RICE UNIVERSITY

Improving Electrical Performance of Carbon Nanotube Fibers Using Liquids

by

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ABSTRACT

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Since the discovery of carbon nanotubes in 1991, carbon nanotube-based fibers have been put forth as candidates as a lightweight replacement for metals in electrical wiring. While a tremendous amount of progress has been made in developing these CNT-based fibers for copper replacements, they are still not ready for ubiquitous use. Thus far, the properties of carbon nanotube fibers that are made in industrial quantities typically fall below meticulously-made laboratory samples. Even these small-scale samples fall short of copper’s absolute conductivity value. If copper is to be replaced by an alternative conductor, it is of vital importance that this conductor’s performance equal or exceed copper. In pursuit of this goal, new methods to manipulate the electronic properties of CNTs in a fiber using liquids were investigated. Enhancing conduction using liquids is a nearly unexplored area as liquids have a very limited role in energy transmission. It has been shown that liquids are able to infiltrate the void space inside of several types of carbon nanotube fibers and alter the electrical properties. In so far, this inherent structural feature of CNT fibers has yet to be fully explored in regard to conduction. In this work, the composition, porous structure, and initial electronic properties of direct spun carbon nanotube fibers was obtained. A systematic study showing how solvent properties
effect iodine doping in CNT fibers was performed. A novel method of creating liquid proof electrical contacts between CNT fibers and metals was developed. Experiments illuminating the changes in carbon nanotube fiber structure and resistance upon immersion in liquids were performed. And a liquid-phase doping scheme was examined and showed a decrease in fiber resistance as well as an increase in current carrying capacity. These electrical property changes induced by liquids have tremendous potential for large scale improvements. The understanding generated in this project of the effects that liquids have on conduction in carbon nanotube fibers resulted in an increase in the fiber's electrical performance and will ultimately aid in the implementation of carbon nanotube fibers as conduction wires.
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I would first like to acknowledge my thesis advisor, Prof. Enrique Barrera. Throughout this program, he always provided meaningful guidance and bestowed me with his vast enthusiasm for scientific research. He has been a constant source of challenging questions, which drove me to be creative and was essential to my success. I am very grateful to have been his student.

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# Nomenclature

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<td>CNT</td>
<td>Carbon Nanotube</td>
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<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>HiPCO</td>
<td>High Pressure Carbon Monoxide</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methyl-2-Pyrrolidone</td>
</tr>
<tr>
<td>RBM</td>
<td>Radial Breathing Mode</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
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<td>XPS</td>
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Of the grand challenges that humanity must face in the coming century, energy is quite possibly the most important. Yet, it is arguably the most complex and an ever-evolving challenge. Rice University’s own Richard Smalley characterized energy as such over a decade ago and that sentiment has only risen since. A vast amount of effort is currently being applied to discovery and development of alternative and renewable energy sources. And even when these energy sources have been fully implemented, efficiency and conservation will be paramount in ultimately solving the energy grand challenge. It has been postulated that ultra-lightweight, super strong, multifunctional materials could enable a 40% savings in fossil fuel consumption in the United States alone. Carbon nanotubes (CNTs) are a class of materials that have already made a significant impact on the realization of those multifunctional materials.
CNTs possess the multifunctionality of composite materials but do not have to be artificially combined with any other material. They are incredibly strong, light, and are electrically conductive. Two areas that can benefit from such materials are transportation and energy distribution, i.e. replacing metal conductors used for electrical wiring and electricity transmission lines with lightweight, multifunctional alternatives. Copper conductors have not changed very much in the last half century. Their properties are well established as well as its limitations. One such limitation is weight. The additional weight of copper conductors in wiring harnesses and electrical machines, for example, is limiting their performance, as energy consumption is undeniably related to weight. Additionally, copper generates a vast amount of heat due to Joule heating. Power cables for high amperage applications must manage this heat or risk cable failure. It is for these reasons as well as the others presented above that there is a need for a material that conducts electricity like copper and weighs significantly less and possesses the inherent ability to better manage the heat generated due to current flow. This need could be met by CNT-based materials, which are currently in the development phase.

Taking electrical machines as an example, replacing the copper fiber with carbon nanotube fiber in them has several distinct advantages. A CNT-based fiber can be seen in figure 1.1 a. The first and biggest advantage is weight. The density of copper is much larger than carbon and given how much copper fiber is contained within a modern electric motor (shown in figure 1.1 b), replacing it with CNT fiber would result in a significant weight savings. This would be especially true for motors that do not contain permanent magnets, like induction motors. In addition, this difference in
density means that more CNT fiber can packed into a motor, thereby increasing motor torque. Another advantage of using carbon nanotube fiber in an electric motor is that its resistance varies less with changes in temperature compared to copper fiber. This means that the efficiency of a motor made using CNT fiber would fluctuate less over a wide temperature range. As well, since copper’s resistance increases more quickly with increasing temperatures\(^1\), using CNT fiber in an electric motor would likely increase its efficiency at higher operating temperatures and longer operation times (less machine loss due to ‘copper losses’). To put this concisely, using CNT fiber in electric motors would result in a motor that has equal or better properties but would weigh significantly less.

Although the above example focuses specifically on electrical machines, there are many other industries that could utilize CNT fiber technology. For instance, there is over a mile of copper wiring in currently manufactured vehicles and switching to a
CNT conductor (approximately 1/6 the weight of copper) represents a significant reduction in weight and fuel consumption. Similarly, since CNT current density is much higher than copper, these wires could be thinner and carry the same amount of current. Thus, representing an even greater weight savings without compromising function. This principle can apply to aerospace industry as well. Power distribution lines utilizing CNT fiber would need less reinforcement as this fiber weighs less, is plenty strong already, and lengthens and shortens less with changing temperature. Thus, reducing reinforcement reduces overall weight and the energy needed to install and transport these lines. Furthermore, since the resistance of CNTs increases less quickly with increases in temperature compared to copper, wires made from CNTs would be better equipped to handle higher amperage loads. Currently, the copper cables that supply the high amperage needed to operate furnaces and other high-power electrical equipment need to get rid of the excess heat that the wires generate due to Joule heating, or the cable could fail. This same principle applies to transformers. Heat exchange systems based on oil, water or air are essential to the successful operation of a transformer. A fully developed CNT-based cable of equal size and conductivity could supply the same amount of current and would operate with a decreased rate of failure due to excess heat.

While a tremendous amount of progress has been made in developing these CNT-based fibers for copper replacements, they are still not ready for ubiquitous use. Several manufacturing processes that are capable of making kilometers of CNT fiber have been developed. But thus far, the properties of these nanotube fibers that are made in industrial quantities typically fall below meticulously-made laboratory
samples. Even these small-scale samples fall short of copper’s absolute conductivity value. If copper is to be replaced by an alternative conductor, it is of vital importance that this conductor’s performance equal or exceed copper. In pursuit of this goal, I investigated new methods to manipulate the electronic properties of CNTs in a fiber using liquids. Enhancing conduction using liquids is a nearly unexplored area as most conductors are not porous and do not interact very well with liquids. Besides being a method for heat exchange, liquids have a very limited role in energy transmission. In contrast, when applied to CNT fibers, liquids can be the substances responsible for positive electrical property change. Many three-dimensional CNT-based materials have a porous structure and a very high surface area. In CNT fibers, this porous structure is described as yarn-like. And with this structure comes the opportunity for interactions with liquids and gases within the pores of the CNT fiber. It has been well documented that many substances in close proximity to CNTs can drastically change their electrical properties, including liquids. In so far, this inherent structural feature of CNT fibers has yet to be fully explored in regard to conduction. The electrical property changes induced by liquids have tremendous potential for large scale improvements. Because of this conductor’s unique and exploitable interaction with liquids, new and potentially useful energy transmission products can be developed based on porous CNT conductors and liquids. This project aimed to explore this possibility. In doing so, a comprehensive understanding of the effects that liquids have on conduction in CNT fibers has been generated and it will be shown that application of this knowledge resulted in an increase in the fiber’s electrical performance.
1.1. Thesis Outline

This thesis focuses on the development of a comprehensive understanding of the interaction between CNTs in a fiber and liquids and how this interaction affects the CNT’s electrical properties. Insights gained from this experimental work were then used in the development of two systems where liquids can be used enhance conduction in CNT fibers.

Chapter 2 presents background information for this thesis. Topics presented will include electronic applications of CNTs, CNT fiber synthesis, characterization of an electric motor that contains CNT fiber, and contact resistance and doping as it relates to CNT fibers.

Chapter 3 contains all of the characterization performed on the CNT fibers used in this thesis. Composition, porous structure, and initial electronic properties will be presented in this section.

Chapter 4 presents a study showing how solvent properties effect iodine doping in CNT fibers. For this study, the solvent will be the dopant delivery vehicle, evaporating after application. This study's conclusions will emphasize the importance of accounting for all of the fundamental interactions in doping of CNT fibers with iodine dissolved in solvent, i.e. the CNT + dopant interaction, the CNT + solvent interaction, and the dopant + solvent interaction.

Chapter 5 outlines a novel method of creating liquid proof electrical contacts between CNT fibers and metals. This method utilizes indium powder and solder to
attach fibers to copper tape. Creating this type of contact proved to be crucial for the completion of many experiments in this thesis.

Chapter 6 presents a study on liquid-phase electrical property modification of CNT fibers. This study differs from the previous as the liquid plays an active role, i.e. the CNT fiber is constantly immersed in liquid during data collection. This section will focus on liquids that have a strong electrochemical doping effect and do not exhibit the elasto-capillary effect discussed in a previous chapter. Time-resolved resistance measurements along with Raman spectroscopy data show that there are liquid-induced charge transfer effects in CNT fibers. The overall effect of this liquid-phase doping is lower fiber resistance and an increase in current carrying capacity.

Chapter 7 containing concluding remarks and discusses future studies.
2.1. Carbon Nanotubes

Since their discovery by Iijima in 1991, investigations into the properties of carbon nanotubes (CNTs) have revealed many superiorities mainly relating to mechanical strength and electrical conduction. This hollow nanoscale tube containing carbon in only the SP2 hybridization state can be visualized as a rolled graphene sheet. CNTs can exist in single or multiwalled versions and in one of three configurations depending on how the sheet is rolled (armchair, zig-zig, and chiral). A single walled carbon nanotube's (SWCNT) tensile strength and modulus far exceed metals- SWCNT Tensile strength $\sim 50$ GPa (Steel: 0.5 GPa) and SWCNT tensile modulus $\sim 1000$ GPa (Steel: 200 GPa). As well, much research effort has gone into investigating the electronic properties of CNTs. Individual CNTs are a type of
quantum wire and their electrical properties are different depending on the nanotube’s structure. CNTs in the armchair configuration are metallic while those in the zig-zag or chiral configuration are semiconducting. This can be seen in figure 2.1-a graph showing the density of states at different energy levels. Armchair CNTs have a finite number of charge carriers in the density of states at the Fermi level, a characteristic of metals, while the zig-zag CNTs show no charge carriers in the density of states at the same level, a characteristic of semiconductors. The charge carriers are free to travel along the axial directions of the nanotube. And since the CNTs are one-dimensional conductors, there are two conduction channels (energy sub-bands at the Fermi level in a laterally confined system). Figure 2.2 presents a band structure of an
armchair CNT. Note that the $a_1$ and $a_2$ bands cross at the Fermi energy, indicative of metallic character. CNTs can also exhibit ballistic conduction in which the electrons travel without scattering. In conjunction, these properties are responsible for the exceptional electronic properties—Electrical Resistivity $\sim 1 \times 10^{-8} \Omega \cdot m$ (Copper $1.7 \times 10^{-8} \Omega \cdot m$). A single metallic carbon nanotube's current density is vastly greater than that of copper, about 1,000 times larger\(^5\). Considering all these extraordinary properties, a natural next step is to bundle many CNTs together and make a fiber for conduction. Even given these extraordinary properties, non-ideal growth and packing of carbon nanotubes into fibers has yielded the opposite result—a resistivity that is lower than copper wire. But the issues at the foundation of this non-ideal formation
of fibers are essentially solvable and there are many good reasons to develop CNT-based fibers.

**2.2. Electrical Applications of CNTs**

Being such a multifunctional material, CNTs have been used in many diverse applications. As mentioned above, CNTs possess unique characteristics that make them particularly useful for electrical applications. In general, CNTs are very good field emitters\(^6\), which makes them good candidates for use in flat television and computer screens. Semiconductor single-wall CNTs are very sensitive to molecules in their immediate vicinity due charge transfer that occurs with these molecules. This trait is the basis of single wall CNT gas sensors which are typically orders of magnitude more sensitive than standard solid-state sensors\(^7\). Chemical\(^8\) and biochemical\(^9\) sensors based on this principle have also been developed. Semiconducting single wall CNTs can also be used to create field-effect transistors\(^10,11\). Sensors made from CNT have been shown to be able to accurately monitor the curing of polymers during composite material fabrication\(^12\).

**2.3. CNT Fiber Synthesis**

One of the most exciting ways that the extraordinary properties of CNTs are being applied is through macro-scale continuous fibers. CNT fibers can be fabricated by several methods and each has its own set of advantages. For example, dry spinning
of a CNT aerogel created from a floating catalyst chemical vapor deposition method yields a fiber in a single step. While wet spinning CNTs into a fiber involves an additional step because the CNT have to be made first, then dispersed in solution to make a fiber using a spinneret or similar device. But this extra step allows for the selection of CNTs that have been purified, while the one-step floating catalyst chemical vapor deposition dry spinning process does not. The following sections present a summary of methods to fabricate CNT fibers.

2.3.1. Wet Spinning

Wet spinning procedures that are available in literature typically follow this general scheme: 1) disperse CNTs in solution 2) push that solution through a die into a coagulation bath, which removes the dispersion solution and bundles the CNTs together in the form of a fiber. Figure 2.3 shows a CNT fiber wet spinning setup established by Behabtu et al. in 2013. This process involves dispersing CNTs in

Figure 2.3 CNT Fiber Wet Spinning Setup

a) Light micrograph of spinning dope b) CNT fiber wet spinning setup. The coagulation bath is seen in the middle. The spinning dope is extruded from the device on the left and the drum is seen on the right c) collection drums d) single fiber spinneret e) 19 fiber spinneret
chlorosulfonic acid (producing a liquid crystal) and extrusion through a spinneret in a coagulation bath. Superacids like chlorosulfonic or fuming sulfuric acid are used here because they produce a homogenous CNT solution without damaging the CNT structure. Once extruded, the fibers enter a coagulation bath of water or acetone. This bath removes the acid from the nanotubes and bundles them together. CNTs possess strong intertube van der Waals attractions, which limit solubility in many liquid mediums. The fibers are then removed from the coagulation bath and spun on a drum. Figure 2.4 shows the produced CNT fiber. Fibers produced in this manner are generally dense with little internal void space and contain nanotubes that are well aligned. These properties combined with the use of very high aspect ratio CNTs produces a fiber with a tensile strength of 2.4 GPa and the highest reported conductivity for this type of material- 8.5 MS/m. This value is roughly 15% of copper’s conductivity.

Another wet spinning method is referred to as surfactant-based coagulation spinning. Here, CNTs are dispersed in a surfactant solution and recondensed in a polymer solution, which forms a CNT mesh. This mesh is then collected and turned
into fibers. Vigolo et al. proposed this process in 2000 whereby the CNTs were dispersed in a solution of sodium dodecyl sulfate and polyvinyl alcohol was used as the polymer solution. A schematic of this process can be seen in Figure 2.5. Fibers produced by this process possess properties much lower than ones produced using superacids (Tensile Strength: 0.23 GPa for Surfactant-Based vs. 2.4 GPa for superacid, Electrical Conductivity: 1000 S/m for Surfactant-based vs. 8.5 MS/m for superacid).

2.3.2. Dry Spinning

Dry spun CNT fibers are typically made by either a one or two step process. The one step process, mentioned earlier, is the direct spinning of a CNT aerogel created by a continuous floating catalyst chemical vapor deposition process. The
fibers that will be used in this proposal are made by this method. The two-step process is commonly known as forest spinning. This process will be described first.

Jiang et al. in 2002 were the first group to report that CNT fibers could be spun from a vertically aligned CNT array, referred to as a CNT forest, brush, or carpet\textsuperscript{17}. Fabricating fibers in this way is a two-step process as the forest has to be made first-typically using a chemical vapor deposition method. Once this forest has been grown, fibers are made by carefully pulling out some of the CNTs at the edge and friction between the CNTs keeps them together as the fiber is being made. This process can be seen in figure 2.6. Material properties of fibers made by this method are lower in value when compared to both the one step dry spinning method and the superacid wet spinning method (Tensile Strength: 1.1 GPa; Electrical Conductivity: 90 kS/m\textsuperscript{18}).

The one step method of dry spinning CNT fibers involves collecting and spinning a CNT aerogel produced by a floating catalyst chemical vapor deposition (CVD) process. This is a continuous fabrication method and can make fibers that are kilometers (or longer) in length. Figure 2.7 shows an overview schematic of this process\textsuperscript{19}. Here, carbon, iron, and sulfur sources as well as the carrier gas (H\textsubscript{2}) are introduced into the hot zone (>1000 °C) of the vertical CVD furnace. At this high temperature, the carbon source decomposes in the H\textsubscript{2} reducing atmosphere. The iron source is the catalyst on which these carbon atoms attach and nanotubes grow.
Figure 2.6 Forest Spinning of CNT fiber

Top Left: Spinnable CNT array. Top Right: Initial step of pulling out the CNTs on the edge of the forest. Bottom Left: fiber twisting. Bottom Right: High magnification images of twisted fibers

Figure 2.7 Overview of the vertical floating catalyst chemical vapor deposition process for one-step dry spinning of CNT fibers

The right side highlights the decomposition of precursors that leads to the formation of the CNT aerogel
And sulfur is the promotor of this growth. Sulfur is particularly important at this high
temperature as it enhances the attachment of carbon atoms to the growing ends
of the nanotube. The carbon nanotubes grown at this part of the furnace then form an
aerogel. Van der Waals forces keep this aerogel together as it flows away from the hot
zone toward the exhaust. At this point, this aerogel is densified by a 360° solvent
spray and spooled. Figure 2.8 shows SEM images of the CNT fibers produced by this
method at various length scales. This dry spinning method produces fibers with very
good mechanical and electrical properties (Tensile Strength: 8.8 GPa\textsuperscript{21}; Electrical
Conductivity: 6.7 MS/m\textsuperscript{22})

Figure 2.8 SEM Images of CNT Fibers Produced by the One Step Dry Spinning Method
A) Low magnification image of a CNT Fiber tow of 150-200 fibers B) Image A with higher magnification C) Image of a single CNT Fiber D and E) high magnification images of a CNT fiber showing bundles of CNTs
2.4. Mechanical Property Enhancement of CNT Fibers

Enhancement of CNT fibers strength using solvents and polymers has also been demonstrated. Li and colleagues used a variety of solvents, as N,N-dimethylformamide, dimethyl sulfoxide, and N-methyl-2-pyrrolidone, to densify the array spun CNT fibers. They reported that fibers densified in this method were 100-200 MPa stronger than ones densified with ethanol. The strongest fiber they produced was densified by ethylene glycol (Fiber Strength - 1.45 GPa). They then reported that strength could be increased even further by polymer infiltration utilizing polar solvents. The strongest fiber reported used bismaleimide as the polymer and registered a strength of 2.38 GPa. Similar to this polymer infiltration, monobenzene molecular crosslinker can be employed to increase the specific tensile strength and Young's modulus of CNT fibers beyond commercially available carbon fiber (Specific Tensile Strength: 3.7 N/tex CNT fiber vs. 3.6 N/tex carbon fiber; Young's Modulus: 210 N/tex - CNT fiber vs. 180 N/tex - carbon fiber).

This liquid infiltration trait can also be used for the incorporation of bio-inspired materials into CNT fibers. Ryu and colleagues synthesized CNT forests by plasma enhanced chemical vapor deposition. Then they directly spun fibers from these forests and then processed them by the following method: 1) mechanical twisting, 2) application of the mussel-inspired catecholamine polymer, and 3) heated to 120 °C to evaporate the solvents used. They report a 65% increase in tensile strength with the use of the catecholamine polymer.
2.5. CNT Fibers as Electrical Wiring and in Electrical Machines

Several successful applications of CNT fibers as electrical wiring have already been demonstrated. Uncoated fibers have been used to light up a lightbulb\textsuperscript{22}. Ethernet\textsuperscript{1} and universal serial bus\textsuperscript{26} cables have been fabricated and showed to have comparable performance to standard cables. Solenoids\textsuperscript{1}, a transformer\textsuperscript{27}, and a generator\textsuperscript{28} have also been developed. Additionally, lightweight coax cables\textsuperscript{29} have been produced as well as large diameter wires with a current rating that exceeds 20 amps\textsuperscript{30}. For this thesis, an electric motor was made as a proof-of-concept demonstration. Much research effort has been expended attempting to extract the theoretical conduction from a CNT-based fiber. And even the highest reported level still falls short of the theoretical mark and the conduction of its metal competitors. Table 2.1 shows a summary of the current highest reported material properties of CNT fibers next to its metal competitors, copper and aluminum. This point can be demonstrated by creating an electric motor from CNT fiber. As seen in figure 2.9 a tow of CNT fiber was jacketed using a red enamel paint, coiled and placed over a permanent magnet. When current is applied to the paper clips and the coil is given a little bit of motor starting rotation, this motor will begin to spin on its own until it is stopped, or power is lost. Although, this motor runs just as one would with copper wire, characterizing the CNT fiber motor reveals important differences. Table 2.2 shows a summary of this characterization. While the CNT fiber is lighter, the power required to run the motor
### Table 2.1 Summary of the highest report CNT Fiber material properties alongside its two major metal conductor competitors

<table>
<thead>
<tr>
<th>Property</th>
<th>CNT-Based Wire</th>
<th>Copper (5)</th>
<th>Aluminum 6201-T81 (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity</td>
<td>$1.2 \times 10^{-7} , \Omega \cdot \text{m}$ (8)</td>
<td>$1.7 \times 10^{-8} , \Omega \cdot \text{m}$</td>
<td>$3.16 \times 10^{-8} , \Omega \cdot \text{m}$</td>
</tr>
<tr>
<td>Conductivity</td>
<td>$8.5 \times 10^6 , \text{S/m}$ (8)</td>
<td>$5.88 \times 10^7 , \text{S/m}$</td>
<td>$3.16 \times 10^7 , \text{S/m}$</td>
</tr>
<tr>
<td>Specific Conductivity</td>
<td>$19.6 , \text{kS-m}^2/\text{kg}$ (1)</td>
<td>$6.59 , \text{kS-m}^2/\text{kg}$</td>
<td>$11.8 , \text{kS-m}^2/\text{kg}$</td>
</tr>
<tr>
<td>Current Carrying Capacity</td>
<td>$10^4$ to $10^5 , \text{A/cm}^2$ (1)</td>
<td>$3 \times 10^4 , \text{A/cm}^2$ (6)</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>$0.33 , \text{g/cm}^3$ (1)</td>
<td>$8.93 , \text{g/cm}^3$</td>
<td>$2.69 , \text{g/cm}^3$</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>$1230 , \text{W/m-K}$ (2)</td>
<td>$385 , \text{W/m-K}$</td>
<td>$205 , \text{W/m-K}$</td>
</tr>
<tr>
<td>Specific Thermal Conductivity</td>
<td>$451 , \text{mW/m}^2/\text{kg-K}$ (3)</td>
<td>$44.6 , \text{mW/m}^2/\text{kg-K}$</td>
<td></td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>$8.8 , \text{GPa}$ (2)</td>
<td>$344 , \text{MPa (ultimate)}$</td>
<td>$330 , \text{MPa (ultimate)}$</td>
</tr>
<tr>
<td>Specific Strength</td>
<td>$9.8 , \text{GPa/SG}$ (2)</td>
<td>$0.0385 , \text{GPa/SG}$</td>
<td></td>
</tr>
<tr>
<td>Stiffness</td>
<td>$357 , \text{GPa}$ (2)</td>
<td>$110 , \text{GPa}$</td>
<td>$69 , \text{GPa}$</td>
</tr>
<tr>
<td>Specific Stiffness</td>
<td>$397 , \text{GPa/SG}$ (2)</td>
<td>$12.3 , \text{GPa/SG}$</td>
<td>$25.7 , \text{GPa/SG}$</td>
</tr>
<tr>
<td>Toughness</td>
<td>$121 , \text{J/g}$ (2)</td>
<td>$12.3 , \text{GPa/SG}$</td>
<td></td>
</tr>
<tr>
<td>Strain at Break</td>
<td>$3%-4%$ (conductivity spec) (4)</td>
<td>$14%$</td>
<td>$6%$</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion</td>
<td>$2 \times 10^{-5} / \text{K (DWCNT)}$ (7)</td>
<td>$1.64 \times 10^{-5} / \text{K}$</td>
<td>$2.34 \times 10^{-5} / \text{K}$</td>
</tr>
<tr>
<td>Crossover Temperature ($T_0$)</td>
<td>$60 , \text{K}$ (1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) (Zhao et al. 2011)$^{22}$
(2) (Koziol et al. 2007)$^{21}$
(3) (Behabtu et al. 2013)$^{13}$
(4) Nanocomp Technologies, Inc. Miralon® Yarn Technical Data Sheet
(5) [www.matweb.com]$^{31}$
(6) (Lekawa-Raus et al. 2014)$^{1}$
(7) (Deng et al 2014)$^{32}$
(8) (Tsentalovich et al. 2017)$^{14}$

**Notes:**

**SG:** Specific Gravity (dimensionless parameter that represents the density of the material divided by the density of water)

**Crossover Temperature:** In general, the resistivity will drop with decreasing temperature down to a crossover temperature $T_0$
is much higher that an equivalent copper coil motor- even one where the coils weigh the same. This is to be expected since the measured resistance of the CNT fiber is much higher than the copper coil. Another group that made a similar prototype motor with CNT fiber noted much of the same conclusions\textsuperscript{33}. This group also measured the magnetic flux density of the CNT fiber and noted that its curve was different from copper's. Typically, the relationship between applied current and magnetic flux density is linear. In their experiments, the curve for the CNT fiber was quadratic. The suspected reasoning for this difference was due to temperature changes within the CNT fiber coil.
Table 2.2 Summary of Electric Motor Characterization

<table>
<thead>
<tr>
<th></th>
<th>CNT Cable</th>
<th>Copper (Eq Turns)</th>
<th>Copper (Eq Weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>0.45 g</td>
<td>1.53 g</td>
<td>0.45 g</td>
</tr>
<tr>
<td># of turns</td>
<td>13</td>
<td>13</td>
<td>3</td>
</tr>
<tr>
<td>Resistance</td>
<td>75 - 125 Ω</td>
<td>3.4 - 3.6 Ω</td>
<td>0.4 - 0.75 Ω</td>
</tr>
<tr>
<td>Current (no load)</td>
<td>0.06 - 0.08 A</td>
<td>0.1 - 0.14 A</td>
<td>0.1 - 0.14 A</td>
</tr>
<tr>
<td>Speed (no load)</td>
<td>450 RPM</td>
<td>1200 RPM</td>
<td>430 RPM</td>
</tr>
<tr>
<td>Volts</td>
<td>19V</td>
<td>3V</td>
<td>6V</td>
</tr>
</tbody>
</table>
Many of the interesting abilities of CNT fibers that will be presented in this thesis are due to its unique morphology. Unlike traditional solid metal conductors, CNT fibers contain some void space. Three-dimensional CNT materials can be described as hierarchical. Individual CNTs form small bundles with relatively little space in-between each of the CNTs. These bundles will group together with small yet significantly sized void spaces that result in the characteristic yarn-like structure of CNT fibers synthesized by the one-step floating catalyst chemical vapor deposition process. This chapter outlines the structural and electrical property characterization of the CNT fibers used for this thesis and highlights the unique structural features that will remain a central theme throughout this thesis.
3.1. Morphology and Porosity

CNT fibers used in this thesis were acquired from NanoRidge Materials. They were synthesized by a vertical floating catalyst chemical vapor deposition process using xylene as the carbon source, ferrocene as the iron source, and sulfur with hydrogen as the carrier gas. An overview of the fiber synthesis process was presented in chapter 2.3.2. All of the images presented in figure 2.8 are of these fibers.

Figure 3.1 Medium Magnification SEM Image Showing Porous Structure
Additionally, Figures 3.1 and 3.2 show medium and high magnification SEM images of the CNT fibers that highlight the characteristic porous hierarchical nature of these materials. The morphology of these fibers is similar to other fibers made by a similar process\textsuperscript{34}. Figure 3.3 presents energy-dispersive X-ray spectroscopy (EDS) data on the chemical composition of these CNT fibers. In fibers that were synthesized by a similar method, values for surface area (76 m\textsuperscript{2}/g), lateral pore size (30-40nm) and percent porosity (55%) have been reported\textsuperscript{34}. It is expected that the CNT fibers used in this project have similar values. Scanning Electron Microscopy (SEM) Imaging and

![Figure 3.2 High Magnification SEM Image Showing Porous Structure](image)

Scanning Electron Microscopy (SEM) Imaging and
Energy Dispersive X-Ray Spectroscopy (EDS) was performed on a FEI Quanta 400 Environmental SEM.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>78.54</td>
<td>93.10</td>
</tr>
<tr>
<td>Al</td>
<td>1.42</td>
<td>0.75</td>
</tr>
<tr>
<td>Si</td>
<td>1.71</td>
<td>0.86</td>
</tr>
<tr>
<td>S</td>
<td>1.92</td>
<td>0.85</td>
</tr>
<tr>
<td>Ca</td>
<td>2.53</td>
<td>0.90</td>
</tr>
<tr>
<td>Fe</td>
<td>13.88</td>
<td>3.54</td>
</tr>
</tbody>
</table>

Figure 3.3 EDS Data Showing the Atomic Composition of the CNT Fibers

3.2. X-ray Photoelectron Spectroscopy Analysis

To further understand the chemical composition, these CNT fibers were characterized by x-ray photoelectron spectroscopy (XPS). This preliminary full spectrum scan of the CNT fibers coincides with the EDS data in that it shows the fibers are composed of carbon with a small amount of oxygen. This data is presented in figure 3.4. X-ray photoelectron spectroscopy (XPS) analysis was performed using a PHI Quantera XPS.
3.3. Thermogravimetric Analysis

In order to obtain additional CNT fiber composition information, thermogravimetric (TGA) analysis was performed. TGA results indicate that the CNT fibers are composed of 13.2% amorphous carbon impurities (this includes absorbed gas molecules and moisture), 77.2% carbon nanotubes, and 9.6% iron impurities. Figure 3.5 shows this data graphed along with a curse showing derivative weight. The two highest peaks on the derivative weight curve indicate the temperature where the greatest rate of change of weight loss occurs. For these fibers, the greatest rate of weight loss occurred around 575° C, which coincides with the typical temperature of
CNT oxidation (between 500°C and 800°C). Thermogravimetric analysis (TGA) was performed using a Q-600 Simultaneous TGA/DSC from TA Instruments.

![Figure 3.5 TGA Data of CNT Fibers](image)

### 3.4. Raman Microscopy Analysis

Figure 3.6 shows Raman microscopy spectra for CNT fibers. For this analysis, three laser wavelengths were used - 514 nm, 633 nm, and 785 nm. The peaks that appear in this analysis give insights into some specific characteristics of the CNTs that make up the fiber. The G-band is a characteristic feature of graphitic carbon, which is the primary allotrope of carbon in CNTs. The D-band intensity is characteristic of defective, broken, or short nanotubes and loose carbon atom. The ratio of these two peaks (G/D ratio) is an indicator of quality. Higher quality CNTs will have more graphitic carbon and less defects. Hence, a high G/D ratio indicates high quality CNTs.
The ratio for each laser is displayed in the figure. It should be noted that these ratios are comparatively low as the fibers used for this analysis (and all of the experiments in this thesis) were not purified. The radial breathing mode (RBM) portion of the 633nm spectrum (from 100 cm\(^{-1}\) to 300 cm\(^{-1}\) shift) indicates that there are CNTs with two different diameters, 1.12nm and 1.26nm. The following equation was used to determine these diameters:
Equation 3.1 – Relation between RBM Frequency and CNT Diameter

$$\omega_{RBM} = \frac{248}{d_{cnt}}$$ \(^{35}\)

Where $$\omega_{RBM}$$ is the Raman frequency shift and $$d_{cnt}$$ is the diameter of the CNTs in nanometers. This data suggests that the type of CNTs in the characterization area are either single walled or two different diameters or are double walled. Although, the peaks that indicate larger diameter tubes (which would indicate multiwalled CNTs) are not seen here because this Raman spectrum does not go below 100 cm\(^{-1}\) shift. Raman spectroscopy was performed using a Renishaw inVia confocal Raman microscope equipped with 3 lasers – 532nm, 633nm, and 785nm.

3.5. CNT Fiber Conductivity

The carbon nanotube fibers provided by NanoRidge Materials were in the form of a tow that contained 150 to 200 individual fibers. Only individual fibers were
used for the experiments presented in this thesis. Accordingly, the individual fibers must be separated from the tow before use. The conductivity of the individual fibers was determined using a 4-point resistance measurement technique as shown in figure 3.7. Resistivity ($\rho$) was calculated using the following equation:

**Equation 3.2 – Resistivity**

\[ \rho = \Omega (A/l) \]

Where $\Omega$ is resistance as measured by the 4-point probe, $A$ is the cross-sectional area of the sample, and $l$ is the length of the sample. Conductivity ($\sigma$) is the inverse of resistivity:
Equation 3.3 – Conductivity

\[ \sigma = \frac{1}{\rho} \]

Diameter measurements for determining cross-sectional area were measured by light microscopy and the length of the samples were measuring by a Vernier caliper. For this calculation, it is assumed that the fibers are a cylinder of uniform diameter. Realistically this is not true, so an average diameter is calculated from 10 different, random spots along the fiber. The average conductivity of 40 samples measured is $1.6 \times 10^5$ S/M (Siemens per meter). This value can be compared to the values in table 2.1 for the state-of-the-art CNT fiber, copper and aluminum. Transmitted light microscopy was performed using a Zeiss AxioImager M2 and the associated software package. Resistance measurements were obtained using a Keithley 2400 SourceMeter.

### 3.6. Current Carrying Capacity

Current at failure measurements were performed using a 2-point measurement scheme. Voltage sweeps were performed starting from 1 volt and the ending voltage is dependent on the initial resistance of the samples, ranging from 30 volts to 100 volts. Current carrying capacity was calculated using the following equation:
Equation 3.4 – Current Carrying Capacity

\[ \text{Current Carrying Capacity} = \frac{I}{\left(\frac{\pi D^2}{4}\right)} \]

Where \( I \) is the current at failure and \( D \) is the diameter of the fiber. The average current carrying capacity for the fibers used here is \( 3.83 \times 10^3 \text{ A/cm}^2 \).
Chapter 4

Solvents as dopant delivery vehicles: Effects of solvent properties in iodine doping of CNT fibers

4.1. Introduction

Electrical wires made from CNTs have been predicted to revolutionize energy transmission due to the CNT’s intrinsic characteristics of high conductivity, low density, flexural strength and high thermal conductivity. Although, bulk CNT materials typically fall short of the single CNT’s values in these categories. Much effort has been put into improving CNT fiber properties, especially its conductivity. Optimization of the fiber fabrication parameters and chemical doping have worked exceedingly well. The use of strong mineral acids, halogens (Br₂ and I₂), interhalogens, Au³⁺, alkali metals (Li and K), hydrazine, polymers and KAuBr₄ as dopants have shown significant increases in conductivity of CNT fibers and films. Iodine doped CNT fibers have been shown to exceed the specific conductivity of copper. In their work and several others, the iodine doping was
performed in the gas phase over several hours at high temperature in a sealed container. Although, easier and more industrially scalable doping techniques have been developed, such as solution-phase doping. In this method, solid-phase dopants are dissolved in solvent which is applied to the CNT material and the solid dopant is left behind when the solvent evaporates. However, solution-phase doping is typically considered a post-synthesis method of increasing conduction in CNT fibers. One notable exception are the CNT fibers that are wet spun from a liquid crystalline solution of CNTs and chlorosulfonic acid\textsuperscript{13}. When this solution is pushed through a spinneret in a coagulation bath, the acid is incorporated into the fiber and acts as a dopant. Additionally, another advantage to using volatile solvents in solution-phase doping is their evaporation leads to densification of CNT materials, a process called solvent induced capillary densification\textsuperscript{45}. While the wet spinning method uses liquids to both densify the fiber and deliver dopants, the dry and direct spinning methods use liquids to only densify the CNT fibers. But incorporating a dopant, like iodine, into these liquids is easy and both the delivery of the dopant and the densification will result in increases in conductivity. As well, there is strong evidence to suggest that including a dopant in the solvents would increase the amount of densification caused by solvent evaporation\textsuperscript{38}. This work presents a systematic study into the fundamentals of solution phase iodine doping for the purpose of incorporating it into the direct CNT fiber synthesis process. This chapter will survey each of the three fundamental interactions (CNT-Solvent, CNT-Dopant, and Dopant-Solvent) and present new correlations between solvent properties and iodine doping efficacy.
Ultimately, the information generated here will be used to incorporate dopants into the direct CNT fiber spinning process, which will allow these CNT fibers to benefit from liquid densification/dopant incorporation similar to wet spun CNT fibers.

4.2. Results and Discussion

The direct CNT fiber spinning process presented in chapter 2 uses 360° solvent sprayers to densify the CNT aerogel that exists the furnace into a fiber before spooling. So far, the solvents used in this spinning process have been pure solvents. It follows that any dopant that can be dissolved in a solvent can be applied to the CNT fiber at this stage of the spinning process. The solvent-dopant combinations that can be considered here are numerous and must be narrowed down systematically. In order to do this, each of the fundamental interactions of solution-phase CNT doping will be investigated individually, as seen schematically in figure 4.1. The information obtained will be combined to determine a suitable solvent-dopant combination that can be tested in a full-scale direct CNT fiber spinning setup.

4.2.1. CNT-Solvent Interaction

The CNT-solvent interaction is based on the physical compatibility of the two components. There are several methods to determine this compatibility quantitatively. One method is to determine the interfacial energy by measuring the contact angles of solvents when applied to the surface of CNTs. The interfacial energy can be calculated as follows:
Equation 4.1 – Interfacial Energy

\[ \gamma_{s/l} = \gamma_{s/a} - \gamma_{l/a} \cos \theta. \]

Where \( \gamma_{s/l} \) is the interfacial energy between the CNTs and the liquid, \( \gamma_{s/a} \) is the surface energy of the CNTs, \( \gamma_{l/a} \) is the surface tension of the liquid and \( \theta \) is the contact angle. Generally, systems to tend minimize total energy. Thus, a low interfacial energy suggests a high degree of compatibility between the CNTs and the solvent, as shown here\textsuperscript{34}. In this publication, N-methyl-2-pyrrolidone (NMP) is shown to have the lowest interfacial energy of the solvents tested. As well, NMP has been established as a powerful agent for dispersing individual CNTs, which implies high CNT-solvent compatibility\textsuperscript{46,47}. Relatedly, solvent infiltration into CNT fibers has an effect on the

![Figure 4.1 Schematic of Fundamental Interaction in CNT Fiber Doping](image-url)
fiber internal structure. Qiu et al. in 2013 took a group of various organic solvents (acetone, cyclohexane, cyclohexanone, ethanol, methanol, N-methyl-2-pyrrolidone (NMP), and toluene) and water and were able to determine ingress of liquids by measuring changes in fiber dimensions and contact angles. They were also able to determine the effects of liquid infiltration on the internal structure of the CNT fiber by both wide- and small-angle X-ray scattering. Their results show that each of the organic solvents readily wicked into the fiber while water did not. This was confirmed by the observance of radial swelling (measurement of fiber diameter). Also noted that adding liquid to a tensioned fiber results in a decrease in stress. Small-angle X-ray scattering studies were able to confirm liquid infiltration by determining an increase in the lateral size of void space inside of the fiber. Wide angle X-ray scattering measurements were able to show that the organic solvents did not intercalate between individual nanotubes. Intercalation of liquids would be recognizable in the wide-angle X-ray scattering data by a shift in the 002 peak at lower scattering angles (Scattering between stacked graphene layers of flattened nanotubes causes the 002 reflection). They were not able to observe this peak shift. As a consequence of these structural changes, fiber resistance increases as resistance increases are related to the length of the junction that opens between bundles. This observed increase in fiber resistance is another metric that can be used to determine CNT-solvent compatibility. In many cases, the amount of resistance increase is inversely proportional to the interfacial energy. Similarly, Zhang and colleagues in 2017 studied the influence of capillary effects on the electrical properties on ordered CNT films.
They found that the electronic transport of a CNT film can be adjusted by structural changes at the CNT junctions caused by capillary effects. Their mechanism explains the resistance change and recovery of a CNT system through an immersion and then evaporation process\(^{51}\).

As the scheme of relating resistance increase to increases in bundles gap distances was determined using a small number of solvents, this study found it necessary to expand upon this knowledge by testing more solvents. Structural changes upon solvent infiltration into CNT fibers was determined by measuring the increase in fiber diameter. This data is presented in figure 4.2. As expected, the dimensional changes and corresponding increases in CNT bundle gap distances were accompanied by increases in fiber resistance. The % change in resistance as a function of time data is presented in figure 4.3. Careful inspection of these two graphs show a correlation between fiber diameter increase and resistance increase. This result agrees with previous research cited above. It should also be noted that the values are displayed as percent change from the original pre-immersion value. Although all the CNT fibers used in this project are a part of the same batch, any given section of CNT fiber can have different inherent properties – the starting resistances and fiber dimensions can vary significantly. But the percent change in resistance values are very consistent. Meaning that a fiber reported to have a 100% change in fiber resistance upon immersion in solvent will have its resistance double consistently regardless of the fiber’s initial resistance.
Figure 4.2 Changes in Fiber Diameter Upon Liquid Infiltration

Figure 4.3 Change in Fiber Resistance Over Time Upon Liquid Infiltration
4.2.1.1. Hansen Affinity Parameters

While determining the interfacial energy is a good indicator of the CNT-solvent compatibility, a contact angle measurement still needs to be made to calculate these values. However, another method of determining this compatibility has been identified that does not require any measurements. This method involves using Hansen solubility parameters to calculate corresponding affinity parameters. Hansen solubility parameters were originally developed to predict solvent compatibility with polymers, i.e. they are used to predict if one material will dissolve in solvent, making a solution\textsuperscript{52}. These solubility parameters are based on dispersions forces (atomic), polarity forces (molecular dipole-dipole forces), and hydrogen bonding (electron exchange) character. Each material and solvent has its own values for each of these parameters. These values are essentially coordinates in a three-dimensional space. The ‘distance’ between two points in this space relates to the compatibility of the material and solvent – the shorter the distance, the more compatible. This distance between points is known as a Hansen Affinity Parameter and is calculated in the following manner:

\textbf{Equation 4.2 - Hansen Affinity Parameter}

\[ R_d = \sqrt{4(\delta_d^{NT} - \delta_d^{L})^2 + (\delta_p^{NT} - \delta_p^{L})^2 + (\delta_h^{NT} - \delta_h^{L})^2} \]
Qiu and colleagues showed that calculating the Hansen affinity parameter of CNTs and solvents is a good indicator of the level of resistance increase. As this study evaluated new solvents, Hansen affinity parameters were calculated, and a similar pattern was seen in regard to resistance increases. A couple of solvents that were used in Qui’s work were also tested in this study to serve as comparative markers. Figures 4.4 shows a graph comparing maximum % resistance increase to calculated Hansen affinity parameters. As the previous section showed, the increase in
resistance is accompanied by an increase in fiber diameter. Figure 4.4 also shows a graph comparing % fiber diameter increase to calculated Hansen affinity parameters. Both of these graphs show that there is inverse relationship between the affinity parameter and both the amount of increase in fiber resistance and diameter – a result that agrees with previously published studies. A table containing relevant properties and Hansen solubility parameters of all solvents used in this thesis as well as the parameters for single, double, and multi-walled CNTs is located in Appendix A. This table also contains the calculated affinity parameters.

4.2.2. CNT – Dopant Interaction

The ideal CNT fiber will be made entirely of long aspect ratio metallic CNTs that are impurity and defect free as well as being perfectly aligned and densified\textsuperscript{28}. When considering this ideal fiber for the real world, this theory doesn’t mention much on how to get an extremely large number of carbon nanotubes to effectively ‘communicate’ with each other. The coordinated placement of an extremely large number of discreet particles is a daunting task, especially considering the forces between individual CNTs and small bundles. It has been theorized by Xu et al. that CNT organized in a fiber could nearly act as one long ballistic conductor\textsuperscript{53}. But the fibers could only act this way if a certain set of circumstances was met. Those being that fiber would be made of only armchair chirality CNTs that were very long and contact each other at a precise overlap length. This recommendation of a precise overlap length is meant to minimize intertube contact resistance. Buldum and Lu
calculated that the lowest resistance is achieved when the contacts between nanotubes resemble an A-A stacking of graphite. Although, achieving this precise overlap length is very difficult and Xu et al. stipulated that it would be sufficient to have a very long overlap length. This is an interesting point about intertube contact resistance and how difficult it can be to minimize in real samples. Lekawa-Raus et al. estimated that there were 31 million CNTs in the cross-section of a 10µm diameter fiber. The simultaneous coordination of millions of CNTs in a fiber has proven to be a difficult task and can be remediated by chemical doping. Application of a chemical dopant to CNT change intra-tube electronic properties by shifting the Fermi level. In addition to this, a chemical dopant also influences the transport of charge between individual CNTs in a CNT fiber or other 3-dimensional CNT materials. The unique properties of liquids can aid and optimize the delivery of a chemical dopant. The chemical nature of super acids and surfactants overcome the forces between CNTs and allow them to move freely in those liquids as individual tubes. The fact that a liquid can do this task is something that can be utilized in methods for increasing conduction in CNT fibers. Liquids are unique in that they can flow freely but do not try to occupy the entire volume they are placed in. Liquids can be a medium through which coordination is applied to CNT fibers. And the unique porous nature of direct spun CNT fibers is one route where liquids can exert their unique abilities. That is, the liquid that has infiltrated the fiber effectively connects all of the bundles, which makes liquids an efficient way to chemically dope CNT fibers.
Several electrical property modifiers were considered for this thesis. A selection of studies on property modifiers that were ultimately not pursued beyond preliminary studies are presented in Appendix B. Iodine was chosen for this study for several reasons. Iodine has historically been used to increase conductivity in CNTs with great effect. The highest reported specific conductivity of a CNT fiber was doped with iodine\(^{22}\). And several other studies have shown iodine’s potency as a dopant. Considering that the iodine is going to be applied to the fibers in liquid form, it is relatively safer to use that some other iodine containing dopants, such as iodine monochloride and iodine monobromide. While both are very effect chemical dopants for CNTs, these compounds are corrosive. While solutions containing iodine are used in the medical field as disinfectants. This coupled with the highest specific conductivity study provides motivation to refine a solution-based method for iodine doping.

4.2.3. Dopant – Solvent Interaction

Although iodine can be applied to the fiber in gaseous form, this method typically takes many hours at high temperatures. Iodine is a solid at room temperature and has good solubility in many different solvents. As well, iodine interacts differently with different solvents depending on the solvent’s properties. Iodine will typically accept electrons from solvent molecules, which creates donor-acceptor complexes\(^{59}\). Depending how good of an electron donor the solvent is, the color of the iodine solution will change. That is, absorption bands will be observed at
different wavelengths. Iodine dissolved in hydrocarbons will appear purple in color (520-540nm). This indicates that iodine in hydrocarbons retains more of the diatomic iodine character as the color of gaseous iodine is also purple. Iodine dissolved in aromatic solvents appear in the 490-510nm range. And iodine dissolved in good electron donors like alcohols and amines and polar solvents will appear dark brown at 450-480nm. Additionally, charge-transfer complexes will form with very good electron donors. A good example is pyridine, which forms [pyr-I-pyr]+I$_3^-$ when combined with I$_2$. A recent study showed that charged iodide chains are responsible for effective doping in CNTs$^{60}$. It is hypothesized that the donor-acceptor and charge-transfer complexes that are formed when iodine is dissolved in solvents that are good electron donors will decrease fiber resistance more than neutral solvents because the donor-acceptor and charge-transfer complexes formed resemble the iodine species responsible for the doping response. The study presented in the next section will test this hypothesis and show that solvent selection is an important consideration for chemically doping CNT fibers with iodine.

4.2.4. Solvent Selection in Solution-Phase Doping of CNT Fibers with Iodine

In order to evaluate the cumulative action of the three fundamental interactions in CNT fiber doping, iodine dissolved in different solvents was applied to a CNT fiber and the fiber resistance is measured at all stages of this process. Two versions of this experiment were performed to effectively gage how the fundamental interactions affect fiber resistance. The first version applied a small amount of the
iodine solutions to the center of the fiber, away from the contacts. The second version treated the entire length of the fiber between the contacts. Figure 4.5 shows the experimental setup. The graph shown in figure 4.6 summarizes the center application experiment and relates the average maximum fiber resistance decrease (in percent) to solvent dipole. Appendix C shows an example of how these maximum resistance decreases were obtained. These values are an average of at least 6 different fibers. Percent change in resistance (and later in conductivity) is reported here for similar reasons mentioned in section 4.2.1. Resistance change, rather than resistivity change, is reported in this experiment because the solutions are applied to the center of the fiber only. Resistivity accounts for an entire volume and since this treatment doesn't affect the whole volume, reporting change in resistance is more appropriate. This graph clearly shows that iodine dissolved in polar solvents decrease fiber resistance.
more than when dissolved in non-polar solvents. The maximum resistance decrease achieved with heptane and cyclohexane were 2.9% and 4.5%, respectively. While the maximum resistance decreases for the polar solvents (pyridine, acetone, ethyl acetate, isopropanol and acetic acid) are all

over 8.5%, maximum 11.3%. In this case, the polarity of the solvent is related to the solvent’s ability to donate or accept electrons. This data confirms the hypothesis presented in the previous section. The graph in figure 4.7 shows the same average maximum fiber resistance decrease data but relates it to the Hansen affinity parameter. A rough correlation can be observed with this data – a low affinity parameter correlates to a larger resistance decrease. But this observation is an
artifact of the experimental design. By applying the iodine solution to only the center of the wire, a test of solvent compatibility is built in. A low affinity parameter implies a higher degree of compatibility with the CNT fiber and presumably a higher degree of solution wicking. In this case, the solvents with low affinity parameters will deliver the iodine to more of the fiber, thus decreasing fiber resistance more. As this effect appears to be dependent on applying the iodine solution to the center of the fiber, another version of the experiment was performed where the entire fiber is treated

![Graph](image)

**Figure 4.7 Maximum Fiber Resistance Decrease (%) to Hansen Affinity Parameter (Center Application)**

and the change in fiber conductivity was determined. In this version of the experiment, the same relationship is observed with average maximum conductivity increase and dipole moment, shown in figure 4.8. Conductivities of the fibers, before
and after treatment, were determined as described in chapter 3 and an average of 4 fiber’s change is the average maximum conductivity value graphed. Figure 4.8 shows another confirmation that solvents that are good electron donors will cause a larger decrease fiber resistance when compared to neutral solvents at similar dopant concentrations. The differences between the two solvent types is even clearer than in the center application experiment. The gap between the two solvent groups grew from 4% change in resistance (4.5% for cyclohexane $\rightarrow$ 8.5% for ethyl acetate) to 11.1% change in conductivity (3.7% for cyclohexane $\rightarrow$ 14.8% for pyridine). These two terms are comparable as the length and cross-sectional area terms remain the same in the full fiber application experiment. The only term that changes in the

![Figure 4.8 Maximum Fiber Conductivity Increase (%) to Dipole Moment (Full Fiber Application)](image)
calculation of conductivity is fiber resistance. Although, a correlation between percent conductivity increase and low affinity parameters is not observable like in the previous experiment, as seen in figure 4.9. The solvent with the highest percent conductivity increase (isopropanol - 25.1%) has the highest affinity parameter (11.25 MPa\(^{1/2}\)) of the polar solvents. While the lowest affinity parameter, pyridine (2.2 MPa\(^{1/2}\)), has the lowest percent conductivity increase of the polar solvents (14.8%). This result confirms that the center application experiment was influenced by solvent compatibility. And considering that the intention is to use this solution in the solvent sprayers that densify the fiber, solvent compatibility isn’t the largest concern if it wets the CNTs, which all the solvents used in this study will. The information obtained from

![Figure 4.9 Maximum Fiber Conductivity Increase (%) to Hansen Affinity Parameter (Full Fiber Application)](image)
these studies suggests that isopropanol would be the best solvent to use if iodine is going to be included into the densification process of direct spinning CNT fibers.

4.3. Conclusions and Future Studies

This chapter surveyed each of the fundamental interactions associated solution-phase iodine doping. Results show that established methods for determining solvent compatibility with CNTs apply to some other solvents that have never been tested. This chapter was also able to recommend an iodine-solvent combination that could potentially have the biggest impact on conductivity if used to densify fibers in the direct spinning method. Although, one potential drawback of this recommendation has been identified – the stability of iodine. Iodine will sublimate at room temperature and given the small amount of iodine used in these studies, the doping effect of the iodine did not last very long. Some preliminary studies on how to increase dopant stability have been performed. Just like with pyridine, combining iodine and triphenylphosphine (PPh\textsubscript{3}) results in a charge-transfer complex. PPh\textsubscript{3} is a solid at room temperature and the charge-transfer complex that’s made with iodine is more stable than iodine alone. Although the stability of the iodine – PPh\textsubscript{3} complex is more stable, the resistance does not decrease as much compared to pure iodine. However, with some experimenting with the ratio of iodine to PPh\textsubscript{3}, the resistance is expected to decrease as much as pure iodine. Determining the best ratio between these two compounds would be a worthwhile future study. Another would be to try
this doping method in full scale – comparing the electrical properties of CNT fibers densified by pure and iodine containing solvents.

4.4. Methods

Liquid Infiltration

The CNT fiber samples were set up in the same 4-point resistance measurement scheme as presented in chapter 3, except that the CNT fiber is soldered to the copper tape. This is shown in figure 3.7. The soldering protocol is presented in the next chapter. The solder makes the contacts liquid proof as the binder in the silver paint dissolves in the solvents that are used in this study. The fiber was then lowered into a solvent bath. The resistance was constantly measured at a rate of one measurement per 1.7 seconds for the first 20 minutes. Measurements were taken each minute for the next 10 minutes, then every 2 minutes for the next 20 minutes, then every 5 minutes for the next 10 minutes. Measurements were taken for a total of 60 minutes. At the end of this time, the fiber was removed from the solvent bath and the resistance was measured in a similar fashion for 30 minutes. Resistance measurements were constantly taken at a rate of one measurement per 1.7 seconds for the first 10 minutes. Measurements were taken each minute for the next 10 minutes, then every 2 minutes for the next 10 minutes. Each fiber-solvent combination was evaluated twice.
Structural Changes

Changes in the diameters of CNT fibers was measured using transmitted light microscopy (Zeiss AxioImager M2). CNT fibers were placed on a glass microscope slide and covered with a coverslip. A before solvent exposure image was taken to determine the diameter of the fiber. Then, solvent was applied to the edge of the coverslip, which flows into the volume between the slide and coverslip by capillary action. This exposes the CNT fiber to the solvent. An after-exposure image was taken of the same portion of the CNT fiber as the before-exposure image to determine the change in fiber diameter. Average fiber diameters were determined by measuring the area of the fiber in the image and dividing that area by the length. The area of the fiber is determined using National Institutes of Health ImageJ image processing software. These images contain a calibrated scale bar of 0.11 μm/pixel for the 20x objective used in this study. Percent diameter increase was calculated by the standard percent change equation – after exposure diameter – before exposure diameter divided by the before exposure diameter, multiplied by 100%. A schematic of this process is shown below. Heptane, isopropanol, acetone, and pyridine were acquired from Millipore Sigma.

Evaluation of Resistance Decrease from Solution-Phase Iodine Doping

Voltage, current and resistance measurements will be taken by a Keithley 2400 SourceMeter. The data generated by this meter will be collected on a connected computer using LabView software. In general, the CNT fibers were affixed to
conductive copper tape by silver paint and mounted on a glass microscope slide. The iodine solutions (15.75mM) were applied to the CNT fibers in the center. In a subsequent experiment, the same iodine solutions were applied to the entire fiber. An example of how maximum resistance values were obtained in these experiments is shown in Appendix C. The Keithley SourceMeter is attached to the 4 copper tape strips in the typical 4-point measurement scheme to measure the electrical properties. This experimental setup is able to measure the electrical properties during all phases of the experiments described above and all data was saved to a connected computer at a rate of one reading every 1.7 seconds. By using this universal system, external forces can influence the wire while still connected to the SourceMeter. This system of mounting the CNT fibers on microscope slides gives this system adaptability. Iodine and all solvents (Heptane, Cyclohexane, Acetone, Isopropanol, Ethyl Acetate, Acetic Acid and Pyridine) used in this experiment were obtained from Millipore Sigma. Silver paint and copper tape was obtained from Ted Pella.
Chapter 5

Soldering of CNT Fibers

5.1. Introduction

Carbon nanotube-based materials have shown enormous potential as candidates to replace copper and other metals as electrical wires. Robust electrical connections are a critical piece of any electrical wiring system. To date, very few methods exist to create these strong electrical connections with carbon-based materials. These methods involve mechanical bonding, use of conductive paints, adhesive bonding, cold welding, brazing, and soldering. While each of these methods does create a stable electrical connection, each has its own drawbacks. Adhesives are typically insulators and introduce resistance into the electrical connection. Conductive paints, which are metal particles held together with a polymeric binder, are not suited for high temperature applications and will dissolve in the presence of certain solvents. Although brazing works well for other carbon-based materials, this process typically involves temperatures that exceed the breakdown temperature of nano-structured carbon materials. Cold welding with thin metal foils also creates very
good electrical connections to carbon materials but they are not mechanically robust enough for some applications. The most ideal method of creating mechanically and electrically sound connections is through soldering. Soldering temperatures are generally lower than the breakdown temperatures of nanosized carbon materials. As well, soldering creates strong electrical connections with a wide range of materials including metals and printed circuit boards. However, commercially available soldering alloys do not wet carbon materials very easily. One method gets around this problem by incorporating several percent of transition metals (Cr and Ni) into the solder. While this method does suit each of the criteria set for ideal electrical connections between CNT fibers and metals, obtaining a custom formula solder wire is not feasible for most laboratories that are not specifically setup for making this type of material. Additionally, this type of solder is not commercially available yet as there isn’t a large enough market for soldering CNT-based materials. For this thesis, completion of many experiments depended on the development an easy method of electrically connecting CNT fibers to metals that was both mechanically stable and liquid proof. This chapter outlines this development as it presents a novel method for creating mechanically strong, liquid proof electrical connections for CNT fibers using solder and indium powder.

5.2. Method

CNT fibers were obtained as previously described in chapter 3 – general background. CNT fibers, as a single fiber or as a tow of fibers, are placed on top of a
Figure 5.1 CNT Fiber Method Schematic
strip of copper tape (figure 5.1A). Next, a small amount of indium powder was placed on top of the CNT fiber (figure 5.1B). This powder was then compacted together by applying pressure (figure 5.1C). This pressure cold welds the indium powder together into a disk. Finally, commercially available Sn60/Pb40 ‘No clean’ resin flux cored solder was applied to the area of the fiber that is covered by the indium (figure 5.1D and E).

Copper tape was obtained from Ted Pella. Indium powder was obtained from Millipore Sigma. The solder used for this study is manufactured by MG Chemicals and the solder iron was set to 315.5 °C.

5.3. Results and Discussion

Typical commercially available solder is a low melting alloy composed of lead and tin or silver along with other transition metals, like gold, indium and gallium. Solder is nonreactive and has a high surface tension. These two characteristics make solder's wetting of carbon-based materials very poor. But incorporating metals into CNT-based materials can be completed by other means, such as electrochemical methods\textsuperscript{67} and sputtering\textsuperscript{68}. As well, mercury\textsuperscript{69} was used as an electrical contact during one of the early determinations the conductivity of a single CNT. Considering this, carbon and CNT-based materials should compatible with liquid metals if the procedure promotes the proper interaction. The typical procedure for joining materials with solder doesn’t work very well for CNT fibers. Since the solder and CNT do not wet
very well, it is difficult to heat the CNT fiber with the solder, a key aspect in the spreading of the solder on the base material. Additionally, since the CNT fiber's density is very low it tends to float on the liquid solder. The method presented above gets around this difficulty by applying indium powder. Indium has a low melting point (156.6°C) and it is one metal that can cold weld to itself in bulk form. By applying pressure, the indium forms a cohesive disk that surrounds the CNT fiber and allows it to be incorporated into the solder much more easily. The indium ensures that the CNT fiber does not float on the solder when it is applied. The liquid solder heats up the indium and it incorporates into the liquid solder along with encasing the CNT fiber in the solder-indium mixture. In this case, the indium powder is acting like traditional solder flux in that flux aids in wetting. Figure 5.2 shows an image of a soldered CNT tow that zooms in on the edge of the solder where the tow exits. Figure 5.3 shows an SEM image of a cross section of a CNT fiber that has been soldered to a copper tape base. It is clearly shown that the CNT fiber is encased in solder and that solder is
securely attached to the copper base. Additionally, this image of fiber encased by solder looks nearly identical to the images presented in the only other CNT fiber soldering publication. They determined through this image that the transition metal laden solder they created wet the CNT fiber. Since these images look nearly identical, it can be concluded that the soldered method presented here also enabled wetting of CNT fibers. Figure 5.4 are zooming in on the fiber and its interface with the solder. This data also confirms the wetting of the CNT fiber by the solder as there aren’t any observable indications that the fiber and solder are repelling each other (no
observable separations). Upon careful inspection of figure 5.4F, it can be seen that some of the CNTs in the fiber have attached to the solder (indicated by red arrows). Figure 5.5 shows an SEM image with an EDS overlay of atomic makeup as taken across the red line. Moving from left to right along this red line, the EDS data shows the atomic composition goes from carbon to a mixture of Pb, Sn, and In, as expected. Figure 5.6 shows EDS data for the entire SEM image shown in the right side of figure 5.5. This data reiterates that the expected atomic composition for this image.

As mentioned above, the indium in this method effectively acts like flux in the soldering process in that it promotes wetting of the solder on a material. Although in this case, the indium is a wetting agent for the CNT fiber, not for the base material.
(copper in this case). A special note should be made here that the solder used in this experiment contains traditional soldering resin flux core. This resin flux is included to enhance wetting on the base material by negating the oxides that form on the surface of uncoated copper (oxides prevent wetting of solder on copper). This resin

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Net Int.</th>
<th>Error %</th>
<th>Kratio</th>
<th>Z</th>
<th>A</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>24.35</td>
<td>78.08</td>
<td>165.50</td>
<td>6.91</td>
<td>0.2543</td>
<td>1.4930</td>
<td>0.6994</td>
<td>1.0000</td>
</tr>
<tr>
<td>PbM</td>
<td>21.38</td>
<td>3.97</td>
<td>36.70</td>
<td>12.32</td>
<td>0.1719</td>
<td>0.7457</td>
<td>1.0703</td>
<td>1.0073</td>
</tr>
<tr>
<td>InL</td>
<td>30.51</td>
<td>10.23</td>
<td>36.10</td>
<td>15.08</td>
<td>0.2634</td>
<td>0.8800</td>
<td>0.9798</td>
<td>1.0012</td>
</tr>
<tr>
<td>SnL</td>
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<td>7.71</td>
<td>23.50</td>
<td>20.48</td>
<td>0.2014</td>
<td>0.8641</td>
<td>0.9810</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

Figure 5.6 EDS Data for Whole Image in Figure 5.5
flux has no effect on the wetting of the CNT fiber. The same problems described above are applicable to both resin-cored and non-resin-cored solder alloys. This was confirmed in attempts to solder the CNT fiber with different types of fluxes and flux-cored solder wire without indium. Using additional rosin flux, additional tinning flux, acid-cored lead-free solder and solid core silver solder all failed to solder the CNT fiber.

Finally, in order to show this method’s versatility and viability, a CNT fiber tow was cut in the middle and a joint was made. This process is shown in figure 5.7. Figure 5.7A shows the fiber tow cut in half. Figure 5.7B shows the fiber tow with the cold-welded indium powder making the joint. Figure 5.7C shows the joint made by soldering. The initial 4-point resistance of the fiber was 10.1 Ω. After the fiber was cut and repaired with solder, the resistance rose to 11.6 Ω. This increase is small but significant and is likely caused by operator error. Although the solder iron is set to a lower temperature than the breakdown temperature of the CNTs, excess heat can damage and result in an increase in resistance. According to the TGA data presented in chapter 3, the solder iron temperature of 315.5 ºC is hot enough to burn amorphous carbon impurities. This TGA provides some evidence that prolong exposure to this level of heat can change the CNT fiber structure. As well, similar damage can be observed when soldering circuit boards and the soldering iron is used for too long. More care will be taken in future attempts to make soldered joints in this manner and the increase in fiber resistance is not expected.
Figure 5.7 Soldered Joint

5.4. Conclusion

The results presented in this chapter show that this novel method for affixing CNT fibers to copper tape by soldering is useful in a variety of settings. All the materials needed to solder these CNT fibers to many metal bases are commercially available, suggesting that this method could be translated to an industrial setting. This novel
technique may enable the use of CNT fibers in areas that would benefit from a lightweight conductor, such as automotive wiring harnesses and electrical machines.

As it pertains to this thesis, soldering fibers using this method has enabled the completion of many studies that would otherwise be impossible to perform. These soldered electrical contacts are liquid proof and allow entire CNT fibers to be immersed in liquids. And as the next chapter will show, very interesting features of these CNT fibers are observed when fully immersed in liquids.
Chapter 6

Liquid-Phase Doping of CNT Fibers

6.1. Introduction

Since their discovery by Iijima in 1991\(^2\), investigations into the properties of carbon nanotubes (CNTs) have revealed many superiorities on the nanoscale mainly relating to mechanical strength and electrical conduction. CNTs possess a high degree of multifunctionality- they are incredibly strong, light, and are electrically conductive. Numerous methods have been developed to combine these nanosized hollow tubes of carbon into three dimensional hierarchical structures that are able to effectively transfer their exceptional small-scale properties to a macroscopic scale product. One example product would be CNT fibers\(^{13,17,19}\). CNT fibers can be made at kilometer lengths at laboratory scale and even longer industrially. These fibers are able to achieve very high strengths\(^{21}\) and conductivity\(^{22,14}\). As well, they have been developed for many diverse applications such as sensors\(^{70,71}\), energy storage\(^{72,73}\), functional textiles\(^{74,75}\), multifunctional composites\(^{76,77,78,79,80,81}\), and signal\(^{29,82}\) and energy transmission\(^{22,83}\).
Generally, CNT fibers made by direct spinning from the floating catalyst chemical vapor deposition (FC CVD) reactor have very high surface areas and contain large, continuous pores. This yarn-like characteristic imparts these fibers with additional properties not seen in non-porous fibers. It is this void space inside of the CNT fiber which allows for intrafiber interactions with liquid mediums. To date, much research effort has been spent on understanding the fundamentals of this fiber-liquid interaction. It has been shown experimentally that the electrical properties of porous hierarchical CNT materials will change in the presence of liquids. One explanation for this phenomenon is based on elasto-capillary effects. It was shown that many organic solvents will readily infiltrate into the CNT fiber and cause increases in fiber resistance by separating the weakly bound bundles of CNTs in the fiber. This was confirmed by observation of radial swelling and an increase in the lateral size of void space inside of the fiber, shown by small-angle x-ray scattering. Another study looked at the influence of capillary effects on the electrical properties on ordered CNT films upon application of solvent. It was concluded that the electronic transport of a CNT film can adjusted by structural changes at the CNT junctions caused by capillary effects. Their mechanism explains the resistance change and recovery of a CNT system through an immersion and then evaporation process. This effect was further confirmed by the observation of a non-ohmic effect when a CNT fiber is immersed in polar solvents and a varying electric field is applied. That is, the electric field is able to modulate the resistivity of the CNT fiber when polar solvents are present. They concluded that the electric field was able to control the gap...
distance between CNT bundles. Another explanation for how liquids alter electrical properties is based on electrochemical doping where the liquids will induce changes to the electronic structure of the CNTs within the fiber\textsuperscript{12}. It has been shown that the use of different types of solvents will allow for tailoring of electronic properties of CNTs\textsuperscript{84,85}. As well, polar liquids and ones that contain ions are known to induce changes in conductance upon immersion by electrostatic gating\textsuperscript{86}. This is the basic operating principle behind CNT-based fluidic\textsuperscript{87} and biochemical sensors\textsuperscript{9}.

The work presented here has used and expanded upon the information presented above. It will show that there isn’t one single explanation for the changes in electrical properties of CNT fibers upon liquid infiltration. It confirms that both electrocapillary and electrochemical doping effects will dominate when certain liquids infiltrate CNT fibers. It will also demonstrate that the non-ohmic effect previously observed polar liquids will disappear if certain conditions are met – meaning that CNT fibers immersed in polar liquids can exhibit ohmic behavior as well. All this information taken together was then used to show that CNT fibers immersed in liquids can carry more current without failing when compared to fibers in open air – an initial step in the development of fluidic conduction wires.
6.2. Results and Discussion

6.2.1. CNT Fibers

CNT fibers were acquired from NanoRidge Materials. They were synthesized by a vertical floating catalyst chemical vapor deposition process using xylene as the carbon source, ferrocene as the iron source, and sulfur with hydrogen as the carrier gas. The morphology of these fibers and their characteristic porous hierarchical nature was shown in chapter 3 along with other characterization data.

6.2.2. Liquid Infiltration and the Elasto-capillary Effect

Previous experimental research supporting the elasto-capillary effect established that a good indicator of resistance increase in CNT fibers is a low Hansen affinity parameter\(^3^4\), as presented in chapter 4. Most of the solvents evaluated in this manner matched this trend. It was also shown that there are two other values that can be used to predict the level of increase in fiber resistance – a comparatively lower interfacial energy and the characteristic lateral size (Porod length) obtained from small angle x-ray scattering. This study set out to expand on this knowledge base by evaluating nine other solvents. Time-resolved graphs of five new solvents plus two from previous studies (for comparison) are shown in figure 6.1 along with their Hansen affinity parameters. Calculation of these parameter is presented in chapter 4 and appendix A. A number of new solvents evaluated in this work also followed this trend. NMP and acetone were used here to establish a consistent pattern from prior
Figure 6.1 Resistance of CNT Fibers Immersed in Solvents as a Function of Time

published research. Although the absolute value of the percent change in resistance differs with NMP and acetone, the overall pattern is the same and the results generated are comparable. As shown before, NMP increases fiber resistance more than acetone - the result that is predicted by the Hansen affinity parameters. Pyridine, hexylamine, isopropanol, toluene and heptane also adhered to this prediction. It should be noted that only the change in fiber resistance is reported here (and for the rest of the chapter) rather than a change in resistivity. Although, it can be reasonably assumed that the changes in resistance reported would be equal to resistivity changes. Equation 3.2 outlines how resistivity is calculated. In the experiments presented in this chapter, the cross-sectional area (amount of solid material carrying charge) and length of the fibers remain constant and only the resistance changes. Hence, the changes in resistance are equal to changes in resistivity as the resistance

<table>
<thead>
<tr>
<th>Hansen Affinity Parameter (MPa 1/2)</th>
<th>SWCNT</th>
<th>DWCNT</th>
<th>MWCNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>3.22</td>
<td>2.38</td>
<td>2.21</td>
</tr>
<tr>
<td>NMP</td>
<td>4.83</td>
<td>6.60</td>
<td>2.52</td>
</tr>
<tr>
<td>Hexylamine</td>
<td>3.32</td>
<td>6.37</td>
<td>6.31</td>
</tr>
<tr>
<td>Acetone</td>
<td>5.47</td>
<td>8.96</td>
<td>6.23</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>9.77</td>
<td>13.27</td>
<td>11.25</td>
</tr>
<tr>
<td>Toluene</td>
<td>8.29</td>
<td>6.97</td>
<td>10.36</td>
</tr>
<tr>
<td>Heptane</td>
<td>11.79</td>
<td>12.03</td>
<td>14.21</td>
</tr>
</tbody>
</table>
is the only term that changes. Additionally, reporting changes in resistance is what is generally reported in literature for similar experiments\textsuperscript{34}. An interesting observation can be made by looking at the shape of the pyridine and hexylamine lines, as seen in figure 6.2. These two lines are unique among the solvents tested as they have an initial spike in resistance then a relaxation, then level out. And the resistance to which they settle at is consistent with what the affinity parameter would predict. The solubility parameters for hexylamine are not available, but values for a similar solvent, propylamine, are listed. Comparing these two values, the resistance increase with pyridine should be higher than with hexylamine, which is the case here. One possible explanation for this behavior is the nitrogen in these solvents.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{resistance.png}
\caption{Resistance of CNT Fibers Immersed in Pyridine and Hexylamine as a Function of Time}
\end{figure}
NMP has a nitrogen as well but it is a pyrrolidone which contains a carbon-oxygen double bond, which changes its behavior in this case.

There is also a correlation between the amount of measured increase in diameter and the Hansen affinity parameter, as seen in chapter 4 figure 4.4. That is, the lower affinity parameters would signify a greater increase in diameter, which is what is observed with pyridine, acetone, isopropanol and heptane. To measure this diameter change, CNT fibers were placed under a cover slip and initial diameter measurements were taken. Then solvent was applied to the outside of the coverslip and immersed the fiber in that solvent by capillary action. After this, another measurement was taken then compared to the original. This result also concurs with previously published research 34.

6.2.3. Liquid Infiltration and the Electrochemical Doping Effect

However, as figure 6.3 shows, not all of the solvents tested coincide with what is predicted by evaluating the Hansen affinity parameter. Each of the solvents shown here demonstrate a decrease in resistance for most of the one hour of immersion. These results are in support of the electrochemical doping effect that has been previously reported. Noticeably, all of the solvents presented here that do not fit with the electrocapillary trend contain halogens. Graphs comparing similar solvents are shown in figures 6.4 and 6.5. Toluene is compared to chlorobenzene and methanol is compared to dichloromethane and diiodomethane. These graphs are meant to demonstrate the difference in electrical property response between solvents with
and without halogens. It has been well established that the electrical properties of CNTs can change in the presence of halogens\textsuperscript{37,22}. Halogens are one of the most common dopants for CNTs and can produce very large gains in conductivity. It is also well established that solvents can be used to tailor the electronic properties of CNTs. Although, in these two cases\textsuperscript{85,84}, the solvents are not present when the data is being collected. The data presented here, while the solvents are present, seems to indicate that the halogens in these solvents exhibit a similar doping effect, although it is not a very large effect. This electrochemical doping effect has been presented previously with propylamine. Although the study was not able to replicate this result with a similar solvent (hexylamine). Rather than a decrease in resistance, a large increase is observed with hexylamine. Brief decreases in fiber resistance upon immersion have been observed before\textsuperscript{34,49} and in this study as well. The cause of this brief decrease
was determined to be an increase in capacitance due to the rapid influx of a material with a higher dielectric constant between current carrying wires. The dielectric constants of the solvents used here are listed in appendix A. In the case of CNT fibers, the current carrying wires are bundles of CNTs. This increase in capacitance leads to additional current in the fiber as charge leaks out the ‘capacitor’ that is formed. But this charge leak is short-lived and cannot explain the behavior exhibited by these halogen containing solvents. For most of the halogen containing solvents tested, the resistance initially decreases and stays below the pre-immersion resistance value. This behavior indicates that there is an electrochemical doping effect present.

Figure 6.4 Resistance Measurements of CNT Fibers Immersed in Solvents Containing Halogens as a Function of Time - Similar Solvent Comparison 1
To add support to this claim, Raman microscopy analysis was employed. High pressure carbon monoxide (HiPCO) produced CNTs were processed into a film by dissolving them in different solvents and filtering. It should be noted that different CNTs were used this experiment because the established method for determining this charge transfer using Raman microscopy involves dispersing the CNTs in a particular solvent and making the CN'TS into a film through filtration. The HiPCO produced CNTs used here are stored unprocessed in a container and will disperse in solvents much more easily, a key step in making films. The CNTs in the fibers already have structure and density. Changing the CNTs in the fiber from a fiber to a film is not the ideal method for making films. Full Raman spectra show that the CNTs in the fibers and the
HiPCO produced CNTs are different. This can be seen by inspecting the shape of the $G$ band at 1590 cm$^{-1}$, shown in figure 6.6 (red arrow). Although this is the case, charge transfer effects as seen by Raman microscopy are not CNT type depended and a reasonable conclusion can be made that if charge transfer can be seen with HiPCO produced CNTs, it can be seen with the CNTs in the fiber. Using Raman microscopy equipped with a 633nm laser, charge transfer was observed as indicated by $G$ band shifts, as seen in figure 6.7. The data presented here is of the $G$ band of CNTs processed in diiodomethane and hexylamine. In CNTs, electron donor and acceptor molecules

![Graph showing Raman Microscopy Analysis of CNT Fiber and HiPCO-made CNTs](image)

Figure 6.6 Raman Microscopy Analysis of CNT Fiber and HiPCO-made CNTs
cause opposite shifts in the G peak\textsuperscript{64}, which is what is seen here. Diiodomethane is electron withdrawing while hexylamine is electron donating. Since the decreases in fiber resistance here seem to be associated with the inclusion of halogens, I wanted to know if I can induce the same decrease in resistance by artificially adding a halogen to a halogen-free solvent. In order to test this, a 15.75 millimolar solution of iodine pyridine and isopropanol was prepared as well as a 0.475% Lugol’s solution. (For this experiment, Lugol’s solution is iodine and potassium iodine dissolved in 50:50 mixture of water and isopropanol. The stated percentage relates to a total iodine content that is equivalent to the amount of iodine that was included in the 15.75 mM solutions). The fibers were immersed in these solutions and fiber resistance was measured in the same manner as before. The graphs for these experiments are shown in figure 6.8. Adding iodine to pyridine resulted in a large increase in fiber resistance.

Figure 6.7 Raman Microscopy Analysis Showing G-band shift – 633nm Laser
Although, this resistance increase is around half of the resistance increase of pure pyridine. An increase was also observed when the fiber was immersed in the Lugol’s solution. The interesting result here is that adding iodine to isopropanol decreases fiber resistance by almost 20%. In comparison, pure isopropanol will increase fiber resistance by about 15%. The results with iodine in pyridine and isopropanol further confirm that the inclusion of halogens, whether dissolved or as a part of the solvent molecule, change the electrical properties of CNT fibers immersed in liquids by electrochemical doping.

Another topic that needs to be considered at this point is the ability of halogen containing solutions to purify CNTs. In 2006 a CNT purification technique using liquid bromine was reported. This method reduced the iron content of the CNTs from 27% to 1.7%. In this case, liquid bromine proved to be a strong enough oxidant in that it would remove the iron, but not strong enough to damage the CNTs. This study also considered liquid iodine and showed that this liquid would decrease the iron content to 9%. While this was not the lowest iron content achieved in this study, it still represents a significant decrease. Bromine solutions were also considered in this study and showed an 8-16% final iron content. It is possible that the iodine solutions used in this study are purifying the CNT fibers to a certain extent. Although the decrease in iron content that was shown by purifying with iodine was obtained using pure liquid iodine. The iodine content in the solutions used in the present study are much lower (15.75 mMolar). It is reasonable to conclude that the purification and iron removal by the solutions used here will not be as pronounced as was observed.
with pure iodine (or bromine) and the elasto-capillary and electrochemical doping effects are the main drivers of electrical property change.

Figure 6.8 Resistance of CNT Fibers Immersed in Pyridine with Iodine, Isopropanol and Iodine and Lugo's Solution as a Function of Time

6.2.4. Ohmic and Non-Ohmic Behavior of CNT Fibers in Liquids

Another established characteristic of CNT fibers submersed in polar liquids is the exhibition of a non-ohmic effect. In traditional ohmic conductors that obey Ohm's law (Voltage equals Current multiplied by resistance), material resistance remains the same at a given temperature (resistance will rise with temperature). The I-V characteristic curve of an ohmic conductor is a straight line and the slope of this line is the resistance of the material. CNT fibers behave like an ohmic conductor in air, as
seen in figure 6.9. In 2014, Terrones et al. showed that CNT fibers when immersed in polar solvents behaves non-ohmically. They showed that an electric field is able to modulate the resistivity of the CNT fiber. Specifically, they showed that fiber will resistance will decrease if the applied current is increased. And they concluded that

![Figure 6.9 I-V Curve of CNT Fiber in Air](image)

the electric field was able to control the gap distance between CNT bundles. However, this effect was observed after the fiber’s resistance was given sufficient time to stabilize while immersed. And as discussed earlier, nearly all the solvents that have been examined in this manner show an increase in fiber resistance over time. The resistance decreases shown by Terrones et al. still represent an overall resistance increase compared to the pre-immersion value. Conversely, this study has shown there are several solvents that behave differently than the solvents used to establish
these characteristic behaviors. Considering this, I wanted to find out if this non-ohmic effect is retained with solvents that display different trends. To that end, I took two of the liquids that were most different from the others, iodine in isopropanol (due to the resistance decrease) and Lugol’s solution (due to its electrolytic nature, a liquid that hasn’t been tested in this manner), and performed current sweeps with fibers immersed in them. Similar sweeps were performed on fibers in air and in NMP as a comparison to the previously published study by Terrones. This data is shown in figure 6.10. Just as Terrones showed, a fiber resistance when immersed in NMP decreases when the current is increased. As well, the fiber’s resistance increases with current while in air, just as expected due to Joule heating. The behavior of the fiber immersed in Lugol’s solution matches that of NMP. But this non-ohmic effect is not observable with iodine dissolved in isopropanol. Considering the results presented in the previous section on fiber resistance decreases due to electrochemical doping, immersion in liquids that will dope CNT fibers in situ causes the characteristic non-ohmic effect to disappear and the fibers behave ohmically.
6.2.5. Increases in Current Carrying Ability of CNT Fiber in Liquids

As presented in the previous section, the resistance of a CNT fiber in air will increase when the current is increased. This is due to the heat that builds through Joule heating. In characterizing these CNT fibers, current carrying capacity was calculated, as shown in chapter 3. In each of the samples tested, the fiber's resistance dramatically increases around 30 milli Amps during the sweep. This can be seen in figure 6.11 as the I-V curve of the fiber in air dramatically changes slope. And the fiber typically fails at a current amount just above this value. The current sweeps that are performed to calculate current carrying capacity are the same as the ones performed to evaluate the non-ohmic effect in the previous section except that the current level was kept below this in-air failure level, as failure of the CNT fiber was not the desired
outcome. Upon careful inspection of figure 6.10, the curve of the current sweep of the fiber that is in air has a noticeable increase in resistance at the higher current values.

![I-V Curve of a CNT Fiber in Air During a Current Carrying Capacity Evaluation](image)

**Figure 6.11 I-V Curve of a CNT Fiber in Air During a Current Carrying Capacity Evaluation**

This resistance uptick is an early sign of fiber failure from heat. However, in all 3 liquids tested, fiber resistance either remained constant (iodine in isopropanol) or decreased with increasing amounts of current (Lugol's solution and NMP). As this feature where overall fiber resistance decreases as the current increases could be a very useful for power transmission, a current carrying capacity analysis was performed on the fibers immersed in liquids. This data is shown in figure 6.12. Both the fiber submersed in iodine dissolved in isopropanol and in Lugol's solution were able to carry 3 times as much current as the CNT fiber in air. Additionally, the fibers immersed in liquids did not fail. The failure point of the CNT fiber in air is indicated
by the red arrow. Data using higher currents were unable to be obtained as the current limit of the equipment was reached.

Figure 6.12 I-V Curve of CNT Fibers in Air and Immersed in Liquids During a Current Carrying Capacity Evaluation

Although this ability to carry more current while immersed in liquids is an achievement in and of itself, it is worthwhile to look at fiber resistivity as well. Current carrying capacity and how it relates to wire failure is based on heat generation. Cables that provide high amperage current to furnaces often need to be cooled in some way or too much heat will build up and the cable or jacketing will fail. Considering this, it makes sense that the CNT fibers immersed in liquids will be able to carry more current without failing as the liquid would provide some heat exchange. But for most of the solvents and liquids considered here, immersion raises resistance and thus raises fiber resistivity. This increase in resistivity means that more voltage would be
needed to get to that current level in the fiber, which decreases efficiency. Figure 6.13 analyses the resistivity of CNT fibers immersed in isopropanol with iodine and Lugol’s solution with a resistance ‘timeline’. This graph shows the monitoring of resistance of a single CNT fiber during the initial stages of immersion and then through a current sweep. The dashed line represents the starting resistance of the fiber in air. Any time the curves in this graph go above this dashed line, resistivity increases. Going below this line means a decrease in resistivity (or an increase in conductivity). Immersing a CNT fiber in isopropanol with dissolved iodine increases conductivity at most points during this experiment. This increase remains mostly unchanged with changing current as well. Its overall behavior is what would be expected of an ohmic conductor. Conversely, the Lugol’s solution significantly decreases fiber conductivity until a certain current is applied to the fiber. Then an increase in conductivity is observed, which is larger than the increase in conductivity seen with the iodine in isopropanol.
Figure 6.13 Resistance 'Timeline' of CNT Fibers in Isopropanol with Iodine and Lugol's Solution
The rightmost portion of figure 6.13 shows the resistance of the fibers when the current is lowered to the value used for portion A. The observed increase in conductivity for the Lugol’s solution returns to the large decrease in conductivity observed just after immersion. The isopropanol/iodine combination experiences a similar return to its original immersed value. The two methods presented here for increasing conductivity and current carrying capacity in CNT fibers immersed in liquids serve as the initial step in the development of fluidic conduction wires.

6.3. Conclusion and Future Studies

This chapter presented a study on liquid-phase electrical property modification of CNT fibers. This study differs from the previous as the liquid plays an active role, i.e. the CNT fiber is constantly immersed in liquid during data collection and use. This section focused on liquids that have a strong electrochemical doping effect. The overall effect of this liquid-phase doping is lower fiber resistance and an increase in current carrying capacity. In fact, the current level achieved without failure is higher than the recommended amperage for a jacketed copper wire twice the diameter of the CNT fiber. This recommendation is admittedly conservative and is to make sure the heat generated in the fiber doesn’t melt the jacketing. But for a fiber that has a conductivity value that is 2 orders of magnitude lower than copper, the amount of current it withstood without failing is remarkable. Additionally, the electric field strength has been shown to change the characteristic capacitance of CNT fibers as well as the resistance. A future study would be to evaluate this liquid-phase
doping scheme with alternating current, as CNT fibers are also being developed for power and signal transmission. A preliminary study using iodine monochloride in acetic acid showed that signal attenuation decreased over a very large frequency range. This is shown graphically in figure 6.14. Transformers that are used power transmission are one product where this porous CNT fiber and liquid-phase doping scheme can be implemented. In some transformers, the copper coils sit in large tanks of oil, which is used to keep them cool. Replacing those copper coils with CNT fiber coils and replacing the oil with a liquid that can decrease resistance and increase current carrying capacity (like the liquids investigated here) would represent a significant advancement in the energy transmission field.

![Frequency Attenuation Graph](image)

**Figure 6.14 Frequency Attenuation Comparison of an Iodine Monochloride Treated and an Untreated CNT Fiber**
6.4. Methods

Liquid Infiltration

The CNT fiber samples were set up in the same 4-point resistance measurement scheme as presented in chapter 3, except that the CNT fiber is soldered to the copper tape. This is shown in figure 3.7. The solder makes the contacts liquid proof as the binder in the silver paint dissolves in the solvents that are used in this study. The fiber was then lowered into a solvent bath. The resistance was constantly measured at a rate of one measurement per 1.7 seconds for the first 20 minutes. Measurements were taken each minute for the next 10 minutes, then every 2 minutes for the next 20 minutes, then every 5 minutes for the next 10 minutes. Measurements were taken for a total of 60 minutes. At the end of this time, the fiber was removed from the solvent bath and the resistance was measured in a similar fashion for 30 minutes. Resistance measurements were constantly taken at a rate of one measurement per 1.7 seconds for the first 10 minutes. Measurements were taken each minute for the next 10 minutes, then every 2 minutes for the next 10 minutes.

Raman Microscopy Analysis

Raman spectroscopy was performed using a Renishaw inVia confocal Raman microscope with the 633nm laser.
Changing Electric Field Evaluation and Ampacity Measurements

Changes in electrical properties with changing electric field strength was measured using a Keithley 2400 SourceMeter and LabView Software. Current sweeps were performed between 0.1mAmp to 20mAmp. A 4-point resistance measurement scheme was employed for these tests. These sweeps were performed after sufficient time was given for the resistance to remain constant.

Current at failure measurements were performed similarly to the changing electric field studies. A 2-point measurement scheme was used for these tests. Voltage sweeps were performed starting from 0.1 volts and the ending voltage is dependent on the initial resistance of the samples, ranging from 30 volts to 100 volts.
Chapter 7

Concluding Remarks

Research done to date on carbon nanotube-based fibers are showing that they will be ideal metal conductor replacements once they achieve comparable performance. These limiting factors of nanotube-based fibers are becoming less of a hindrance, but improvement is still needed. This thesis has contributed solutions to this problem by utilizing the unique properties of liquids and CNT fibers. By investigating and understanding the fundamental electrical property changes of porous CNT fibers that have been infiltrated with liquids, approaches for ultimately increasing the conduction and current carrying capacity in these fibers has been developed. The understanding generated in this project of the effects that liquids have on conduction in CNT fibers resulted in an increase in the fiber’s electrical performance and will ultimately aid in the implementation of carbon nanotube fibers as conduction wires.
**Thesis Outcomes**

1. Characterized the composition, porous structure, and initial electronic properties of direct spun CNT fibers

2. Expanded knowledge on the structural and electrical property changes of CNT fibers due to liquid infiltration. Showed that the mechanism for electrical property change is a combination of both electrochemical doping and elasto-capillary effects.

3. Showed how solvent properties affect iodine doping efficacy in CNT fibers by emphasizing the importance of accounting for all the fundamental interactions.

4. Developed a new method to solder CNT fibers to metals.

5. Evaluated a liquid-phase CNT fiber doping technique that showed that liquids can decrease overall fiber resistance and increase current carrying capacity.
References


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Appendix A

Table Appendix A.1 Physical Parameters for Various Liquids

<table>
<thead>
<tr>
<th>Substance</th>
<th>Density (g/cm³)</th>
<th>Vapor Pressure (kPa)</th>
<th>Dipole Moment (Debye)</th>
<th>Surface Tension (mN/m)</th>
<th>Viscosity (mPa s)</th>
<th>Dielectric Constant at 20°C</th>
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<tr>
<td>N-Methyl-2-Pyrrolidone</td>
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<td>Acetone</td>
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<td>22.72</td>
<td>0.306</td>
<td>21.01</td>
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<td>0.53</td>
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<td>34.57</td>
<td>2.02</td>
<td>16.1</td>
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<td>7.87</td>
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<td>21.97</td>
<td>1.074</td>
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<td>2.76</td>
<td>2.215</td>
<td>36.56</td>
<td>0.879</td>
<td>13.26</td>
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<td>20.93</td>
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<td>0</td>
<td>19.66</td>
<td>0.387</td>
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<td>-</td>
<td>-</td>
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<td>6.0814</td>
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<td>Acetic Acid</td>
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<td>1.7</td>
<td>27.1</td>
<td>1.056</td>
<td>6.20</td>
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Information in this table was sourced from the CRC Handbook of Chemistry and Physics⁸⁹.

Table Appendix A.2 Hansen Solubility Parameters for Various Liquids and CNTs

<table>
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<th>Substance</th>
<th>Hansen Solubility Parameters (MPa 1/2)</th>
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<td>Dispersion</td>
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<td>Pyridine</td>
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</tr>
<tr>
<td>Isopropanol</td>
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</tr>
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<td>Heptane</td>
<td>15.3</td>
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<tr>
<td>Chlorobenzene</td>
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<td>Dichloromethane</td>
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<td>Diiodomethane</td>
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</tr>
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<td>Methanol</td>
<td>15.1</td>
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<tr>
<td>Toluene</td>
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</tr>
<tr>
<td>Cyclohexane</td>
<td>16.8</td>
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<tr>
<td>Ethyl Acetate</td>
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<td>Acetic Acid</td>
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<td>Single Wall CNT</td>
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<td>Double Wall CNT</td>
<td>19.5</td>
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<tr>
<td>Multi Wall CNT</td>
<td>18.6</td>
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</table>
Hansen Solubility Parameters were obtained from ‘Hansen Solubility Parameters: A Users Handbook’\(^5\).

Single wall CNT Hansen Solubility Parameters were obtained from Bergin et al\(^9\).

Double and Multiwall CNT Hansen Solubility Parameters were obtained from Detriche et al\(^9\).

**Table Appendix A.3 Hansen Affinity Parameters**

<table>
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<th>Substance</th>
<th>Hansen Affinity Parameter (MPa 1/2)</th>
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<td>N-Methyl-2-Pyrrolidone</td>
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<td>Ethanol</td>
<td>12.53</td>
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<td>3.22</td>
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<td>Ethyl Acetate</td>
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<tr>
<td>Acetic Acid</td>
<td>8.87</td>
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</table>

As presented in chapter 4, Hansen affinity parameter are calculated as follows:

\[
R_\delta = \sqrt{4(\delta_d^{NT} - \delta_d^L)^2 + (\delta_p^{NT} - \delta_p^L)^2 + (\delta_h^{NT} - \delta_h^L)^2}
\]
Appendix B

CNT-Antimony Fiber

Antimony is commonly recognized as a metalloid and is found on the periodic table between tin and tellurium. It also shares a row with iodine, a common dopant for CNT fibers that increases conduction. It was originally believed that antimony could serve a similar dopant function as iodine in CNT-containing materials. Some supporting evidence for this belief came from Vogel and colleagues in 1977. They showed that graphite intercalated with acid fluorides (an example being antimony pentafluoride) would produce high conductivity. Other more recent support of antimony use in carbon materials: a tin/antimony/CNT material as a lithium ion battery anode; antimony nanoparticle modified CNTs as a material for electrochemical sensing; antimony doped graphene nanoplatelets that are being developed as stable carbon-based electrocatalysts.

In this preliminary study, antimony pentafluoride was applied to a CNT fiber tow to determine if antimony could act as a dopant and decrease the resistance of the CNT fiber tow. The weight, length and 4-point resistance of a CNT fiber tow was determined. In a low moisture environment, this CNT fiber tow was placed in a boiling flask and antimony pentafluoride was applied to it using a pipette. The boiling flask was sealed and removed from the low moisture environment and a vacuum was applied. The flask was then heated to 80°C and left for 72 hours. After this, the weight,
length and 4-point resistance of the CNT fiber tow were determined again. This procedure was performed on two CNT fiber tows. The before and after weight and resistance measurements are presented in appendix B figure 1. Before and after scanning electron microscopy images are presented in appendix B figure 2. Data from both tows shows that there was a gain in weight and decreased resistance. This resistance decrease supports the dopant hypothesis. Additionally, the weight increase suggests that a considerable amount of antimony was added to the CNT fiber tow (more than would be expected for a dopant). This inference is supported by the electron microscopy images where a distinct change in morphology is observed. This is further supported by the energy-dispersive X-ray spectroscopy (EDS) data.
presented in figure 3, which show an antimony content of nearly 30 atomic %. Given that antimony pentafluoride is a liquid when applied to the CNT fiber, it is possible that antimony has formed in the pores where this liquid could penetrate. Although these results were positive, the weight added to the fiber as well as the hazardous nature of the synthesis were the reason that this CNT-Antimony fiber was not pursued further.

Figure 2: Scanning electron microscopy images of control, untreated fibers (top) and antimony pentafluoride treated fibers (bottom). a) and d) low magnification images b) and e) medium magnification images c) and f) high magnification images
Metal Particle Delivery with Solvents

In this experiment, gold nanoparticles suspended in ethanol and silver particles in acetone were applied to a CNT fiber and the resistance change was measured. The purpose for performing this experiment was to test the theory that adding conductive particles to the CNT fiber will increase its conductivity. Metal particles have been shown to increase conductivity in CNT fibers before, but those particles were applied to the fiber by a different method. Since the gold and silver particles are suspended in an organic solvent, it is hypothesized that some of these particles could get carried into the void space as the organic solvent infiltrated and decrease resistance. Filling these pores with something that is conductive is likely to be better for current flow than air. In order to examine the effect of applying this conductive paint, a four-point resistance measurement method was used whereby a
CNT fiber was attached to copper tape using conductive paste and mounted on a glass slide. This setup is shown in chapter 4. The gold nanoparticles and silver particles were applied to the CNT fiber using a pipette. The fiber resistance was measured constantly during both experiments.

The results show that the silver particles decreased the resistance of the CNT fiber. The gold nanoparticles increase the CNT fiber resistance. These results are summarized graphically below in appendix B figure 4 and 5. These results partly support the hypothesis that application of conductive particles dispersed in organic solvents will decrease the resistance of a CNT fiber. The gold nanoparticles increased fiber resistance. This is due to the PVP capping step in the synthesis process that’s meant to stop the gold nanoparticles from growing. This PVP coating would likely make the particles nonconductive. SEM images of the fibers taken after the experiments are shown in appendix figure 6. Although the silver particles decrease fiber resistance significantly, this decrease comes with increased weight and bulk, which would decrease the specific conductivity. It was for this reason that the inclusion of silver particles in CNT fibers would not be pursued further.
Figure 4: Resistance change as a function of time for the application of silver particles to a CNT fiber

Figure 5: Resistance change as a function of time for the application of gold nanoparticles to a CNT fiber
Gold particles were graciously provided by a collaborator and this synthesis procedure was provided. The gold nanoparticles were synthesized by modifying a polyol process. Poly(vinyl pyrrolidone) (PVP) was dissolved in diethylene glycol (DEG) and refluxed for 5 min while stirring. Then a solution of Tetrachloroaurate trihydrate (HAuCl4•3H2O) dissolved in DEG was added and was allowed to react for 10 min. The resulting product was used as-made for the experiment.
Appendix C

This appendix presents an example of how the maximum resistance and conductivity values were obtained. These values were used in graphs shown in chapter 4. The figure below is an example of the type of graph that is generated during the experiment. It is a graph of change in resistance as a function of time. The red arrow in the figure signifies the point of maximum resistance decrease. This value is either made into a percentage (center application experiment) or used to calculate fiber conductivity (full wire application).

![Graph of change in resistance as a function of time](image-url)