state: a fraction of the rods enter the liquid crystalline phase, while the rest remain in the isotropic phase. These coexisting phases may separate from one another, but in many cases the time scale for complete separation is months or years; instead, the mixture of the two phases typically consists either of liquid crystalline domains within an isotropic bulk or the reverse. At the highest concentrations, above some threshold $\phi_{\rm IC}$, the solution becomes entirely liquid crystalline. Even in the fully liquid crystalline regime, however, there are kinetic barriers that prevent the merging



Figure 3.1: Schematic illustrating the concentration regimes that can be found in rigid rod solutions. From left to right these are: dilute, semidilute, concentrated isotropic, biphasic, and fully liquid crystalline. (Reproduced from Davis *et al.* (2004) without permission, adapted from Doi and Edwards (1986)).

of separate liquid crystal domains (Behabtu, 2012). The interfaces between aligned domains, which are often referred to as defects in the liquid crystal structure, are significant sources of elasticity when such a solution is subjected to strain.

Equations 3.1-3.3 represent the expected phase boundaries for a monodisperse sample of purely rigid rods with a single length and diameter and with no attractive interactions. Real systems may diverge from this ideal in several ways; polydispersity in length or diameter leads to phase boundaries which are less clearly defined. For example, at concentrations near ϕ_{dilute} short rods may be able to rotate freely without entanglement, while long rods, which sweep out a larger area, encounter others and are impeded (Marrucci and Gizzuti, 1983). Similarly, rods with a higher aspect ratio are expected to enter a liquid crystal phase at lower concentrations then shorter rods within the same sample (Wensink and Vroege, 2003). The existence of attractive interactions may shift ϕ_{I} and ϕ_{IC} to lower concentrations, because alignment between neighboring rods will be more energetically favorable (Green *et al.*, 2009). Finally, flexibility in the rods may be expected to decrease the degree to which they impede or collide with one another at all concentrations, leading to a higher effective value for ϕ_{dilute} , ϕ_{I} , or ϕ_{IC} ; this is a

plausible explanation for the appearance of the empirical factor $\alpha \approx 30$ in equation 3.1.

3.2.2 Sources of Viscoelastic Stress

Orientational stress in rigid rods

Viscoelastic stress arising from orientational entropy in a rigid rod solution has been described by Doi & Edwards (Doi and Edwards, 1986). A solution of rods at thermodynamic equilibrium will exhibit some distribution of rod orientation; if the solution is subject to strain, hydrodynamic forces on the rods will cause them to re-orient, shifting the orientation distribution from the equilibrium state. Orientational stress arises from the collective Brownian rotational motion of the rods as they return to the equilibrium distribution. For a rod solution undergoing oscillatory shear strain with frequency ω , the complex shear modulus arising from rotational entropy is

$$G^*(\omega) = \frac{1}{i\omega} \left[\eta_s + G\tau_{\rm rot} \left(\frac{1}{1 + i\omega\tau_{\rm rot}} + \frac{1}{3} \right) \right]$$
(3.4)

where τ_{rot} is the rotational relaxation time of the rods and *G* is the instantaneous rotational shear modulus, which depends on the rod number concentration *v* and the temperature *T*:

$$G = \frac{3}{5} \nu k_B T \tag{3.5}$$

The real and imaginary parts of G^* , which are respectively the elastic modulus G' and the viscous modulus G'', are given by

$$G'(\omega) = G \frac{(\tau_{\rm rot}\omega)^2}{1 + (\tau_{\rm rot}\omega)^2}$$
(3.6)

and

$$G'' = \eta_s \omega + G \left[\frac{\tau_{\rm rot} \omega}{1 + \tau_{\rm rot} \omega} + \frac{1}{3} \tau_{\rm rot} \omega \right]$$
(3.7)

In the dilute concentration regime, in which the rotational motion of rods is not hindered by neighboring rods, the rotational relaxation time is

$$\tau_{\rm rot} = \frac{\zeta L^3}{72k_B T} \tag{3.8}$$

in which ζ represents the friction coefficient between the rod and the surrounding fluid. In this regime, τ_{rot} is independent of concentration. In the semidilute regime, however, rotation is hindered by the presence of other rods; in this regime, rotational relaxation can be described by a so-called reptation model. Each rod may be considered to be confined to a virtual tube created by neighboring rods, and the diameter D_t of this tube depends on total rod concentration. In this case, rotational relaxation is carried out by a series of movements of the rod along its axis in the confining tube, each of which allows a rotation through a small angle roughly equal to D_t/L . The rotational relaxation time of the rod is given by

$$\tau_{\rm rot} = \frac{\zeta L^3}{72k_B T} \left(\frac{L}{D_{\rm t}}\right)^2 \tag{3.9}$$

The confinement length D_t for a given rod in a semidilute or concentrated isotropic solution can be estimated by considering the number of other rods which intersect a virtual cylinder of radius *r* around that test rod, denoted N(r). This number will be determined by the length of the rod in question, the number concentration of rods in the system, and the orientation distribution of the rods. In the most general case, for a set of rods with a length probability distribution P(L), number concentration v, and orientation distribution $\Psi(\mathbf{u})$, the number of rods intersecting a cylinder of radius *r* around a test rod of length *L* is

$$N(r) = \frac{1}{2} \int \int \int \Psi(\mathbf{u}') \nu P(L') L' | \mathbf{u}' \cdot \mathbf{n} | d\mathbf{u}' dL' dA$$
(3.10)

where the factor of $\frac{1}{2}$ is included to account for the fact that most rods pass through the cylinder twice (Doi and Edwards, 1986; Marrucci and Gizzuti, 1983). The integration accounts for all possible lengths & orientations of the intersecting rods over the surface area of the virtual

cylinder. In the case of an isotropic solution,

$$N(r) = \frac{\nu \pi r L}{2} \int P(L') L' dL'$$
(3.11)

The confinement length at a given concentration is determined to be the radius at which the number of rods intersecting the cylinder is on the order of 1, $N(D_t) \simeq 1$. In the simple case of monodisperse rod length,

$$D_{\rm t} = \frac{\alpha}{\nu L^2} \tag{3.12}$$

in which α is the empirical factor which appears in equation 3.1. In this context, this factor may be interpreted as the number of rods that must intersect the virtual cylinder in order to effectively cage the rod within that cylinder. Rheometry of rod solutions has indicated that α is approximately 30 (Teraoka and Hayakawa, 1989; Larson, 1999).

Orientational stress in semiflexible rods

For rigid rods, equation 3.9 indicates that the rotational relaxation time increases quadratically as the confinement length D_t shrinks. If the slight flexibility of rod-like molecules is taken into account, however, this is only expected to hold true up to a certain limit of confinement. Flexibility results in transverse undulations along the contour of a semiflexible rod, with the amplitude and wavelength of the undulation determined by the rod's stiffness. If the size of the virtual tube confining a rod is comparable to this transverse undulation, escape from a confining tube will be easier due to the ability of the rod to bend slightly and find pathways through which it can reptate (Odijk, 1983). In this case, the rotational relaxation time of the rod is

$$\tau_{\rm rot} = \frac{\zeta L^2 L_p}{12k_B T} \tag{3.13}$$

The onset of very tight entanglement therefore represents the start of a third regime of rotational relaxation behavior, in which the rotational relaxation of a rod is expressed by equation 3.13 for all concentrations. The transition to this flexibility-enabled rotational relaxation
behavior has recently been observed in individual HiPco SWNTs confined in porous media (Fakhri *et al.*, 2010).

Tension stress in semiflexible rods

Many semiflexible rod systems have a complex shear modulus which follows the power law scaling $G^*(\omega) \propto \omega^{3/4}$ at high frequencies, indicating a source of viscoelastic stress with a relaxation time $\tau \propto t^{-3/4}$. This has been identified as a stress arising from longitudinal stretching and compression of the rods — not due to stretching of the molecular structure of the rod itself, but due to a change in the amplitude of transverse fluctuations that arise due to rod flexibility (Gittes and MacKintosh, 1998; Morse, 1998a,b). Rods which are extended or compressed (depending on how they are oriented with respect to a strain deformation) will either bunch up or extend slightly; the rods subsequently relax by propagation of excess contour length along the chain.

Simulations of rod relaxation indicate that this tension stress actually exhibits two regimes of relaxation time. $G'(\omega) \propto G''(\omega) \propto \omega^{3/4}$ at the shortest time scales; however, after a time τ_{\parallel} given by

$$\tau_{\parallel} = \frac{\zeta L^8}{k_B T L_p^5} \tag{3.14}$$

the moduli adopt the scaling behavior $G'\omega \propto \omega^{5/4}$ and $G''(\omega) \propto \omega$, with some crossover region of intermediate behavior separating the two regimes (Pasquali *et al.*, 2001). This time scale represents the time it takes for a change in contour density (excess bunching or stretching) to diffuse to the ends of the rod. For very stiff or very short rods, with $L \ll L_p$, this crossover time becomes very short and the $G^*(\omega) \propto \omega^{3/4}$ behavior may only be observed at very high frequencies.

3.3 Materials and Methods

3.3.1 Preparation of CNT/acid Solutions

This study was performed using solutions of CNTs in ClHSO₃, which is an aggressive and hygroscopic acid. Materials and procedures for sample preparation and testing were carefully designed to avoid health risks, damage to equipment, and degradation of the quality of the solutions themselves. ClHSO₃ reacts readily with ambient atmospheric moisture to create H_2SO_4 , resulting in an acid mixtures which may which may act as a weaker solvent for CNTs (Davis *et al.*, 2009). This reaction also results in the release of HCl gas, which is highly corrosive as well as an inhalation hazard. To prevent this reaction, solutions containing ClHSO₃ were mixed within an enclosed glove box flushed with dessicated air (dew point -50 °C). The materials used to work with the acids were those with little or no susceptibility to corrosion in ClHSO₃, such as glass, PTFE, Hastelloy C, and 316 stainless steel.

99% ClHSO₃ was used as received from Sigma Aldrich. CNT solutions were prepared by mixing acids with dry CNTs in glass vials within a glove box flushed with desiccated air. Solutions with mass concentrations below 1% were mixed on magnetic stir plates using Teflon-coated stir bars for 24 hours. Solutions with mass concentrations above 1% were mixed using a DAC 150.1 FV-K speed mixer (FlackTek, Inc.). Note that in section 3.4 the rheology of the Unidym solutions prepared for this study is compared to the rheology of HiPco CNT solutions in ClHSO₃ and 102% H₂SO₄, some of which were which were mixed different methods; see Davis (2006), Banzola (2008), and Young (2012) for details.

Mass fraction of CNTs was converted into volume fraction based on an average density of the CNTs in each batch, calculated according to the formula

$$\langle \rho_{\rm CNT} \rangle = \frac{4000}{A_s (\langle d \rangle + \delta_{\rm vdW})^2} \left[\langle n \rangle \langle d \rangle - 2\delta_{\rm vdW} \sum_{i=0}^{\langle n \rangle - 1} i \right]$$
(3.15)

in which $A_s = 1315 \text{ m}^2/\text{g}$ is the specific surface area of one side of a graphene layer, $\langle n \rangle$ is the average number of walls and $\langle d \rangle$ the average external diameter of the CNTs, and $\delta_{\text{vdW}} = 0.34$ nm is the spacing between concentric CNT walls (Laurent *et al.*, 2010).

CNTs from two different sources were used in this study and in the studies reported in Davis (2006), Banzola (2008), and Young (2012); these are referred to as HiPco CNTs and Unidym CNTs. The distribution of diameter and number of walls of each batch has been assessed by TEM imaging; aspect ratio and length distribution have been determined by extensional viscosity measurements (Tsentalovich *et al.*, 2016). The isotropic-nematic cloud point ϕ_{dilute} for each batch was estimated by examination of a range of solution concentrations under polarized light microscopy (Tsentalovich *et al.*, 2016). Average persistence length for each batch was calculated using the formula (Fakhri *et al.*, 2009)

$$\langle L_{\rm p} \rangle = \langle n \rangle \frac{\pi C \langle d \rangle^3}{8k_B T} \tag{3.16}$$

in which C = 345 N/m is the in-plane graphitic stiffness. The stiffness of CNTs with multiple walls is assumed to be the sum of the stiffnesses of the individual walls; additional bending stiffness arising from friction between the concentric walls is neglected.

HiPco CNTs were synthesized the HiPco reactor at Rice University (with the designation batch 188.3) and were oxidized and purified by an HCl wash as described in Xu *et al.* (2005). This batch is composed of SWNTs with an average diameter of 1.15 nm. The lengths of the CNTs follow a log-normal distribution with $\langle L/d \rangle = 383$, implying that $\langle L \rangle = 440$ nm. The average persistence length is $\langle L_p \rangle = 51 \ \mu$ m. The isotropic-to-nematic transition concentration is $\phi_I = 1250$ ppm. The average density of Hipco CNTs given by equation 3.15 is 1.58 g/cm³. Note that this is slightly different from the density used to calculate volume fraction in Young (2012), which was 1.42 g/cm³. The latter represents the density of a hexagonally closed packed bundle of these CNTs; the density of 1.58 g/cm³ is more accurate for a solution of individually dispersed CNTs.

Unidym CNTs were obtained from Unidym, Inc. in a purified form. This batch is composed primarily of double-walled CNTS, with some single-walled and triple-walled CNTs present ($\langle n \rangle$ is approximately 2). The average diameter is 2.11 nm; the length distribution is log-normal with $\langle L/d \rangle = 4008$, implying $\langle L \rangle = 8460$ nm. The average persistence length is $\langle L_p \rangle = 600 \ \mu$ m. The isotropic-to-nematic transition concentration is $\phi_I = 61$ ppm. The average density of Unidym CNTs given by equation 3.15 is 1.79 g/cm³.

3.3.2 Polarized Optical Microscopy

Light microscopy of acid solutions was performed on a Zeiss Axioplan microscope. Samples were prepared for microscopy by drawing the solution into rectangular glass capillaries with inner cross-section dimensions of 50 nm x 200 nm; after influx of solution by capillary forces, the ends of the glass capillary were melted with a flame to form an air-tight seal. Microscopy was performed by imaging through the smaller capillary dimension.

Polarized microscopy was performed in transmission mode through the use of independently rotatable polarizing filters placed in the light path before and after the sample (termed the polarizer and analyzer, respectively). This technique exploits the optical properties of anisotropic materials, in which the refractive index differs for light polarized in different planes; such materials are known as birefringent materials. Polarized light that is transmitted through a birefringent sample is split into two components, with polarizations parallel and perpendicular to the optical axis of the sample. When the light subsequently passes through a second polarizing filter, only the components of these two waves which are parallel to this polarizer's axis will pass through. If the polarizing filters before and after the sample are oriented with optical axes orthogonal to one another, then the only light that is able to pass to the objective is that which has had its polarization changed by transmission through birefringent areas in the sample. This technique was employed to visualize the birefringent liquid crystalline domains in CNT solutions.

3.3.3 Dynamic Shear Rheology

Dynamic shear rheology was performed on solutions of Unidym CNTs in ClHSO₃ with volume fraction concentrations between $\phi = 1 \times 10^{-5}$ and $\phi = 3 \times 10^{-3}$ using an ARES strain controlled rheometer (TA Instruments, Wilmington, DE) with a 100 g Force Rebalance Transducer (FRT). The geometry used for testing was a double-walled concentric cylinder couette with an inner and outer cup diameter of 27.95 mm and 34 mm, and an inner and outer bob diameter of 29.5

mm and 32 mm; both parts of this geometry were made of stainless steel 316. Sample loading was accomplished with the use of a Plexiglas chamber to temporarily enclose the geometry. To prevent reaction of ambient moisture with the sample during the test, the acid solutions were covered with a layer of Fluorinert FC-72, which was itself covered with a layer of low viscosity silicon oil (4.7 cP) in order to prevent evaporation of the volatile Fluorinert. Because the central shaft of the double-walled couette is hollow and presents an additional pathway for moisture to reach the sample on the interior of the bob, Fluorinert FC-72 was added to this central shaft. Section 3.3.5 provides further details and describes the rationale behind this loading procedure.

Dynamic shear rheology for the highest concentration Unidym solution tested, with $\phi = 0.0147$, was performed using an RDA III strain-controlled rheometer (TA Instruments, Wilmington, DE) with a convection oven attachment. The tests were performed at room temperature, but the convection oven attachment was used to enclose the testing geometry and flush the atmosphere around it with anhydrous nitrogen during the test. The geometry used for testing was a modified version of a parallel plate geometry with a diameter of 40 mm, made out of stainless steel 316; in order to enable the use of Fluorinert and silicon oil covering fluids the bottom plate was replaced with a shallow cup with an inner diameter of 42 mm.



Figure 3.2: A & B: Photographs of the testing geometries used for rheological measurements on $CIHSO_3$ solutions; these are (A) a double-walled concentric cylinder couette and (B) a 40 mm diameter parallel plate testing fixture in which the bottom plate has been replaced by a shallow cup. All parts are made out of stainless steel 316 in order to avoid excessive corrosion by the liquid acid or acid fumes. C: Cartoon schematic demonstrating how these geometries are loaded with acid samples and with covering fluids to protect that acid from atmospheric moisture. In the case of the double walled couette, the surface of the acid on the inner portion of the hollow couette bob was covered by injecting Fluorinert (red) down the hollow upper shaft. This schematic also indicates the basic use of the geometry as a part of the rheological test: each case the bottom portion of the geometry is moved by an oscillating motor, shearing the rheology sample (black) between two closely separated surfaces; the total shear stress exerted by the fluid sample on the upper portion of the geometry is recorded by a torque transducer.

In section 3.4 the rheology of the Unidym solutions measured in this study is compared to the rheology of Hipco CNT solutions in $ClHSO_3$ and 102% H₂SO₄, which were tested on either the same ARES rheometer or an AR 2000ex rheometer (also TA instruments), using a variety of testing geometries (Davis, 2006; Banzola, 2008; Young, 2012).

For all solutions, the critical strain value γ_c defining the upper limit of the linear viscoelatic strain regime was determined using a strain sweep test between $\gamma = 0.001$ and $\gamma = 1$. Frequency-dependent viscoelastic properties were measured for each sample using a strain value within the linear regime (i.e., less than γ_c).

3.3.4 Experimental Limitations & Challenges

In this study and in other studies performed on CNT solutions in ClHSO₃ (Davis, 2006; Banzola, 2008; Young, 2012), the viscoelastic response of CNT solutions was measured over a frequency range of 0.1 rad/s to 100 rad/s; however, the useful experimental range was narrower than this for many of the solutions tested. There are three important limits beyond which the results of dynamic shear measurement on a sample will no longer reflect the material properties of that sample; these are 1) the frequency below which the stress from the sample creates a torque on the geometry which is below the torque sensitivity limit of the rheometer, 2) the frequency above which inertial effects within the sample lead to non-uniform shear in the gap, and 3) the frequency above which torque associated with the acceleration and deceleration of the oscillating rotor dominates the torque measurement (Ewoldt et al., 2015). The third of these effects is only an issue for rheometers in which the torque transducer is connected to the geometry rotor, as was the case for the AR 2000ex rheometer used in Young (2012), rather than the geometry stator, as is the case for the ARES rheometer used in this study. These effects place an upper and lower limit on the range of frequencies at which reliable data can be obtained for any given sample. For low-viscosity samples these upper and lower limits may converge, in which case the rheology of the fluid cannot be reliably measured.

Figure 3.3 demonstrates the limits of the experimental window for two concentrations of Unidym CNTs in ClHSO₃. The torque sensitivity limit of the rheometer, T_{min} , places a lower



Figure 3.3: Measurements of elastic modulus (G', circles), viscous modulus (G'', squares), and complex shear modulus (G^* , triangles) as a function of frequency for Unidym CNTs in CIHSO₃ at a concentration of (A) 80 ppm by volume and (B) 500 ppm by volume. In each case, data below the dashed blue line (denoted by solid black fill) indicates data for which the measured torque falls below the sensitivity limit of the rheometer; data points for which G^* falls under the dashed red line (indicated by unfilled data points) are unreliable due to fluid inertia effects. Reliable data is indicated by solid gray fill. Shear rheology can be measured reliably over a broader range of frequencies (and thus a broader range of time scales) for the 500 ppm solution.

limit on the magnitude of sample modulus that can be reliably measured (either $G'(\omega)$ or $G''(\omega)$), expressed as

$$G_{\min} = \frac{K_{\tau} T_{\min}}{\gamma_0} \tag{3.17}$$

in which K_{τ} is the conversion factor between the sample shear stress and measured torque and γ_0 is the strain amplitude of the test (Ewoldt *et al.*, 2015). In Figure 3.3, measurements of $G'(\omega)$ and $G''((\omega))$ taken beyond this limit are represented by solid black symbols.

The limit at higher frequencies arises from the propagation of shear waves through the sample. In order for the shear in the sample to be homogeneous, the wavelength of shear waves propagating away from the moving surface of the geometry should be more than 10 times the thickness of the gap in which the sample is sheared, D (Ewoldt *et al.*, 2015; Schrag, 1977). The wavelength depends on the frequency and on the material properties, resulting in unreliable

measurement for any frequency at which

$$|G^*(\omega)| > \left(\frac{10}{2\pi}\right)^2 \cos^2\left(\frac{\delta}{2}\right) \rho \,\omega^2 D^2 \tag{3.18}$$

in which δ is the phase difference between the torque measurement and the strain applied to the sample and ρ is the density of the sample (Ewoldt *et al.*, 2015). In Figure 3.3, measurements of $G'(\omega)$ and $G''(\omega)$ taken below this limit are represented by hollow symbols.

As a result of the combination of these effects, the measurable frequency range for solutions of Unidym CNTs became progressively narrower as concentration decreases; solutions with concentration lower than 20 ppm could not generate reliable data at any frequency.

3.3.5 Challenges of rheological testing with ClHSO₃

The ability of ClHSO₃ to form true solutions of individualized CNTs was first reported in (Davis *et al.*, 2009). Since that time several attempts have been made to design an experimental procedure suitable for performing shear rheology in this aggressive acid; each procedure attempted to date has exhibited only partial success. The challenges that must be faced in order to run a test in ClHSO₃ in a typical shear rheometer include:

- · preventing corrosion of the testing geometry in contact with the sample
- preventing damage to the electrical and mechanical components of the instrument itself from HCl gas that arises from the sample
- preventing the ingress of atmospheric moisture to the sample, which degrades the solvent strength and results in production of excessive amounts of HCl gas
- preventing solvent strength from degrading due to the thermodynamic decomposition of ClHSO₃ into HCl and H₂SO₄, with subsequent loss of volatile HCl gas

The first of these challenges, preventing corrosion of the rheometer geometry, can be overcome by using corrosion-resistant materials. Geometries made out of stainless steel 316 have been used successfully in this study and previous studies; this material tends to show some signs of corrosion and discoloration after several uses, but this corrosion has not been observed to progress far enough to damage the geometry or affect the accuracy of measurements. The primary drawback of using steel geometries is the significant mass of the rotors, which contributes to the instrument inertia effect discussed in section 3.3.4.

The other challenges posed by $CIHSO_3$ are more difficult to overcome. The essential operation of rotational shear rheometers makes the prospect of sealing the atmosphere around the sample very difficult, since the two pieces of the testing geomtery (the rotor and the stator) must be free to move relative to one another. The only ways to control sample atmosphere are to enclose the entire rheometer in a sealed and regulated atmosphere or to protect the sample from the atmosphere with some additional covering fluid (either a liquid or gas) which will not produce significant additional torque during the rotation.

The first attempt to measure the rheology of CNT solutions in ClHSO₃ was reported in Banzola (2008). In that study, and in Young (2012), rheology was performed by enclosing an AR 2000ex stress-controlled rheometer (TA Instruments, New Castle, DE) entirely in a Plexiglas box flushed with dessicated air (dew point -50 °C). The removable front plate of this box was fitted with rubber gloves for loading and operation of the rheometer while the box was sealed. The box was sealed and flushed with dried air overnight before loading and testing the acid samples.

After a prolonged period of use (several months) the body and electronic components of this rheometer began to suffer corrosion and malfunction. Although the air that was flushed through the glove box has a dew point of -50°C, corresponding to a relative humidity level of 1-2%, this level of moisture produced enough HCl gas upon contact with the sample to cause progressive damage to the rheometer. Additional precautions instituted to minimize the production of HCl gas during testing and subsequent unloading of the sample were not sufficient to prevent this damage from progressing (Young, 2012).

A similar technique with an additional layer of precaution was employed during the early portion of this work; CNT solutions in ClHSO₃ were tested on an RDA III strain-controlled

rheometer with a convection oven attachment. The convection oven closes around the sample geometry (without forming a seal) and flushes the space around the sample with gas, which may be heated or at room temperature. This rheometer was enclosed within a large sealed glove bag, and both the bag and the convection oven were flushed continuously with anhydrous nitrogen gas. This setup was suitable for keeping moisture away from the samples during testing itself, when the convection oven was closed around the geometry and flushed with nitrogen; however, the atmosphere in the glove bag surrounding the rheometer rarely fell below 5% relative humidity, even after many hours of anhydrous nitrogen flow. This residual moisture caused HCl gas production from the sample while the convection oven was open during loading and unloading of the geometry. This period of exposure was enough to cause progressive corrosion damage to the rheometer, and it began to experience electrical malfunction over time.

The damage caused to the electrical components of the AR 2000ex and the RDA III rheometers during these studies underscored the importance of maintaining a strict separation between the atmosphere of the acid sample and the atmosphere of the rheometer body, not only during testing but also during loading and unloading. It also demonstrated that applying local exhaust section near the sample during loading and unloading was not a sufficient precaution. In order to avoid this problem a loading procedure was developed which allows an airtight environment to be temporarily placed around the testing geometery itself, isolating it from the body of the rheometer.

After early tests on the RDA III, the rheological measurements for this study were performed on an ARES strain controlled rheometer using a double-walled concentric cylinder couette geometry, with the following procedure: for sample loading, two halves of a Plexiglas chamber are clamped around the geometry. PTFE gaskets create a seal between the two halves of the chamber and around the upper and lower shafts of the rotational test geometry. Two tubes are connected to this chamber: one through which the chamber may be flushed with anhydrous Nitrogen gas, and the other connected through an acid trap to a mechanical air pump, and thereby to an exhaust vent. The sample of acid or acid solution to be tested is loaded into the cylindrical cup via a syringe through a hole in the Plexiglas which is also covered by a PTFE gasket.

This chamber serves several purposes; it keeps the atmosphere around the geometry dry, it presents a barrier between the sample and the atmosphere of the lab and rheometer, and it provides a channel by which suction can be applied to remove any HCl gas that may be produced while loading. However, this chamber only serves its purpose during the initial loading of the sample; the seal around the geometry shaft allows the upper part of the geometry to be lowered or raised, but it does not allow the geometry to rotate freely and thus cannot remain in place during the test. In order to prevent moisture ingress into the sample or the release of acid fumes from the sample during testing, the loading procedure is completed as follows: after the sample is loaded by syringe into the cylindrical cup, and the upper shaft of the geometry is lowered to immerse the cylindrical bob into the sample until it reaches the prescribed depth for testing. A low-viscosity Fluorinert solution (FC-72) is then loaded into the cup to cover the acid; this fluid does not react with the acid and is immiscible with water, and so should prevent atmospheric moisture from diffusing into the sample. Unfortunately, Fluorinert FC-72 is rather volatile at room temperature; less volatile species of Fluorinert are able to react with the acid, and thus are not suitable for this purpose. In order to prevent Fluorinert evaporation, a low viscosity silicon oil is loaded on top of the Fluorinert layer.

The densities of ClHSO₃, Fluoirinert FC-72, and silicon oil are 1.75 g/cm³, 1.68 g/cm³ and 0.9166 g/cm³, respectively, so the three fluid layers stable and avoid inversion or contact between the silicon oil and the acid. Accidental contact between silicon oil and acid results in partial polymerization of the oil, darkening its color and increasing its viscosity to the point at which it significantly affects the test. As long as this does not occur, the low viscosities of the silicon oil and Fluorinert (4.7 cP and 0.64 cP, respectively), coupled with the fact that they are in contact only with the top portion of the rotor and not between the shearing surfaces, ensure that the addition of these fluids creates negligible additional torque during movement of the rotor.

After the covering fluid layers are in place, the Plexiglas chamber may be removed and the test may proceed as normal. After the test is completed, unloading of the geometry can be ac-

complished by detaching the upper part of the geometry (the couette bob) from the rheometer and gently lowering it into the cup until it rests on the bottom; if this is done with care the separate layers of covering fluid can be maintained without mixing as the bob is lowered into the cup. Strong suction provided by an exhaust vent is kept near the geometry during unloading to serve as a precaution in case the acid layer is exposed during the lowering of the bob shaft. After the bob is lowered into the acid, the cup can also be detached from the rheometer and the entire geometry can be removed to a fume hood or dry air glove box for cleaning.

The above procedure was used with some success over the course of this study, allowing measurements to be preformed on solutions of Unidym CNTs in $ClHSO_3$ without significant release of HCl fumes or damage to the rheometer. However, this procedure has one major drawback: it is adequate to keep atmospheric moisture out of the acid sample during every step of the procedure, but it does not prevent the spontaneous evolution of HCl gas from the sample over the course of time. HCl may evolve in $ClHSO_3$ even without the addition of water through the reversible reaction

$$ClHSO_3 \leftrightarrow HCl + H_2SO_4$$
 (3.19)

Over the course of time HCl produced by this reaction can enter a gas phase and escape from the solution, leaving behind a mixture of $ClHSO_3$ and H_2SO_4 which acts as a weaker solvent for CNTs. This was observed in acid samples loaded onto the ARES under covering fluid layers of Fluorinert and silicon oil: a slow process of bubble formation occurs at the interface between the acid and the Fluorinert, and these bubbles are able to rise through the Fluorinert and silicon oil to reach the surface (an exhaust vent was placed above the sample during the course of the test). This process led to a degradation of solvent strength over the course of several hours and eventually caused the CNT solutions to flocculate.

In order to confirm that this degradation in solvent strength was indeed due to the escape of gas from the acid rather than to some unforeseen chemical reaction between the $ClHSO_3$ and Fluorinert, two glass vials of CNT solution in $ClHSO_3$ topped with Fluorinert and silicon oil layers were set in a fume hood overnight; one vial was capped, and the other vial left open.

After a period of 12 hours the solution in the uncapped vial had flocculated, indicating reduced solvent strength. The solution in the capped vial had not visibly degraded. One possibile explanation for this is that some species of gas evolved from the acid fluid and passed through the Fluorinert (such as HCl evolving from the ClHSO₃) and that this gas was able to escape the open vial but built up within the sealed vial until an increase in pressure caused the gas production to stop. A second possibility is that atmospheric moisture was actually able to diffuse through the layers of covering liquid to react with and weaken the ClHSO₃, and the vial sealed off from room air became depleted of atmospheric moisture before this process caused the acid to degrade much. In either case, the process in question would proceed if the sample were loaded onto a rheometer under covering fluid in otherwise open lab air.

The stability of sample properties over time was monitored by conducting repeated dynamic shear tests in the linear strain regime at a fixed frequency. Figure 3.4 plots a series of measurements performed on solutions of Unidym CNTs at concentrations of (A) 100 ppm and (B) 300 ppm by volume; these samples were subjected to a series of tests in which the solution was subjected to several seconds of steady shear, allowed to rest for a variable period of time, and then subjected to a strain sweep measurement at a frequency of 10 rad/s. After shear the complex modulus G^* evolved to a steady state as the sample relaxed; this process took < 10 minutes for the 100 ppm solution and about 1 hour for the 300 ppm solution. Once the samples had undergone more than 8 cumulative hours of testing G^* began to increase by orders of magnitude over this initial steady state value.

Data collected during this 8 hour window appears to be trustworthy, but this process creates a hard limit on the length of time over which rheological testing can be conducted. Even with the rigorous loading procedure described above, it is not possible to test very long-time relaxation modes of CNT/ClHSO₃ solutions.



Figure 3.4: Complex shear modulus G^* measured at a frequency of 10 rad/s at varying time points after the cessation of steady shear in (A) 100 ppm and (B) 300 ppm solutions of Unidym CNTs in CIHSO₃. Samples were tested in a double-walled couette geometry with Fluorinert and silicon oil covering fluids, as depicted in 3.2. In each case the structure of solution recovers over the course of several minutes after the cessation of shear, resulting in the development of a steady-state modulus; this steady state value was repeatably attained after the shear step was repeated, so long as the cumulative time after sample loading was under ≈ 8 hours. At a total time of 8 hours after initial loading the samples begin to coagulate, leading to a progressive and irreversible increase in sample modulus; this was taken as a sign of solvent strength degradation.

3.4 Results

Figure 3.5 shows the results of dynamic shear rheology carried out on solutions of Unidym CNTs in ClHSO₃ at varying concentrations, plotted on a logarithmic scale. For comparison, Figure 3.6 shows the analogous set of measurements performed on HiPco CNTs in ClHSO₃ (originally reported in Banzola (2008) and Young (2012)).

The quantity G''_{CNT} reported in these figures and in the remainder of this section represents the contribution of the CNT solute to the viscous modulus of the sample. $G''_{CNT}(\omega) = G''(\omega) - \eta_s \omega$, in which $G''(\omega)$ is the frequency-dependent viscous modulus of the solution as a whole and η_s is the viscosity of the acid solvent, which is a Newtonian fluid; $\eta_s \omega$ is the contribution of the solvent to the viscous modulus measured in dynamic shear.

For both data sets the frequency range for reliable measurement narrows with decreasing concentration due to the effects described in section 3.3.4. Due to this limitation, it was not possible to measure the rheology of solutions in the dilute regime in ClHSO₃ for either HiPco or Unidym CNTs. Substituting $\langle L \rangle$ and $\langle d \rangle$ for these CNT batches into equations 3.1 - 3.3 yields



Figure 3.5: Overlay of the elastic modulus (G', black symbols) and the CNT contribution to the viscous modulus (G'_{CNT} , blue symbols) measured for solutions of Unidym CNTs in CIHSO₃ as a function of angular frequency.

 $\phi_{\text{dilute}} = 56 \text{ ppm}, \phi_{\text{C}} = 2100 \text{ ppm}, \text{ and } \phi_{\text{I}} = 9200 \text{ ppm for HiPco CNTs, and yields } \phi_{\text{dilute}} = 0.46 \text{ ppm}, \phi_{\text{C}} = 196 \text{ ppm}, \text{ and } \phi_{\text{I}} = 830 \text{ ppm}.$ These values of ϕ_{I} over-predict the actual onset of the biphasic regime by around 1 order of magnitude in each case; this may be attributed to the polydispersity of aspect ratio in each sample, which shifts ϕ_{I} to lower concentrations due to the presence of long CNTs (Tsentalovich *et al.*, 2016; Wensink and Vroege, 2003). The predicted values of ϕ_{dilute} and ϕ_{C} , and the experimentally determined values of ϕ_{I} , indicate that the lowest measurable concentration in each system is in the semidilute regime, and that in both cases the concentration range considered encompasses a portion of the semidilute regime, the concentrated isotropic regime (near ϕ_{C}), and the biphasic regime; it is likely that they also encompass the onset of the fully liquid crystalline regime, since the biphasic window is expected to be 1-2 orders of magnitude in concentration.

The evolution of $G'(\omega)$ and $G''_{CNT}(\omega)$ with increased CNT concentration is similar for Unidym and HiPco CNT solutions, reflecting a similarity in the microstructure and physics of the two



Figure 3.6: Overlay of the elastic modulus (G', black symbols) and the CNT contribution to the viscous modulus (G'_{CNT} , blue symbols) measured for solutions of HiPco CNTs in CIHSO₃ as a function of angular frequency. This data was previously reported in Banzola (2008) and Young (2012) with slightly different values of volume fraction, based on a different calculation of CNT density (see section 3.3).

systems; the rheology of HiPco solutions in 102% H₂SO₄ which is reported in Davis (2006) followed the same basic evolution. The rheology of these solutions is also similar to the viscoelastic rheology of aqueous CNT dispersions stabilized by surfactant (Hough *et al.*, 2004; Hobbie and Fry, 2007). The most obvious differences between the rheology of Unidym CNT and HiPco CNT solutions in this concentration range are a) the Unidym CNTs attain a shear modulus on the order of 1 Pa at a much lower concentration, b) for concentrations less than $\phi = 0.01$ Unidym CNTs maintain a much larger modulus than HiPco CNTs, and c) for concentrations greater than $\phi = 0.01$ the modulus of HiPco CNT solutions is greater than that of Unidym CNT solutions. The reversal of relative magnitude will be discussed in section 3.4.1.

At low concentrations the moduli have a positive power law dependence with frequency, indicating the existence of a viscoelastic stress that is relaxing on a time scale of 0.01 - 10 seconds. At higher concentrations the frequency dependence of the moduli decreases or vanishes, indicating that the stress being measured either does not relax over time or relaxes on a time scale much longer than 10 seconds. This plateau behavior and the fact that elastic modulus G'is much greater than the viscous modulus G''_{CNT} in that concentration regime are both signs of an elastic network structure. Unfortunately, the experimental window for low-concentration solutions is too narrow to show whether and how the samples transition to other behavior at different time scales. It is possible that the lower concentration solutions represent samples in which the CNTs do not form a significant elastic network, and that such a network only forms above a certain value of ϕ in each system; however, it is also possible that the lowest concentration solutions do contain an elastic network and would exhibit plateau behavior at lower frequencies, if those frequencies could be measured. If the elastic network stress of entangled CNTs increases more rapidly with concentration than does the source of stress which gives rise to the relaxation power law behavior, then the crossover between the two behaviors would shift to higher frequency with increasing concentration; this could result in a case in which the plateau modulus behavior shifts increasingly into the measurable range as concentration increases.

There are several indications that the latter picture is the correct one for CNT/superacid

systems. In Unidym solutions, and below $\phi = 7.2 \times 10^{-3}$ in HiPco, the power law dependence of $G'(\omega)$ and $G''_{CNT}(\omega)$ on ω decreases gradually with increasing concentration, and the crossover between the two moduli shifts to higher frequencies; this is an indication that each separate data set reveals only a portion of a transition between high-frequency (short time scale) relaxation behavior and low-frequency (long time scale) network plateau behavior, that the transition occurs over a range of times scales that extends across many orders of magnitude, and that the transition is shifted to higher frequencies as concentration increases due to the growth of the network stress. The highest concentration Unidym CNT solution samples also exhibit a gradual increase in the slope of $G'(\omega)$ and $G''_{CNT}(\omega)$ consistent with such a transition.

On the other hand, the magnitude and frequency dependence of $G'(\omega)$ and $G''_{CNT}(\omega)$ for HiPco solutions go through a rather rapid change between concentrations of $\phi = 7.2 \times 10^{-3}$ (7200 ppm by volume) and $\phi = 1.1 \times 10^{-2}$ (1.1% by volume); this indicates that some other change takes place in this concentration regime place beyond an increase in the relative magnitude of the elastic plateau, or that the concentration dependence of the elastic network modulus is very strong in this regime. A similar rapid change in viscoelastic behavior was reported for solutions of HiPco CNTs in 102% H₂SO₄ at concentrations around $\phi = 1 \times 10^{-3}$ (Davis, 2006). These changes have been interpreted as hallmarks of a rigidity percolation in HiPco/superacid systems (Davis, 2006; Young, 2012). Interestingly, a sudden transition of this sort does not appear in the rheology of Unidym CNT solutions in ClHSO₃.

The remainder of this section covers two topics: Section 3.4.1 compares the development of elastic network structure in HiPco and Unidym CNT solutions and relates the network elasticity to the development and specific microstructure of the liquid crystal phase in each system. Sections 3.4.2 and 3.4.3 analyze the frequency-dependent relaxation behavior observed at lower concentrations and higher frequencies using models of semiflexible rod viscoelasticity, and identify the source of viscoelastic stress in this regime.

3.4.1 Elastic network development and percolation

Davis (2006) and Young (2012) reported that solutions of HiPco CNTs in ClHSO3 and 102%

 H_2SO_4 undergo a rigidity percolation transition at $\phi = 7.20 \times 10^{-3}$ and $\phi = 1.13 \times 10^{-3}$, respectively; with a corrected density value of 1.56 g/cm³ for HiPco CNTs, these concentrations are more accurately expressed as $\phi = 6.47 \times 10^{-3}$ and $\phi = 1.02 \times 10^{-3}$. These concentrations fall into the biphasic concentration regime of for HiPco CNTs in ClHSO₃ and 102% H₂SO₄, respectively (i.e., the concentration regime in which liquid crystal phase and isotropic phase coexist). In both cases the authors suggest that the rigidity percolation is caused not by percolation of individual CNTs, but by percolation of the liquid crystal domains in the biphasic solution.

The difference in the percolation threshold concentration and the difference that was observed in the concentration dependence of the network elasticity for these two systems can be attributed to the difference in morphology of the biphasic liquid crystal domains in each acid. In 102% H_2SO_4 HiPco CNTs form long, thread-like liquid crystal domains (Davis, 2006); in ClHSO₃ they form elongated droplet domains with much shorter aspect ratio, which may be expected to form a percolated network at higher concentrations than the threadlike domains present in 102% H_2SO_4 (Young, 2012). In both cases, separate liquid crystal domains which encounter one another typically cannot merge or interpenetrate, due to differences in alignment director, but instead will entangle and stretch around one another, leading to a significnat elastic response (Behabtu, 2012).

The rheological hallmarks of percolation identified in Davis (2006) and Young (2012) were:

- a dramatic increase in the magnitude of the G' and G''_{CNT}
- the emergence of the elastic modulus *G*′ as the dominant modulus
- the loss of frequency dependence in the viscoelastic response
- a decrease in the critical strain $\gamma_{\rm C}$ which marks the limit of the linear viscoelastic regime

Some of these hallmarks also appear in the rheology of Unidym CNTs in ClHSO₃, but they appear to arise from a less dramatic change in solution microstructure.

Figure 3.7 plots the magnitude of G' and G''_{CNT} for Unidym CNTs and HiPco CNTs in ClHSO₃ as a function of concentration. The isotropic-nematic transition concentration in each system



Figure 3.7: Elastic modulus (G', red squares) and the CNT contribution to the viscous modulus (G''_{CNT} , blue diamonds) measured for (A) solutions of Unidym CNTs in CIHSO₃ and (B) solutions of HiPco CNTs in CIHSO₃ as a function of concentration. All data was measured by dynamic shear at an angular frequency of 2.5 rad/s. Vertical dashed lines indicate the lowest volume fraction ϕ_1 at which liquid crystalline phase can be identified by polarized optical microscopy (Tsentalovich *et al.*, 2016). In both systems the elastic modulus begins to dominate over the viscous modulus at a concentration which is roughly 5-6 times ϕ_1 ; in HiPco this crossover coincides with a rapid increase in shear modulus magnitude, whereas in Unidym the increase in modulus is more gradual at all concentrations.

is indicated by arrows. In both cases the viscoelasticity is dominated by the viscous modulus at low concentration and by the elastic modulus at higher concentrations, and in both cases the scaling of shear modulus with ϕ is nearly linear at low concentrations. The key difference between the two data sets is that the crossover point between G' and G''_{CNT} for HiPco solutions coincides with a steep increase in the magnitude of both moduli, whereas there is no such increase in the Unidym solution modulus curves. Unidym solutions exhibit shear moduli which are much greater than that of HiPco solutions at low concentrations but which are surpassed by the shear moduli of HiPco solutions at concentrations higher than $\phi = 0.01$.

The relative magnitude of viscosity and elasticity in rheological samples is often described using the loss modulus $\tan(\delta) = G''/G'$ in which δ is the raw phase angle between sinusoidal stress and strain in the dynamic shear measurement. A modified form of the loss modulus which expresses the ratio of viscosity and elasticity arising exclusively from the CNTs may be given by

$$\tan(\delta_{\rm CNT}) = \frac{G_{\rm CNT}''}{G'} \tag{3.20}$$



Figure 3.8: Modified loss modulus $\tan(\delta_{\text{CNT}})$ expressing the ratio of the CNT contribution to elastic and viscous modulus for solutions of (A) Unidym CNTs and (B) HiPco CNTs in ClHSO₃ as a function of CNT concentration. Dashed lines indicate the $\tan(\delta_{\text{CNT}}) = 1$. A value of $\tan(\delta_{\text{CNT}}) > 1$ indicates that the viscous modulus is dominant; $\tan(\delta_{\text{CNT}}) < 1$ indicates that elasticity dominates, and is a sign of elastic structure. The rapid decrease of $\tan(\delta_{\text{CNT}})$ around $\phi = 10^{-2}$ in HiPco solutions coincides with the rapid increase in the magnitude of G' and G''_{CNT} in Figure 3.7 B.

in which δ_{CNT} represents the phase angle between strain and stress curves if the contribution of the Newtonian solvent is subtracted from the stress. Figure 3.8 plots the values of $\tan(\delta_{\text{CNT}})$ corresponding to the data shown in Figure 3.7.

At low concentrations the viscous modulus arising from the CNTs, G''_{CNT} , is larger than the elastic modulus G', resulting in $\tan(\delta_{CNT}) > 1$. As concentration increases, the relative magnitude of G' with respect to G''_{CNT} increases; the point at which the elastic modulus becomes the dominant corresponds to the point at which $\tan(\delta_{CNT})$ falls below 1. It should be noted that at intermediate concentration these solutions exhibit a crossover point between the G' and G''_{CNT} frequency sweep curves (see Figures 3.5 and 3.6); G' dominates at low frequencies G''_{CNT} dominates at high frequencies, with the crossover point shifting to higher frequencies as concentration increases. As a result the concentration at which $\tan(\delta_{CNT})$ falls below 1 depends on the frequency considered; within the window of frequencies used in this study, crossover was observed between $\phi = 3x10^{-4}$ and $\phi = 3x10^{-3}$ in Unidym solutions and between $\phi = 4.7x10^{-3}$ and $\phi = 7.2x10^{-3}$ in HiPco solutions.

Figure 3.9 plots the change in the dependence of G' and G''_{CNT} on radial frequency as ex-



Figure 3.9: Change in the frequency scaling parameters of elastic and viscous modulus in solutions of (A) Unidym CNTs and (B) HiPco CNTs in CIHSO₃ as da function of CNT concentration. The power laws p and q were determined by power law fits to $G'(\omega)$ and $G_{CNT''}(\omega)$, respectively. Both moduli become less dependent on the frequency of dynamic applied strain as concentration increases, indicating the formation of an elastic structure.

pressed by the power law exponents p and q, with

$$G'(\omega) \propto \omega^p$$
 (3.21)

$$G_{\rm CNT}''(\omega) \propto \omega^q$$
 (3.22)

These power law exponents were determined by fitting the data in Figures 3.5 and 3.6; the two lowest concentration Unidym solutions were omitted from this analysis since they only two reliable data points were available for each. The frequency dependence of G' and G''_{CNT} becomes weaker as concentration increases; high concentration HiPco solutions exhibit a frequency-independent plateau both moduli, and the moduli of Unidym solutions also trend towards frequency-independence; this loss of frequency dependence is a signature of a dominantly elastic network structure.

Figure 3.10 plots $\gamma_{\rm C}$, the critical strain which marks the limit of the linear viscoelastic regime, as a function of volume fraction. The critical strain provides a measurement of how much a



Figure 3.10: Critical strain $\gamma_{\rm C}$ marking the limits of the linear viscoelastic strain regime for solutions of (A) Unidym CNTs and (B) HiPco CNTs in CIHSO₃ as a function of CNT concentration. In each system $\gamma_{\rm C}$ begins to decrease once concentration rises above a certain threshold, indicating that the viscoelastic behavior arises increasingly from a structure which can be broken or altered by strain. The rapid decrease of $\gamma_{\rm C}$ around $\phi = 10^{-2}$ in HiPco solutions coincides with the rapid increase in the magnitude of G' and $G''_{\rm CNT}$ in Figure 3.7 B.

sample's structure can be deformed before it is significantly disrupted or broken; lower critical strain is an indication of a more tightly-entangled and interconnected structure.

For HiPco CNT solutions in ClHSO₃ the sharp increase in viscoelastic moduli that begins at $\phi = 6.8 \times 10^{-3}$ coincides with a) a sharp decrease in tan(δ_{CNT}), which indicates the rapid emergence of a dominant elastic modulus, b) a sharp decrease in γ_{C} , indicating a transition to a solution in which the stress arises primarily from connections and entanglements which can be easily broken by strain, and c) a sharp decrease in the power law exponents *p* and *q*, indicating a transition to a solid-like structure with a frequency-independent viscoelastic stress response. These changes collectively indicate that at this concentration some rigidity percolation has occurred, resulting in the creation of a significant elastic structure.

Unlike HiPco solutions, Unidym CNT solutions do not exhibit a dramatic increase in G' and $G_{\text{CNT}''}$ at any point in the concentration range that has been investigated. Other hallmarks of elastic network evolution do appear in Unidym CNT rheology, and they coincide with each other to a certain extent: $\tan(\delta_{\text{CNT}})$ falls below a value of 1 between $\phi = 5 \times 10^{-4}$ and $\phi = 1 \times 10^{-3}$; γ_{C} decreases by almost 1 order of magnitude between $\phi = 1.5 \times 10^{-4}$ (slightly above ϕ_{IN}) and $\phi = 5 \times 10^{-4}$; the power law exponents p and q also decrease over this concentration range. It is

clear that Unidym solutions do form an elastic network; however, that network is softer than the network formed by HiPco CNTs, and it appears to develop more slowly as concentration increases.

The rheology of the elastic network that forms in biphasic Unidym CNT soltions in $ClHSO_3$ reflects the morphology of its liquid crystal phase, just as is the case for HiPco CNT solutions in 102% H_2SO_4 and $ClHSO_3$. Figure 3.11 shows polarized optical microscopy images which are typical of Unidym CNT and HiPco CNT biphasic solutions in $ClHSO_3$. Unlike HiPco solutions, Unidym CNTs in the biphasic regime do not separate into well-defined droplets of liquid crystal phase in an isotropic matrix. Instead, the isotropic and aligned CNT phases appear to form something closer to a bi-continuous phase. Without distinct liquid crystal domains which resist interpenetration, Unidym solutions lack the interaction between domain interfaces which produces rigidity percolation in HiPco solutions.

These results, taken together with the results of Davis (2006) and Young (2012), illustrate the dominance of liquid crystal domain morphology over the linear viscoelastic response of high-concentration CNT solutions in superacids. Beyond a certain concentration this emergent collective behavior becomes more important in determining solution viscoelasticity than the relaxation behavior of the individual CNTS.



Figure 3.11: A-C: Light microscopy images of a biphasic solution of Unidym CNTs in ClHSO₃ in unpolarized light (A) and between crossed polarizers (B & C). The solution concentration is $\phi = 1.5 \times 10^{-4}$, roughly $2.5 \times \phi_1$. White arrows indicate the optical axes of the polarizer and analyzer with respect to the sample; bright portions of the solution indicate the presence of CNT liquid crystal phase with a local alignment director oriented 45° with respect to the alingments of both polarizers. An occlusion appears on the capillary glass surface in the upper left hand corner, appearing dark in the unpolarized light image and bright in the polarized image. D-F: Light microscopy images of a biphasic solution of HiPco CNTs in ClHSO₃ in unpolarized light (D) and between crossed polarizers (E & F). The solution concentration is $\phi = 3.1 \times 10^{-3}$, roughly $2.5 \times \phi_1$. The liquid crystal phase in the HiPco solution takes the form of discrete tactoid-shaped droplets in an isotropic medium; the liquid crystal phase in Unidym CNTs is more diffuse, forming a bi-continuous phase with the isotropic phase. Light microscopy of Unidym CNT solutions is courtesy of Dmitri Tsentalovich.

3.4.2 Comparison to predictions of rotational entropy stress

Young (2012) compared the frequency-dependent viscoelastic modulus observed in low concentration HiPco CNT solutions in ClHSO₃ and 102% H_2SO_4 to a theoretical prediction for the viscoelastic stress arising from orientational entropy in semiflexible rod solutions. In that study, G' and G''_{CNT} were calculated using the equations outlined in section 3.2.2 as a function of volume fraction for a sample of rods which are monodisperse in diameter but polydisperse in length. The agreement between the theoretical prediction and experimental results was poor, with the theory significantly over-estimating the measured modulus.

Here, this calculation is applied to the case of Unidym CNTs. G' and G''_{CNT} were calculated using the algorithm described in Young (2012). Briefly, the calculation is performed by considering CNTs with a distribution of lengths to have a distribution of rotational relaxation times. The degree of rotational confinement is calculated separately for each length of CNT according to equation 3.10; depending on the concentration and length distribution of the CNT population, the rotational relaxation for a CNT of a given length may be calculated according to equation 3.8, equation 3.9, or equation 3.13. The expected values of G' and G''_{CNT} are then calculated based on the sum of contributions from each length population of CNT, each weighted by the total number concentration of rods of that length. Calculations for HiPco and Unidym CNTs were based on parameters of the length distribution determined by extensional viscosity measurements (Tsentalovich *et al.*, 2016)

Figure 3.12 shows the results of this calculation, with the analogous result for HiPco CNTs in ClHSO₃ for comparison. In both cases there is a large discrepancy between predicted and measured viscoelastic moduli. For HiPco CNTs the model over-predicts the moduli for all but the lowest concentration, and the predicted scaling of G' and G''_{CNT} with concentration does not match that of the measured behavior. For Unidym CNTs the prediction for elastic modulus G' is not far off in magnitude and the theoretical curves have the correct scaling with concentration, but the magnitude for the viscous modulus G''_{CNT} is predicted by the model to be 2 orders of magnitude higher than the measured modulus.



Figure 3.12: Comparison between theoretical predictions for the viscoelastic modulus arising from rotational Brownian motion in semiflexible rods with lognormal length distribution and experimentally determined modulus values for CNTs in superacids as a function of concentration. Dashed red lines and solid blue lines show the predicted value of $G''_{\rm CNT}$ and G', respectively, based on a dynamic strain frequency of $\omega = 2.5$ rad/s. Red squares and blue crosses show the values of $G''_{\rm CNT}$ and G', respectively, measured at $\omega = 2.5$ rad/s.

3.4.3 High-frequency viscoelastic response

Given the discrepancy between the modulus values and predictions based on rotational entropy which was reported in Young (2012), and reported in this study in Figure 3.12, it is doubtful that the shear modulus of low concentration CNT solutions arises from the orientation stress described in Doi and Edwards (1986). On the contrary, there is strong evidence that it arises instead from the longitudinal tension stress arising from contour fluctuations in individual CNTs (see section 3.2.2). The frequency scaling power laws reported in Figure 3.9 are consistent with this interpretation, given that the scaling exponents p and q tend toward values near 3/4 in the low concentration regime.

A more detailed analysis of the concentration and frequency scaling of G' and G''_{CNT} can be performed to determine whether this apparent scaling of $\approx \omega^{3/4}$ is indeed due to highfrequency tension stress. It is helpful to consider the possibility, mentioned briefly above, that the viscoelastic data reported in Figures 3.5 and 3.6 are all part of a single "master" curve of viscoelastic behavior; if this were the case, it could imply that the behavior observed at low concentrations for a given frequency has the same physical origin as the behavior observed at a much higher frequency in a higher concentration solution.

Each of the individual data sets plotted in Figures 3.5 and 3.6 is of course only a short segment of a longer curve which describes the shear modulus of that particular solution as a function of frequency. It is possible that all of the data sets in each separate solution system are part of a single behavior curve which is identical, or nearly identical, at all concentrations, aside from a shift in magnitude and characteristic frequency. The proposed curve is one in which an elastic plateau modulus dominates the frequency response at long times (low frequency) and a frequency-dependent relaxation modulus dominates the response at short times (high frequency), with a gradual period of transition between the two regimes of behavior; the transition region is centered around some crossover frequency ω_0 . The physical requirements for such a unified behavior to arise are:

• the frequency-dependent modulus in CNT/superacid solutions over a range of concentrations arises from the same kind of stress

- this stress decays (relaxes) in the same manner at all concentrations, with a negative power law dependence on time expressed as $\sim t^{-E}$
- the magnitude of this transient stress scales positively with CNT concentration with some power law ~ ϕ^{F}
- · the sample also exhibits a stress arising from an elastic network which decays very slowly
- the magnitude of the elastic network stress scales positively with CNT concentration with a power law ~ ϕ^{J} , with J > F

It is the rapid scaling of elastic network stress with CNT concentration that results in a shift of the crossover ω_0 to higher frequencies as concentration increases.

The existence of a single "master curve" of viscoelastic behavior has been reported in several other systems, including colloid particles (Trappe and Weitz, 2000), surfactant-stabilized CNTs (Hobbie and Fry, 2007; Ao *et al.*, 2016), actin (Gardel *et al.*, 2004), and liquid crystalline cellulose (Urena-Benavides *et al.*, 2011). For each of these samples, the viscoelastic modulus curves can be collapsed into the master curve by multiplying the frequency and the magnitude by a set of concentration-dependent scaling factors, $a(\phi)$ and $b(\phi)$. The resulting master curve of complex modulus G^* (for example) would be $bG^*(a\omega)$. If the master curve does indeed represent a underlying behavior, i.e., if the hypothesis of unified behavior across all the concentrations involved is correct, then identifying the appropriate scaling parameters *a* and *b* can be a powerful analysis technique, especially for solutions with a very narrow experimental range; measurements from solutions at different concentrations may stand in for measurements in a single solution across a broader range of times scales (or vice versa).

In Gardel *et al.* (2004) the authors used a master curve scaling analysis to demonstrate that the frequency-dependent viscoelasticity crosslinked actin networks arose from the collective effect of tension stress relaxation in the individual actin filaments. A modified version of this analysis method begins with the hypothesis that the viscoelastic system in question has two primary sources of stress, as outlined above in general terms: a frequency-independent elasticity $G'_0 \sim \phi^J$ in which the unknown power law J arises from the details of the network structure, and a transient stress produced by longitudinal tension relaxation in the individual rods, which exhibits a frequency scaling $G^*(\omega) \propto G'(\omega) \propto G'' \propto \omega^{0.75}$, and which, because it arises from the sum of individual rod behavior, has a linear dependence on ϕ (i.e., F = 1).

If scaling factors $a(\phi)$ and $b(\phi)$ can be found for this system such that the rescaled modulus curves for each concentration of solution fall onto a single pair of master curves $bG'(a\omega)$ and $bG''(a\omega)$ it implies that $b \sim \phi^{-J}$ and $a \sim \phi^{(1-J)/0.75}$; thus, if the assumptions above hold, they lead to a prediction that $b\phi \sim a^{0.75}$ (Gardel *et al.*, 2004).

This analysis was applied to the viscoelastic modulus data reported in Figures 3.5 and 3.6, as well as to the viscoelastic modulus data reported in Davis (2006) for HiPco CNTs in 102% H_2SO_4 ; the results are shown in Figures 3.13 - 3.15. In each case, the data were re-scaled onto master curves by arbitrarily choosing the set of scaling factors $a(\phi)$ and $b(\phi)$ which led to the smoothest continuous curve for $bG_{CNT}^*(a\omega)$.

In the case of Unidym CNTs, the same set of scaling factors produced good collapse of G_{CNT}^* , G', and G_{CNT}'' ; however, in the case of HiPco CNTs in ClHSO₃ and 102% H₂SO₄, rescaling based on G_{CNT}^* led to poor collapse of the separate modulus curves. The decision to base the rescaling on the total complex modulus G_{CNT}^* means that $a(\phi)$ and $b(\phi)$ reflect the scaling of the dominant modulus, which is G' at low values of $a\omega$ and G_{CNT}'' at high values of $a\omega$. This discontinuity implies that for HiPco CNTs in either of these solvents, the shape of the viscoelastic response curve changes within this range of concentrations; in other words, the sources of viscoelastic stress change in their nature rather than merely shifting in magnitude and in time scale as concentration increases.

To a certain extent this mismatch between the scaling of G' and G''_{CNTS} is to be expected, given that over the range of concentrations considered the solutions are evolving from an isotropic to a liquid crystalline phase. A similar discontinuity in the rescaled master curve was reported by Urena-Benavides *et al.* (2011) for liquid crystalline solutions of cellulose; the authors in that case suggest that the impossibility of rescaling both G' and G'' onto master curves using the

same set of scaling factors was a result of the development of liquid crystal domains with increasing concentration. In contrast, Hobbie and Fry (2007) found that for surfactant stabilized solutions of MWNTs, which are isotropic at all concentrations, the same set of scaling parameters result in good collapse for both G' and G''. It is interesting to note that the discontinuity in the G' curves at high values of $a\omega$ (at which G''_{CNT} is slightly dominant in G^*_{CNT}) is not large (see Figure 3.13 C and Figure 3.14 C), but the discontinuity in the G''_{CNT} curves at low values of $a\omega$ (at which G' is dominant in G^*_{CNT}) is much worse; this shows that the mismatch between the scaling of G' and G''_{CNTS} becomes much more significant at concentrations above the identified percolation threshold for the liquid cystal domains in those solutions. It may be that no remarkable mismatch appears in the Unidym curves precisely because those solutions undergo the transition from isotropic to liquid crystal phase without the appearance of such well-defined domains.

In each of these three systems, $b\phi$ vs. a follows a well-defined power law for at low concentrations. This power law scaling begins to fail above $\phi = 0.011$ for HiPco in ClHSO₃ (shortly above the percolation transition), above $\phi = 0.0011$ for HiPco in 102% H₂SO₄ (just below the percolation threshold) and above $\phi = 5 \times 10^{-4}$ in Unidym CNTs (just below the elastic modulus becomes dominant). It is difficult to draw conclusions about the reason for this failure, even though the concentrations at which this occurs suggest that it is related to the percolation of liquid crystal phase, because these are also concentrations at which the elastic plateau modulus dominates the rheology at all measured frequencies, particularly in HiPco solutions. Because the high frequency behavior is not included in these modulus curves it is difficult to say whether the data have actually been rescaled "correctly". Measurements over a broader frequency range may be needed to distinguish whether the scaling factors b and a are meaningful beyond these concentrations. On the other hand, the concentrations for which the power law scaling is observed include the lowest concentration data sets for each system, which show only the frequency-dependent modulus, and the intermediate concentration data sets, which show the crossover regime and thus contain enough information to reveal the scaling of the plateau modulus.



Figure 3.13: A: master curve of $G^*_{\text{CNT}}(\omega)$ for solutions of HiPco CNTs in CIHSO₃. The same concentrationdependent scaling factors $b(\phi)$ and $a(\phi)$ were used to rescale $G'(\omega)$ (**C**) and $G''_{\text{CNT}}(\omega)$ (**D**). **B**: $b\phi$ vs. a for solution concentrations up to $\phi = 0.011$. A power law fit to this relationship indicates a high-frequency scaling of $\sim \omega^{0.68}$.



Figure 3.14: A: master curve of $G^*_{CNT}(\omega)$ for solutions of HiPco CNTs in 102% H₂SO₄. The same concentrationdependent scaling factors $b(\phi)$ and $a(\phi)$ were used to rescale $G'(\omega)$ (**C**) and $G''_{CNT}(\omega)$ (**D**). **B**: $b\phi$ vs. a for solution concentrations up to $\phi = 0.0011$. A power law fit to this relationship indicates a high-frequency scaling of $\sim \omega^{0.72}$.



Figure 3.15: A: master curve of $G^*_{CNT}(\omega)$ for solutions of Unidym CNTs in CIHSO₃. The same concentrationdependent scaling factors $b(\phi)$ and $a(\phi)$ were used to rescale $G'(\omega)$ (**C**) and $G''_{CNT}(\omega)$ (**D**). B: $b\phi$ vs. a for solution concentrations up to $\phi = 5 \times 10^{-4}$. A power law fit to this relationship indicates a high-frequency scaling of $\sim \omega^{0.68}$.

Power law fits of $b\phi$ vs. *a* for each system are shown in Figure 3.13 B, Figure 3.14 B, and Figure 3.15 B. For HiPco CNT solutions in ClHSO₃ and in 102% H₂SO₄ the empirically determined power laws are \approx 0.68 and \approx 0.72, respectively. While these do not exactly match the expected tension regime power law of 3/4, they are reasonably close, and suggest that the frequency-dependent relaxation observed in these solutions is indeed a result of longitudinal tension on the individual CNTs.

The power law fit in the case of Unidym CNT solutions in ClHSO₃ is higher, ≈ 0.93 . This may indicate that the Unidym CNTs on this range of time scales exhibit the tension relaxation moduli scaling as $G'\omega \propto \omega^{5/4}$ and $G''(\omega) \propto \omega$ expected at times $t > \tau_{\parallel}$ rather than tension relaxation moduli scaling as $G'(\omega) \propto \omega^{7/4} = 0$ and $G''(\omega) \propto \omega^{3/4} = 0$. However, if this is the case it would indicate that the apparent scaling of $\sim \omega^{3/4}$ observed for HiPco CNTs is an anomalous result, because τ_{\parallel} for HiPco CNTs should be a much shorter time than τ_{\parallel} for Unidym CNTs; the Unidym CNTs have a larger $\langle L_p \rangle$, but HiPco CNTs have a shorter average length $\langle L \rangle$ and a smaller value of $\langle L/L_p \rangle$. In fact, using $\langle L \rangle$ and $\langle L_p \rangle$ for each batch into equation 3.14 yields $\tau_{\parallel} \approx 10^{-7}$ seconds for Unidym and $\tau_{\parallel} \approx 10^{-12}$ seconds for HiPco CNTs, which would imply that the experimentallyu accesible range is far from the $\sim \omega^{3/4}$ scaling regime in either case.

It is possible that the average CNT batch parameters $\langle L \rangle$, $\langle d \rangle$, and $\langle L_p \rangle$ present a misleading picture of the time scales that are relevant for relaxation. For example, if there were a significant sub-population of HiPco CNTs with $L > \langle L \rangle$ and $d < \langle d \rangle$ for which tension stress relaxed more slowly, this sub-population might be responsible for the stress contribution that results in the observed ~ $\omega^{3/4}$ scaling.

3.5 Conclusion

3.5.1 Summary of key results

The rheology of Unidym and HiPco CNT solutions in ClHSO₃ presented in this work leads to the following physical picture:
Within the range of concentrations tested, the rheology of both systems appears to include an elastic plateau modulus at low frequencies which transitions into a frequency-dependent relaxation modulus at high frequencies. The crossover between these regimes of behavior shifts to shorter time scales as concentration increases, with the result that only the relaxation modulus can be measured in low concentration solutions and only the plateau modulus can be measured in high concentration solutions. This leads to some ambiguity as to the true origin of the relaxation modulus measured at low concentrations, since the lack of measurable elastic plateau may be taken to mean that these solutions are only loosely entangled, have no elastic plateau, and exhibit more fluid-like behavior. However, several lines of evidence indicate that the origin of viscoelastic stress is indeed the same as that of the high-frequency stress at higher concentrations. These are

- the fact that *G*′ and *G*[″]_{CNT} do not match the modulus values that are predicted for orientation stress
- the fact that $G' \propto \omega^p$ and $G''_{CNT} \propto \omega^q$ with scaling exponents p and q which are similar to one another, which would not be expected for fluid-like behavior
- the continuous evolution of *p* and *q* from low concentrations through moderate concentrations at which the crossover to plateau modulus is explicitly observed, which makes it possible to scale the behavior for the entire concentration range onto a master curve.

Master curve scaling analysis presented in Section 3.4.3 seems to confirm that the source of viscoelastic stresses measured in low concentration solutions, and at high frequencies in higher concentration solutions, do indeed have the same origin, and that the behavior is consistent with tension stress in semiflexible rods.

The elastic plateau modulus grows in magnitude as concentration increases. The dependence of this modulus on concentration does not appear to be strongly impacted by the appearance of the liquid crystal phase (note the consistency of slopes in Figure 3.7 A & B near the onset of liquid crystal phase at ϕ_I). However, the development of the plateau modulus is strongly affected by percolation of discrete, non-interpenetrating liquid crystal domains, which form in

HiPco CNT solutions in both $ClHSO_3$ and 102% H_2SO_4 but do not appear to form in Unidym solutions. The interaction of these domains, once they reach their particular percolation concentration threshold, creates a major additional source of viscoelastic stress in HiPco/superacid solutions which is not present in Unidym/superacid solutions. This additional liquid crystal domain interaction creates the following effects:

- It is responsible for the rigidity percolation transition that appears in solutions of HiPco CNTs in both $CIHSO_3$ and 102% H₂SO₄, but which is absent in Unidym CNT solutions in $CIHSO_3$.
- It causes solutions of HiPco CNTs in both ClHSO₃ and 102% H₂SO₄ to have a shear modulus at high (liquid crystal) concentrations that is several orders of magnitude larger than that of Unidym CNT solutions at the same volume fraction; Unidym liquid crystal solutions exhibit a softer network and flow more easily.
- It alters the shape of the viscoelastic behavior curve in the time domain, such that the behavior curves at either end of the biphasic concentration regime are not self-similar. This results in discontinuity in either G' or G''_{CNT} for HiPco solutions if the viscoelastic moduli are scaled onto a master curve using the same scaling factors; the behavior of Unidym solutions, on the other hand, remains self-similar throughout the concentration range considered in this work.

This work, taken together with the reports of Davis (2006) and Young (2012), illustrates the the particular morphology of the liquid crystal phase plays a huge role in determining CNT/superacid solution rheology and behavior. At low concentrations (in the semidilute and concentrated isotropic regime, and even in the first portion of the biphasic regime), rheology is directly determined by the characteristics of the CNT batch (such as $\langle L \rangle$ and $\langle L_p \rangle$); at some concentration in the biphasic regime this ceases to be the case and rheology is determined instead by liquid crystal domain size, domain shape, and presumably also the resistance of domains to stretching, bending, and interpenetration, all of which are only partially determined by CNT batch properties. This leads to the somewhat counter-intuitive result that solutions containing longer CNTs may flow and deform more easily at high concentrations than solutions containing shorter CNTs; this has major implications for processing of high-concentration CNT/superacid solutions into solid materials, for which the use long CNTs is an important potential route to improving properties. It also means that the rheology of even a stable superacid solution is not a fundamental solution property but rather is determined by the shear history, because the liquid crystal phase may go through slow evolution over the course of time: liquid crystal domains may grow, merge, or change in shape over the course of time.

3.5.2 Unexplained results

The two major findings of this work which remain puzzling or in need of further explaination are the severe over-estimation of the rotational relaxation modulus that comes from analysis of rod theory, and the observation of relaxation behavior similar to $G'(\omega) \propto G''(\omega) \propto \omega^{3/4}$ in HiPco solutions, which seems to violate the expectation that such a scaling would be found only at $t < \tau_{\parallel} \approx 10^{-12}$ seconds. It is possible that one or both of these puzzling results could be explained by a misunderstanding of the range of lengths or diameters present in these CNT batches.

It should be noted that there are other reasons to conclude that the low concentration solutions measured in this work do not exhibit a viscoelastic stress dominated by orientation stress. One is the success of scaling the moduli for low concentration solutions into the high-frequency portion of a master curve that includes a network plateau modulus. This rescaling implies that the transient stress being measured is larger in magnitude than the network plateau stress, which is consistent with the assumption that it is a tension relaxation stress rather than an orientational relaxation stress (Morse, 1998b). The values of loss modulus $\tan(\delta_{CNT})$ and the particular combination of frequency scaling factors p and q that are exhibited by both Unidym and Hipco solution are also reasons to doubt that these are orientation modulus curves, because those values are difficult to achieve for moduli arising from equations 3.6 and 3.7. What remains puzzling is the fact that the CNT tension and elastic network stresses measured for these solutions are apparently so much smaller in magnitude than the expected orientational stress; essentially, it seems as if the orientation stress is either absent, or is much lower in these samples than theory suggests.

3.5.3 Outlook for rheological study of CNT/superacid solutions

There are several ways in which the study of CNT/superacid solution rheology may be advanced by future work. This section outlines a few possible directions for further research efforts

Firstly, the rheology of dilute solutions has been very difficult to investigate, especially because of the low viscosity of ClHSO₃. For solutions of CNTs with aspect ratios of 10^2 to 10^4 , the dynamic shear stress produced by the sample at achievable experimental frequencies is evidently below the limit of commercial shear rheometers. It may be possible to examine this behavior regime in one of two ways: either by measuring a sample of CNTs with much higher aspect ratio, which might generate orientation stresses large enough in magnitude to be measured by dynamic shear, or by measuring the rheology of dilute and semidilute solution using a microbead optical rheology technique.

Secondly, the study of CNT/superacid rheology thus far has suffered from a limitation which is common to many branches of CNT research, which is the polydispersity of the available CNT samples in terms of length and diameter. Monodisperse samples are difficult or impossible to obtain; if in the future such samples become available, then the rheology of superacid solutions containing monodisperse CNTs could be assessed and used to generate less ambiguous conclusions about the relaxation behavior of these molecules.

Thirdly, as the parameter space of CNT/superacid solution is more fully explored, a greater variety of liquid crystal microstructures may be observed with a variety of novel rheological behavior. The results presented here have demonstrated the profound effect that liquid crystal domain morphology can have on CNT/superacid solution rheology. Several distinct liquid crystal domain morphologies have been observed to date in CNT/superacid solutions, with morphology depending on aspect ratio and solution strength (Davis *et al.*, 2009; Behabtu, 2012;

Jamali *et al.*, 2015). The discovery of different morphology in other regimes of parameter space remains a possibility. Additionally, the influence of domain morphology on rheology should be taken into account when the effect of shear history on CNT solution behavior is considered: any development or merging of these domains over time, and any disruption of their shape due to high shear, is likely to affect the linear viscoelasticity of the sample.

Finally, it must be reiterated that the techniques applied thus far for the shear rheometry of ClHSO₃ have each failed to completely meet the challenges posed by this aggressive acid. The loading procedure outlined in section **3.3.5**, which was used in this study, appears to be adequate for testing over short periods of time; a more intense set of precautions needs to be taken if samples are to be subjected to test over longer periods of time. It is possible that the best way to avoid the degrading effects of gas species evolution in acid samples is to combine the use of a covering fluid with the use of a pressurized cell to inhibit the evolution of gas bubbles from the acid; another possibility is to enclose the testing geometry with gas flow manifolds that are capable of blanketing the exposed acid with a pressurized flow of HCl gas, which is itself separated from the atmosphere outside the manifold with a high pressure flow of anydrous nitrogen, in order to prohibit the evolution of HCl gas from the sample. Such solutions will need to be undertaken with the utmost care if they are to ensure reliable data collection, avoid health risks for the researcher, and prevent damage to the testing apparatus.

Chapter 4

Electrochemical Circuit Behavior of CNT Fiber Electrodes

4.1 Introduction

An electrochemical interface between a solid electrode and organic tissue is a central component of many medical treatments and devices. Any application which involves detection and recording of the body's electrical activity on the cellular or multi-cellular scale, or which uses the input of electric current to stimulate or regulate cellular activity, will include some electrochemical current exchange across an interface of this kind between the body and the device. In the realm of medicine such applications include the use of cardiac pacemakers, electrocardiograms (EKGs), and neural electrodes which allow for the detection, recording, or stimulation of neuronal electrical activity in the brain or peripheral nervous system.

Several considerations are important when designing an electrode for medical use. Firstly, the total impedance of the electrode itself and of the interface between the electrode and biological tissue should be low. The impedance of an electrical circuit may be defined as the function which relates the electric current flowing through a circuit at $t = t_0$ to the electric potential difference across the circuit during the time period $t \le t_0$. Low impedance ensures low

loss of signal in sensing and recording applications. Low impedance is critical for pacemakers and other devices which stimulate tissue by delivering electric current because it allows for adequate current flow without the application of very high potentials, which can lead to hydrolysis and tissue damage near the electrode. Keeping the required voltage output low can also extend battery life, or allow for equivalent battery life with a smaller battery size, thereby making the implanted device less intrusive (Webster, 1995).

Secondly, the material used should be biocompatible, meaning that it should not be acutely toxic or damaging to the tissue around it in the short term, that it will not generate an extended or harmful immune response, and that it should impose minimal risk of long-term health issues (such as cancer) for the patient. In addition to the chemical biocompatibility of the component materials, the size and mechanical properties of the implant must be considered. Mechanical mismatch between stiff electrodes and the soft tissue surrounding them can lead to damage to that tissue (Polikov *et al.*, 2005; Harris *et al.*, 2011).

If an electrode is intended for long-term implantation, its usage lifetime and durability are also important. Corrosion in physiological environments or mechanical fatigue due to motion of the tissue in which it is embedded may cause the components of a device, in particular the electrode itself and any wires passing to and from the electrode, to lose function over time or eventually fail. Implanted device failure may pose an immediate hazard (if the broken parts are jagged or if they migrate in the body) and creates a need for an additional medical intervention for device replacement. Implantable electrodes are typically composed of corrosion-resistant metals and alloys such as stainless steel, cobalt-chromium alloys, titanium alloys, and platinum alloys. The strength and geometry of implanted materials should be carefully designed to maximize mechanical durability and minimize fatigue (McClain *et al.*, 2011; Kilgore *et al.*, 2003; Kozai *et al.*, 2015). A natural dilemma arises between the need for device durability and the need for a flexible device which will match the mechanical motion of embedded tissue; larger and thicker metal parts are more durable, but less flexible.

Continuous CNT fibers show great promise for use as electrochemical electrodes, particularly in the realm of medicine. They have been shown or may be expected to possess many of the properties that are typically sought in medical electrode design: small profile, high inherent conductivity (i.e., low inherent impedance) (Behabtu *et al.*, 2013), low contact impedance with biological tissue (Vitale *et al.*, 2015), flexibility, durability, and chemical stability in biological environments (Voge and Stegemann, 2011; Vigolo *et al.*, 2000; Wang *et al.*, 2003b; Viry *et al.*, 2007; Harreither *et al.*, 2013). Replacing the current state-of-the-art materials with CNT fibers could result in increased performance and safety in many applications; this is especially true of applications requiring an implant in areas of the body that undergo continuous or repeated motion, such as joints, spine, neck, or muscle tissue. CNT fiber may even enable medical therapies that were previously impossible to implement, given the susceptibility of metal parts to fatigue. Characterization and understanding of the electrochemical properties of CNT fiber is necessary to assess the viability of such novel applications and to provide guidance for design and development of CNT-fiber based medical devices.

The treatment of cardiac arrhythmias is an example of an application in which the development of CNT fibers has led to the promise of novel medical procedures. Many instances of cardiac arrhythmia arise when the tissue in a region of the heart muscle loses the ability to carry the electric signals that regulate cell contraction (Kleber and Rudy, 2004; Dhein *et al.*, 2014). Treatment through the addition of conductive implants that directly supplement the transmission of these signals has not been possible with conventional materials because of the fragility of metal conductors in repeated bending strain (which is unavoidable in a beating heart). CNT fiber, on the other hand, may provide a novel treatment for this condition by serving as a flexible and biocompatible implant which can carry electric signal through a region of conduction block.

This chapter presents a study of the electrochemical properties and equivalent circuit behavior of CNT fibers used as electrodes in explanted cardiac tissue and in physiological saline. The remainder of this introduction summarizes recent investigations into CNT-based electrodes and the medical applications of CNT fiber electrodes, which motivated the present work. Section 4.2 describes the basic physics of electrochemistry at an electrode/electrolyte interace. Section 4.3 describes the apparatus and measurement techniques used in this work to assess the electrochemical properties of CNT fiber. Section 4.4 presents the results of the electrochemical measurements, the interpretation of those results to reveal the underlying equivalent circuit behavior, and a discussion of how electrochemical properties may be expected to scale with the dimensions of a CNT fiber electrode. Finally, Section 4.5 discusses the manner in which treatment or aging of the fiber may change the degree to which its internal porous structure is accessed by the conductive electrolyte solution, and describes a post-processing procedure by which the electrochemical properties of CNT fiber can be optimized.

4.1.1 CNT-based electrochemical electrodes

CNTs and other graphitic materials have been investigated for use in a wide variety of electrochemical applications, including electrodes for medical uses (Fung *et al.*, 2010; Musa *et al.*, 2012; Minnikanti *et al.*, 2009), chemical detection (Nugent *et al.*, 2001; Wang *et al.*, 2003a; Hu *et al.*, 2007), and energy storage (Ambrosi *et al.*, 2014; Obradovic *et al.*, 2009). CNTs are prized in these applications for a number of reasons. The most common motivation for the use of CNT materials in electrochemical electrodes is their high surface area 3D structure, which presents the possibility for greatly decreased interfacial impedance compared to other materials. In many tests CNT electrodes have been reported to attain lower interfacial impedance than bare metal electrodes of the same size (Fung *et al.*, 2010; Musa *et al.*, 2012; Vitale *et al.*, 2015).

Many of the CNT electrodes that have been reported in electrochemical literature are arrays or mats of CNTs gown through chemical vapor deposition (CVD) (Fung *et al.*, 2010; Musa *et al.*, 2012) or coatings of CNTs deposited onto solid electrode surfaces from a solution or suspension (Keefer *et al.*, 2008; Minnikanti *et al.*, 2009). In some cases the CNT electrode materials comprised large bundles of MWNT (Nugent *et al.*, 2001) or macroscopic CNT fibers fabricated by wet-spinning into a polymer coagulant (Wang *et al.*, 2003a).

Continuous, macroscopic CNT fiber represents a single material that can be used as both an electrode and the conducting lead wire connecting that electrode to the main body of a medical device. Electrodes that are constructed using CNT films or CNT arrays grown by CVD require a metallic substrate which is electrically connected to the CNTs and metallic conducting wires, and are subject to the danger of mechanical failure and fatigue damage inherent to metals. A CNT fiber electrode can combine the excellent electrochemical interface properties demonstrated by CNT structures with the flexibility and durability exhibited by CNT fiber, without sacrificing the conductivity of the conducting wire; it can also obviate the need for any physical or electrical connection point between electrode and the conducting lead, which may eliminate a possible point of failure.

4.1.2 Wet-spun CNT fibers as medical electrodes

CNT fibers as neural electrodes

CNT fibers fabricated using the wet-spinning acid process have recently been used in a lab setting as microelectrodes for recording and stimulation of electrical signals in rodent neuronal tissue, with a particular investigation into their potential use as deep brain stimulation (DBS) electrodes for treatment of Parkinson's disease (Vitale *et al.*, 2015). The small diameter of the CNT fibers allowed for the creation of a flexible microelectrode with a small profile, consisting of two separately insulated fibers twisted to form a long, thin electrode, with the ends exposed for electrochemical contact with neural tissue. These electrodes demonstrated good performance *in vivo* over a time period of 6 weeks. The application of CNT fibers in this case demonstrates their multi-purpose utility as both an electrochemical electrode and a flexible, durable connection between the electrochemical interface and the neurostimulation device.

In the same study the electrochemical properties of CNT fiber were compared to those of platinum-iridium (Pt-Ir) wire; CNT fiber electrodes were found to have a much lower electrochemical impedance over a broad range of frequencies (lower by one order of magnitude), and a much higher charge storage capacity (greater by two orders of magnitude, for both cathodic and anodic charge), indicating their superior performance as electrochemical electrodes. The impedance of CNT fibers measured at a sinusoidal AC voltage frequency of 1 kHz, when normalized by electrode surface area, was also lower than that reported in other literature for tungsten and carbon fiber neural electrodes (Prasad and Sanchez, 2012; Kozai *et al.*, 2012). The electrochemical impedance of CNT fiber electrodes had a negative power law scaling with frequency in the range of frequencies considered, as did that of Pt-Ir, indicative of capacitive behavior; however, the broader equivalent circuit behavior of the electrodes was not investigated.

Biocompatibility of CNT fibers

Regardless of electrochemical performance, an electrode can be of no use in a medical setting if it produces a destructive toxic or immune response when placed in contact with tissue. This requirement is particularly true of electrodes designed for long-term implantation, such as pacemaker or DBS electrodes. Toxicity has been and remains a major concern in discussions of the medical use of nanostructured materials in general, and CNTs in particular. The toxicity of CNT materials has been reported to vary depending on the size, dosage, and agglomeration density of the CNTs in question (Kunzmann *et al.*, 2011; Krug and Wick, 2011; Kostarelos, 2008; Bianco *et al.*, 2011; Lacerda *et al.*, 2008).

Wet-spun CNT fibers have thus far demonstrated excellent biocompatibility in toxicity and immunological tests. Vitale *et al.* (2015) reports that in the course of 6 week *in vivo* implantations in rodent neural tissue, CNT fibers elicited lowered inflammatory and immune response from the tissue surrounding them compared to Pt-Ir wires (considered a state-of the art material in terms of performance and biocompatibility). A more thorough investigation of CNT fiber biocompatibility has recently been performed through acute and chronic implantation in rodent muscle tissue (McCauley *et al.*, in preparation). Neither implanted CNT fiber nor injections of saline in which CNT fiber had been aged produced any inflammation or immune response beyond that measured using negative controls (silk).

CNT fibers as cardiac electrodes

The work presented in this chapter is one part of an ongoing research effort to assess the suitability of wet-spun CNT fibers for use in cardiac applications. The preliminary studies in that effort included examination of the exchange of current between CNT fibers and cardiac tissue in a variety of models: *in vitro, ex vivo* (i.e., in explanted organs from sacrificed animal subjects) and *in vivo*. *In vitro* tests revealed that myocardial cells deposited on CNT fiber in a cell culture medium would attach to and grow on the fiber surface with no signs of toxicity, and that current passed through the fiber could induce synchronized contraction in these cells. Individual CNT fiber filaments embedded in the epicardium of an explanted rodent heart, or even in non-invasive contact with the outer surface of the epicardium, were able to detect an EKG trace from the spontaneously beating heart and could induce contraction in the heart with a moderate input voltage signal (1 V). These preliminary results indicate that the physical and electrochemical contact between CNT fiber and myocardial tissue is quite good.

More recently, *in vivo* trials in ovine hearts have demonstrated that CNT fibers can act as a bridge through regions of conduction block in myocardial tissue. In these trials the conduction velocity of the action potential, the electrical signal which propagates through heart tissue and induces orderly muscular contraction, was measured using electrodes placed on the exposed epicardium of a beating heart before and after an ablation catheter was used to induce damage to the tissue. The reduction in action potential velocity caused by the damaged tissue was substantially reversed when a CNT fiber bundle was placed across the scar, indicating that action potentials can be transmitted across the region of conduction block through the fiber. This is a significant result: it indicates that the total impedance of the fiber bundle (which may be considered to be an electrode with a continuous surface of contact to the tissue) was low enough to transfer a large fraction of the current output from activating cells on one side of the conduction block to the passive but healthy cells on the far side (Figure 4.1) (a more in-depth description of cellular electrical signaling in myocardial tissue is provided in 5.2).

Objectives of the current work

The specific goals of the work presented in this chapter were

• to obtain accurate measurements of electrochemical impedance and charge injection capability for CNT fiber electrodes of various sizes in mammalian cardiac tissue and in physiological saline (that is, saline with a concentration that makes it suitable for use as a surrogate for extracellular fluid)



Figure 4.1: A: Photograph of epicardially implanted CNT fibers in a sheep heart. CNT fibers were sewn across a semi-circular scar at the 10:30 o'clock position, whereas the semi-circular opening is opposite at the 4:30 o'clock position. CNT fiber pacing leads are implanted in the center of the scar, and four decapolar sensing catheters are placed around the scar. Numbers 1-10 correspond to the position of bipolar electrograms recorded circumferencially around the scar. B: Example of a CNTf tied onto 6-0 prolene monofilament curved surgical needle, which was used for implantation. C: Graphical representation of CNTf pacing and four decapolar sensing catheter setup prior to, and (D) after scar formation by radiofrequency ablation. E: Representative example of epicardial electrograms and conduction intervals from pacing artifact recorded from bipole position 4 at baseline (red), post-ablation (black), post-ablation with CNT fiber (blue), and with silk control (green). F: Polar plot of average myocardial conduction time to bipolar sensing electrodes (decapolar catheters) at positions 1-10 at baseline, (G) post-ablation, (H) post-ablation with CNT fiber, and (I) with silk suture control (n = 3). The yellow ellipses in indicate the area where CNT fiber or silk suture were implanted. J: Representative 3D Carto mapping of latent activation time (LAT) for baseline condition, (K) post-ablation, (L) post-ablation with CNT fiber, and (M) post-ablation with silk suture control. *Figure and caption reproduced from McCauley et al. (in preparation)*.

- to use these measurements to elucidate the physical processes responsible for the electrochemical impedance, and describe the equivalent circuit of a CNT fiber electrode
- to use the information obtained about the equivalent circuit to determine how electrochemical performance can be expected to vary with the size and surface area of CNT fiber electrode in the most general case.

This work presents a characterization the of the specific electrochemical properties CNT fiber. The inherently porous structure of the CNT fiber and the way in which fiber is treated, aged, or stored play a significant role in determining these properties. These effects are explored, and a procedure which can be used to optimize CNT fiber electrochemical properties by exploiting this porous structure is presented.

4.2 Background: Electrochemistry

Electrochemical electrode interfaces are surfaces at which electric current may be exchanged between a solid conducting material and a fluid electrolyte. Electric current in a metallic conductor consists of a migration of free electrons; electric current in an electrolyte consists of the diffusion of ions or other charged species. Current can be exchanged across such an interface through two mechanisms: Faradaic charge transfer processes, in which electrons are actually exchanged through redox reactions between the conductor and various chemical species in the electrolyte, and capacitive (non-Faradiac) charge transfer, in which charge is gradually built up on either side of the interface through the creation of a Helmholtz double layer (analagous to the charging of a capacitor) (Stern, 1924; Merrill *et al.*, 2005). The simplest circuit that may be used to model an electrode/electrolyte system (known as the equivalent circuit of the system) consists of two resistors connected in series with a capacitor, which is itself bridged by a third resistor; this simple model is shown in Figure 4.2. The series resistors R_S and R_{el} represent the resistances associated with diffusion of ions through the solution and drift of electrons in the



Figure 4.2: Models depicting an electrochemical electrode interface at the molecular scale. A: Depiction of a redox reaction by which an electron is extracted from the solid conductor and transferred to a positive ion in the electrolyte. In aggregate, reactions of this type give rise to Faradaic charge transfer current. Kinetic barriers to the completion of the reaction create an effective resistance R_{CT} to this current, which is connected in series with the bulk resistances of the electrode and electrolyte. B: More complete model, in which the electrode/electrolyte interface exhibits both charge transfer current due to aggregate redox reactions and polarization due to the creation of a Helmholtz double layer. The flow of charge to create the double layer serves as a current pathway parallel to that of the charge transfer current, and the double layer itself can be modeled as a capacitor, C_{DL} .

electrode, respectively; the capacitor C_{DL} and resistor R_{CT} set in parallel represent the capacitance of the Helmholtz double layer which is "shorted" by the Faradaic current associated with charge transfer reactions at the electrode surface.

In practice, a variety of additional physical processes may play a role in determining the equivalent circuit behavior of an electrode/electrolyte system. If the electrolyte must diffuse through a porous barrier in order to reach the electrode surface, it will experience an access resistance R_a (Ovadia and Zavitz, 1998). If the flow of current results in local inhomogeneities in ionic concentration then transient diffusion currents may be created, resulting in a so-called Warburg impedance, which is described in more detail below (Taylor and Gileadi, 1995). A certain subset of reversible Faradaic charge transfer reactions which self-limit due to the buildup of an adsorbed layer on the electrode surface may behave as an essentially capacitive circuit element rather than a resistive one; this is often referred to as a pseudocapacitance (Taylor and Gileadi, 1995). In addition to these physical processes the circuit behavior may be com-

plicated by the fact that the electrolyte solution resistance R_S has several components R_{S1} , R_{S2} , etc, which may each scale differently with electrode size or geometry; for example, one of these components may be a resistance associated with the spread of ionic current into the bulk electrolyte from a μ m-scale electrode, while another may be the true bulk resistance of the electrolyte cell (Franks *et al.*, 2005).

Constant phase elements

Physical processes which give rise to non-Faradaic currents are essentially capacitive, in that they involve build up and storage of electric charge at the electrochemical interface; however, they may exhibit behavior that distinct from that of an ideal capacitance. A capacitive process that allows some current to flow through the circuit, i.e., a capacitor with some leakage current, can be modeled as a capacitor in parallel with a resistor; however, a number of commonly observed electrochemical processes cannot be modeled in this way, or indeed by any combination of ideal resistors and capacitors. Such processes are represented instead by an empirically derived circuit element known as a constant phase element (CPE).

In general, CPEs behave like capacitors in which some portion of the charge accumulated in a given time is lost to mechanisms outside of the circuit. A CPE may be characterized as a circuit element with an inverse power law dependence on complex frequency, having impedance

$$Z_{\text{CPE}}(\mathscr{S}) = \frac{1}{Y \mathscr{S}^n}$$
(4.1)

where complex frequency $\mathscr{S} = \sigma + j\omega$, $j = \sqrt{-1}$, and 0 < n < 1. Y is a parameter with units of (Siemens)*(seconds)ⁿ (or S*sⁿ) An ideal capacitor is a CPE for which n = 1 and for which Y is the capacitance, C, in units of S*s; in that case, equation 4.1 reduces to the classical formula for the impedance of a capacitor:

$$Z_{\rm C}(\mathscr{S}) = \frac{1}{\mathcal{C}\mathscr{S}} \tag{4.2}$$

In the case of an input current or input voltage with a sinusoidal AC voltage of constant amplitude (i.e., $\sigma = 0$), equations 4.1 and 4.2 may be written in the more familiar forms

$$Z_{\rm CPE}(\omega) = \frac{1}{Y(j\omega)^n}$$
(4.3)

and

$$Z_{\rm C}(\omega) = \frac{1}{Cj\omega} \tag{4.4}$$

The impedance of an ideal capacitor exposed to a sinusoidal AC voltage of constant amplitude with radial frequency ω is a purely imaginary number, and the resulting current passing through a circuit consisting of only that capacitor would be a sine wave with a constant phase shift of -90° with respect to the the phase of the input voltage. The impedance of a CPE is a complex number, and the current it produces corresponds to a sine wave with a constant phase of -90° * n with respect to the driving potential.

CPE behavior in electrochemical electrodes is frequently observed in the double layer capacitance; the deviation from ideal capacitive behavior in this case is attributed to the roughness of electrode surfaces (McAdams *et al.*, 1995). Another common source of CPE behavior is the Warburg impedance, which arises as a result of accumulation or depletion of ions near the electrode over time as current flows along with the diffusion of ions against the resulting concentration gradient. The physical origins of the Warburg impedance are described in Taylor and Gileadi (1995); it appears in EIS measurements as a CPE with n = 0.5. The Warburg impedance has been observed in biological electrode systems, including platinum electrodes in explanted heart tissue (Ovadia and Zavitz, 1998). In general, it tends to appear in the circuit behavior of any electrode with a sufficiently low R_{CT} , since a significant charge transfer current is required for rapid creation or depletion of charged species at the electrode surface, which in turn gives rise to significant diffusion effects.

4.3 Materials & Methods

4.3.1 Measurement with a 3-electrode potentiostat

The apparatus used for the electrochemical measurements described in this chapter was a Gamry Reference 600 potentiostat from Gamry Instruments operating in a "3-electrode" configuration. The three electrodes referred to here are a "working" electrode (W), which is commonly the electrode being characterized, a "counter" or "auxiliary" electrode (C), from which current passes to the working electrode through the intervening electrolyte, and a "reference" electrode (R), which is in contact with the same electrolyte sample and which should be maintained at a constant electric potential. There is in fact a fourth electrode in this configuration, the "working sense" electrode (WS), which is attached directly to the working electrode; the working sense and the reference electrodes together comprise a 2-probe voltmeter that allows for measurement of the electric potential at the working electrode with respect to the potential of the reference electrode. In practice, different samples of conductive material may be selected for the working electrode, counter electrode, and reference electrode; the Gamry potentiostat is then connected to these electrodes by metallic alligator clips (or some other suitable connection to the appropriate wire leads). A simplified schematic of an electrochemical cell with a 3-electrode configuration is shown in Figure 4.3.

Porous glass or plastic electrochemical cells in which a redox reaction occurs at a constant, well-known potential between a metal conductor and a locally saturated electrolyte are typically used as reference electrodes in electrochemical experiments. In these studies a porous glass Ag/AgCl aqueous electrode from Sigma Aldrich served as the reference electrode.

Once a set of electrodes has been connected appropriately to an electrolyte sample, measurements are performed by imposing a certain voltage signal across the cell and monitoring a) the current between the counter and working electrodes and b) the potential difference between the reference and working sense electrodes. The instrument may be operated either in potentiostatic mode, in which the input voltage signal is modified through a feedback mechanism in order to achieve a controlled working electrode potential, or in galvanostatic mode, in which the input voltage signal is modified through a feedback mechanism in order to achieve a



Figure 4.3: A & B: Depictions of the Gamry Reference 600 potentiostat and the set of electrodes available for use with this measurement system. C - E: Simplified schematic of an electrochemical cell measured using a 3-electrode configuration. The circle represents an electrolyte cell, and the C, R, W, and WS represent the counter, reference, working, and working sense electrodes. In many measurements a circuit is closed by the potentiostat device between the working and counter electrodes, as shown in D; the dotted line in E denotes the portion of the system that is interrogated by EIS measurement. Image source for A & B: www.gamry.com

controlled current between the counter and working electrodes. Measurements of both steady state and transient responses can be performed using this technique, which allows for a variety of measurement methods probing DC and AC impedance, stability, reaction kinetics at the electrode interface, etc. The two measurement modes employed in the present work, cyclic voltammetry and electrochemical impedance spectroscopy, are briefly described below.

Open circuit potential

When current is not allowed to flow from the working electrode through a closed circuit, cathodic and anodic charge transfer reactions between the electrode material and reactant species in the electrolyte result in positive or negative charge accumulation on the electrode over time. This results in a non-zero open circuit potential E_{oc} at the working electrode (defined relative to the potential at the reference electrode, E_{ref}). The sign of the accumulated charge depends on the relative reaction rates of cathodic and anodic processes; either a net positive or net negative charge accumulates on the working electrode until the faster reactions self-limit, at which point the net charge becomes constant and E_{oc} attain an equilibrium value. When a circuit is closed, anodic or cathodic charge transfer current may be induced by setting the potential of the working electrode above or below this equilibrium value of E_{oc} ; holding the electrode at E_{oc} causes a net current of 0 A.

Cyclic voltammetry

A cyclic voltammetry (CV) experiment is carried out in potentiostatic mode by sweeping the electric potential at the working electrode linearly between two extremes and recording the resulting transient current through the working electrode. Typically the limits chosen are some positive and negative value of equal magnitude around either the open circuit potential E_{oc} or the potential at the reference electrode (denoted V_{ref} or E_{ref}). A highly simplified schematic of the measurement technique and its relation to the 3-electrode potentiostat configuration is given in Figure 4.4.

In the case of a purely resistive system a CV measurement would result in a single-line I-V curve, which would be linear in the case of an Ohmic conductor. In the case of an electrochemical system or any other circuit which includes some capacitance, the cyclic curve will instead exhibit hysteresis due to the charging and discharging of the various capacitive elements. In principle, the shape of the CV curve from an electrode depends on a combination of factors including the total capacitance of the electrode, the kinetics of the chemical reactions that may occur between the electrode material and the electrolyte under study, the diffusion rates of reactants in the electrolyte, and the rate at which the voltage sweep is carried out (Cogan, 2008).

One of the relevant parameters derived from CV measurements is the charge storage capacity (CSC), which can be divided into cathodic and anodic charge storage capacity (CSCc and



Figure 4.4: Summary of the basic chain of events comprising a CV measurement: Potential at the working electrode is subjected to a controlled, approximately linear sweep (actually a rapid stepwise change). The resulting transient current between the counter and working electrode is then plotted as a series of independent current vs. voltage curves, one for each completed voltage cycle.

CSCa). CSC is the total charge added to or removed from the electrolyte during the cyclic voltage sweep, measured by integrating the area within the hysteresis curve. Total CSC provides an indirect measurement of the total capacitance of the electrode, although the correspondence between the two is not perfect: the resistance-dependent time constants of the electrode circuit also affect CSC through their effect on charging and discharging times of those capacitors. CSCc is important in the characterization of electrodes intended for electrical stimulation of biological tissue because such stimulation is usually carried out with cathodic currents. Reliable stimulation of cellular tissue requires a certain threshold current, but large voltages and prolonged application of voltage can damage that tissue; CSCc provides an indication of how much charge can be delivered by a given electrode with a given voltage stimulation pulse, and is therefore one essential figure of merit for medical electrodes, alongside raw impedance (Cogan, 2008).

Except where noted, CV results reported in this chapter were obtained by performing a cycle of 5 linear voltage sweeps with $V_{max} = V_{ref} + 0.5$ V and $V_{min} = V_{ref} - 0.5$ V, with the initial ramp starting at V_{ref} and sweeping toward positive voltages. CSC values were computed by

first averaging together the 4 complete cycles between V_{min} and V_{max} , then integrating the area between the positive and negative arm of the curve. CSCc was computed as the integral of the portion of this curve in which current was negative. Note that there is typically a difference between V_{ref} and equilibrium E_{oc} , which means a certain amount of charge transfer current will flow from the working electrode at $V-V_{ref}=0$. In practice this can produce a CV curve which is not centered around zero on the current axis; this is the case in Figure 4.10.

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is performed either by imposing a sinusoidal AC current of fixed magnitude and monitoring potential (galvanostatic mode) or by imposing a sinusoidal varation of fixed magnitude in the working electrode potential and monitoring the current through the cell (potentiostatic mode). This allows for a measurement of system impedance as a function of AC frequency. Current passes between the counter electrode and the working electrode; however, changes in potential resulting from this current are monitored only in the section of the cell between the reference and working sense electrodes; this produces a measurement of impedance which excludes the impedance of the counter electrode. The impedance measured is that of a portion of the electrolyte itself, a portion of the working electrode, and interface between the two. A highly simplified schematic of the measurement technique and its relation to the 3-electrode potentiostat configuration is given in Figure 4.5.

EIS tests were carried out in potentiostatic mode by applying a very small amplitude (2 mV) sinusoidal variation in the potential at the working electrode, varied around the value of E_{oc} measured immediately before the start of the test; E_{oc} was monitored for 100 seconds before each EIS test to ensure that the potential was at or near the equilibrium value (see Section 4.4.2 for a discussion of measured E_{oc} values).



Figure 4.5: Summary of the basic chain of events comprising an EIS measurement: a sinusoidal electric potential of small amplitude and constant frequency is imposed at the working electrode. The magnitude and phase shift of the resulting sinusoidal current through the cell provide a measurement of the magnitude and phase of AC impedance at that frequency; this measurement is repeated across a range of input frequencies to produce a plot of the impedance spectrum. The portion of the system probed is indicated by the dashed line in the cartoon schematic of the electrochemical cell.

4.3.2 Measurements in saline & explanted heart tissue

The electrochemical properties of CNT fibers were measured in two settings that approximate human cardiac tissue: explanted porcine (pig) hearts, and beakers of so-called normal saline solution (aqueous NaCl, 0.9% NaCl by mass). Porcine hearts provide a good surrogate for human cardiac tissue in terms of total size and thickness of the heart walls; swine are often used as an animal model for *in-vivo* test of medical techniques, devices and treatments. Normal saline is an electrolyte solution commonly used in medical settings for a variety of applications, with closely approximates the ionic content of blood plasma as well as extracellular and intracellular fluid. While porcine cardiac tissue corresponds more closely to human cardiac tissue in terms of structure, ionic content, and the presence of cell membranes and other solid biological material, saline offers a measurement system in which is more easily controlled, avoiding changes over time due to tissue degradation, changes of chemical content due to necrosis of the tissue, and dehydration.

Porcine hearts were obtained from a butcher immediately after slaughter and kept on ice in a sealed plastic bag for 1.5 hours during transport to the lab; measurements were performed at room temperature. The positioning of electrodes for electrochemical tests on heart samples mimicked the setup described in Ovadia and Zavitz (1998), and is depicted in Figure 4.6 (A); a stainless steel syringe needle was inserted into the left ventricle to serve as the counter electrode, and the porous end of the Ag/AgCl reference electrode was inserted into the cavity of the right atrium, in contact with the tissue of the atrial wall. Single filaments of CNT fiber or 25 micron diameter platinum wire (99% platinum) were used as working electrodes, and were inserted tangentially through the outer wall of the right atrium by stitching with a surgical needle; a straight needle was used so that the embedded length of the working electrodes could be measured. The other end of the working electrode wires were secured to the contact surfaces of the Gamry lead wires with insulating tape. Measurements were carried out on heart samples at times ranging from 1.5 hours to 7 hours after explantation. During this time the hearts were periodically re-wetted with room temperature saline solution to counteract dehydration.

Tests in saline were carried out by immersing the counter, reference, and working electrodes in a beaker of normal saline solution at room temperature (Figure 4.6 B). Stainless steel syringe needles served as the counter electrode, with the porous Ag/AgCl electrode serving as the reference. In order to expose a controlled length of the CNT fiber and Pt wire working electrodes to the saline, these samples were encased in cylindrical glass capillaries sealed at either end with insulating epoxy with a known length of electrode exposed (Figure 4.6 (C)).

4.3.3 CNT Fiber and platinum electrode samples

The CNT fibers used in this study were fabricated through the the wet spinning process described in Section 2.4. Fibers created from three different CNT sources were used in these experiments.

The first set of fibers was created using CNTs purchased from Continental Carbon Nanotechnologies, Inc. (CCNI); this CNT batch consists of a mixture of single, double, and triplewalled CNTs with an average length of 4.4 μ m and an average outer diameter of 1.69 nm, de-



Figure 4.6: A: Setup used for electrochemical measurements in explanted porcine hearts. One end of a thin CNT fiber is sutured into the epicardial surface of the ventricle on the near side of the heart as a working electrode, with the other end affixed to the Gamry working electrode alligator clip (green) by adhesive tape; the CNT fiber is barely visible at this scale, and is indicated by the black arrow. B: Setup used for electrochemical measurements in normal saline. C: CNT fiber enclosed in a glass capillary, sealed at the end with epoxy, for the sake of measuring a known length of fiber immersed in normal saline

termined by TEM analysis and extensional viscosity measurements performed by colleagues at Rice University (Tsentalovich *et al.*, 2016). The second set of fibers was created using Tuball CNTs obtained from OCSiAl and purified according to the method described in Tsentalovich (2015); this CNT batch consists of single wall carbon nanotubes (SWNTS) with an average length of 3.5 μ m determined by extensional viscosity technique and an average outer diameter of 1.5 nm reported by the manufacturer. The third set of fibers was created using CNTs obtained from Unidym; this CNT batch consists primarily of double wall nanotubes with an average length of 4.17 μ m and an average outer diameter of 1.89 nm.

Physical and electrical properties of the CNT fibers were assessed using techniques described in Behabtu *et al.* (2013). Fiber diameters and cross sectional areas were determined using scanning electron microscopy (SEM). Fiber density was determined by measuring the mass of known lengths of fiber on a Citizen CM21 Micro Balance. Fiber resistivity was measured using a linear 4-point probe connected to a Hewlett-Packard 34401a Multimeter.

Tests were performed using Platinum wire (99% platinum) obtained from the California Wire Company, with an outer diameter of 25 μ m, as a conductive metal control.

4.3.4 Equivalent circuit modeling

Equivalent circuit modeling is a technique in which the impedance spectrum of a particular physical system is used to derive an equivalent circuit for that system; that is, a collection of distinct classical circuit elements which would produce the same responses to the application of current and voltage as does the system under study. For a complex physical system with many sources of resistance, capacitance, or inductance, a simple equivalent circuit will provide only an approximation of the true circuit behavior; some degree of degeneracy is to be expected, since there may be multiple circuit configurations that would produce similar or identical impedance spectra. For cases in which some initial guesses can be made about the dominant processes effecting current flow in the system, equivalent circuit modeling is an effectively tool to quantify the magnitude of those effects or to distinguish between proposed models.

Circuit model fitting was performed using the Gamry Echem Analyst software package, which was designed for use with the Gamry Reference 600 potentiostat; circuit models were constructed and circuit parameter values set using the Gamry software's model editor. Initial parameters were chosen using a preview mode to generate spectra closely approximating the data curve; fitting was then performed using a simplex method (Nelder and Mead, 1965) until the χ^2 value of the fit could not be improved by additional iterations (in all cases presented here this occurred within 100-300 iterations).

4.4 Results

This section describes the results of electrochemical measurements performed on CNT fiber samples and platinum wire samples of a comparable size in both explanted heart tissue and normal saline. The CSC and CSCc of the electrodes are compared, and an equivalent circuit model suitable for each class of electrode material is constructed based on the results of EIS measurements. These results indicate that the very low impedance exhibited by CNT fiber electrodes in comparison to platinum, previously reported in Vitale *et al.* (2015), is primarily a result of the porous structure and large surface area of the CNT fiber. The results also indicate that the wettability of the CNT fiber has a large effect on its electrochemical impedance, and that the post-processing and environmental history of the CNT fiber sample may have a significant affect on this wettability and thereby on electrochemical performance. A set of post-processing procedures are presented by which this wettability can be controlled to achieve reliable, optimally low impedance.

4.4.1 Normalization by electrode surface area

EIS and CV measurements were performed in porcine heart tissue and in normal saline using CNT fibers with differing outer diameters (14.08 μ m, 23.48 μ m, and 44.66 μ m, hereafter referred to for convenience as thin, medium, and thick CCNI fiber), as well as Pt wire with a diameter of 25 μ m. Because the ultimate goal of these experiments is to understand the behavior at the electrode/electrolyte interface in particular, it is useful to normalize measurements to the

surface area of the electrode used; this is necessary in order to accurately determine the specific properties of the interface.

Two difficulties arise in this normalization. The first is that the measurements are performed on a system that includes not only the electrode/electrolyte interface but also some portion of the bulk electrolyte and the bulk of the working electrode wire/fiber (i.e., the portion between the interface and the actual instrument electrode lead). The impedance arising from the interface itself may be expected to have an inverse linear relationship with its total surface area, but the impedance of the other portions of the system may depend on this surface area only weakly or not at all. For this reason, normalizing the total response of the system to the electrode area is not a perfect solution. Equivalent circuit modeling analysis, presented in Section 4.3.4, helps relieve this situation by making it possible to identify and quantify the circuit components that represent different physical processes within the system, allowing for an investigation of the scaling behavior of each.

The second difficulty is that the true surface area of an electrode may not be obvious due to roughness on the microscopic and nanoscopic scales; this is certainly true in the case of CNT fibers. Measurement of the surface area of a nanostructured material can be provided by a BET technique (Dollimore and Heal, 1978), but it is not clear that such a measurement, based on accessibility of the surface by gas molecules, would necessarily provide information about the accessibility of the surface by an aqueous solution or other liquid. We may well expect a CNT fiber to have an electrochemical interface area much greater than that of a smooth Pt wire electrode, but it is not trivial to determine how much greater without a thorough understanding of the roughness, porosity, and wettability of that fiber.

For most of the experimental results presented in this work the measured current (in CV results), the measured impedance modulus (in EIS results), and the magnitudes of fitted circuit elements (in circuit modeling of the EIS results) have been normalized by the "geometric" surface area of the samples; that is, a naïve calculation of electrode outer surface area based on the diameter of the wire/fiber and the length embedded in the heart tissue or immersed in saline. This type of analysis is typical in discussing the properties of electrodes made of solid

materials such as platinum or platinum black (see Fig. 1 in Franks *et al.* (2005)). Platinum black, for example, typically has much lower contact impedance than "bright" platinum due to its surface roughness; however, because platinum black has a fairly standard surface roughness, i.e., because a platinum black electrode's actual surface area is roughly the same multiple of its geometric surface area from sample to sample, it is still useful to normalize its properties to geometric surface area in making comparisons to other solid electrodes and in reporting area-specific properties. This approach leads to a useful set of specific properties and provides a good indication of how electrode performance will vary between electrodes with the same macroscopic ("geometric") size and shape if material is varied.

Unfortunately, normalizing interfacial properties by geometric surface area is not appropriate in the case of porous electrodes such as gold powder (Song *et al.*, 1999) or conducting polymer (Sharifi-Viand *et al.*, 2012) in which the electrolyte can penetrate a significant distance into the bulk of the electrode. For porous electrodes the actual surface area of the electrochemical interface depends not only on the geometric surface area of the electrode but also on its thickness or volume, its porosity, its wettability, and the accessibility of the pores to the electrolyte. This is in fact the case with CNT fibers: the porous inner structure contributes significantly to the active interfacial surface area; evidence of this effect and a quantitative assessment of its extent is presented in sections 4.3.4 and 4.5.

As an initial standard of comparison with Pt wire, the CNT fiber results presented in this section will be normalized by geometric surface area. From those results and analysis a case will be built that CNT fibers do in fact act as porous electrodes, and the factors that affect the accessibility of their internal structure will be examined.

4.4.2 Electrochemical characterization

Measurement of open circuit potential

CNT fiber and Pt wire working electrodes in normal saline were both observed to have an open circuit potential (E_{oc}) within the range of 200 mV - 400 mV with respect to the reference potential. This indicates that when no external potential is applied and the circuit is closed, cathodic



Figure 4.7: Relaxation of open circuit potential E_{oc} for Pt wire (red curves) and CNT fiber (blue curves) working electrodes in normal saline immediately after application of a working electrode potential of +1.5 V (solid curves) or -1.5 V (dashed curves). Initial E_{oc} measurements for Pt wire and CNT fiber are given by black X's and Blue squares, respectively.

charge transfer reactions (reduction of the electrode) occur at a more rapid rate than anodic charge transfer reactions (oxidation of the electrode) until the working electrode accumulates a positive net charge; at this point an equilibrium is reached between cathodic and anodic reactions.

Figure 4.7 depicts the return of CNT fiber and Pt wire open circuit potential to equilibrium when the circuit is disconnected after the application of moderate positive or negative working electrode potential (\pm 1.5 V). In both cases the return to equilibrium is an asymptotic approach to the value of the initial potential measurement, but this evolution is much slower in CNT fibers than it is in Pt wire; this indicates that the electron transfer kinetics of redox reactions are much faster for the Pt wire than for the CNT fiber.

In explanted porcine hearts, the E_{oc} of CNT fiber and Pt wire working electrodes was not stable; rather, the open circuit potentials for working electrodes of either material became increasingly negative over time, indicating that the native rate of anodic charge transfer reactions gradually increased as the tissue sample aged (see Figure 4.8). This drift in E_{oc} was gradual, resulting in a change of 20 - 30 mV over the time period of each EIS measurement. Such a small



Figure 4.8: Open circuit potential E_{oc} vs. time for Pt wire and CNT fiber working electrodes implanted in explanted porcine hearts.

change over the course of the measurement should not have affected the EIS results; however, the negative potential did have a progressive effect on CV measurements, as noted below.

EIS and CV measurements

Figure 4.10 displays area-normalized CV curves obtained for medium CNT fiber and 25 μ m Pt wire working electrodes in explanted heart tissue (**A**) and normal saline (**B**). Area-normalized EIS results from the same systems, averaged over at least 4 samples in each case, are shown in Figure 4.11. It is clear from the EIS results that systems with CNT fiber working electrodes exhibit much lower electrochemical impedance than systems with Pt wire working electrodes over most of the measured frequency range. This is reflected in the CV results of Figure 4.10 by the ratio of current density produced by the two materials: the CNT fiber electrodes produce current density that is more than 2 orders of magnitude greater than that produced by Pt wires. The difference in the impedance magnitude curves for the two materials shown in Figure 4.11 and the narrowing of that difference at high frequencies are both consistent with the results reported in Vitale *et al.* (2015).



Figure 4.9: Cyclic Voltammetry of a CNT fiber working electrode in normal saline between 2.2 V and -2.3 V with respect to V_{ref} , with an Ag/AgCl reference electrode. Beyond $V-V_{ref}=1.5$ and $V-V_{ref}=-1.5$, significant Faradaic current flows due to oxidation or reduction of water; in this voltage range significant gas production from hydrolysis is observed.

Figure 4.9 shows a representative CV curve of CNT fiber in normal saline over an extended voltage range, illustrating the limits of the water window; the water window is the range of potentials a working electrode of a given material can attain without significant oxidation or reduction of H₂O. At the positive voltage edge of the water window (in which the working electrode serves as an anode), water can be reduced at the electrode surface, leading to the formation of O₂ gas and H⁺ ions. At the negative voltage edge of the water window free H+ ions can be reduced, leading to the formation of H₂ gas and an excess of solvated OH⁻ ions (Brummer and Turner, 1977; Hudak, 2011). The water window presents a limit to the range of voltages that can be considered for the operation of an electrode in physiological conditions, because the gas production and shift in local electrolyte pH associated with it can cause significant harm to surrounding tissues (Brummer and Turner, 1977). The water window for CNT fibers consists of the range of potentials between approximately +1.5 V and -1.5 V with respect to the potential of the Ag/AgCl electrode; this is consistent with the water window reported in Vitale et al. (2015) Beyond these voltage limits Faradaic current can flow through these charge transfer reactions, and the CV curve transitions from an essentially capacitive curve to the I-V curve of an Ohmic resistor. Significant production of gas bubbles was observed along the length of CNT fiber working electrodes set to potentials outside of this window.

Voltage limits of +0.5 V and -0.5 V were chosen for the measurements reported in Figure 4.10 in order to assess the performance of the electrodes within the water window. For Pt wire in explanted heart tissue some Faradiac current appears at either end of this voltage range (labels 1 and 2), with primarily capacitive current dominating at low voltages; these peaks are consistent with surface oxidation of platinum at positive voltages and hydrogen plating at low voltages, respectively (Brummer and Turner, 1977; Hudak, 2011). In contrast, the CV curve of CNT fibers in explanted heart tissue is purely capacitive over the entire voltage range; the only asymmetry around the midline at $V = V_{ref}$ consists of a slightly larger cathodic current appearing at negative voltages. The total CSC is 0.797 μ C/mm² for the platinum and 83.2 μ C/mm² for the CNT fiber.

For the Pt curve the capacitive region around $V = V_{ref}$ is offset towards anodic currents, and has a slightly positive overall slope (see label 3). This is consistent with the observation that E_{oc} is lower than V_{ref} . A constant anodic charge transfer current is promoted in this range of potentials, and this Faradaic current is superimposed with the current produced by capacitive charging and discharging. It is likely that the same is true for the CNT fiber electrode, but in that case the background Faradaic current is so much smaller than the capacitive current that it produces no appreciable offset. As a result of this offset, the CSCc for platinum wire from this curve is extremely small (5.93 nC/mm²), while the CSCc for CNT fiber is 39.7 μ C/mm². If the progressively increasing negative E_{oc} is an artifact produced by degradation of tissue, then the CSCc for Pt electrodes *in vivo* could be many times greater, likely on the same order of magnitude as the CSC. Even taking this artifact into account, CNT fiber electrodes exhibit a CSCc which is more than one order of magnitude greater than that of the Pt wire electrodes.

Tests of cyclic voltammetry in normal saline produce results which are similar in most respects to the results of testing in cardiac tissue; CNT fiber working electrodes exhibit much larger current density and CSC than Pt wire elctrodes of the same geometric surface area (Figure 4.10 (B)). In this case, a significant cathodic Faradaic current is generated from both kinds of electrodes at negative voltages (see labels 4 and 5). For CNT fibers this produces a deflection of the capacitive curve as Faradaic currents are superimposed onto it. For Pt wire there



Figure 4.10: Cyclic voltammetry of medium thickness CNT fiber (right-hand axis) and 25 μ m Pt wire (left-hand axis) working electrodes in (A) explanted porcine hearts and (B) normal saline. Current measurements are normalized to the geometric surface area of the working electrodes. V–V_{ref} represents the applied difference between electric potential at the working electrode and electric potential at the Ag/AgCl reference electrode. Plotted curves represent results averaged over 4 complete linear voltage sweeps, with a ramp rate of 0.1 V/s. Labeled features represent oxidation (1), hydrogen plating (2), and evidence of small anodic Faradaic current around V = V_{ref} from Pt wire electrodes in explanted cardiac tissue (3), and cathodic current in both species of working electrode at negative potentials in normal saline (4 & 5).

is a similar deflection accompanied by an increase in the area between the cathodic and anodic current density curves; this increase in area indicates that the resistive Faradaic current is linked to a reversible pseudocapacitive process such as a redox reaction or the formation of a partial coating of adsorbed species. Anodic current from Pt wire electrodes in this range of potentials is consistent with the adsorption of H^+ as observed in Kolthoff and Tanaka (1954), Hudak *et al.* (2010), and Brummer and Turner (1977).

Figure 4.11 presents the results of EIS measurement in the form of a pair of Bode plots, which display the magnitude and phase of a system's AC impedance as a function of frequency. For systems in which the impedance arises primarily from a capacitor or a CPE the magnitude exhibits a negative power law dependence (linear on the log-log plot) and the phase attains some negative phase value, with a minimum of -90° in the case of an ideal capacitor (see Equations 4.1 and 4.2). For systems in which the impedance arises mainly from resistive effects the magnitude curve exhibits a plateau and the modulus curve attains a small negative phase value, with a phase of 0° for a pure resistor.

The averaged impedance spectra in Figure 4.11 represent the impedance of the complete electrode/electrolyte systems under measurement, as described in Section 4.3.1. In each case, impedance magnitude is normalized by the geometric surface area of the working electrode. Each of the systems measured exhibited a primarily capacitive impedance at low frequencies and a transition to resistive impedance at higher frequencies. This transition occurred near the middle of the measured range for systems incorporating CNT fiber electrodes, but only occurred at the highest frequencies for systems incorporating Pt wire electrodes. Aside from these dominant capacitive and resistive regions, there are indications of other regimes of behavior at the edges of the measured range. At the highest frequencies the slight downturn in phase exhibited by systems with CNT fiber electrodes indicates that there may be a second region of capacitive dominance at higher frequencies. At the lowest frequencies an upturn in phase and an indication of a plateau in the magnitude curves for systems with Pt wire electrodes indicates the presence of a low-frequency resistive region.

It is clear from Figure 4.11 that the capacitance dominating the low-frequency impedance



Figure 4.11: Bode plots showing impedance magnitude |Z| (**A** & **C**) and phase (**B** & **D**) of medium thickness CNT fiber and 25 μ m Pt wire working electrodes in explanted porcine hearts (**A** & **B**) and normal saline (**C** & **D**). Impedance magnitude has been normalized by the geometric surface area of the working electrodes.

of systems incorporating CNT fiber electrodes has a significantly lower impedance magnitude (i.e., higher capacitance) than that which dominates the impedance of systems incorporating Pt wire electrodes. At higher frequencies the resistive impedance of systems with CNT fiber electrodes exceeds that of Pt wire electrodes.

Figure 4.12 shows an overlay of averaged EIS results obtained from CNT fibers with three diameters ("thin", "medium", and "thick" CNT fiber), with results normalized by geometric surface area of the electrode wire. The separation between the three curves indicates that neither the dominant capacitive impedance nor the dominant resistance of these systems scale linearly with geometric surface area when the diameter of the working electrode is varied; it also appears that the magnitudes of these impedances do share the same diameter scaling. The trend exhibited by the capacitive impedances magnitudes in Figure 4.12 is reflected in CV measurements from these fibers (Figure 4.13). Thin and medium CCNI fiber working electrodes produced current densities which were approximately similar, while the current density from thick CCNI fiber was larger (implying a larger capacitance, with a lower capacitive impedance).

Normalizing impedance magnitude by working electrode geometric surface area does lead
to a good collapse of the capacitive portion of the impedance curves within each individual data set (the set of data from electrodes of a given material and given diameter) plotted in Figure 4.12. This can be observed from the fact that there is much smaller variation in the capacitive portions of the averaged EIS curves than there is in the resistive portions of the curves. The success of geometric area rescaling can also be observed when the area-normalized impedance curves from individual electrodes within each data set are plotted separately and overlaid (see Figure 4.14); in each case, the capacitive regions of the impedance magnitude curves collapse to a single curve after area normalization. In other words, the dominant capacitive impedance in each system remains proportional to the working electrode geometric surface area if that area is varied by changing the length of electrode exposed to the electrolyte; this strongly suggests that the dominant capacitive impedance in each of these systems is indeed associated with a physical process occurring at the electrode/electrolyte interface. The divergence in the area-normalized impedance of CNT fibers of different diameter must still be accounted for. The resistive portions of the impedance curves in Figure 4.14 are not collapsed by normalization by electrode geometric surface area and are therefore not associated with that interface.



Figure 4.12: Bode plots showing impedance magnitude |Z| (**A**) and phase (**B**) of CNT fibers with varying diameter, measured in normal saline. Impedance magnitude has been normalized by the geometric surface area of the working electrodes. The failure of normalization indicates that both the dominant capacitance and the dominant resistance of the measured system scale super-linearly with CNT fiber electrode diameter.



Figure 4.13: Cyclic voltammetry of CNT fiber with varying diameter in normal saline. Current measurements are normalized to the geometric surface area of the fiber. $V-V_{ref}$ represents the applied difference between electric potential at the working electrode and electric potential at the Ag/AgCl reference electrode. Plotted curves represent results averaged over 4 complete linear voltage sweeps, with a ramp rate of 0.1 V/s.



Figure 4.14: Overlaid curves of area-normalized impedance magnitude |Z| measured for normal saline with CNT fiber working electrodes. The CNT fibers used for measurement were Thin CCNI (A), medium CCNI (B), and Thick CCNI (B). Each data set represents a series of measurements on a single CNT fiber working electrode as the length of the working electrode filament was progressively shortened.

4.4.3 Equivalent Circuit Modeling

The physical meaning of the EIS results shown in Figures 4.11, 4.12, and 4.14 can be better understood through equivalent circuit modeling. Fitting the impedance magnitude and phase curves to a circuit model allows for identification of the origin of the various capacitive and resistive impedances in the spectrum, and provides a framework within which the scaling of impedance with electrode dimension can be explained.

This section explores two approaches to modeling the working electrode/electrolyte interface. The first approach is to model this interface as an essentially 2-dimensional (2D) surface. The second approach takes into account the porous structure of CNT fiber electrodes, modeling the electrochemical interface with a transmission line model that takes into account the resistance associated with ionic diffusion into and out of the structure. The latter approach presents a framework in which the failure of area-normalization demonstrated in Figure 4.12 can be explained.

2D interface models

The basic circuit model that is most commonly applied to describe the physics of an electrochemical electrode is the Simplified Randles Cell model (Figure 4.15 (A)), which consists of a resistor and capacitor connected in parallel, with a second resistor set in series with this parallel combination. The parallel resistor and capacitor represent the electrode/electrolyte interface itself, in which the Helmholtz double layer is represented by the capacitor C_{DL} ; this capacitance is bridged by ions diffusing across the double layer to reach the electrode surface and participate in charge transfer reactions, with an associated resistance R_{CT} . The current flowing between the counter electrode and working electrode must also pass through the bulk of the electrolyte (or heart tissue), through the bulk electrode material, and through any resistive barriers presented by contact resistance between the electrode wires and the measurement apparatus; this represents a set of resistors connected in series which act as a single "baseline" resistance, R_B . Because it is common for the double layer capacitance to behave like a CPE



Figure 4.15: Various circuit models that may potentially describe the equivalent circuit behavior of electrochmical cells. In each case, a dashed line indicates the circuit elements which represent the interface between the electrolyte and the working electrode. A: Simplified Randles Cell, in which the Helmholtz double layer is assumed to act as an ideal capacitor; B: A modified version of the Simplified Randles Cell in which the double layer is assumed to act as a CPE; C: Full Randles Cell, in which the double layer treated as a CPE and in which diffusion arising from ion creation and depletion is represented by a Warburg impedance; D & E: Two of the circuit models used for fitting in the present study, denoted Model 1 and Model 2, respectively; these consist of a parasitic capacitance set in parallel with either a Simplified Randles Cell or a full Randles Cell.

rather than like a pure capacitor, electrochemical circuits are often described using a modified form of the Simplified Randles Cell, shown in Figure 4.15 (B) (Kovacs, 1994; Randles, 1947).

The impedance spectrum produced by a Simplified Randles Cell is shown in Figure 4.16. At low frequencies the frequency-dependent impedance of the capacitor or CPE is extremely high and the current flows predominantly through the series combination of the two resistors, leading to a region of resistive behavior with total impedance $\approx (R_{CT} + R_B)$. As frequency increases the impedance of C_{DL} falls below R_{CT} , leading to the emergence of a capacitive region in which the total impedance is $\approx (C_{DL}(\omega) + R_B)$; in this regime the current flow at the electrode/electrolyte interface itself consists primarily of charging and discharging of the Helmholtz double layer, connected in series with current flow through the bulk materials on either side of the interface. At the highest frequencies the contribution of C_{DL} to this combined impedance becomes minimal and the frequency-independent R_B becomes the dominant component of the total impedance.

Both Pt wire electrodes and CNT fiber electrodes have an impedance spectrum with fea-



Figure 4.16: Bode plot showing the theoretical EIS behavior of a Simplified Randles Cell (see Figure 4.15 (A)) with $R_B = 1 \Omega$, $R_{CT} = 100 \Omega$, and $C_{DL} = 10 \mu F = 10 \mu S^*s$. The spectrum is divided into three regimes of behavior: plateau impedances of $\approx R_B$ and $\approx (R_B + R_{CT})$ dominate at high and low frequencies, respectively, and a frequency-dependent impedance, $\approx (C_{DL} + R_B)$, dominates at intermediate frequencies.

tures similar to that of the Simplified Randles Cell. Every sample measured displays the characteristic behavior of a circuit containing a resistance in series with a capacitance; furthermore, the Randles Cell model is consistent with an impedance spectrum in which a capacitive impedance scaling with electrode surface area (arising from the electronic double layer) gives way at higher frequencies to a resistive impedance (arising from the baseline series resistance) which does not scale with working electrode area. In no case is there an obvious transition to a lower-frequency resistance-dominated plateau as would be expected in a Simplified Randles Cell, but the slight downturn in slope that appears in the modulus curve for Pt wires at the lowest frequencies, accompanied by an increase in phase value, indicates that such a region does exist just beyond the experimental range. For CNT fibers the indication of a low-frequency resistance is fainter, consisting only of a moderate upturn in the phase at low frequencies.

Many electrodes in physiological environments, including platinum electrodes in explanted rodent hearts, exhibit the behavior of a full Randles Cell model rather than that of a Simplified Randles Cell (Ovadia and Zavitz, 1998). In this model, a Warburg impedance element W is placed in series with R_{CT}. This Warburg element represents the pseudocapacitive impedance associated with a depletion or excess creation of ions at the electrode surface over time due to charge transfer reactions, along with the resulting diffusion current caused by this local change in ion concentration; it is modeled as a CPE with n = 0.5. The signature of the Warburg impedance is not clearly evident in the EIS spectra shown in Figures 4.11 and 4.12; nevertheless, fitting was performed using both the full Randles Cell and the Simplified Randles Cell in order to rule out the possibility that ionic diffusion was in fact playing a role in the measured impedance.

The EIS curves depicted in Figues 4.11 and 4.12 exhibit one feature that does not fit the expected behavior of either of the Randles Cell models: the indication of an additional capacitancedominated regime at high frequencies. This implies the existence of an additional capacitive element in a circuit branch parallel to R_B , which in turn implies that it is parallel to the entire electrolyte/electrode system. This may be attributed to a series of so-called parasitic capacitances. Parasitic capacitance is often observed in electrochemical measurements or other high-frequency impedance measurements; it represents capacitance due to charge buildup at contacts between conductors or between nearby conductors within the measurement apparatus and system (Musa *et al.*, 2012). As such, it can be considered a measurement artifact.

The EIS curves of each electrode sample were fit to the two models shown in Figure 4.15 (D) & (E), hereafter referred to as Model 1 and Model 2. Model 1 consists of a Simplified Randles Cell with the double layer modeled as a CPE, in parallel with an additional CPE that represents the parasitic capacitance. Model 2 is the same circuit with a Warburg impedance placed in series with the charge transfer resistance R_{CT} . In these circuits, the double layer capacitance is represented by CPE_{DL} , a circuit element with frequency dependent impedance given by

$$Z_{\rm DL}(\omega) = \frac{1}{Y_{\rm DL}(j\omega)^{\rm n_{\rm DL}}}$$
(4.5)

Likewise, the parasitic capacitance is represented by CPE_P, a circuit element with impedance

$$Z_{\rm P}(\omega) = \frac{1}{Y_{\rm P}(j\omega)^{\rm n_{\rm P}}} \tag{4.6}$$



Figure 4.17: χ^2 values derived from fitting EIS data to the equivalent circuit models shown in Figure 4.15; χ^2 values were averaged separately for each class of CNT fiber working electrodes (**A**) and Pt wire working electrodes (**B**) in explanted porcine hearts and normal saline. For each class of working electrode measured, model 1 provides an adequate fit, indicating that Warburg impedance resulting from diffusion of ions contributes negligibly to the total impedance within the measured frequency range.

The values that can be determined by a successful fitting procedure, therefore, are R_B , R_{CT} , Y_{DL} , n_{DL} , Y_P , n_P , and, in the case of Model 2, W.

2D model fitting results

The individual EIS spectrum for each working electrode in the data sets described by Figures 4.11 and 4.12 were fit to both Model 1 and Model 2. Averaged χ^2 values from these fitting attempts are displayed in Figure 4.17. The average χ^2 values are extremely similar in all cases; this indicates that the simpler model, which excludes the Warburg impedance, adequately describes the observed EIS behavior. When Model 2 was used to fit EIS curves from these electrodes the algorithm was unable to identify a value for the Warburg impedance, resulting in error ranges much larger than the reported fit parameter — this too is a sign that within this frequency range ionic diffusion does not have a measurable impact on the impedance of either species of electrode.

Table 4.1 reports the averaged fit parameters (circuit element parameters) derived from fitting EIS curves to Model 1. The normalized magnitude parameter of the double layer capac-

itance, Y_{DL}/A , is much greater for CNT fiber electrodes than for Pt wire electrodes, by a factor of at least 200. The magnitude of the double layer capacitance depends on the properties of the electrolyte and the (real) surface area of the electrode, but not on electrode material (Franks *et al.*, 2005; Bard and Faulkner, 2001); therefore, this disparity in magnitude implies that the actual surface area of CNT fiber working electrodes (accessed by the electolyte) exceeds the surface area of a Pt wire of the same geometric surface area by more than 2 orders of magnitude. The double layer capacitance is roughly similar for thin and medium CNT fibers, but much greater for the thicker fiber (reflecting the relative magnitudes of the various curves in Figures 4.12 and 4.13); this indicates that the thickest CNT fibers have the greatest available surface area, even after normalizing for geometric surface area.

The power law exponents n_{DL} for CNT fiber and Pt wire fall into a range of 0.88 - 0.97, which is typical for other electrodes made of these materials (Franks *et al.*, 2005; Fung *et al.*, 2010; Musa *et al.*, 2012). Y_{DL}/A for Pt wire in saline is of the same order of magnitude as that reported in (Franks *et al.*, 2005; Musa *et al.*, 2012) for Pt wire in physiological saline (which range from $2x10^{-7}$ to $2x10^{-6}$ S*sⁿ), and Y_{DL}/A for Pt wire in explanted heart tissue is slightly higher (by a factor of ≈4) than the primary capacitance that has been reported for Pt wire electrodes in explanted and perfused rodent hearts in (Ovadia and Zavitz, 1998).

The charge transfer resistance R_{CT} /A for CNT fiber is likewise much larger than that of Pt wire, but only by 1 order of magnitude rather than 2. This parameter should have the same dependence as Y_{DL} /A on the total actual surface area of each electrode exposed to the electrolyte, but it is also influenced by electron transfer kinetics of the two materials. As shown by 4.7, the CNT fiber electrodes used in this study have much slower reaction kinetics than Pt wire. Hence, CNT fiber has a much higher actual surface area than Pt wire, but also a greater charge transfer resistance per unit of actual surface area (possibly greater by an order of magnitude).

The baseline resistance R_B should be composed of several components connected in series; these include the resistance of the bulk electrolyte (saline or heart tissue), a spreading resistance associated with divergence of current from the thin working electrode fiber/wire into the bulk of the electrolyte, the metallic resistance of the portion of working electrode wire/fiber between the electolyte and the Gamry lead electrode, and the contact resistance between that working electrode wire and the metallic Gamry lead. Several things are clear from the fitted values of area-normalized baseline resistance, R_BA : first, R_BA is significantly larger for working electrodes in explanted heart tissue than for working electrodes in normal saline. This may be attributed to a larger resistivity for heart tissue (which for human tissue lies in the range of 2.9 - 5.88 Ω m) than for normal saline (0.75 Ω m) (Franks *et al.*, 2005; Roth, 2000). Second, R_BA is much larger for CNT fibers than for Pt wire, by a significant factor. This is the case even after the known wire resistance between the Gamry lead and the exposed area of working electrode is accounted for; the CNT fibers do have a resistance per unit length that is between 1.5 and 8 times larger than that of the Pt wire, leading to much greater wire resistance R_W , but $R_W \ll R_B$ in each case. Finally, the baseline resistive impedance appears to have a nearly quadratic dependence on the diamter of the CNT fiber working electrodes, leading to a roughly linear dependence for the area-normalized value R_BA in Figure 4.14.

Both of the latter observations, the large difference in R_BA between Pt wire and CNT fiber and the scaling of R_B with CNT fiber diameter, indicate that the contact resistance at the metalto-metal interface between the working electrode wires and the Gamry lead is the dominant component of R_B , at least for CNT fiber. The point of electrical contact was maintained by simple mechanical contact between a length of the working electrode wire and the outer, flat surface of a metallic alligator clip. A series of two-point probe measurements conducted on CNT fiber and Pt wire held between two such contacts with varying wire length revealed that the electrical contact achieved between CNT fiber and the alligator clips by this method was significantly worse than that achieved for Pt wire, that it depends strongly on CNT fiber diameter, and that it can exhibit significant variation. Contact resistances measured for Pt wire for a 0.5 cm length of contact varied from 0.02 - 0.6 Ω ; contact resistance for thick, medium, and thin CCNI fiber for the same length of contact ranged from 1.5 to 150 Ω , from 5 to 500 Ω , and from 17 to 25000 Ω , respectively. This extreme variation in contact resistance may be a consequence of a) the non-uniform surface and b) the malleable structure of the CNT fibers (i.e., their ability to flatten to varying degrees under applied mechanical pressure). The dependence of the contact resistance on fiber diameter may arise from a combination of difference in the tangential surface area of the fiber pressed into the metal or from the fact that electrons need to spread laterally from the contact suurface into the fiber, perpendicular to the alignment of the individual CNTs, in order to reach a fully developed uniform current flow within the fiber. The large values and extreme variation in contact resistance for CNT fibers indicate that simple mechanical contact between the fiber and a flat metal surface is far from an optimal method for achieving electrical contact, especially for precise measurement. In the future, lower and more uniform contact resistance could be achieved by using a higher pressure mechanical crimping technique to thoroughly flatten the fiber structure against the metal surface, or a colloidal metal paint could be applied at the point of contact.

The parasitic capacitance in measurements of CNT fiber electrodes is much greater than in measurements of Pt wire electrodes, by around the same factor as the difference in the double layer capacitance. The origin of this effect is not clear from these results, but this does indicate that charging on the surfaces of the working electrodes (either at the point of contact with the Gamry lead electrode or elsewhere along their surface) is involved.

	R _B *A	Y _P /A	n _P	Y _{DL} /A	n _{DL}	R _{CT} *A
	$(\mathbf{\Omega} * \mathbf{mm}^2)$ $(\mathbf{S} * \mathbf{s}^n)$			$(S*s^n/mm^2)$		$(\Omega * mm^2)$
Pt Wire	826 ± 342	4.49 ± 2.11	0.785	2.56 ± 0.85	$0.937 \pm$	3.48 ± 3.14
Explanted Heart		x10 ⁻⁸	± 0.040	x10 ⁻⁷	0.013	x10 ⁻⁷
Pt Wire	1.11 ± 66	1.30 ± 0.42	1.000	6.82 ± 1.49	$0.896 \pm$	2.48 ± 0.86
Normal Saline		x10 ⁻⁸	± 0.024	x10 ⁻⁷	0.022	x10 ⁻⁷
Medium CNT Fiber 3140 ± 1200 3.62 ± 0.99		0.417	5.29 ± 1.65	$0.889 \pm$	—	
Explanted Heart		x10 ⁻⁶	± 0.024	x10 ⁻⁵	0.025	
Thin CNT Fiber	1640 ± 999	1.92 ± 1.61	0.460	3.31 ± 0.65	$0.971 \pm$	1.36 ± 0.50
Normal Saline		x10 ⁻⁶	± 0.116	x10 ⁻⁵	0.011	x10 ⁻⁶
Medium CNT Fiber	852 ± 408	0.95 ± 0.59	0.548	3.79 ± 0.54	$0.940 \pm$	2.82 ± 0.16
Normal Saline		x10 ⁻⁶	± 0.048	x10 ⁻⁵	0.015	x10 ⁻⁶
Thick CNT Fiber	391 ± 204		_	1.54 ± 1.14	$0.918 \pm$	
Normal Saline		—	—	x10 ⁻⁴	0.024	—

Table 4.1: Average circuit model parameters derived from fitting EIS results from a selection of CNT fiber and Pt wire working electrodes to Model 1 (depicted in Figure 4.15 (C)). Averages were calculated using at least 5 measurements in each category and, in the case of CNT fiber and Pt wire in explanted hearts, 3 different tissue samples. Error values were calculated by considering both the variation in values fit to each separate electrode and the uncertainty reported by the fitting algorithm for each quantity. For some individual electrode measurements certain elements could not be identified by the fit (typically either Y_p , n_p , or R_{CT}), resulting in a fit value with a reported uncertainty much larger than its own magnitude; these values were not included in the averaging. In some cases this was true for all measurements in a given data set, and therefore the value of the element in question could not be determined (R_{ct} for medium CNT fiber in heart tissue, Y_p , n_p and R_{CT} for thick CNT fiber in normal saline).

Porous electrode interface model

The failure of normalization in Figures 4.12 and 4.13 and the disparity of the area-normalized values of Y_{DL} for CNT fiber electrodes of varying diameter reported in Figure 4.1 indicate that electrochemically active surface area of CNT fiber electrodes differs significantly from their geometric surface area. Furthermore, the discrepancy cannot be attributed to mere roughness of the outer surface on the scale of tens or hundreds of nanometers; if this were the case then the ratio of active surface area to geometric surface area would be similar for each of the three classes of CNT fiber and area normalization would have been effective. From this it may be concluded that some significant amount of the internal surface of the porous structure of the fiber is accessed by the electrolyte, contributes to the total capacitance of the Helmholtz double layer, and takes part in any charge transfer reactions giving rise to Faradaic current. In other words, the penetration depth of electrolyte into the fiber is some significant fraction of its thickness.

The interface of an electrolyte with a porous electrode in which the inner pore surfaces are electrochemically active (as should be the case for CNT fibers) can be modeled using a transmission line circuit, as shown in Figure 4.18. Because current can be exchanged at the inner pore surface over a range of pore depths, the distributed resistance through the electrolyte channel connecting the pore to the bulk electrolyte must be taken into account. The inset in Figure 4.19 (A) depicts the transmission line model proposed by Bisquert in Bisquert *et al.* (1999), known as the Bisquert Open model. In this model, the electrochemical circuit at each point along the inner surface of the pore (double layer capacitance bridged by charge transfer resistance) and the resistance through the electrolyte channel into the pore are modeled with a collection of transmission line elements; r_{pore} represents a resistance per unit length for ionic diffusion through the electrolyte into and out of the pores, r_{CT} represents charge transfer resistance for Faradaic current on all of the surfaces within one unit of pore depth, and cpe_{DL} , a CPE with magnitude parameter y_{DL} and power law parameter n_{DL} , represents the Helmholtz double layer over the surfaces contained in one unit of the pore's depth. The resistance through the bulk conductor within the wall of the pore itself is assumed to be small compared to the



Figure 4.18: Cartoon model describing the general case of transmission line circuit behavior in an electroactive pore, reproduced from https://www.gamry.com/application-notes/ElS/use-of-transmission-lines-for-eis/. In this circuit, the impedance χ_1 represents the impedance per unit length of the electrolyte solution in the porous channel, χ_2 represents impedance per unit length for current flow within the conductive pore wall, and ζ represents the impedance of interface at the face of the electrolyte and the pore wall. Z_A and Z_B represent the impedance of interface at the face of the electrode outside of the pore and at the base of the pore, respectively. The Bisquert Open Model depicted in Figure 4.19 (A) is a specific case of this model in which $\chi_1 = r_{pore}$, ζ is a parallel combination of r_{ct} and cpe_{DL} , and Z_A , Z_B , and χ_2 are neglected.

resistance through the electrolyte, and is neglected.

In order to model the effect of fiber porosity on the equivalent circuit behavior of the system, EIS results from CNT fiber electrodes were fit to the model depicted in Figure 4.19 (A), hereafter referred to as Model 3. This model is similar to Models 1 and 2, but with a Bisquert Open transmission line used to represent the circuit behavior of the electrode/electrolyte interface. A Bisquert Open transmission line is typically used to model electrodes in which a porous layer with a certain depth L is placed over an insulating base which does not interact with the electrolyte; this model is appropriate in the case of CNT fiber because in this case there is no "base" at all, and the entirety of the fiber structure accessed by the electrolyte serves as the electrochemically active "wall" of the pore. The depth L in this case represents the penetration depth of the electrolyte into the fiber. L cannot be determined from fitting; it must be measured independently by some other means.

The average goodness of fit achieved by fitting CNT fiber electrode data to Model 3 is compared in Figure 4.21 to the goodness of the fits achieved using Models 1 and 2; average parameters derived from these fits are provided in Figure 4.2. EIS spectra from thick and medium CNT fiber are much better fit by this model than by models based on a simpler, solid electrode in-



Figure 4.19: A: Circuit model representing the interface between CNT fiber and electrolyte as a Bisquert Open transmission line model, appropriate to a porous electrode with high conductivity in the pore walls. B: Sample Bode plot of impedance magnitude and phase from a CNT fiber in normal saline, fit by both Model 1 and Model 3; the latter is able to achieve better fitting with the shape of both curves.



Figure 4.20: Theoretical impedance spectrum calculated using the fit parameters derived from Model 3 shown in Figure 4.19, overlaid with two curves calculated using identical parameters but with $r_{pore}L$ arbitrarily increased by 10x and 100x.



Figure 4.21: Average χ^2 derived from fitting EIS data from CNT fiber working electrodes in both explanted porcine hearts and normal saline to Model 1 and Model 2, given in Figure 4.15 (D) & (E), and Model 3, given in Figure 4.19. For medium and thick CNT fiber Model 3, which takes porous electrode structure into account, produces a significantly better fit; there is minor improvement in goodness of fit for thin CNT fibers as well.

terface; the improvement for thin CNT fiber is not as meaningful. Qualitatively, it can be seen from Figure 4.19 (B) that the impedance spectrum of model 3 is able to reproduce some of the features observed in CNT fiber EIS curves better than Model 1; this is particularly true in the region of intermediary behavior between the frequency ranges in which either R_B or the double layer capacitance dominate the impedance. The value of the product r_{pore} *L has a significant effect on the impedance in this range of frequencies, as illustrated by Figure 4.20.

	R _B *A	Y _P /A	n _P	y _{DL} * L/A	n _{DL}	r _{pore} *L*A	r _{ct} *A/L
	$(\Omega * mm^2)$	$(S*s^n/mm^2)$		$(S*s^n/mm^2)$		$(\mathbf{\hat{\Omega}} * \mathbf{mm}^2)$	$(\Omega * mm^2)$
Medium CNT Fiber	2430 ± 1080	1.35 ± 0.91	0.474	5.79 ± 1.83	$0.932 \pm$	5110 ± 1660	
Explanted Heart		x10 ⁻⁶	± 0.044	x10 ⁻⁵	0.012		
Thin CNT Fiber	1390 ± 1102	1.43 ± 1.11	0.450	3.44 ± 0.10	$0.970 \pm$	298 ± 251	
Normal Saline		x10 ⁻⁶	± 0.055	x10 ⁻⁵	0.044		
Medium CNT Fiber	765 ± 413	—	—	3.85 ± 0.81	$0.944 \pm$	372 ± 69	—
Normal Saline				x10 ⁻⁵	0.031		
Thick CNT Fiber	378 ± 173	1.16 ± 0.36	1.000	10.08 ± 0.28	$0.928 \pm$	190 ± 43	
Normal Saline		x10 ⁻⁹	± 0.007	x10 ⁻⁵	0.029		

Table 4.2: Average circuit model parameters derived from fitting EIS results from CNT fiber working electrodes to Model 3, depicted in Figure 4.19 (A), which takes into account electrolyte penetration into a porous electrode. Averages were calculated using at least 5 measurements in each category and, in the case of CNT fiber and in explanted hearts, 3 different tissue samples. Error values were calculated by considering both the variation in values fit to each separate electrode and the uncertainty reported by the fitting algorithm for each quantity. The fitting algorithm failed to determine a value for r_{CT} in all cases. Note that the magnitudes of y_{DL} and r_{pore} are both given in terms of the pore depth L, which must be determined independently.

The physical interpretation of the difference between the transmission line circuit behavior of a porous electrode and the circuit behavior of a planar electrode is that the tortuosity of the pores hinders ions in the electrolyte from diffusing between the bulk electrolyte and the inner structure of the fiber. For very high frequencies charging and discharging of the double layer occurs extremely quickly, with a small total charge $Q(\omega)$ attained by the double layer capacitor in each cycle and minimal diffusion of ions required to achieve this charge; essentially, positive and negative ions already within the pores of the fiber move short distances as they change place in the cyclic formation of positive or negative double layers on the pore wall. Current flows through the electrolyte and electrode as a result of this cyclic polarization, and the resistance to that current consists only of the resistance to diffusion of electrons in the conductor and the resistance to movement of ions on a nanometer scale; i.e., the bulk resistances which sum to R_B . At lower frequencies more total charge must flow over the time period of the oscillation if the same current amplitude is to be maintained, so the buildup of the polarized layer requires more significant diffusion of ions through the pores; the total impedance in this frequency regime includes not only R_B but also the pore diffusion resistance r_{pore} and some impedance Z_{DL} arising from the buildup of the double layer itself. Finally, below a certain threshold frequency, the frequency-dependent capacitive impedance Z_{DL}, which represents the energy barrier of adding further charge to the already polarized double layer over the time period of each cycle, becomes overwhelmingly dominant over the other impedances, and the circuit behavior becomes similar to that of a simple planar electrode.

Penetration depth and diameter scaling

The improvement that can be achieved in fitting the EIS behavior of CNT fibers by using a transmission line model provides confirmation that the porous 3D structure of the fiber is involved in electrochemical interactions. Unfortunately, the circuit parameters determined from this fitting do not provide a quantitative measurement of the electrode properties unless they can be coupled with an understanding of the penetration depth L. An estimation of L can be made by determining the fraction of the CNT fiber's total internal surface area that is electrochemi-



Figure 4.22: Y_{DL} from thin, medium, and thick CNT fiber (derived from fits to Model 1) plotted against either geometric surface area (A & B) or total electrode volume (C & D). The data is plotted on either a linear (A & C) or a log scale (B & D). Overlaid lines in the log scale plots indicate the slope for linear scaling. Measurements were performed in normal saline; in each case the length of CNT fiber exposed to the saline was controlled by encasing the electrode in a class capillary with the end exposed, as shown in Figure 4.6 (C).

cally active. This can be done by examining how the total capacitance of the Helmoltz double layer (as measured by Y_{DI}) varies with fiber electrode volume.

When performed with as-spun fiber (that is, CNT fiber produced according to the procedure described in Section 2.4 with no additional treatment steps) the scaling of interface properties with fiber diameter revealed an unexpected feature of CNT fiber electrochemical behavior. Figure 4.22 plots the magnitude of Y_{DL} (obtained from measurements in normal saline, fit to Model 1) against both the geometric surface area and total working electrode volume for thin, medium, and thick as-spun CNT fibers with varying working electrode length. The double layer capacitance has a super-linear scaling with with geometric surface area, as would be expected if there is significant infiltration of the electrolyte into the porous structure; however, the scaling with total electrode volume is also super-linear. This result can only be explained by differences in the accessibility of the internal porous surface between thin, medium, and thick CNT fibers. Naively, the difference in accessibility of the internal fiber structure may be explained by one of two things: a difference in the wettability of the CNT sidewalls or a structural difference in porosity or pore size. The former explanation seems unlike, given that the fibers in question are composed of the same species of CNT, from the same acid solution, and fabricated with identical processing steps. The latter explanation is a possibility that cannot be ruled out, in spite of the similarity in fabrication and in measured density of the fibers. However, a third explanation exists: that the internal pores of as-spun fibers are not in fact void of other materials when the tests are carried out. In fact, this is known to be the case for wet-spun CNT fiber: some residual aqueous acid remains in the interstitial spaces of the fiber in spite of the removal of acid during the coagulation step and subsequent washing and drying of the fiber (Ericson *et al.*, 2004; Behabtu *et al.*, 2013). The results presented in the following section demonstrate that the presence or absence of this residue, or of other liquids in the porous internal structure of CNT fiber, does indeed have a strong effect on wettability and electrochemical performance of the fiber.

4.5 Effect of CNT fiber wettability on electrochemical properties

Sections 4.4.2 and 4.4.3 show that CNT fiber electrodes can have electrochemical impedance far lower than that of smooth metal electrodes, that this low impedance is primarily due to large double layer capacitance, and that this large capacitance results from the fact that some amount of the internal surface structure of the fibers is accessed by the electrolyte fluid and participates in electrochemical current exchange. This implies that the performance of CNT fiber electrodes in electrochemical applications is strongly dependent on the wettability of this internal porous structure with respect to the electrolyte. If the wettability is high, capillary forces will drive the electrolyte into all of the pores to which it has an open channel, and the interfacial surface area will be maximized; if wettability is low then capillary forces will prevent the electrolyte from flooding any pores below a certain size, the interfacial surface area will be minimized, and the electrochemical impedance will be high.

Experimental samples from several batches of CNT fiber exhibited two extremes of behavior: some samples from each batch exhibited high double layer capacitance and low impedance in EIS measurements and large CSC in CV tests; other samples from the same batches exhibited very low double layer capacitance, much higher impedance in the range of frequencies below 100 Hz, and drastically lower CSC. There were no observable differences in diameter or density between the two groups of fiber in each case, but there was a small (15-40%) increase in the DC resistivity of the group of samples which exhibited lower capacitance and higher EIS impedance.

The essential difference which leads reproducibly to this divergence in properties is the set of conditions which has been applied to the fiber after fabrication, in particular the conditions in which the fiber has been stored and aged. Fibers which have been stored in sealed plastic containers after their date of fabrication exhibit consistently high double layer capacitance; fibers from the same batch which have been exposed to lab air for a period of 6 or more months between fabrication and the month in which the electrochemical tests were performed exhibit decreased double layer capacitance and charge storage capacity, along with slightly increased impedance. The resistivity and density of as-spun fibers and of fibers that have been aged in this manner, referred to here as dessicated fibers, are given in the first 4 columns of Table 4.3; CSC/A and Y_{DL}/A (derived from fits of EIS in saline using Model 1) for these fibers are given in the first 4 columns of Table 4.4.

In order to understand the mechanism by which different aging conditions might affect the electrochemical capacitance of CNT fiber in this manner, it is important to recall the fabrication process used to produce this material: wet-spun CNT fibers were derived from a highconcentration solution of CNTs in ClHSO₃ acid that was extruded into acetone; the acetone provides a solvent channel for the acid to diffuse away, causing the CNTs to densify and solidify into a fiber filament; these fibers are subsequently washed with water and dried at a temperature of 115 °C. It has previously been observed that wet-spun CNT fibers retain some amount of residual aqueous acid content after this fabrication, washing, and drying process, and that this residual acid is responsible for electrically doping the fiber (Ericson *et al.*, 2004; Behabtu *et al.*, 2013). This aqueous residue is fairly stable; heating the fiber at temperatures of 100-200 degrees does not remove the doping effect. Annealing fiber at high temperatures (800-1000 °C) appears to remove some or all of this residue; this can be observed primarily from an increase of 3x-10x in fiber resistivity after annealing.

Based on the effect of fiber aging on electrochemical properties it is reasonable to hypothesize that the bimodal variation in the electrochemical properties of CNT fibers is due to a change in effective wettability, and that this change in wettability arises from a change in internal water content. The CNT fibers which exhibit low capacitance are those which have been stored in conditions that allow for a gradual evaporation or leeching of aqueous acid out of the fiber. Removal of dopant from the CNT structure explains the overall increase in resistivity for those fibers which had been stored outside of sealed conditions and the lack of such increase for those that had been stored in sealed spools (see Table 4.3). This increase in resistivity is too small to explain the observed increase in electrochemical impedance, but it does point to a loss of aqueous dopant.

The loss of water from internal pores of the fiber might affect the wettability, or more precisely the accessibility of the internal structure with respect to aqueous electrolytes, in the manner depicted in Figure 4.23. If the fiber has a dry internal structure and a moderately hydrophobic surface, the small channels into and throughout its structure may be inaccessible to surrounding water. On the other hand, if water already exists in the pores in the form of trapped droplets or flooded channels then an aqueous solution in which the fiber is submerged may come into contact with it, forming fluid channels that connect the internal pores to the bulk of the surrounding aqueous environment. Once this occurs, ions in the aqueous solution can diffuse into the porous structure of the fiber, and it will become electrochemically active.

In this proposed picture, therefore, a CNT fiber will present a large amount of surface area accessible to an electrolyte solution, and thus achieve a low electrochemical contact impedance, only if it is already pre-wetted by solvent. Due to their method of fabrication wet-spun CNT fibers are generally wetted in this way with aqueous acid residue when they are created. The loss of electrochemical capacitance observed for the fibers stored outside of sealed conditions



Figure 4.23: Cartoon model depicting how pre-existing water content may influence the accessibility of fiber pore structure by an external aqueous electrolyte. A totally dessicated fiber structure (A) or a fiber in which the outer layers of structure are dessicated (C) may remain inaccessible to external electrolyte due to the hydrophobicity of CNT surfaces and the small sizes (<1 μ m) of the porous channels into the fiber. B: If many fiber pores are already filled with water, there may be many points of ingress for an external electrolyte to access those pores without having to overcome a significant energy barrier due to surface tension. D: Applying a large bias voltage between a dessicated fiber electrode and the external electrolyte can induce electrowetting.

may be due to water gradually evaporating or wicking out of these channels over a long period of time, or perhaps due to water being depleted in the area near the outer skin of the fiber such that a fluid connection can no longer occur between the internal wetted surface and an external aqueous electrolyte (see Figure 4.23 C). Furthermore, If it is indeed the case that the number of pre-wetted internal channels affects the total area of the electrochemical interface, it is possible that small variations in water content (leading to small changes in overall density) lead to large variations in effective wettability and thereby produce the discontinuities in the scaling shown in Figure 4.22.

4.5.1 Change in wettability due to annealing or dessication of CNT fiber

In order to test the above hypothesis, EIS and CV measurements were performed on CNT fiber electrodes before and after annealing at 1000 °C. Columns 5 & 6 of Table 4.4 report CSC/A and Y_{DL}/A (derived from fitting to model 1) for 3 fiber batches: two sets of CNT fiber fabricated with Tuball CNTs and one fabricated with Unidym CNTs (insufficient material from the CCNI CNT fiber batches discussed in Sections 4.4.2 and 4.4.3 was available for annealing be applied). The fiber samples chosen for annealing had been stored in sealed plastic containers, and are assumed to have retained the properties of as-spun fiber. Table 4.3 reports resistivity and density of these fibers before and after annealing. The change in resistivity of the fiber (approximately a factor of 3 in each case) indicates a loss of dopant consistent with the removal of aqueous acid. In each case the annealing process decreased the double layer capacitance and charge storage capacity of the fiber, indicating that much less total surface area is accessible by the electrolyte; the magnitude of the change was smallest in the case of the Unidym fiber, being less than a factor of 2. For Batch 1 Tuball, fiber dessicated by aging in the lab actually attained a much lower CSC value than annealed fiber; this may be an indication that 1 hour of annealing at 1000 °C is not sufficient to remove all water from the fiber structure.

	As-Spun Fiber		Dessicate	d Fiber	Annealed Fiber		
Fiber Batch	Resistivity Density		Resistivity	Density	Resistivity	Density	
	$(\mu \mathbf{\Omega cm})$	(g/cm³)	$(\mu \mathbf{\Omega cm})$	(g/cm³)	$(\mu \mathbf{\Omega cm})$	(g/cm ³)	
Thin CCNI	61.22 ± 28.40	1.31 ± 0.08	82.40 ± 37.95		—	—	
Fiber							
Medium	49.79 ± 14.26	1.29 ± 0.10	64.01 ± 18.21				
CCNI Fiber							
Thick CCNI	49.51 ± 19.15	1.27 ± 0.10	57.90 ± 22.49		—		
Fiber							
Tuball Fiber	50.39 ± 3.41	1.10 ± 0.04	67.62 ± 4.80	1.09 ± 0.05	124.3 ± 10.8	1.06 ± 0.11	
Batch 1							
Tuball Fiber	43.85 ± 5.57	1.50 ± 0.16	61.22 ± 7.72	1.43 ± 0.13	—	—	
Batch 2							
Tuball Fiber	44.98 ± 7.11	1.31 ± 0.14	57.35 ± 9.12	1.38 ± 0.17	148 ± 7.1	1.03 ± 0.11	
Batch 3							
Unidym	105.7 ± 2.5	0.71 ± 0.02	—		328.7 ± 12.1	0.57 ± 0.01	
Fiber							

Table 4.3: Resistivity and volumetric density measured for fiber samples that were stored in sealed containers after fabrication ("As-Spun"), stored in open air for 6 or more months ("Dessicated") or annealed in an atmosphere of Ar & H at 1000° C for 1 hour (plus heating and cooling ramp time). Blank cells indicate conditions in which that fiber species has not yet been tested.

	As-Spun Fiber		Dessicated Fiber		Annea	led Fiber	Electrowetted Fiber	
Fiber	CSC/A	Y _{DL} /A	CSC/A	Y _{DL} /A	CSC/A	Y _{DL} /A	CSC/A	Y _{DL} /A
Batch	$(\mu C/mm^2)$	$(\mu Ss^n/mm^2)$	$(\mu C/mm^2)$	$(\mu Ss^n/mm^2)$	$(\mu C/mm^2)$	$(\mu Ss^n/mm^2)$	$(\mu C/mm^2)$	$(\mu Ss^n/mm^2)$
Thin								
CCNI	102	5.9 ± 2.1	2.0	2.5 ± 0.2			78.3	33.1 ± 6.5
Fiber								
Medium								
CCNI	194	22.6 ± 3.7		_		_	103	37.9 ± 5.4
Fiber								
Thick								
CCNI	758	96.5 ± 5.0	9.3	12.6 ± 0.9		_	332	154 ± 114
Fiber								
Tuball								
Fiber	51.7	17.9	1.2	_	16.6		390	212
Batch 1								
Tuball								
Fiber			5.2	_		_	473	173
Batch 2								
Tuball								
Fiber	22.8	21.4	14.3	_	13.3	9.5	495	192
Batch 3								
Unidym								
Fiber	205	80.5		_	140	64.4	483	253

Table 4.4: Charge storage capacity and double layer CPE magnitude, normalized by geometric surface area, measured for fiber samples that were stored in sealed containers after fabrication ("As-Spun"), stored in open air for 6 or more months ("Dessicated"), annealed in an atmosphere of Ar & H at 1000° C for 1 hour (plus heating and cooling ramp time), or re-wetted by conditioning in normal saline in which working potential was ramped to ± 5 V ("Electrowetted"). In each case, the electrowetting procedure was performed on previously annealed fiber if available, and otherwise on dessicated fiber. Blank cells indicate conditions in which that fiber species has not yet been tested.

4.5.2 Electrowetting of CNT fibers

The prospect that storage conditions, aging, or other post-processing of CNT fibers can have such a large effect on their electrochemical properties could present a major challenge to their use in high-performance electrode applications; fortunately, this aging/drying process can be reversed by a simple conditioning step: water can be introduced or re-introduced into the structure of a dessicated CNT fiber using an electrowetting procedure as described in (Mugele and Baret, 2005) and applied to CNT fiber structures in (Dhindsa *et al.*, 2006; Zhu *et al.*, 2006). When a potential difference is applied between an electrode and a surrounding electrolyte an electronic double layer is formed at the interface; the electrostatic force attracting the ions in that layer to the electrode material surface changes the effective interfacial tension. If there is another fluid in contact with the electrode or within its pores, such as air, this change in effective interfacial tension leads to a change in electrolyte contact angle and increased wetting of the electrode by electrolyte; increasing the wettability of porous structures beyond a given threshold can induce spontaneous capillary-driven filling of the pores. Once these pores are flooded the bias voltage can be removed and the fluid may remain in place due to the thermo-dynamic barriers to de-wetting; this process is illustrated in Figure 4.23.

Preliminary electrowetting procedure

A modified form of the procedure for a CV measurement was used to electrowet CNT fibers: CNT fiber working electrodes were immersed in saline as a part of the standard 3-electrode potentiostat configuration, and working electrode potential was swept linearly from 0 V (with respect to V_{ref}) to an upper limit V_{max} , then to a lower limit $-V_{max}$, and finally back to 0 V. The efficacy of this treatment can be assessed by comparing the electrochemical properties of the fiber electrode before and after it is applied. Figure 4.24 A overlays CV curves obtained from a previously annealed CNT fiber electrode before and after electrowetting via a CV sweep with a nominal V_{max} of 5 V (the actual voltage limit was not well-controlled; see discussion below). Initially the CNT fiber has a low CSC due to dessication from annealing. After a high-amplitude voltage sweep cycle is applied the next standard CV measurement sweep within the water window results in a large positive (anodic) current with subsequent cycles moving towards a symmetric, capacitive, steady-state CV curve; Figure 4.24 B shows the first 5 cycles after electrowetting, and Figure 4.24 A compares the subsequent 5 cycles, in the steady state, to the initial measurment on annealed fiber. All subsequent CV measurements follow this steady-state curve.

This increase in CSC must arise from the creation of, or some significant increase in the magnitude of, a capacitive current channel at the interface between CNT fiber and electrolyte; under the assumption that the primary capacitance is still the double layer capacitance, this implies that the amount of wettable surface area is significantly and stably increased by electrowetting at V_{max} of 5 V. Figure 4.24 C shows a comparison of EIS measurements on annealed fiber before and after electrowetting; this comparison demonstrates that electrowetting greatly increases Y_{DL} without affecting R_B , i.e., that the electrode interface has greatly increased in actual surface area, with no change in the resistance of the bulk electrolyte or of the CNT fiber itself. Columns 7 and 8 of Table 4.4 provide average values of CSC/A and Y_{DL} /A for CNT fibers after electrowetting with the above procedure.

The large transient anodic current observed in Figure 4.24 B during the first sweep to positive voltages after electrowetting may be understood as an artifact resulting from the manner in which electrowetting was achieved. The electrowetting procedure begins with a sweep to a large positive voltage, which causes attraction of negatively charged ions (CI^-) to the electrode, decreases the surface tension between the locally electronegative solution and the CNT electrode surface, and induces capillary wetting of the internal porous fiber structure. This is followed by a sweep to negative voltages, which causes a net diffusion of CI^- out and a net diffusion of Na⁺ into the flooded fiber channels; the voltage is then returned to 0 V, leaving an excess of positive ions in the fiber structure. When a subsequent CV sweep begins and a positive voltage is applied at the fiber electrode the excess positive ions are driven out into the surrounding solution, resulting in a large transient anodic current out of the CNT fiber due to ionic diffusion.



Figure 4.24: A: CV measurement performed on an annealed CNT fiber working electrode (Batch 3 Tuball fiber) before and after undergoing an electrowetting procedure. Electrowetting was carried out by sweeping electrode potential linearly at 1 V/s from 0 V to +5 V, then to -5 V, and finally back to 0 V (with respect to V_{ref}). The initial CV measurement carried out immedaitely after this procedure, shown in B, exhibits very large anodic current during the first sweep from 0 V to 0.5 V, which is interpreted as a consequence of the fiber pores containing an excess of Na⁺ after the sweep to negative potentials in the second half of the electrowetting procedure; the post-electrowetting CV curve shown in A was carried out immediately after the 5 cycles shown in B, and represent a stable state. CSC/A increased from 1.33 ×10⁻⁵ C/mm² to 49.5 ×10⁻⁵ C/mm² after electrowetting, indicating a large increase in total capacitance. C: EIS specta measured for the same fiber before (red squares) and after (blue circles) electrowetting is applied. Y_{DL} /A increased from 0.95 ×10⁻⁵ S*sⁿ_{DL}/mm² to 19.2 ×10⁻⁵ S*sⁿ_{DL}/mm², resulting in an order of magnitude decrease in the capacitive impedance of the electrode interface at low frequencies.



Figure 4.25: CV curves obtained for a sample of dessicated thick CCNI CNT fiber after electrowetting procedure is applied, and again after the sample was removed from saline and heated in an oven at 115 °C for 12 hours. The increase in apparent capacitance induced by electrowetting is almost entirely retained.

Stability of CNT fiber properties after electrowetting

Once water has been introduced to the internal structure of the CNT fiber its presence is relatively stable in normal lab conditions; the degradation of wettability over time that results in the properties of dessicated fiber reported in Table 4.4 only occurs after a long period of exposure to open air, accompanied by close contact with a hygroscopic paper container (further study would be required to determine which of these factors, time or capillary wicking, was more influential). Figure 4.25 displays the results of CV measurement performed in normal saline on a dessicated CNT fiber before electrowetting, after electrowetting, and once more after the fiber had been removed from saline and dried overnight in an oven at 115 °C. The decreased current and CSC observed after oven heating indicates that the fiber structure is slightly less accessible to the saline; this suggests that a certain amount of the water introduced by electrowetting has been removed, but that the majority of it remains, or at least that it is still present in a majority of the channels that are allowing saline access to the internal structure.

4.5.3 Specific properties of CNT fiber electrodes after electrowetting treatment

We may now return to the scaling analysis attempted in Figure 4.22 in order to determine, first, whether and to what extent the electrowetting procedure diminishes the differences in effective wettability of structure that are apparent in measurements of as-spun fiber, and second, the



Figure 4.26: Y_{DL} from thin, medium, and thick CNT fiber (derived from fits to Model 1) plotted against either geometric surface area (A & B) or total electrode volume (C & D). The data is plotted on either a linear (A & C) or a log scale (B & D). Overlaid lines in the log scale plots indicate the slope for linear scaling. Measurements were perfomed in normal saline using electrowetted fiber; in each case the length of CNT fiber exposed to the saline was controlled by encasing the electrode in a class capillary with the end exposed, as shown in Figure 4.6 (C).

proportion of the total electrode volume which is accessed by an aqueous electrolyte in the case of an electrowetted fiber. Figure 4.26 plots the double layer capacitance (determined by fitting EIS results with model 1) from CNT fibers of different exposed lengths and different diameters used as working electrodes in normal saline. In contrast to the variety of scaling behaviors exhibited by as-spun fibers in Figure 4.22, the data for electrowetted fibers falls onto a single master curve of capacitance vs. electrode volume; furthermore, this curve has linear scaling behavior (a power law fit to the aggregated data results in a power law of 1.02, with an R² value of 0.9709).

Figure 4.26 implies that, for electrowetted fiber in the range of diameters studied, normal saline is able to access portions of the porous structure extending through the full thickness of the fiber; electrochemical current exchange, including the formation of the Helmholtz double layer, occurs throughout this wetted portion of the porous structure. We may presume that

there are also portions of the fiber's internal structure which are not accessed by saline, or which perhaps are accessed by the saline but which do not contribute to the effective capacitance of the Helmholtz double layer - for example, the spaces between surfaces of two neighboring CNTs may be smaller than the characteristic thickness (Debeye length) of the double layer. Given what is known about the sub-micron geometry of the fiber, namely that the CNTs are arranged in well-aligned, tightly packed filaments with less dense packing between separate filaments, it is possible that the interstitial spaces between the filaments is wetted by the saline, but that the interstitial spaces between individual CNTs within the filaments is not.

The linear scaling of double layer capacitance with fiber volume revealed in Figures 4.26 implies that the value of L appropriate to use in fitting the EIS curves of electrowetted fiber to Model 3 is the radius of the fiber itself. Average values of fitted circuit model parameters for electrowetted fibers based on this conclusion are given in Table 4.5. With this appropriate estimation of the parameter L, we can finally use these fitted parameters to draw conclusions about the specific equivalent circuit properties of the CNT fiber/saline interface.

	R _B *A	Y _P /A	n _P	y _{DL} /A	n _{DL}	r _{pore} *A	r _{CT} *A
	$(\Omega * mm^2)$	$(S*s^n/mm^2)$		$(S*s^n/mm^3)$		$(\mathbf{k} \hat{\mathbf{\Omega}} * \mathbf{m} \mathbf{m})$	$(\Omega * mm^3)$
Medium CNT Fiber	2430 ± 1080	1.35 ± 0.91	0.474	4.93 ± 1.71	$0.932 \pm$	435 ± 154	—
Explanted Heart		x10 ⁻⁶	± 0.044	x10 ⁻³	0.012		
Thin CNT Fiber	1390 ± 1102	1.43 ± 1.11	0.450	4.89 ± 1.13	$0.970 \pm$	42.3 ± 36.9	—
Normal Saline		x10 ⁻⁶	± 0.055	x10 ⁻³	0.044		
Medium CNT Fiber	765 ± 413		_	3.28 ± 0.83	$0.944 \pm$	31.7 ± 7.4	—
Normal Saline				x10 ⁻³	0.031		
Thick CNT Fiber	378 ± 173	1.16 ± 0.36	1.000	4.83 ± 0.94	$0.928 \pm$	8.51 ± 2.53	
Normal Saline		x10 ⁻⁹	± 0.007	x10 ⁻³	0.029		

Table 4.5: Average circuit model parameters derived from fitting EIS results from CNT fiber working electrodes to Model 3, depicted in Figure 4.19, with pore depth L equal to the radius of the fibers in question.

 y_{DL} is a parameter with units of (CPE) capacitance per unit length, and represents the amount of double layer capacitance afforded by all of the surface available within each unit of penetration depth into the porous structure of the fiber; y_{DL} /A may therefore be considered to be the total amount of double layer capacitance afforded by all available surfaces within a unit volume of a fiber (after conditioning with the electrowetting procedure). The fit parameters reveal that in this appropriately normalized metric, electrowetted CCNI fibers are roughly equivalent to one another. The total amount of surface area that can be accessed by aqueous electrolyte within the porous structure of these fibers is equivalent on a per unit volume basis (and, given the similarity in the densities, on a per mass basis as well).

 r_{pore} is a parameter with units of impedance per unit length, and represents the resistance associated with ionic diffusion along one unit length of the parallel arrangement of all of the electrode's pores; $r_{pore}A$ represents the resistance over the same unit length of pore depth for a parallel arrangement of all of the pores in a single unit of geometric surface area on the electrode surface - hence, it is a resistivity for the flow of ionic current through the porous structure of the fiber. The fitted results indicate that the pores are somewhat more accessible for larger diameter fiber (although there is too much uncertainty in the error of the value for thin fiber to conclude that this is necessarily a trend with diameter.) Interestingly, there is a significant difference between the fitted values of $r_{pore}A$ for medium CNT fiber in explanted heart tissue and normal saline. This is somewhat surprising given the similarity in y_{DL}/A for the same two cases, which indicates that there are not unexpected differences in ionic content for the two electrolytes. This could be related to a decrease in diffusivity in the case of the extracellular heart tissue; the possible source of this effect, and the question of whether or not the same difference would appear *in vivo*, are not clear from these results.

Given that the penetration depth L is on the same order as the fiber radius in electrowetted CNT fibers, one caveat must be made concerning the analysis of these fibers using the Bisquert Open model. Although Model 3 does provide a good fit for the EIS of CNT fibers, the Bisquert Open model was derived to describe planar electrodes in which the pores are perpendicular to the electrode surface and in which every slice of electrode "depth" is uniform in terms of total porous surface area. In a cylindrical porous structure there is more total pore volume and more total porous surface area at shallow penetration depths than there is at greater penetration depths. A more sophisticated way of modeling the CNT fiber interface, therefore, would be one which allows for depth-dependent values of $r_{pore}A$, y_{DL}/A , and $r_{CT}A$.

The fact that electrochemical performance of CNT fiber electrodes appears to scale with the total volume of those electrodes rather than with their outer surface area (after appropriate treatment) allows for increased efficiency in the design and fabrication of electrodes using this material, as it may obviate additional design steps intended to increase geometric surface area. The electrowetting procedure allows for the electrochemical properties of CNT fiber electrodes to be improved and standardized after fabrication. This procedure may also be particularly important if it is observed in the future that annealing (which removes residual acid) also reduces CNT fiber toxicity. If annealing of CNT materials before implantation in the body is discovered to be necessary, electrowetting can be applied as part of a two-step processing procedure in order to preserve or even enhance the electrochemical properties of the material.

4.5.4 Limitations and drawbacks of current electrowetting procedure

After the data presented above was collected, two sets of experiments revealed drawbacks inherent in the method that was used for application of electrowetting to CNT fiber. Both are related to problems encountered at high voltages. Analysis of these problems provides clues as to how the a "second generation" electrowetting procedure should be designed.

Poor control/measurement of V_{max}

The wettability of surfaces induced by electrowetting, as measured by either interfacial tension or contact angle, typically increases quadratically with applied potential until some plateau is achieved; this phenomenon is known as contact angle saturation (Mugele and Baret, 2005). Measurements of CNT fiber CSC and Y_{DL} post-electrowetting are not direct surrogates for measurement of achieved contact angle, in that the scaling of these quantities with contact angle or with effective surface tension is not currently known; however, it is straightforward to assume that they are correlated, and that extent of surface that can be wetted using this technique will ultimately be limited by the phenomenon of contact angle saturation.

In order to assess the dependence of final properties on applied voltage, the electrowetting procedure described above was performed in stages on several annealed and several dessicated fibers, using progressively greater values of V_{max} in each stage. Figure 4.27 A plots the average specific CSC of these CNT fiber electrodes as determined by standard CV tests (5 complete cycles with $V_{max} = 0.5$ V, within the water window) which were performed between these higher-limit potential sweeps. For applied voltages of 1.5 V or less the increase in CSC is negligible; for larger values of V_{max} the treatment results in progressively larger values of CSC, indicating that an increasing amount of internal fiber surface is being accessed by the electrolyte, with an apparent plateau when large potentials are applied. The range of intermediate CSC values attained at intermediate potentials implies that some but not all of the pores are wetted at those potentials, or that the fluid penetrates more deeply into all of the pores as applied potential is increased.

The basic shape of the post-electrowetting CSC curves in Figure 4.27 A is indeed similar to the scaling of contact angle with applied voltage that is commonly observed for electrowetting (Mugele and Baret, 2005; Zhu *et al.*, 2006), which may serve as an indication that contact angle saturation was achieved. Unfortunately, this method of assessing the effect of V_{max} , and indeed the use of the Gamry potentiostat as a tool to apply the electrowetting procedure in the first place, has a fundamental flaw: for each of the samples shown in Figure 4.27 A an instrument limitation arose which prevented the controlled application of large potentials.

In a 3-electrode potentiostat the potential difference $V - V_{ref}$ between the working and reference electrodes is some fraction of the total potential difference between the working and counter electrodes; the Gamry 600 potentiostat is able to apply potential differences of up to ± 22 V between the working and counter electrodes, but is unable to apply currents larger than 600 mA in total (according to manufacturer's specifications). If the total impedance between the working electrode and the counter electrode is sufficiently small, this limit on applied current effectively lowers the limit on achievable applied potential. In each of the the progressive
electrowetting trials depicted in Figure 4.27 A, $V-V_{ref}$ suffered from this limitation once the applied $V-V_{ref}$ exceeded a threshold of ≈ 2.75 V (with some variation from sample to sample). Beyond this point, the potential was not well-controlled. In Figure 4.27 A, voltage sweeps with well-controlled voltage are indicated by open symbols, and sweeps in which the voltage exceeded limits of good instrument control are indicated by solid symbols. The majority of the change in wettability evidently occurs in the latter regime; it is apparent, therefore, that the degree of wetting induced by each successive high-voltage sweep continued to increase, implying that the actual value of V_{max} did continue to increase by some fraction of the intended increment.

Examples of cyclic voltammetry curves generated during these electrowetting voltage sweeps for one particular sample, Tuball Batch 1 Dessicated, are given in Figures 4.27 B - E, and the same data sets are plotted as a function of time in 4.27 F. In each plot, the data ranges in which the potentiostat current limit was reached can be clearly observed as flat current plateaus; the current limit reached in these plateau regions was ± 655 mA, slightly higher than the nominal instrument. In light of this limit, the horizontal axes of Figures 4.27 B - E should be understood to represent "nominal potential", the potential which the instrument attempted to impose, which only corresponds to the actual potential when the instrument is not at the current limit. During the time periods in which the instrument applied this maximum current the actual potential of the working electrode should have continued to increase due to progressive charge accumulation in the Helholtz double layer. The actual peak working electrode potential V_{max} achieved during any of the sweeps in which the current limit was reached should therefore be proportional to the amount of charge accumulated (resulting from prolonged time of exposure to the current I = 655 mA) and inversely proportional to the effective double layer capacitance. During these procedures the CNT fibers were exposed to the maximum current for an increasing duration with each step, but also experienced a progressive increase in double layer capacitance (as measured indirectly by the metric of CSC).

There are two possible explanations for the observed plateaus in post-electrowetting CSC exhibited in Figure 4.27 A. One possibility is that the achieved values of V_{max} were large enough



Figure 4.27: A: CSC derived from a series of CV measurements on CNT fiber working electrodes in between applications of the electrowetting procedure with increasingly large values of V_{max} . Open symbols indicate measurements of CSC following an electrowetting voltage sweep in which the voltage was well-controlled; closed symbols indicate measurements of CSC following voltage sweeps in which the instrument current limit was reached, during which working electrode voltage was not well-controlled. B-E: samples of current vs. nominal voltage during the application of electrowetting procedure on a dessicated Batch 1 Tuball CNT fiber, with nominal V_{max} of 1 V, 2 V, 3 V, and 4 V. Each sweep consisted of 2 full cycles, beginning at V = V_{ref} . Plateaus at ±655 mA indicate portions of the sweep in which the potentiostat was unable to apply sufficient current to achieve the nominal voltage F: Plots of current vs. time corresponding to the electrowetting sweeps shown in B-E. During sweeps with a higher nominal V_{max} the CNT fiber working electrode was exposed to the maximum current, ±655 mA, for longer sustained periods.

to reach contact angle saturation and the actual limits of induced wettability, and that this limit is achieved at some value of V_{max} between 2.75 V and 5 V. The second possibility is that wettability continued to increase with applied V_{max} , but that V_{max} itself reached a plateau value between 2.75 V and 5 V as a result of a self-limiting process in which the increase in total accumulated charge combined with the progressive increase in Y_{DL} yielded a progressively smaller increase in the total potential of the double layer with each step. Further experiments with better design and an apparatus that can reach sufficient current levels will be necessary to resolve this ambiguity. It is possible that an apparatus capable of generating larger currents would successfully induce a greater increase in fiber wettability, CSC and V_{max} .

Damage to CNT fiber structure due to hydrolysis of water

There is one more possible explanation for the increasing effectiveness of electrowetting at high voltages, which unfortunately seems to be the most likely; that is damage to the CNT fiber structure caused by gas production from hydrolysis. As shown in Figure 4.27, the best results for electrowetting were obtained by sweeping the working electrode potential to $V_{max} > 4$ V. This potential is well above the limits of the water window (see Figure 4.9), resulting in a significant current due to the hydrolysis of water and significant production of O_2 or H_2 gas during the positive and negative arm of the voltage cycle, respectively. This gas could be observed as aggressive bubble formation along the length of the immersed CNT fiber working electrode.

In light of this aggressive bubble formation, and in light of the drawbacks caused by the current limit of the Gamry potentiostat which are described above, an alternate electrowetting procedure was applied to a test portion of annealed CNT fiber in an attempt to achieve optimal properties without exceeding the water window. Before the application of electrowetting, the fiber had a CSC of $11.8 \,\mu$ C/mm². Instead of being subjected to a cyclic sweep, the fiber was then held at a constant potential of -1.5 V with respect to the E_{oc}, a potential that was confirmed to be immediately inside the water window, for 2 hours. The current required to maintain this steady state current value reached a steady state of 90 mA after 30 minutes, indicating that the electronic double layer had become fully charged by that time. After this period of time, the CSC has increased to $178 \,\mu$ C/mm².

After this the fiber was subjected to a single quick sweep (16 seconds in duration) to \pm 4V; as expected, significant gas production occurred at the high and low potential ends of this sweep as the potential exceeded the water window. After this sweep, the CSC of the fiber had increased again to a value of 701 μ C/mm². After this treatment, a segment of the original annealed fiber and the test fiber which had been subjected to high-voltage electrowetting, and thereby used to induce hydrolysis current, were both examined under SEM. The annealed fiber has a surface and structure which is typical of CNT fiber; the fiber which had been used to induce hydrolysis current was marked by many rifts in the structure, presumably created by the rapid expansion of gas bubbles from gas production within the porous structure of the fiber. Obviously, clefts



Figure 4.28: A & B: SEM images of the surface of an annealed CNT fiber before the application of electrowetting. The fiber surface exhibits shallow grooves due to the spacing between the thin CNT bundles that make up its sub-structure, but there are no holes, cracks, or voids in the fiber skin. Image B is a higher magnification of a portion of image A. C - **F**: SEM images of an annealed CNT fiber after an electrowetting procedure in which the fiber was swept linearly to $\pm 4V$ vs. E_{oc} , and during which it produced a significant amount of gas from hydrolysis. A number of cracks were opened in the fiber structure, attributed to rapid expansion of gas bubbles from created by hydrolysis within the porous fiber. These cracks improve the ability of saline to access the interior fiber structure, and are partially, though not solely, responsible for the improvement in fiber wettability after high-voltage electrowetting.

produced in the fiber structure will make it easier for saline to access the interior porous structure; this may be the primary reason for the improvement in CSC from 178 to 701 μ C/mm².

This test revealed that electrowetting can be applied with a moderate effect at potentials within the water window, resulting in more than an order of magnitude improvement in the CSC of a previously annealed fiber. This demonstrates that the basic premise and theory of operation of electrowetting, that it is able to stably increase wettability of the internal porous structure of the fiber, is valid. Pushing the fiber to higher potentials allows electrowetting to be more "effective", but it appears that this is accomplished at least in part by cracks being opened

in the structure of the fiber by rapid expansion of gas bubbles.

The opening of the fiber structure by gas bubble production is not necessarily a drawback; it may be a useful tool for improving the access of saline or other electrolyte fluid to the interior of the fiber for electrochemical applications. However, it may have significant drawbacks, particularly if it has weakened the mechanical properties or the fatigue life of the fiber. In addition, the creation of clefts in the fiber structure creates ambiguity in the electrochemical properties of the fiber that have been derived from circuit model fitting of electrowetted fibers, because it means that the fiber is no longer a uniform porous structure; the electrochemical current exchange between the fiber and the electrolyte is most likely concentrated at places where such clefts open access to a greater amount of the interior porous surface. Future study should be performed to investigate whether the penetration depth L is equivalent to the fiber radius if only "gentle" electrowetting within the water window is applied.

4.6 Conclusion

This work has demonstrated that CNT fibers exhibit low electrochemical impedance primarily due to the large specific surface area they present for electrolytic current exchange. This surface area allows for the formation of very high-capacitance Helmholtz double layers when the fibers are used as working electrodes in physiological systems. Scaling of the capacitance with fiber diameter reveals that the internal porous surface of the fiber, rather than the roughness of the outer skin, is the primary source of this large electroactive surface. Furthermore, tests on annealed and dessicated CNT fiber show that the wettability of this internal surface with respect to saline is strongly determined by the amount of water that is already trapped in the structure.

An electrowetting procedure has been described which is able to reliably and reproducibly achieve high CSC, high Y_{DL} , and low electrochemical impedance in CNT fiber. There is a great deal of room for more precise understanding of the electrowetting process and optimization of the electrowetting procedure; the procedure used in this work introduces cracks in the fiber

structure which may be responsible for a significant portion of the measured properties improvment; a better version of the technique should avoid voltages outside of the water window in order to prevent the hydrolysis and rapid gas bubble expansion that presumably created these cracks.

Optimization of electrowetting as a post-processing treatment for CNT fiber should focus not only on optimizing final electrochemical properties but also on developing a scalable method to treat large amounts of fiber; this could potentially be achieved with a continuous roll-to-roll process in which the CNT fiber passes through an aqueous electrolyte bath. Ideally, the voltage difference between the fiber and the bath should be maintained at a level that avoids the production of gas species, and the residence time of fiber in the bath should be sufficient to ensure maximum charging of the Helmholtz double layer to reach this potential.

The efficacy of electrowetting in decreasing the electrochemical impedance of wet-spun CNT fibers that have been dessicated or annealed suggests that a similar procedure could be used to decrease electrochemical impedance of other CNT materials of a similar dimension, whether those materials were created using a solution-based process or an entirely dry solid-state process. Larger scale CNT materials may not exhibit the same trend; for a CNT fiber or other CNT structure of sufficient thickness it may not be the case that the entire volume can be suffused with electrolyte through electrowetting, or it may be the case that the resistance $r_{pore} *L$ associated with ionic diffusion into the deepest part of the structure becomes large enough to limit the participation of that structure in the electrochemical current exchange over a wider range of frequencies (as illustrated in Figure 4.20).

Chapter 5

Modeling CNT Fiber Electrode Performance in Cardiac Tissue

5.1 Introduction

Understanding the specific equivalent circuit behavior of a given material's electrochemical interface is only the first step in engineering medical electrodes using that material; once this behavior is understood one may consider the precise way in which the electrode will interact within the more complex electrochemical circuit behavior of cellular tissue (which may be either healthy or diseased). This chapter presents a derivation and analysis of the electrical transfer function that underlies the performance of CNT fiber in one particular medical application: treatment of ventricular arrhythmia arising from cellular conduction block. This kind of treatment is not feasible without a material that can combine low contact impedance, long fatigue life, suitable biocompatibility, and a small spatial dimension suitable for implantation in tissue; therefore, it represents an entirely novel application which may be enabled by the development and optimization of CNT fiber electrodes.

In recent animal trials, bundles of CNT fiber have been used to restore conduction velocity through scar tissue in sheep hearts *in vivo*, as depicted in Figure 4.1. In this case, "conduction velocity" refers to the speed with which the action potential response, described in section 5.2,

propagates through the cellular tissue. CNT fiber is able to aid this propagation by transmitting the currents produced by healthy activating cells across the scar tissue with sufficiently low loss to stimulate polarized cells on the far side. The relevant transfer function to consider is therefore one for which the input signal is either the extracellular voltage or electric current in some region of actively depolarizing cells which are in contact with the fiber, and for which the output signal is, or is directly linked to, the magnitude of membrane depolarization in one or more cells near another section of the fiber, at some distance or across a region of conduction block.

This chapter begins with a basic description of the operation of cardiac cells and the propagation of action potentials in cardiac tissue. Section 5.3 presents a theoretical equivalent circuit model representing a CNT fiber passing through a collection of heart cells interrupted by a region of conduction block; the specific equivalent circuit of a CNT fiber/electrolyte interface, as reported in sections 4.4 and 4.5, is incorporated into this more complex circuit. Based on this circuit a transfer function is derived between the electrical potential in the extracellular fluid immediately surrounding the CNT fiber "upstream" from the conduction block (that is, in the direction from which the action potential is expected to propagate in the course of a normal heart contraction) and the potential in the extracellular fluid surrounding the fiber "downstream" from the conduction block, as a function of frequency and distance; this latter quantity is chosen as a surrogate for the membrane polarization (the difference between intracellular and extracellular potential) of the cells immediately surrounding the fiber in that region. Section 5.4 presents numerical solutions of this transfer function for a variety of parameter values in the physically relevant range. Finally, section 5.5 discusses the limitations inherent in this calculation due to the various assumptions on which it relies, the conclusions that may or may not be be drawn from it, and proposes steps that could be taken to improve its accuracy.

5.2 Background: Electric signaling in cardiac tissue

Muscle contraction in the heart is regulated by the passage of an electric signal through the tissue with orderly timing and an orderly direction of transmission, referred to as action potential propagation (Kleber and Rudy, 2004). This signal does not consist of a direct flow of current on the length scale of the organ; rather, it may be described as a chain reaction of stimulated cellular electrical activity which propagates through the heart tissue.

The characteristic cells of cardiac tissue are referred to as cardiomyocytes, or myocardial cells. These cells spend a majority of time in a "polarized" resting state. In this polarized state, ion pumps in the cell membranes continuously expend energy to transport ions into and out of the cell against a charge gradient, thereby maintaining a net negative potential inside the cell with respect to the extracellular fluid. The resulting polarization of the cell membrane (≈ -90 mV) is referred to as the resting membrane potential. When a local change in ionic concentration inside or outside of the cell decreases this polarization to a threshold of -70 mV on any part of the cell membrane, voltage sensitive ion channels in that portion of the membrane activate and initiate a series of ion exchanges; the resulting series of changes in the cellular membrane potential are collectively referred to as the action potential.

A complete description of the cellular processes in each phase of the action potential response can be found in (Kleber and Rudy, 2004). A plot of (simulated) membrane potential vs. time (inner potential - outer potential) of a single cell undergoing this response, reproduced from that reference, is given in Figure 5.1. A thorough description of the ionic exchanges that give rise to the shape of the curve is not necessary here, but the most important features of the reaction should be noted. One of the these is the very rapid upstroke in the intracellular potential at the beginning of the response, which results from a rapid influx of positive ions (this upstroke is also referred to as depolarization, since the initial resting membrane polarization of the cell is lost, and in fact partially reversed). This rapid upstroke and the currents associated with it are primarily responsible for initiating the action potential response in neighboring cells, since they are capable of inducing a significant decrease in the membrane polarization of those cells.



Figure 5.1: Simulated membrane polarization (internal potential - outer potential) for a myocyte undergoing the action potential response; reproduced with some modification from (Kleber and Rudy, 2004). BCL = 1000 ms refers to the cycle length applied between simulated stimulations of the cell.

A second critical feature of the action potential is that once a cell has depolarized it cannot be activated again for a short time (known as the refractory period); hence, the action potential chain reaction is typically only able to propagate in a single direction out from the source of initiation, towards cells that are in the resting state, and not backwards to the cells that have recently undergone depolarization. Finally, it is important to note that action potential regulates heart muscle contraction because one of the steps in the action potential response is an exchange of calcium ions that mediates cellular contraction. The essential operation of a beating heart is carried out by the initiation of an action potential at a specific location in the organ (a group of specialized cells called the sinoatrial node), followed by rapid propagation of the action potential through the heart tissue in an orderly fashion to produce synchronized contraction, with each cell contracting once and then returning to the resting state to await the next beat.

"Conduction block" and "conduction delay" in cardiac settings refer to any physiological condition that prevents action potential propagation, or which delays its passage through the

heart. If ion uptake in the contracting cell is inhibited, or if any other factor greatly increases the time required for a given cell to complete its action potential upstroke, then the nearby cell membranes may exhibit a weaker transient depolarization which does not bring them to the -70 mV threshold; in this case action potential transmission will fail, resulting in conduction block. Alternately, the weaker transient currents may bring these cells to the threshold, but only after a significant delay. Action potential transmission may fail or be delayed if only one or a few cells in a given region of tissue undergo the response, such that the current dissipates into a large region of polarized cells without producing sufficient depolarization in any of them; this is known as source-sink mismatch. A larger group of cells participating in the exchange creates a greater total local ionic current, and results in more reliable transmission. Conduction block and conduction delay can result from obstructions in the heart, such as non-conducting blood vessels or foreign implanted material, but they most commonly arise from disease or damage to myocardial cells followed by the growth of non-conductive scar tissue replacing either all, or even simply a majority, of the cardiomyocytes in a given region. In this context, "nonconductive" does not imply that the scar tissue or other obstruction is necessarily an insulator; rather, it may simply be incapable of participating and sustaining the action potential response chain reaction (Kleber and Rudy, 2004; Dhein et al., 2014). Conduction block and conduction delay are major causes of cardiac arrhythmia.

Cardiac electrodes are used to interact with this tissue in a variety of ways; the two most basic applications are sensing of voltage signals and delivery of pacing voltage. In a sensing application, two electrochemical electrodes implanted in or on cardiac tissue, with some separation distance between the two, may be used to detect the difference in local potential between those two locations (or at each location and relative to a fixed reference potential). This technique can be used to reveal many details about the passage of action potentials through the tissue, including the beating frequency, the amplitude and transient duration of currents output by the cells around the electrodes (and hence information about whether the cells are acting with good synchronization and without delay), and the direction of propagation (if the orientation of the electrode pair can be rotated or if multiple electrode pairs are employed). In a pacing application, a large transient current or a potential difference is imposed between two electrodes on either side of some region of tissue, creating a local change in extracellular fluid potential sufficient to initiate action potential response in some or all of the cells in that region (Webster, 1995).

For both sensing and pacing applications, electrodes which are capable of delivering large capacitive (non-Faradiac) currents are optimal; it is generally better to avoid charge transfer reactions, which can induce local changes in chemical composition or oxidative and reductive stress on the local biological matter. Therefore, electrodes with large surface areas, which can exhibit extremely high-capacitance Helmholtz double layers when polarized, are optimal for cardiac electrode applications (Webster, 1995).

Low-impedance materials are especially critical for restoration of normal action potential propagation through a region of conduction block, because the input signal in this case would be the rather small currents and voltages output by the cells themselves. In order to be successful in this application, a material must be able to transfer these signals with extremely low loss. The results presented in 4.1 and in McCauley *et al.* (in preparation) indicate that CNT bundles of a sufficient size were able to reliably meet this requirement.

5.3 Derivation of *in vivo* circuit model and transfer functions

5.3.1 Seal resistance and sheet resistance

The exchange of electric current between any organic cell and a nearby solid electrode within an electrolytic medium (such as extracellular fluid *in vivo* or a cell culture solution *in vitro*) is subject to loss due to the diffusion of current into the electrolyte. The impedance associated with this loss pathway is referred to as a seal resistance. More intimate physical contact between the electrode and cell membrane, or some other constriction of the channels available for electrolyte diffusion between those surfaces, leads to higher seal resistance and thus to more efficient current and voltage transfer between electrode and cell. In general, the relative magnitudes of the seal resistance, the impedance associated with the current crossing the cell membrane, and the impedance of the electrode/electrolyte interface is the most crucial physical relationship governing the performance of an electrode designed for sensing and stimulation of electroactive cells.

The calculation of seal resistances in the circuit model derived below is based on the approach found in Braun and Fromherz (2004), Schoen and Fromherz (2007), and Joye *et al.* (2009). A region of extracellular fluid between a cell membrane and a nearby solid surface is treated as a thin sheet of conducting material with some given resistivity (in this case the resistivity of the extracellular fluid, denoted ρ_s) and a uniform thickness *h*, with a resulting sheet resistance

$$\mathbf{r}_{\rm s} = \frac{\rho_{\rm s}}{h} \tag{5.1}$$

to any flow of charge parallel to the surfaces of contact. The actual seal resistance R_{seal} is then governed by this sheet resistance and by the size and geometry of the surface of contact.

Three of the major assumptions made in the construction of the circuit models below are introduced through the use of a sheet resistance to derive seal resistance; all of them are necessary due to a lack of evidence concerning the nature of the contact between CNT fiber and myocytes after implantation of the fiber *in vivo*. First, it is assumed that the area of contact between the cell membrane and the fiber can be treated as a gap with uniform thickness *h*. In reality both myocytes and CNT fiber have curvature (*in vivo* myocytes take the form of cylinders with diameters in the range of 10 - 20 μ m); furthermore, CNT fibers have a surface that is rough on both a μ m and sub- μ m scale. Treating their contact as a gap of uniform thickness is tantamount to assuming a) that the two surfaces are deformable enough to conform to one another when placed in close contact and b) that any variations in the thickness of that gap due to surface roughness of the fiber do not affect the sheet resistance so long as the value chosen for *h* is close to the spatial average. Second, an appropriate value of *h* is not currently known. It is difficult to predict what values this difference will take after *in vivo* implantation of a fiber, particularly after some period of time in which inflammation and/or healing of the cellular tissue occurs around the fiber. The roughness of the fiber surface may result in a value of *h* that

varies throughout the interface, leading to small regions of close contact with high r_s separated by regions in which contact is not close.

Finally, it is assumed that the CNTs in the outer layers of the fiber do not penetrate the cell membrane and gain access to the intracellular fluid. This kind of penetration has been observed in Vakarelski *et al.* (2007) and Skandani *et al.* (2012). In wet-spun CNT fiber the constituent CNTs are well-aligned with the fiber axis, well-packed, and strongly bound to one another by van der Waals forces; the surfaces of the fiber in direct contact with the cell (if any) should therefore be composed primarily of CNT sidewalls, with no individual CNT tips available to penetrate the membrane. However, until further study is performed on the interface between CNT fiber and cellular tissue *in vivo* after an implantation, this remains an assumption. If CNTs do penetrate the cell membrane then the CNT fiber would form an electrical connection between the intracellular fluids of separate myocytes as well as the extracellular fluid around them, complicating the circuit behavior considerably. This would actually be quite useful for assisting action potental propagation, provided that the portions of the fiber exposed to extracellular fluid were insulated and the fiber only electrically connected the intracellular fluids of distant cells, but that possibility will not be discussed in depth here.

For the sake of simplicity the derivation below assumes that the interfaces of contact between CNT fibers and the membranes of neighboring myocytes are conformal contacts separated by junctional gaps of uniform thickness h, filled with extracellular fluid; section 5.4 presents the changes in transfer efficiency that will result from varying the value of h, among other parameters. Because of these assumptions, as well as others involved in the derivation below, the resulting transfer functions should be considered an initial approximation; future research aimed at characterization of the interface between CNT fibers and *in vivo* myocytes on a μ m and sub- μ m scale may lead to a more accurate transfer function based on this starting point.

5.3.2 Area contact & point contact models

There are two approaches for constructing the circuit model of an electroactive cell separated from an electrode surface by a thin layer of conducting fluid. The more strictly realistic approach is an area contact model, which is essentially a two-dimensional transmission line (Weis and Fromherz, 1997). In this model the currents into and out of the cell and the electrode are assumed to be distributed in some way across their surfaces. Within each differential area element of the interface there is an impedance associated with current crossing the cell membrane, a second impedance for current crossing into the electrode, and a third impedance for the flow of current laterally through the gap; the 2D transmission line circuit is formed by these interconnected area elements. This model allows for a description of potentials and currents as functions of position within the interface. For some contact area geometries, such as a circular contact, the spatial distribution of currents and potentials in the gap and at the electrode or membrane surface can be calculated with relative ease (Weis and Fromherz, 1997).

The other possible approach is the construction of a so-called point-contact model, in which the electrical connections between the cell membrane and the extracellular gap, and between the electrode and the gap, are treated as a single circuit connection. In such a model the area-dependent currents, potentials, and impedances are replaced by average "global" values. The global impedances for currents crossing the cell membrane or electrode interface can be determined if their area-specific impedances and the total area of the contact are known; the global seal resistance can be determined for simple geometries, so long as an average of the resistances from each differential area element to the line of "contact" with the extracellular fluid along the gap edge can be calculated (Weis and Fromherz, 1997). The point contact model may be expected to accurately predict circuit behavior so long as the interface is reasonably uniform.

The circuit model given below for a CNT fiber passing through bundles of cardiac cells has been derived using a hybrid approach: the principles of the point-contact model are applied to determine impedance values for the interface within each differential length element of the fiber; these characteristic impedance values are then incorporated into a transmission line model which allows for calculation of the longitudinally distributed currents and potentials.

5.3.3 Transfer function for CNT fiber embedded in aligned myocyte bundle

In the setting of *in vivo* heart tissue, cardiac cells grow together to form continuous bundles; each myocyte takes on a roughly cylindrical form with a length of approximately 100 μ m and a radius of approximately 10 μ m, and these individual cells are linked together end-to end to create continuous chains (Dhein *et al.*, 2014). The end-to-end connections consist of specialized structures known as intercalated disks, which are narrow (\approx 2-5 nm) clefts of extracellular fluid intermixed with connective tissue (Dhein *et al.*, 2014). In any given region of heart muscle the bundles themselves tend to be aligned in a common direction; functionally, this arrangement leads to anisotropic propagation velocity of action potentials (faster in the direction of myocyte alignment) and anisotropic muscle contraction, in which each myocyte contracts along its own axis and transfers force to its end-to-end neighbors through the intercalated disks (Saffitz *et al.*, 1995).

Because the seal resistance at any point along a CNT fiber or other thin filament electrode will depend sensitively on the nature of its contact with the surrounding cells, such an electrode may exhibit markedly different performance depending on the angle between the fiber axis and the local alignment of myocyte bundles. The circuit model derived below represents the limiting case in which the fiber is embedded in a bundle of myocytes aligned parallel the fiber axis. In addition, myocytes are treated as linear chains, whereas in reality they exhibit bifurcation and branching connections with other parallel myocytes; this distinction should not fundamentally change the nature or the amount of area covered by the interface.

Consider a cylindrical fiber of radius u which is surrounded on all sides by continuous chains of connected myocytes. Assume the myocytes closest to the fiber deform in response to its curvature as shown in Figure 5.2, so that they form regions of approximately planar contact; the fiber surface and cell membranes are separated by a gap of extracellular fluid with uniform thickness h, with $h \ll u$. Assume that these regions of contact have a uniform width W_{cell} in the



Figure 5.2: Hypothetical model of the physical interface between a CNT fiber and the adjacent continuous myocyte strands in cardiac tissue *in vivo*. This model assumes that the cell strands are aligned with the fiber axis and that the cell membranes are soft enough to conform to the shape of the fiber to some extent. For the sake of simplifying the associated circuit model, this physical model also assumes a perfectly cylindrical fiber and identical contact with each cell strand. Each cell is assumed to form a surface of close contact with the fiber over an arc length W_{cell} ; within this region it is assumed that the fiber radius *u*. The space between the cells and the fiber is assumed to be filled with extracellular fluid.

azimuthal direction and that the interstitial spaces between neighboring myocytes represent low impedance pathways to the bulk of the extracellular fluid. The fraction of fiber surface exposed to the interstitial fluid between the cells, Q, the fraction which is covered by the cells, P, and the number of parallel cell lines that can be in contact with the fiber in this manner, N, are given by $Q = (2\pi u) * mod(W_{cell})$, $P = 2\pi u - Q$, and $N = P/W_{cell}$, respectively.

These regions of close contact extend longitudinally along the fiber, with the coverage of the cell membrane broken only by narrow clefts of extracellular fluid at the intercalated disks. Because these clefts of extracellular fluid are much narrower than the interstitial spaces between neighboring cells in the azimuthal direction (\approx 2 nm vs. >20 nm), the resistance to current flow outward from the fiber through the intercalated disks is much greater than the resistance to the flow of current out of the gap through the larger interstitial spaces (Dhein *et al.*, 2014). As a first approximation the breaks at the intercalated disks may be ignored, and the regions of close

contact between the cell lines and the fiber may be modeled as continuous strips of width W_{cell} . The seal resistance at each point within these strips of contact arises from the total resistance to the flow of current out of the interfacial gap in the azimuthal direction, toward the nearest interstitial space between the parallel cell lines.

For sufficiently small *h*, this seal resistance is the primary impedance between any given location within the junctional gap and the bulk of the extracellular tissue, which may be considered to serve as a ground potential/current sink. The interstitial spaces between the cells, on either side of each region of close contact, are electrically separated from this ground potential by some smaller resistance r_{bulk} arising from the resistivity of the bulk tissue.

The electrical behavior of this system may be modeled as a transmission line with three distinct, interconnected current channels. Channel 1 represents the flow of current through the fiber itself. Channel 2 represents the flow of current longitudinally along the gaps between the fiber and the cells; in fact this is composed of N identical parallel channels, each representing one of the cell line contacts, and so can be treated as a single channel with the appropriate impedance divided by a factor of N. Channel 3 represents the extracellular bulk, into which current from channel 1 and channel 2 is able to diffuse. Current may flow between channel 1 and channel 2 through the interfacial impedance of the portion of the fiber covered by the cells (the fraction of fiber surface equivalent to P), and likewise, current may flow between channel 1 and channel 3 through the interfacial impedance of the portion of the fiber exposed to the clefts in between the cells (the fraction of fiber surface equivalent to Q), in series with a small bulk resistance. Current may flow between channel 2 and channel 3 through the seal resistance associated with flow of current in the transverse direction through the gap toward the nearest cleft between cells (again, this may be treated as a parallel array of N pathways), also set in series with the bulk tissue resistance r_{bulk}. In order to describe the circuit behavior of the transmission line, therefore, we must identify the impedances described above, as well as the impedances per unit length through channel 1 and channel 2.

This circuit bears some similarity to the transmission line derived by Bisquert et al. to describe the interfaces of porous oxide electrodes with conductive coatings in (Bisquert *et al.*, 2006), but with slightly different boundary conditions, and with the additional complication of the circuit connection between channel 1 and channel 3, which makes the derivation of an analytical solution more difficult. Here we derive the impedance quantities and the system of differential equations which govern the behavior of the circuit, and then rely on numerical methods to solve for the desired transfer function.

The simplest quantity to derive is the impedance per unit length through the fiber, which is given by

$$r_{\rm f} = \frac{\rho_{\rm f}}{\pi u^2} \tag{5.2}$$

in which $\rho_{\rm f}$ is the fiber resistivity.

To find the impedance between the fiber and the electrolyte around it we may start with the area-specific interfacial impedance which was determined through circuit model fitting in Section 4.4 and use it to calculate the interfacial impedance of a longitudinal cylindrical section with circumference $2\pi u$ and differential length dx. We model the fiber/electrolyte interface as a Bisquert Open transmission line, as described in Section 4.4.3 and as depicted in Figure 5.3 (B). For any given circuit element magnitude A, let \bar{A} express its area-specific value and let \hat{A} represent its value specific to a differential length section of the fiber's cylindrical surface; then $\hat{y}_{dl} = 2\pi u \bar{y}_{dl}$, $\hat{r}_{pore} = \bar{r}_{pore}/(2\pi u)$, and $\hat{r}_{ct} = \bar{r}_{ct}/(2\pi u)$. The values of \bar{y}_{dl} , \bar{r}_{pore} , \bar{r}_{ct} , and n_{dl} may be determined from area-normalized EIS fitting results. The interfacial impedance over a differential length section of the fiber is given by

$$\hat{Z}_{inter}(f) = \sqrt{\frac{\hat{r}_{pore}\hat{r}_{ct}}{1 + \hat{r}_{ct}\hat{y}_{dl}(jf)^{n_{dl}}}} \coth\left(u\sqrt{\frac{\hat{r}_{pore}\left(1 + \hat{r}_{ct}\hat{y}_{dl}(jf)^{n_{dl}}\right)}{\hat{r}_{ct}}}\right)$$
(5.3)

in which $f = \omega/(2\pi)$ is AC voltage frequency in Hz. The total impedance to current leaving the fiber and entering the interfacial gaps between the fiber and cell membranes (channel 2) within each differential length section is given by \hat{Z}_{inter}/P , while the impedance to current leaving the fiber directly into the the bulk tissue through the interstitial spaces between parallel cell lines is \hat{Z}_{inter}/Q .

If we assume that the CNT fiber in question has properties equivalent to the medium thickness CCNI CNT fiber examined in Section 4.4, then $\rho_f = 49.79 \,\mu\Omega$ cm and \bar{y}_{dl} , \bar{r}_{pore} , and n_{dl} may be drawn from the the first row of Table 4.5 (with $\bar{y}_{dl} = y_{dl}/A$, etc.); however, because \bar{r}_{ct} could not be determined from fitting of EIS results to the Bisquert Open model it must instead be estimated by another means. A reasonable estimate for this parameter may be generated from the currently available data by taking the values of R_{CT} derived from fitting of EIS results in saline to the simplified Randles model (Model 1) and normalizing by the total volume of the measured electrodes rather than by electrode surface area. Thus,

$$\bar{\mathbf{r}}_{\rm ct} \approx \bar{\mathbf{R}}_{\rm CT} \frac{\pi(\mathbf{u}_0^2)}{2\pi \mathbf{u}_0} \tag{5.4}$$

in which \bar{R}_{CT} is drawn from the 5th row of Table 4.1 and $u_0 = 11.74 \ \mu$ m, the radius of the fiber measured in those experiments.

To determine the impedance to current flow within the interfacial gaps we may consider a differential length section of one gap, with width W_{cell} and length dx. We may construct an approximate point contact model for this rectangular element by considering the longitudinal and transverse (azimuthal) current flows separately. We first consider only the current flow in the azimuthal direction; we define an arbitrary line of electric contact parallel to the fiber axis which is set some distance *y* from the closer outer gap edge, and $W_{cell} - y$ from the further edge. The total seal resistance between such a contact line and the gap edges is equivalent to two sheet resistances set in parallel:

$$R(y) = \frac{1}{\frac{hdx}{\rho_s y} + \frac{hdx}{\rho_s(W_{cell} - y)}} = \frac{\rho_s(yW_{cell} - y^2)}{hW_{cell}dx}$$
(5.5)

The average value of this seal resistance in the domain $0 < y < W_{cell}$, which may be taken as the global resistance between to the flow of current directly from this rectangular element into the extracellular bulk, is

$$r_{\rm gb} = \frac{1}{6} \frac{\rho_{\rm s} W_{\rm cell}}{h dx}$$
(5.6)

Similarly, if we consider the flow of current across the edges in the longitudinal direction, the impedance in each direction is given by the average sheet resistance to one edge from all lines of contact running perpendicular to the longitudinal direction:

$$\mathbf{r}_{\rm gg} = \frac{1}{2} \frac{\rho_{\rm s} \mathrm{d}x}{h \mathrm{W}_{\rm cell}} \tag{5.7}$$

Because the junctional gap around the fiber consists of N gap spaces, the total impedances to current through or out of the gap spaces are given by r_{gb}/N and r_{gg}/N .

It is not immediately clear what value we should assign to the impedance of the bulk tissue around this cylindrical system, because the distance over which current must travel before it is said to reach the "ground potential" of the organ/body is not obvious. Fortunately, the transfer function solutions presented in Section 5.4 reveal that so long as the value chosen for this parameter is not unrealistically large ($\gg 1 \Omega$), it affects only the high-frequency limiting behavior of the transfer function, and has no effect on voltage transfer within the frequency range relevant to cardiac cell function.

Nevertheless, we can at least make an order-of-magnitude estimate of the value by assuming that the current from each point along the fiber needs to disperse into a volume on the order of several cm³ before it becomes negligible. On a macroscopic scale the cardiac tissue is a syncytium with two types of current pathway (interconnected extracellular fluid and interconnected extracellular fluid), both of which have an anisotropic conductivity with the alignment of the cellular strands. A range of values have been reported for the conductivity of each component: 0.12 - 0.62 S/m or 0.08 - 0.24 S/m for extracellular fluid in the directions longitudinal and transverse to the cell strands, respectively, and 0.17 - 0.34 S/m or 0.019 - 0.06 S/m for the connected intracellular fluid in the longitudinal or transverse direction (Roth, 2000). Given this range of conductivities, 10 Ω m is a reasonable order-of-magnitude approximation for the anisotropic resistivity. Therefore, we can assume that each differential length element of the fiber/cell bundle system is separated electrically from ground by a total resistance r_{bulk} which is on the order of 0.1 Ω .

Given the impedances derived above, we may construct a system of simultaneous differ-

ential equations to describe the currents and the electric potentials in the fiber/cell bundle transmission line system as a function of longitudinal position *x* and AC voltage frequency *f*. By choosing appropriate boundary conditions we can use this systems of equations to describe a CNT fiber that is exposed to a region of activated tissue and a region of polarized tissue (awaiting an action potential stimulus) separated by a region of conduction block.

5.3.4 Modeling transmission through conduction block

Assume that a filament of fiber embedded as described in a bundle of aligned myocytes passes through some region of conduction block from $x = -L_{block}$ to x = 0, with healthy tissue on either side, and that the fiber extends over a length L_B past this block in the +x direction and over a similar length in the -x direction. Assume that the nature of the block is such that it prevents both cell-to-cell activation and any flow of current through the extracellular fluid (this implies that the transfer function which will be derived from this circuit represents a worst-case scenario in which the fiber is the only available current pathway). Further assume that the propagation of an action potential wave in the +x direction through the cardiac muscle causes, at some moment, the section of the fiber extending from $x = -(L_{block} + L_A)$ to $x = -L_{block}$ to be surrounded by cells undergoing depolarization, and that this produces a uniform change in electric potential (away from the initial ground potential) around this section of the fiber. We can write this time-dependent potential as a function of frequency, $\phi_0(f)$, and it serves as the input signal for the transfer function we wish to calculate.

There are three possible circuit pathways that electric current may take from this region into the extracellular bulk, which serves as a current sink and may be considered to have a ground potential of $\phi = 0$. Broadly speaking, current may either flow directly away from the CNT fiber out from the interfacial gaps and through the extracellular fluid; it may flow along the fiber branch in the -x direction, which in this case would mean flowing back in the direction from which the action potential had propagated, through groups of fully depolarize cells in their refractory period, and thence into the bulk; finally, it may flow through the fiber branch in the +x direction, across the conduction block and toward the polarized cells on the far side. The total potential drop across each of these pathways is the same, and is equivalent to $\phi_0(f)$; the ratio of the current that flows through the fiber in the +x and -x directions is therefore the ratio of the total impedance to ground along either of these two pathways. In reality this will depend both on the length of fiber in each direction and on the conductivity of the tissue in either direction; if we make the additional assumptions that a) the occlusion of conductivity from the conduction block is a small change in the total impedance of the current pathway and that b) the region of conduction block is near the middle of the implanted fiber, then we may assume that the current flow through the fiber in the +x direction is equivalent to the current injected into the nearer half of the fiber interface within the activated region, a segment of fiber with length L_A/2.

The output function we are interested in calculating is the potential in the junctional extracellular gap space between the fiber and the cells on the far side of the conduction block, $\phi_g(x,f)$, which is a function of both the input voltage frequency and distance from the conduction block. Changes in this potential will shift the membrane polarization of the cells in close contact with the fiber surface, and a sufficiently large change (> 20 mV) will lead to propagation of the action potential response.

The three-channel transmission line model shown in Figure 5.3 (C) begins at the edge of the conduction block, x = 0, and extends to $x = L_B$. Within this domain the current and potential in the fiber are described by the functions $\phi_f(x,f)$ and $i_f(x,f)$, and the current and potential in the junctional extracellular gap spaces are described by the functions $\phi_g(x,f)$ and $i_g(x,f)$. An application of Kirchoff's laws leads to the following set of differential equations:



Figure 5.3: Circuit models relevant to the transfer of action potential through a CNT fiber betwen two regions of cardiac tissue. This system includes numerous electrical contacts that occur over relatively large or extended surfaces; as a result it includes several transmission line model geometries, some of which are nested within others. A: Circuit diagram of the Bisquert Open transmission line that gives rise to the interfacial impedance of the CNT fiber, Z_{inter} ; r_{pore} is the resistance per unit length for current through the electrolyte into the pores of the fiber, r_{ct} is the resistance-length associated with charge transfer (Faradiac) current, and $z_{dl} = 1/(y_{dl}(jf)^{n_{dl}})$ is the impedance-length arising from the double layer capacitance. B: Circuit diagram of the Bisquert Open transmission line that gives rise to the impedance of a section of fiber exposed a uniform extracellular potential in a region activating cells, Z_{A} ; $r_{f} = \rho_{f}/(2\pi u)$ is the impedance per unit length within the CNT fiber. C: Full circuit diagram of a CNT fiber surrounded by aligned myocyte strands, with a region of activating cells and a region of passive cells separated by a region of conduction block. The circuit to the right of the conduction block is a three-channel transmission line with continuous current exchange between the lines, having various impedance values (see text); these lines represent the CNT fiber (1), the extracellular junctional gap between the fiber and the adjacent cells (2), and the bulk of the tissue (3), which is assumed to be an equipotential region which serves as a ground potential current sink. The extracellular fluid near a region of activating cells is assumed to be at a uniform and $\phi_0(f)$, and is separated from the start of channel 1 by the impedances Z_A and $r_f L_{block}$, the latter representing the fiber resistance within the region of block. (4) and (5) represent alternate current pathways of unknown impedance between the activating cells and ground: one through the length of fiber "upstream" from the conduction block, and one directly through extacellular fluid.

$$\frac{\partial \phi_{\rm f}}{\partial x} = -r_{\rm f} i_{\rm f} \tag{5.8}$$

$$\frac{\partial \phi_{\rm g}}{\partial x} = -\frac{\mathbf{r}_{\rm gg}}{\mathbf{N}} \mathbf{i}_{\rm g} \tag{5.9}$$

$$\frac{\partial \mathbf{i}_{\mathrm{f}}}{\partial x} = \frac{\mathrm{P}(\phi_{\mathrm{g}} - \phi_{\mathrm{f}})}{\hat{Z}_{\mathrm{inter}}} - \frac{\phi_{\mathrm{f}}}{\frac{\hat{Z}_{\mathrm{inter}}}{Q} + 0.01}$$
(5.10)

$$\frac{\partial \mathbf{i}_{\mathrm{g}}}{\partial x} = \frac{\mathbf{P}(\phi_{\mathrm{f}} - \phi_{\mathrm{g}})}{\hat{Z}_{\mathrm{inter}}} - \frac{\phi_{\mathrm{f}}}{\frac{\mathbf{r}_{\mathrm{gb}}}{N} + 0.01}$$
(5.11)

The value of ϕ_f at $x = L_{block}$ will depend on the value of the input voltage signal ϕ_0 generated in the extracellular gap around the fiber within the region $(-L_A/2) < x < 0$, the total current flowing from this region into the fiber and across the block (which is given by the value of i_f at $x = L_{block}$), the total impedance to this injection of current into the fiber, and finally the voltage loss within the length of fiber that crosses the region of conduction block. The circuit connection between the fiber and the region of extracellular fluid within the region of stimulating cells can be modeled as a transmission line with the characteristics of a Bisquert Open model, as depicted in Figure 5.3 (A), with a total impedance

$$Z_{\rm A}(f) = \sqrt{r_{\rm f} \hat{Z}_{\rm inter}(f)} \coth\left(\frac{L_{\rm A}}{2} \sqrt{\frac{r_{\rm f}}{\hat{Z}_{\rm inter}(f)}}\right)$$
(5.12)

and the total resistance of the section of the fiber in the region of conduction block is given by $R_{block} = r_f L_{block}$. Thus,

$$\phi_{\rm f}({\rm L}_{\rm block},f) = \phi_0(f) - \left(Z_{\rm A}(f) + {\rm R}_{\rm block}\right) * i_{\rm f}({\rm L}_{\rm block},f)$$
(5.13)

Further boundary conditions for the three-channel transmission line circuit between x = 0 and $x = L_B$ arise from the assumption that current does not flow in channel 1 or channel 2 past the end of the fiber at $x = L_B$, where both the fiber itself and the junctional gap between the fiber and cells terminate, and by the assumption that the conduction block provides a complete barrier

to current flow in the extracellular fluid; these assumptions yield the boundary conditions

$$i_g(0,f) = i_g(L_B,f) = i_f(L_B,f) = 0$$
(5.14)

Using the physical quantities and boundary conditions derived above, it is possible to numerically solve the system of differential equations 5.8 - 5.11 to obtain the value of the transfer function

$$H(x,f) = \frac{\phi_{g}(x,f)}{\phi_{0}(f)}$$
(5.15)

for $0 < x < L_B$. Note that because of the influence of capacitive impedances H is a complex function of frequency, having both magnitude and phase.

5.4 Numerical solutions

This section presents solutions of the transfer function H(x, f) obtained by numerical solution of equations 5.8 - 5.11 with a variety of input parameters, with the goal of revealing the overall form and scaling behavior of the function within the parameter space relevant to CNT fiber electrodes. Numerical solutions were obtained using the dsolve algorithm available in the Matlab R2016a software package.

Based on the derivation presented in Section 5.3 the full list of independent parameters that affect H (*x*,*f*) includes the extracellular resistivity (ρ_s), the thickness of the junctional gaps between the fiber surface and the nearest cell membranes (*h*), the width of the regions of conformal contact between the fiber and nearby cells (W_{cell}), the diameter and resistivity of the fiber (*u* and ρ_f), the electrochemical properties of the fiber/electrolyte interface as revealed by EIS fitting (\bar{y}_{dl} , n_{dl} , \bar{r}_{pore} , and \bar{r}_{ct}), the resistance of the bulk tissue (r_{bulk}), and finally the lengths of the sections of fiber in contact with activating cells, conduction block, and the healthy cells "downstream" from the block (L_A, L_{block}, and L_B, respectively). The values of some of these parameters are known; others represent engineering parameters that may be chosen or controlled

in the design of CNT fiber electrodes. The remainder represent unknown physical quantities with values that must be assumed until they can be measured directly.

In order to elucidate the behavior and scaling of the transfer function in the parameter space corresponding to the use of CNT fiber in cardiac tissue, H(x,f) has been calculated for a series of cases in which each unknown or engineered parameter is varied around some "base-line" value, which in turn is derived from an assumption about what constitutes a realistic or typical value for that parameter. The set of values chosen for the calculation of the baseline curves, and a list of the the measurements or the assumptions on which they are based, is given in table 5.1. The table also indicates what range of values is considered for each parameter in Figures 5.5 - 5.12, which explore variation of the function within the biologically relevant frequency and parameter range.

Parameter	Value	Source	Range considered
			in Figures 5.5 - 5.12
	a a		27/4
$ ho_{ m s}$	0.75 Ωm	(Roth, 1988)	N/A
h	$1\mu{ m m}$	Assumption	0.1 - $10\mu{ m m}$
W _{cell}	$10\mu{ m m}$	Assumption; this is half of the typical diameter for a non-deformed myocite (Roth, 1988)	5 - 20 $\mu \mathrm{m}$
r _{bulk}	0.1 Ω	Assumption based on bulk tissue conductivity (Roth, 2000)	0 - 1 Ω
и	$10\mu{ m m}$	Typical value for a single filament wet-spun CNT fiber. CNT fiber radius varies from 5 - 50 μ m for single filaments.	5 - 50 µm
$ ho_{ m f}$	49.79 μΩcm	4-point probe DC measurement on medium thickness CCNI CNT fiber. Resistivity for wet-spun fiber ranges from. 17 - 100 μ Ωcm (Behabtu <i>et al.</i> , 2013)	N/A
\bar{y}_{dl}	$4.93 \mathrm{mSs^{n_{dl}}/mm^3}$	Fitting of EIS results	N/A
n _{dl}	0.932	Fitting of EIS results	N/A
r _{pore}	435 k Ω mm	Fitting of EIS results	N/A
īr _{ct}	$16.6 \mathrm{k}\Omega\mathrm{mm}^3$	Fitting of EIS results; approximation based on measurement in saline.	N/A
L _A	$100\mu{ m m}$	Equivalent to one cell length. Assumes that only one ring of cells around the fiber activate at the same time.	10 - 500 $\mu { m m}$
L _{block}	1 mm		$100\mu{ m m}$ - 1 cm
L _B	5 mm	Reasonable length for stable implant. Shorter effective lengths may be achievable by partial insulation of the fiber	1 - 10 mm

Table 5.1: Baseline parameters for calculation of H(x, f)

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5.4.1 Transfer function scaling with distance and frequency, limiting behavior

Figure 5.4 plots H(x,f) for 10^{-5} Hz $< f < 10^{5}$ Hz and for $0 < x < L_B$. This frequency range extends beyond the range that is relevant for action potential propagation *in vivo*, which is 1 Hz $< f < 10^4$; however, this expanded range is chosen to illustrate a broader range of the scaling behavior. Figure 5.4 A plots a solution for |H(x,f)| calculated using the baseline parameters in table 5.1. Figure 5.4 B plots the same solution as a function of frequency for a fixed position, x = 1 mm, in order to more clearly illustrate the frequency scaling behavior. Within the window plotted in these figures, the transfer function exhibits several regimes of scaling behavior with frequency. At low frequencies the voltage transfer exhibits a low-value plateau; this is followed by two regimes in which the transfer function exhibits a positive power law scaling with frequency, with power laws of ≈ 0.9 , and ≈ 0.47 , respectively. As shown in Figure 5.4 A, the transfer function is uniform over the length of the fiber, exhibiting a negligible decrease with increasing distance from the conduction block. Figure 5.4 C illustrates that a slight dependence on *x* appears at the highest frequencies if a much larger value is input for the fiber resistivity ρ_f .

The dependence of H (*x*,*f*) on the distance *x* is negligible because the resistance to current flow along the fiber axis is small compared to the impedance of current flow radially outward through the fiber and through the transmission line circuit at the fiber/electrolyte interface, \hat{Z}_{inter} . From equation 5.3 we note that $\hat{Z}_{inter}(f)$ has three regimes of frequency scaling, and these give rise to the regimes of scaling in the solution for |H(x,f)|. At very low frequencies the capacitive double layer impedance $\hat{z}_{dl}(f)$ is large compared to the charge transfer resistance \bar{r}_{ct} (i.e, $\hat{r}_{ct}\hat{y}_{dl}(jf)^{n_{dl}} \ll 1$); in this case equation 5.3 reduces to

$$\hat{Z}_{inter}(f) = \sqrt{\hat{r}_{pore}\hat{r}_{ct}} \coth\left(u\sqrt{\frac{\hat{r}_{pore}}{\hat{r}_{ct}}}\right)$$
(5.16)

This produces the low-frequency plateau behavior in |H(x,f)|; in this regime, current can only flow from the fiber to the extracellular fluid via charge transfer reactions, and the transfer of voltage to the surorunding cells is poor. As frequency increase a transition point is reached at



Figure 5.4: A: Magnitude of the electric potential transfer function |H(x,f)| calculated using the baseline parameters given in Table 5.1, plotted as a function of AC voltage frequency f (log scale) and distance x from the region of conduction block (linear scale). This length range represents the entire section of exposed fiber "downstream" from the conduction block, with the fiber end located at $x = L_B = 5$ mm. B: Values of the same function plotted as a function of frequency at a fixed value of position, x = 1 mm. C: |H(x,f)| calculated using basline parameters, but with the value of CNT fiber resistivity ρ_f increased by two orders of magnitude.

which $\hat{z}_{dl}(f)$ becomes smaller than \bar{r}_{ct} (i.e, $\hat{r}_{ct}\hat{y}_{dl}(f)^{n_{dl}} \gg 1$) and equation 5.3 reduces instead to

$$\hat{Z}_{inter}(f) = \sqrt{\frac{\hat{r}_{pore}}{\hat{y}_{dl}(jf)^{n_{dl}}}} \coth\left(u\sqrt{\hat{r}_{pore}\hat{y}_{dl}(jf)^{n_{dl}}}\right)$$
(5.17)

Equation 5.17 may be divided further into two regimes in frequency space, based on the value of $u\sqrt{\hat{r}_{pore}\hat{y}_{dl}(jf)^{n_{dl}}}$; if $\hat{r}_{pore}\hat{y}_{dl}(jf)^{n_{dl}}$; if $\hat{r}_{pore}\hat{y}_{dl}(jf)^{n_{dl}} \ll$ 1, in which case the hyperbolic cotangent term can be replaced with the approximation $\operatorname{coth}(Y) \approx (1/Y)$, and equation 5.3 reduces to

$$\hat{Z}_{\text{inter}}(f) = \sqrt{\frac{\hat{r}_{\text{pore}}}{\hat{y}_{\text{dl}}(jf)^{n_{\text{dl}}}} \left(u\sqrt{\hat{r}_{\text{pore}}\hat{y}_{\text{dl}}(jf)^{n_{\text{dl}}}}\right)^{-1}} = \frac{1}{u\hat{y}_{\text{dl}}(jf)^{n_{\text{dl}}}}$$
(5.18)

In this regime, the impedance of the fiber/electrolyte interface is dominated by the double layer capactance, and this impedance is large compared to the resistance associated with diffusion of ions into the porous fiber structure. There is a negligible difference in impedance for current reaching surfaces on the outer skin of the fiber and current reaching surfaces deep inside the fiber structure, and as a result the double layer impedance acts as if it were effectively that of a planar electrode. This produces the intermediate behavior in which the scaling of |H(x,f)| with frequency matches the frequency scaling of the electronic double layer capacitance; the power law scaling of |H(x,f)| between $4x10^{-4}$ and 4 Hz is $\approx n_{DL}$.

In the high-frequency limit, $u\sqrt{\hat{r}_{\text{pore}}\hat{y}_{\text{dl}}(jf)^{n_{\text{dl}}}} \gg 1$ and the hyperbolic cotangent term asymptotically approaches a value of 1. In this case equation 5.3 reduces to

$$\hat{Z}_{inter}(f) = \sqrt{\frac{\hat{r}_{pore}}{\hat{y}_{dl}(jf)^{n_{dl}}}} = \hat{r}_{pore}\hat{y}_{dl}(jf)^{\frac{n_{dl}}{2}}$$
(5.19)

In this regime the combination of porous diffusion resistance and the double layer impedance along the transmission line $\hat{Z}_{inter}(f)$ creates an impedance with a fractional power law dependence on frequency. This is an example of so-called 'anomalous diffusion' phenomena, of which the previously described Warburg impedance is also an example. Anomalous diffusion is a label applied to any case in which diffusion of some species violates the ordinary relationship

between mean squared displacement and time, $\langle r^2 \rangle \propto t$, and instead exhibits some relationship $\langle r^2 \rangle \propto t^\beta$, with $0 < \beta < 1$ (Bisquert and Compte, 2001). Various physical effects may give rise to anomalous diffusion of this kind; in particular, this type of scaling arises in cases of diffusion in which the number of diffusing particles is not conserved. This is the case in a transmission line circuit: the diffusion of charged species through the line (either electrons in a conductor or ions in a solution) is subject to a progressive loss to the external channel or sink, leading to a violation of conservation. The transfer function is governed by this anomlous diffusion current for frequencies above 4 Hz. This includes the range of frequencies most relevant to cardiac cell activiation, 1 Hz - 10 kHz (Bu *et al.*, 2009).

The primary conclusions that can be reached from examining the "baseline" transfer function solution in Figure 5.4 are that a) within the frequency regime most important for cell activation the magnitude of the transfer function is small, indicating that only a fraction of the extracellular voltage near the fiber on the proximal side of the block would be transferred to surrounding cells on the far side of the block, and b) whithin this frequency regime the transfer efficiency is strongly affected by the circuit parameters \hat{r}_{pore} and \hat{y}_{dl} , and almost totally unaffected by the fiber resistivity. This suggests that the best way to improve the effectiveness of transfer is not to emphasize the use of CNT fibers with high conductivity, but rather to use fiber that has a large amount of available surface area which can be wet by extracellular fluid, with an open porous structure to allow for facile ionic diffusion into and out of the structure.

5.4.2 Variation of transfer function in the physically relevant range

The range of AC voltage frequencies most relevant to the operation of cardiac cells is 1 Hz - 10 kHz, and the most important portion of this range for the transfer of action potentials is the kHz range, into which the rapid upstroke at the beginning of the action potential is expected to fall (Bu *et al.*, 2009). This is therefore the regime of greatest interest in our consideration of the transfer function H(*x*,*f*). The remainder of this section focuses on the calculation of solutions within this regime of interest, and examines the variation in the transfer function brought about by varying our assumptions about unknown physical parameters, or by varying the assumed



Figure 5.5: Magnitude (A) and phase (B) of the transfer function in the physically relevant frequency regime for several assumed values of junctional gap thickness h. A smaller gap leads to a larger seal resistance r_{gb} , and thereby to larger electric potentials within the gap.

dimensions of the CNT fiber electrode. Figure 5.4 demonstrates that the transfer function in this frequency regime is essentially uniform over the entire fiber length for any physically plausible values of CNT fiber resistivity; the following figures plot solutions of the transfer function as a function of frequency at a fixed distance from the conduction block, x = 1 mm, and it may be expected that the same magnitude of H (*x*,*f*) would be found at other distances.

Figures 5.5 and 5.6 demonstrate the change in magnitude of the transfer function based on different assumptions for the unknown parameters h and W_{cell} . A decrease in h or an increase in W_{cell} both lead to a linear increase in seal resistance for the extracellular fluid gaps between the CNT fiber and the cell membranes, leading to a roughly linear improvement in the transfer function.

Figures 5.7 and 5.8 plot the transfer function for different values of L_A and L_B , respectively. L_B is a parameter that can be controlled to a certain extent by choice of CNT fiber electrode



Figure 5.6: Magnitude (A) and phase (B) of the transfer function in the physically relevant frequency regime for several assumed values for W_{cell} , the width of the regions of close contact between the CNT fiber surface and neighboring myocytes. A wider surface of contact leads to a larger seal resistance r_{gb} , and thereby to larger electric potentials within the gap.



Figure 5.7: Magnitude (**A**) and phase (**B**) of the transfer function in the physically relevant frequency regime for several assumed values of L_A , the length of fiber exposed actively depolarizing cells. Increasing L_A decreases the total voltage drop experienced by current crossing the conduction block through the fiber.

length and implant procedure, coupled with electrical mapping of the conduction block region. L_A, on the other hand, is determined by the physiology of the heart tissue. L_A represents the length of the segment of tissue that is undergoing an action potential response at any given time, and as such it will depend on the conduction velocity of the action potential. It should be reiterated that L_A is a somewhat artificial parameter, arising from the simplifying assumption that $\phi_f(f)$ takes on a uniform value over some area of space. In reality the electric potential generated by activating cells will vary with both position and time as each successive set of cells in the bundle surrounding the fiber initiate their action potential responses, and the injection of current into the fiber will be non-uniform in space at any given moment. In a more complete derivation the nearest analog of L_A would be the length of fiber over which activating cells generate a non-zero $\phi_f(x, f)$.

The magnitude of the transfer function increases with increasing L_A, but decreases with



Figure 5.8: Magnitude (**A**) and phase (**B**) of the transfer function in the physically relevant frequency regime for several assumed values of L_B , the total length of the fiber "downstream" from the conduction block. Increasing L_B increases the total surface area available for current flux out of the fiber, decreasing the current density and thereby the electric potential in the junctional gap around the fiber. Note that the use of equation 5.12 complicates the question to some extent, because it is based on the assumption that that the length of fiber on both sides of the conduction block is equivalent. See Section 5.5 for further discussion.
increasing L_B ; this is a manifestation of the source-sink problem, in that L_A determines the size of the current source, and L_B determines the total area over which the current will be dissipated. A greater amount of fiber surface exposed to activating cells means more total current injected into the fiber. In this frequency range the current flux out of the fiber is uniform from x = 0 to $x = L_B$; large L_B leads to a smaller total current density along the fiber interface and therefore a smaller potential in the interfacial extracellular gap.

Figure 5.9 demonstrates that the spatial extent of the conduction block, L_{block} , does not have a significant effect on the transfer function; this is a consequence of the fact that \hat{Z}_{inter} is large compared to r_f in this frequency regime. However, it is important to note that this is only true for a case in which the conduction block is truly insulating so that there is no current loss from $x = -L_{block}$ to x = 0. If the scar tissue forming the block has some conductivity, or if there are significant channels for extracellular fluid to reach the fiber, then an increase L_{block} will have same effect as an increase in L_B , increasing the total surface area over which current is extracted from the fiber and decreasing transfer efficiency.

Changes in each of the above parameters result in changes in the magnitude of H at all frequencies considered, but they do not change the phase or frequency scaling of the function in this region. In contrast, Figure 5.10 shows that a variation in the fiber diameter *u* has a more complicated effect. Counter-intuitively, an increase in *u* does not lead to a significant increase in the efficiency of voltage transfer at intermediate and high frequencies. This is another manifestation of the source-sink problem. An increase in *u* lowers the total resistance within the fiber by increasing cross sectional area, and it lowers the interfacial impedance \hat{Z}_{inter} by increasing both the outer surface area of the fiber and the depth of fiber structure available for electrolyte intercalation; however, it also means that N, number of myocyte cell strands around the fiber, increases. As a result, the current sink around the fiber is larger, and the electric current transfer to each of the separate cell membranes is increased by only a small amount. The major effect of increasing fiber radius is that the transition from \hat{Z}_{inter} dominated by \hat{z}_{dl} to \hat{Z}_{inter} with significant transmission line behavior is shifted to lower frequencies, and the transfer efficiency in the low frequency range is more significantly increased (a result of decreased \hat{z}_{dl}).



Figure 5.9: Magnitude (A) and phase (B) of the transfer function in the physically relevant frequency regime for several assumed values of L_{block} , the total length of the region of conduction block. This assumes that the region of conduction block is a complete insulator, such that current cannot leak from the fiber into the ground potential within this length of space.



Figure 5.10: Magnitude (A) and phase (B) of the transfer function in the physically relevant frequency regime for several assumed values of fiber radius u. Changing the fiber radius increases the surface area of fiber exposed to both activating and passive cells, with competing effects on the transfer efficiency leading to small net change at moderate to high frequencies. Changing u also impacts the relative contributions of z_{dl} and r_{pore} to Z_{inter} , which shifts the boundary between the two frequency scaling regimes.

The variation with fiber diameter shown in Figure 5.10 can in fact be broken into two competing effects if we dispense with the assumption that the fiber diameter is uniform. Changes in L_A and L_B have inverse effects on the magnitude of the transfer function because they represent the extent of the fiber in contact with a current source and a current sink, respectively; the same is true of the fiber radius in the section exposed to activating cells, which is used in the calculation of Z_A , and the fiber radius in the section of the fiber passing through the conduction block and the region of tissue beyond it. Figure 5.11 and 5.12 show the variations in the transfer function that result if these quantities u_A and u_B are varied independently. Increasing u_A increases the efficiency of voltage transfer; it also causes a shift in phase similar to that which was observed in Figure 5.10. In contrast, increasing u_B leads to a significant decrease in voltage transfer efficiency by dividing the available current into a greater number of cells, but does not change the phase. This implies that the frequency scaling of the transfer function in this regime is determined by the frequency scaling of $Z_A(f)$, the impedance between the fiber and the current source representing the activating cells.



Figure 5.11: Magnitude (A) and phase (B) of the transfer function in the physically relevant frequency regime for several assumed values of fiber radius within the segment exposed to activating cells, u_A , with the radius everywhere else along the fiber set to the baseline value.



Figure 5.12: Magnitude (A) and phase (B) of the transfer function in the physically relevant frequency regime for several assumed values of fiber radius in all segments not exposed to activating cells, u_B , with the radius of the fiber segment that is exposed to activating cells set to the baseline value.

5.5 Conclusion

5.5.1 Sources of uncertainty

The circuit model and transfer function presented here have only limited predictive power due to their reliance on several assumptions and unknown quantities. This section reiterates the major assumptions and limitations inherent in the derived circuit, suggests experimental approaches that could be taken to eliminate some of them in the future, and summarizes the conclusions that can be drawn from the transfer function as it currently stands.

Section 5.3 introduced several major sources of uncertainty in the derivation of the transfer function H(x, f). These include:

- The relative alignment between CNT fibers and the myocyte bundles in the local tissue
- The extent to which cell membranes and the fiber surface conform to one another *in vivo*, and the width of the surface of conformal contact between each cell and the fiber (W_{cell})
- The average thickness of the extracellular gap between the fiber surface and nearby cell membranes (*h*)
- The extent to which other factors may lead to complete fiber encapsulation by the tissue, and the influence of this encapsulation on the total seal resistance in the extracellular fluid near the fiber
- The question of whether individual CNTs in the fiber skin penetrate the cell membranes

Most of these unknowns represent open questions about how the cellular tissue will adhere to and remodel itself around CNT fiber on a μ m and sub- μ m scale after implantation *in vivo*. The first, relative alignment, may be subject to a certain amount of control given a proper implantation mechanism and sufficient information about the local alignment of cells in various regions of the heart muscle. The calculations presented in Section 5.3 do not address cases in which there is misalignment between the fiber and myocyte bundles, but it is reasonable to speculate that the primary difference which would arise in such a case is a large increase

in the factor Q, the fraction of fiber surface area not in close contact with a cell membrane, corresponding to the gaps opened between neighboring cell strands as they are parted by the passage of the fiber through the myocyte bundles. The extent to which the fiber surface would indeed be exposed in such a case is also highly dependent on the precise manner in which the fiber is encapsulated and/or endothelialized by the tissue in the long term after implantation; if other organic tissue around the fiber creates an increase in R_{seal} then alignment may not be crucial.

There is a one more significant source of uncertainty in the use of the transfer function H(x,f) to predict action potential transfer through a CNT fiber electrode: the magnitude of $\phi_0(f)$ itself. H represents the ratio ϕ_g/ϕ_0 ; reliable initiation of action potentials in the cells around the fiber at position *x* requires that ϕ_g reliably achieve values greater than 20 mV. A reliable prediction of both H(x,f) and $\phi_0(f)$ are needed in order to predict whether action potential transfer will be successful.

The peak amplitude of the extracellular potential in strands of guinea pig cardiac muscle has been measured to range from 13 to 24 mV during cellular activation (Knisley *et al.*, 1991). However, the electric potential that would be realized near the skin of an implanted cardiac fiber may be higher than this, depending on the seal resistance between the fiber and the activating cells immediately surrounding it. During the action potential response, current will be exchanged across the cell membranes between the intracellular fluid and the extracellular fluid in the junctional gap until a certain membrane polarization is achieved; the greater the seal resistance, the greater the magnitude of ϕ_0 that will result from this current. Ultimately, then, the transfer function H and the magnitude of the input function ϕ_0 will both depend on the unknown factors that determine the seal resistance, including h, W_{cell}, and any other sources of resistance due to fiber encapsulation.

Investigation of the μ m and sub- μ m scale physiology of the CNT fiber/tissue interface is not a straightforward task, especially given that changes may occur in the days and weeks after *in vivo* implantation due to the immune response or other biological processes. Direct imaging of the interface is not feasible given the length scales involved. A standard SEM technique would require dehydration of the sample, which would dessicate the cells and completely alter the nature of the interface; furthermore, removal of a section of implanted fiber and surrounding tissue from an *in vivo* implant or an *in vitro* culture without mechanically disrupting the interface is difficult due to the toughness of the CNT fiber, which makes it difficult to cut. It may be possible to obtain a good longitudinal cross section of the fiber and surrounding tissue by carefully slicing a down the axis of the fiber, then imaging the sample using a cryo-SEM technique. It may also be possible to use optical microscopy to measure W_{cell} or to gain other information about the gross size and shape of cardiomyocytes around and on implanted fiber.

While understanding the microscopic structure of the interface around an implanted CNT fiber may have other benefits, for the purpose of calculating the transfer function H it would be sufficient to have a measurement of the seal resistance; this may be easier to obtain. *In vitro* measurements of current exchange and seal resistance between myocytes and CNT fiber could be carried out using a patch-clamp technique (Lippiat, 2008), or by studies employing fluorescent voltage sensitive dye, as in Braun and Fromherz (2004).

Ultimately, the most reliable information about seal resistance and about other electrical properties of the CNT fiber/tissue interface can be generated through *in vivo* trials in animal models. Measurements of a) the input voltage required to stimulate cells and b) the amplitude of cellular voltage signals than can be recorded with CNT fiber electrodes of known size and surface area, combined with independent measurements of EIS properties of the fiber in extracellular fluid, may allow for indirect measurement of the seal resistance and of the voltage ϕ_0 experienced as a function of time and frequency by a CNT fiber implanted in a group of activating cells.

5.5.2 Predictions for optimal device design

The transfer function calculations presented in this section cannot be used to make fully accurate predictions about CNT fiber electrode performance *in vivo*; they do, however, lead to several conclusions and testable predictions about which design parameters are important to the performance of such an electrode. The factors that govern electrode performance fall into three

categories: those which determine the impedance between the CNT fiber and the surronding exctracellular fluid, those which determine seal resistance between fiber and cell membranes, and those which determine the balance of current sources and current sinks within the fiber/tissue circuit. Broadly speaking the latter controls the current density out of the fiber, and the former determines the relationship between this current density and the local electric potential at the membranes of the nearest cells.

As noted in Section 5.4.1, the transfer efficiency in the relevant frequency regime is strongly affected by the circuit parameters \hat{r}_{pore} and \hat{y}_{dl} , and almost totally unaffected by the fiber resistivity. This suggests that the best way to improve the effectiveness of transfer is not to emphasize the use of CNT fibers with high conductivity, but rather to use fiber that has a large amount of available surface area which can be wet by extracellular fluid, with an open porous structure to allow for facile ionic diffusion into and out of the structure. The goal of maximizing \hat{y}_{dl} and minimizing \hat{r}_{pore} requires that a distinction be made between the total CNT surface accessible by electrolyte and the total CNT surface that can be easily accessed by ionic diffusion.

Figures 5.5 and 5.6 ultimately demonstrate changes in voltage transfer resulting from changes in seal resistance. In the calculation presented here the seal resistance was governed by the parameters W_{cell} and h; more generally this resistance will be controlled by the degree of encapsulation of the fiber and the extent to which the tissues surrounding the fiber, whether they are myocytes, collagen, or scar tissues, obstruct the flow of current away from the fiber and the myocytes surrounding it. It may or may not be possible to affect the way in which the tissue remodels itself after implantation of a CNT fiber, or the closeness of contact between cell membranes and fiber surfaces; however, to the extent that it is possible, any design feature or treatment that promotes adhesion of cell membranes onto the fiber surface or encourages complete endothelialization of the fiber will be beneficial to performance.

Modifying the physical dimensions of the CNT fiber electrode primarily affects the transfer function by changing either the total current available to be carried by the fiber or the current density leaving the fiber. Increasing the length of fiber or the radius of the fiber in the region of activating tissue "upstream" from a conduction block will improve performance; increasing the length or radius of the fiber (i.e., increasing macroscopic or geometric surface area) within the region of conduction block or within the tissue "downstream" from the block weakens voltage transfer and degrades performance.

If the CNT fiber designed for implantation is a single filament or bundle with a uniform diameter, then the effectiveness of the electrode should be independent of the choice of that diameter. In a therapeutic application there may still be some utility to increasing the diameter of the fiber. Doing so will ensure that, so long as the appropriate voltage thresholds can be achieved to stimulate the cells around the fiber, a greater total number of cells will be stimulated; this will in turn minimize the potential for subsequent source-sink mismatch problems to arise in the tissue itself. Otherwise, it may be best for the diameter of CNT fiber electrodes to be chosen with the aim of optimizing other properties of the device, such as biocompatibility or the ease and stability of implantation. Improved performance could be achieved by using more complex electrode geometries, such as a CNT fiber bundle with non-uniform diameter, or an electrode composed of multiple parallel CNT fiber filaments on one end, to be implanted "upstream" from the block, connected to a single filament which bridges the block.

The maximum value of L_A will most likely be a function of the cardiac tissue, set by the characteristic length λ of the "wave-front" of cells experiencing depolarization at any given moment. Additional length of exposed fiber electrode (in excess of λ) "upstream" from the conduction block will not result in any increase in the instantaneous electric potential $\phi_g(x, f)$ in the junctional extracellular gaps between the fiber and unstimulated cells; in fact, excess length "upstream" from the block may be a liability in terms of performance, in that it could represent an additional region of fiber exposed to a current sink (this is the basis for our assumption that current crossing the conduction block is only injected over a fraction of L_A). From a design perspective, the optimal CNT fiber electrode would be one that maximizes the length of fiber exposed to depolarizing cells when an action potential wave passes through the local tissue, but which minimizes exposed length in excess of that.

Minimizing the lengths of exposed fiber within and beyond the block, L_{block} and L_{B} , is also important to achieving efficient voltage transfer. Theoretically, minimizing L_{B} does have two

drawbacks for device performance, neither of which is considered in the current transfer function calculation. One is an additional manifestation of the source/sink mismatch problem: if L_B is very small and only a small number of myocytes are stimulated by the fiber, this group of cells may not successfully transfer the action potential response into the bulk of cellular tissue around them. The second drawback is that a decrease in L_B without a corresponding decrease in the length of exposed fiber "upstream" of the region of activating cells injecting current into the fiber will increase the relative impedance of the branch of fiber crossing the conduction block (by removing the very low-conductivity pathway through the fiber to a large surface of heart tissue), and will thereby decrease the fraction of the total current from the stimulating cells that passes along that branch. This issue will also arise if an electrode geometry is chosen in which the fiber has a greater radius or a larger number of connected parallel filaments upstream from the conduction block than downstream from it. In the calculations presented in Section 5.4 this current split was assumed to be equal in all cases, which is tantamount to the assumption that the total impedances across each branch of the fiber were roughly equal; in reality total impedance along each branch of the fiber will be determined in large part by the total geometric surface area of fiber available for electrochemical exchange on each side.

From a practical standpoint L_{block} will be set by the local thickness of the scar tissue or other conduction block that necessitates therapeutic treatment, and the minimum values of fiber length upstream and downstream from the conduction block will potentially be set by the requirement that the implantation of the fiber be mechanically stable, with a long enough surface of contact to provide mechanical stability. It may be possible to vary the area of CNT fiber surface available for current exchange in any of these three regions by using fiber coated with an insulating layer of biocompatible polymer. Such a coating, interrupted by short sections of exposed fiber, may allow for a design that optimizes L_A and limits L_B and u_B without compromising the stability of mechanical implantation and without significant current loss in the direction of recently-polarized tissue "upstream" from the conduction block.

The system that has been modeled here is complex, and this model relies on many assumptions; it's purpose is to serve as a starting point for future work on the design of artificial conduction bridges. Ideally, experiments designed to test the predictions of transfer function scaling with the variations outlined above will allow for improvement and modification of this model, allowing it to more accurately reflect reality and to serve as a useful tool in the development of conductive cardiac implants.

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