Electrospun Carbon Model System for a Nanofiber Transparent Conductor

by

William Justin Ritchie

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

The Faculty of Graduate Studies

(Materials Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

January 2013

© William Justin Ritchie, 2013
Abstract

Though absolute quantities of fossil fuels are abundant, the costs of drilling additional oil wells have increased more than 500% since 2000. Building a future that is less reliant on increasingly costly non-renewable energy resources will require the exploration of electricity generation from readily available solar power. Installed photovoltaic (PV) capacity has increased from 700 MW in 1996 to more than 69 GW in 2011. PV is contributing a rapidly growing share of electricity from a renewable source to the global energy picture but the manufacturing process of solar cells require many non-renewable resources and large amounts of energy. Performance of photovoltaic modules and cells are highly dependent on the properties of the transparent conductors. Indium tin oxide (ITO) is widely used in thin film and organic solar cell structures but recent projections for indium supplies show that only a few decades of this material may remain. Materials used in the manufacturing process of photovoltaics will need to use readily abundant resources if they are to become a significant portion of the electricity generation profile over the next century.

This study explores the process of electrospinning and its ability to produce a transparent conductor layer for solar cells by using carbon instead of the scarce materials that constitute many transparent conductors. Thin layers of multi-walled carbon nanotube composites are electrospun, carbonized at temperatures of 700-1000°C and characterized as a transparent conductor (TC) model system. This first iteration of the nanofiber TC system achieves transparencies of greater than 85% and a sheet resistance as low as 700 Ω/□. Polyacrylonitrile (PAN) is evaluated as a carbon fiber precursor against PAN-co-methyl acrylate (PAN-co-MA) for electrical applications. PAN-co-MA is found to have as much as a 700% increase in conductivity compared to homopolymer PAN. The nanofiber transparent conductor model is evaluated in the context of an ITO replacement for solar cells and touch screen devices.
Preface

Results in Chapter 5 are based on work conducted in UBC’s Advanced Fibrous Materials Lab under the supervisions of Dr. Frank Ko.

# Table of Contents

Abstract ........................................................................................................................................... ii
Preface ............................................................................................................................................. iii
Table of Contents ................................................................................................................................. iv
List of Tables ......................................................................................................................................... vi
List of Figures ........................................................................................................................................ vii
Acknowledgements ............................................................................................................................. ix

Chapter 1 Introduction............................................................................................................................. 1

Chapter 2 Objectives ............................................................................................................................. 7

Chapter 3 Literature Review and Background ..................................................................................... 9

3.1 Photovoltaic Cells and Modules in the Global Context ................................................................. 9
  3.1.1 PV as a Scalable Technology ........................................................................................................ 18
  3.1.2 Second Generation Solar PV - Amorphous Silicon ................................................................. 20
  3.1.3 Second Generation Solar PV - Copper Indium Diselenide ..................................................... 22
  3.1.4 Second Generation Solar PV - Cadmium Telluride ................................................................. 23
  3.1.5 Third Generation Solar Cells - Organic Materials ................................................................. 24

3.2 Transparent Conductor Materials and Spectrophotometry .......................................................... 28

3.3 Electrospinning ............................................................................................................................... 36

3.4 Carbon Nanofibers and Composites ............................................................................................. 46

Chapter 4 Materials and Methods ......................................................................................................... 50

4.1 Materials ....................................................................................................................................... 50

4.2 PAN and PAN-co-MA Solution Preparation .............................................................................. 50
  4.2.1 Polymer Solutions with Nanoparticles .................................................................................. 50

4.3 Nanofiber Fabrication .................................................................................................................... 51

4.4 Carbonization Processing Parameters .......................................................................................... 51

4.5 Characterization Methods .............................................................................................................. 52

Chapter 5 Results ................................................................................................................................. 54

5.1 PAN and PAN-co-MA Copolymer Membranes – Microstructural Observations ......................... 54
  5.1.1 Nanofibers Prior to Carbonization ....................................................................................... 54
  5.1.2 After Carbonization ............................................................................................................... 58

5.2 PAN and PAN-co-MA Copolymer Membranes – EDX, Raman Spectroscopy and Electrical Conductivity ......................................................................................................................... 59
  5.2.1 EDX Measured Carbon Content ............................................................................................ 60
  5.2.2 Raman spectroscopy .............................................................................................................. 62
  5.2.3 Electrical Conductivity .......................................................................................................... 64

5.3 PAN Composite Nanofibers as a Transparent Conductor ............................................................ 67
  5.3.1 Microstructural observations ................................................................................................... 67
  5.3.2 Coverage of slides ................................................................................................................... 71
  5.3.3 Optical Transparency .............................................................................................................. 73
  5.3.4 Electrical Conductivity of Nanofiber Thin Layers ............................................................... 76
  5.3.5 Work Function ....................................................................................................................... 78
List of Tables

Table 2-1 – Some Basic Indium Tin Oxide Properties ................................................................. 8
Table 3-1 - Net Energy from Literature of PV Technologies ......................................................... 16
Table 3-2 – Wavelengths that Constitute UV, Vis and IR Bands ................................................... 29
Table 3-3 – Transparent Conductor Performance [70–74] .......................................................... 35
Table 3-4 - Non-Oxide Based TCs ............................................................................................... 35
Table 5-1 – Mean Diameters of PAN and PAN-co-MA after electrospinning ............................. 54
Table 5-2 - Mean Diameter of PAN after Carbonization at 700°C, 900°C and 1100°C .............. 58
Table 5-3 – Mean Diameter of PAN-co-MA after Carbonization at 700°C, 900°C and 1100°C . 59
Table 5-4 – EDX Measured Carbon Content of PAN and PAN-co-MA fibers at 700°C .......... 60
Table 5-5 - Carbon Content of PAN and PAN-co-MA fibers at 900°C ........................................ 61
Table 5-6 - Carbon Content of PAN and PAN-co-MA fibers at 1100°C ...................................... 61
Table 5-7 - Raman Ratio - Note: R=I_g/I_d ............................................................................... 63
Table 5-8 - Conductivity Values for PAN in S/cm ................................................................. 64
Table 5-9 - Electrical Conductivity Values for PAN-co-MA in S/cm ........................................ 66
Table 5-10 - Table of Uncarbonized Diameter MWCNT/PAN-co-MA Distributions .......... 69
Table 5-11 - MWCNT Fiber Diameters at 750°C ................................................................. 70
Table 5-12 - MWCNT Fiber Diameters Carbonized at 850°C .............................................. 71
Table 5-13 - Unit Area Coverage of Nanofibers ................................................................. 72
Table 5-14 - Carbon Nanofiber Work Function Values ............................................................ 78
Table 7-1 - ITO vs. NF TC Properties ......................................................................................... 94
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>Cost of Additional Oil Extraction is Depleting the Excess Wealth Surplus Driving the Consumer Economy [7]</td>
<td>2</td>
</tr>
<tr>
<td>1-2</td>
<td>Yearly Installed PV Capacity Worldwide [8]</td>
<td>3</td>
</tr>
<tr>
<td>1-3</td>
<td>Location of 2009 Installed PV Capacity [11]</td>
<td>4</td>
</tr>
<tr>
<td>3-1</td>
<td>Diagram of the Cz Growth Technique</td>
<td>12</td>
</tr>
<tr>
<td>3-3</td>
<td>Energy Involved in Manufacturing Process of Monocrystalline PV [45]</td>
<td>20</td>
</tr>
<tr>
<td>3-5</td>
<td>Structure of a CIGS solar cell [31]</td>
<td>23</td>
</tr>
<tr>
<td>3-6</td>
<td>Exciton Generation in Organic Polymer Solar Cell</td>
<td>26</td>
</tr>
<tr>
<td>3-7</td>
<td>Common Electrospinning Setup</td>
<td>38</td>
</tr>
<tr>
<td>3-8</td>
<td>Nanofiber Electrospinning Unit (left) and the Nanon (right)</td>
<td>40</td>
</tr>
<tr>
<td>3-9</td>
<td>Electrospinning Processing Parameters [16]</td>
<td>41</td>
</tr>
<tr>
<td>3-10</td>
<td>The structure of polyacrylonitrile transformed by heat into carbon fiber [107]</td>
<td>46</td>
</tr>
<tr>
<td>3-11</td>
<td>Stabilization Stages of PAN [104]</td>
<td>48</td>
</tr>
<tr>
<td>4-1</td>
<td>Graphical Representation of Carbonization Process</td>
<td>52</td>
</tr>
<tr>
<td>5-1</td>
<td>7wt% PAN (left) and PAN-co-MA (right) at 5k magnification uncarbonized</td>
<td>55</td>
</tr>
<tr>
<td>5-2</td>
<td>8wt% PAN (left) and PAN-co-MA (right) at x5k magnification</td>
<td>56</td>
</tr>
<tr>
<td>5-3</td>
<td>9wt% PAN (left) and PAN-co-MA (right) at x10k magnification</td>
<td>56</td>
</tr>
<tr>
<td>5-4</td>
<td>10wt% PAN (left) and PAN-co-MA (right) at x20k magnification</td>
<td>57</td>
</tr>
<tr>
<td>5-5</td>
<td>12wt% PAN-co-MA at x20k magnification</td>
<td>57</td>
</tr>
<tr>
<td>5-17</td>
<td>Plotted Raman Ratio of PAN and PAN-co-MA samples</td>
<td>62</td>
</tr>
<tr>
<td>5-18</td>
<td>Conductivity of PAN Membranes</td>
<td>64</td>
</tr>
<tr>
<td>5-19</td>
<td>Conductivity of PAN-co-MA Membranes</td>
<td>65</td>
</tr>
<tr>
<td>5-20</td>
<td>Conductivity Values for PAN and PAN-co-MA Membranes</td>
<td>66</td>
</tr>
<tr>
<td>5-21</td>
<td>SEM image and Diameter Distribution of 16wt% MWCNT/PAN-co-MA Uncarbonized</td>
<td>68</td>
</tr>
<tr>
<td>5-22</td>
<td>SEM image and Diameter Distribution of 19wt% PAN-co-MA Uncarbonized</td>
<td>68</td>
</tr>
<tr>
<td>5-23</td>
<td>SEM Image and Fiber Diameter Distribution of 22wt% MWCNT/PAN-co-MA..</td>
<td>69</td>
</tr>
</tbody>
</table>
Acknowledgements

I want to thank Dr. Frank Ko and Dr. Peyman Servati for their guidance and support for this work. I’m deeply grateful for the advice and questions of all my lab co-workers and colleagues. This thesis would not have been completed without the support of all the students and staff in the Advanced Fibrous Materials Lab and the Flexible Electronics Engineering Lab.

Portions of this work were made possible through funding from a Strategic Research Grant from the Natural Sciences and Engineering Research Council of Canada along with funding from the Canada Foundation for Innovation and the Asian Office of Aerospace Research and Development.

I want to thank my loving partner Jane for her support and endurance of my graduate work and for my parents to whom I owe my initial inspiration for pursuing a career in engineering and science.
Chapter 1 Introduction

Throughout the last century, the concept of using a photon to generate electricity has gone from the drawing board to the development of a robust industry that focuses on building increasingly efficient and complex forms of photovoltaic (PV) commercial products. Currently, the technology for using PV in the generation of electricity has become reliable enough to provide large-scale commercial power. By developing increasingly more cost efficient production processes, the cost of PV technologies have now been able to realize electric utility scale generating capacity goals of several megawatts (MW) in a single installation. The creation of this entire field began just under sixty years ago in 1955 as Bell Laboratories launched a larger investigation into applying PV concepts towards the generation of electricity for the purpose of powering remote telecommunications systems [1]. At that time, PV was seen as a little more than a potential technology for remote and marginal applications. This goal was realized through low cost silicon based PV modules on remote equipment and through applications in space. For example, nearly all electricity generated for space based technology is through using multijunction solar cells comprised of materials such as Gallium-Indium-Phosphide (GaInP2), Gallium Arsenide (GaAs) and Germanium (Ge) with over 30% efficiency [2].

Now, PV technologies have moved far beyond niche applications; they are sought after in the policy sphere and the utility sector as reliable fossil fuel alternatives to maintain and expand electrical generation capacity while emitting a lower amount of product life-cycle greenhouse gases (GHG) than coal, natural gas, or oil [3]. In 2008, the most recent year that numbers are available for relatively accurate amounts of global electricity generation, 19.1 trillion kilowatthours (kWh) were generated [4]. Out of these 19.1 trillion kWh, coal continues to be the
fuel that is most widely used for electricity generation, constituting 40% of the world electricity supply. Even though generation from nuclear power and renewable grew rapidly in the 1980s and 1990s respectively, coal’s dominance is projected to continue for several more decades. Because our standard of living has been almost entirely reliant on fossil fuel supplies that are becoming more costly to extract, the standard of living in developed nations is slowly decreasing as shown in Figure 1-1. Electricity generation from sources of renewable fuels such as solar PV has been the fastest growing source of global electricity generation and shows the potential to offset fossil fuel dependencies [5], [6].

![Costs per Well, All Wells, 1960-2008](image)

Figure 1-1 Cost of Additional Oil Extraction is Depleting the Excess Wealth Surplus Driving the Consumer Economy [7]
Solar PV technology contributes roughly 12 billion kWh to annual global electricity production or .063% of generated electricity. In 2011, global installed PV nameplate capacity was 69GW as exhibited in Figure 1-2 and the placement of this capacity is roughly the same as in 2009’s installed capacity pictured in Figure 1-3. Photovoltaic technologies are classified based on the type of active layer material used to generate free electrons from the incident energy in an incoming photon [9]. These classifications are broken down to as first generation PV technologies that use silicon, second generation technologies involving thin films such as cadmium telluride (CdTe) or amorphous silicon (a-Si) and third generation technologies that incorporate polymeric materials such as Poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3-hexylthiophene) (P3HT) [10].
Nanotechnology research and development is expected to play a key role in many areas of PV technology development because of expectations that nanomaterials can drive further cost decreases and performance increases through higher conversion efficiencies and through more efficient material use, especially for second and third generation PV devices [5]. Three of the key areas where nanomaterials can have an impact in PV technology is through (I) increases in solar cell efficiency, (II) performance increases for transparent conductor (TC) materials in PV devices or in (III) Anti-reflective (AR) coating layers like ZnO [12]. Transparent conductors are a major factor in the performance and cost of solar cells and related PV technologies, the most common high performing transparent conductor is estimated to impact the cost of an organic solar cell (OSC) by as much as 33-40% [6], [13]. Additionally, an impact in the cost of TC materials can have a major cascade effect on the overall cost of manufacturing solar cells.
In this study, multi-walled carbon nanotubes (MWCNT) are proposed as a method to increase the conductivity of a carrier polymer that can be used as a model system to demonstrate future advances in transparent conductor materials. Nanomaterials such as MWCNT have demonstrated significant and fascinating properties on the nanoscale though much work is still needed to translate their performance to a usable morphology on the macroscale [14], [15]. Because of the discrete nature of nanoparticles, it can be difficult to harness their properties to create meaningful structural forms. There is a significant need to develop carriers that can adapt the properties of nanomaterials to a scale where they can be applied.

Recently, many advances in the process of electrospinning have demonstrated the ability to create multifunctional fibers containing various nanoparticles [16]. Nanocomposite fibers are being explored for their ability to achieve enhanced electronic, chemical and optical properties in one dimension (1D). Electrospinning is one of the most desirable methods for creating 1D fibers because of its scalability and relative simplicity along with its ability to operate at ambient room temperature without requiring a vacuum. Through the process of electrospinning composite fibers are developed through carrier polymers are stretched using electrostatic forces into 1D nanofibers containing nanomaterials that can enhance the properties of the base polymer. These nanoscale fibers are then organized into higher order nanofibrous assemblies [17], [18]. In multifunctional nanofiber membranes, electrical conductivity can be enhanced by using electrically conductive polymer precursors such as PEDOT or Polypyrrole (PPy) or by using a carbon fiber precursor that can be carbonized to create electrically conductive carbon fibers. For this purpose, polyacrylonitrile (PAN) was chosen as the carbon fiber precursor with MWCNT added at increasing levels until the percolation threshold is exceeded [14]. For this work, PAN and an associated co-polymer PAN-co-Methyl Acrylate (PAN-co-MA) is processed with thermal
stabilization and carbonization at temperatures higher than 700°C. These nanofibers are electrospun as thin layers to achieve a balance between transparency and conductivity for use as model system to demonstrate a pathway for future advances in this field for transparent conductor material.
Chapter 2 Objectives

As the depletion rate for non-renewable materials increases in meeting the growth of the PV manufacturing sector, special attention needs to be directed on the ability for the extraction rates of materials to match projected demands in the next few decades. Over the last few decades, policies like feed-in-tariffs (FiTs) have been in place to rapidly increase the rates of installation for grid connected PV [11]. As PV continues to maintain an average growth rate of nearly 40% per year over the last decade, in the next decade the PV manufacturing process will begin to meet material limits in the extraction rates of rare earth materials such as indium, tellurium and even relatively more abundant materials such as copper and silver [19]. In order to offset potential bottlenecks that can lead to price volatility, loss of confidence in the PV market and a possible chain of manufacturer bankruptcies, the PV manufacturing process must be adapted to use as few non-renewable resources (NNRs) as possible. This work examines the NNR requirements of PV manufacturing and explores the ability for the abundant resource of carbon to be incorporated into the manufacturing process through a model system of nanofibers fabrication.

One of the most promising methods of achieving this aim is through replacing the scarce element of indium in the TC layer commonly incorporated into many solar cells. In thin layers, carbon can display high levels of transparency. In order to create absolute reductions in the complexity and cost related to PV manufacturing, the process of electrospinning is proposed because of its advantages as a rapid, inexpensive and simple fabrication method. Much work has been completed in developing carbon composites through electrospinning, yet no work to date has explored using thin layers of carbon composite nanofibers as a TC layer that could be applicable to PV devices [18]. The development of an electrospun TC fabrication technology
opens many possibilities for a low-cost, scalable PV that is less reliant on scarce materials. Additionally, little work has been completed on the alternative co-polymers of PAN for use in electrospinning as conductive membranes [18].

Table 2-1 summarizes some basic properties of indium tin oxide, the leading transparent conductor material. A PAN electrospun TC alternative would need to demonstrate benefits over current values for ITO. In CIGS, ITO films are usually a few hundred nanometers thick on the range of 1000-2000Å. Values for the amount of ITO per megawatt (MW) were calculated using a density of ITO as 7120kg/m³ with 6.25m²/MW for CIGS. ITO was quoted at $26.24/g from Sigma Aldrich.

<table>
<thead>
<tr>
<th>TC</th>
<th>g/MW of CIGS</th>
<th>Sheet Resistance</th>
<th>Transparency</th>
<th>Work Function</th>
<th>$/MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>14.25g ITO/MW*</td>
<td>&lt;100Ω/□</td>
<td>&gt;85%</td>
<td>4.7eV</td>
<td>$372.92*</td>
</tr>
</tbody>
</table>

To expand on the field of electrospun PAN composites and to develop the first systematic study of thin layers of electrospun carbon, this work focuses on the development and characterization of the properties of a MWCNT/PAN and MWCNT/PAN-co-MA electrospun TC layer. For the purpose of exploring an absolute reduction in the cost, complexity and NNR use of PV devices, MWCNT are explored as a model system in using carbon fiber composites as thin layers of electrospun carbon fiber. This study approaches an analysis of the electrical performance of carbon nanofibers based on various precursor polymers and then develops these fibers into thin transparent layers to demonstrate a model system that opens the pathways towards incorporation of renewable materials like lignin.
Chapter 3 Literature Review and Background

3.1 Photovoltaic Cells and Modules in the Global Context

Photovoltaic technologies have undergone a dramatic development since their initial experimental applications in the mid 1950s as developed by Bell Labs. In 1955, the first known PV module was installed in rural Georgia, about 208km south of Atlanta, Georgia, the nearest urban center and consisted of 48 silicon sub-modules, each one tenth of a meter square, encapsulated in silicone oil in a plastic case, under a glass coversheet [20]. This module was capable of producing a final module efficiency of around 2% and little more than 10W of peak power generation. Though radically inefficient by today’s standards, this module demonstrates where the field has grown from over sixty years [21]. The license for this technology was later purchased by National Fabricated Products (NFP), which tried to develop it into a commercially successful technology. Commercial success failed and NFP was bought out by Hoffman Electronics in 1956 which focused on developing this early PV technology into a useful state for PV applications where it has been wildly successful [21].

 Whereas space based PV technologies took the primary focus of the United States industrial development at the time, Sharp, based in Japan began developing PV technologies in the late 1950s and opened a production line in 1964 [20]. By then, module peak power output ($W_p$) had reached levels of several hundred watts, with an output of 225 $W_p$. One of the primary uses of these high power solar modules was in lighting up Japan’s coastal borders, as Sharp installed them at 256 lighthouses [22]. At this point, the modules being produced by Sharp were at a level of efficiency of approximately 4.5% and installation costs were at a level of around
$100/watt, 50 to 100x the current installed cost of today's modules in the year 2012 [23], [24]. By the early 1970s, advances in fabrication technology had pushed the installed cost per watt ($w) down to $w50 for small-scale projects and as low as $w20 for large-scale projects [20].

In early 1973, the United States faced the threat of an energy crisis after an OPEC embargo. This sudden recognition by the United States Government of its fragile U.S energy infrastructure led to the creation of the Solar Energy Research Institute (SERI) through the Solar Energy Research, Development and Demonstration Act of 1974 which began work in 1977 outside of Denver, CO [25]. A sudden awareness of energy swept the United States, which accompanied a large number of PV-centric startups, like the Solar Power Corporation (SPC) that launched in April 1973 [20]. The SPC produced small modules made of cells that were mounted on fibre-reinforced printed circuit boards covered in silicone rubber which produced 1.5 W at roughly 5% efficiency, systems based on this technology were marketed at using as many as 80 of these modules at quantities of over 1000 [20]. As private sector development of PV technologies continued, SERI’s mission found itself vastly underfunded with a 1979 budget of just $25 million USD. After severe funding cuts in the mid-1980s SERI mostly fell apart and was developed into what is now known as the National Renewable Energy Lab (NREL) [25].

The cost of installing PV modules has fallen by a factor of 100 since the 1950s that has outpaced the rate of any other energy technology during that same period [21], [26]. This trend will need to continue if wider scale targets for GHG emission reductions for electricity reductions are to be achieved, some estimates claim that 22TW of solar PV will be needed in the next few decades to meet global energy goals [27]. Because many policy scenarios are planning on large scale increases of installed PV capacity, it is important to note the three major factors that influence PV cost: module efficiency, plant output and silicon material costs. The highest
impact factor on PV cost performance is module efficiency, which is calculated using the equation \( \eta = \frac{W_{\text{out}}}{W_{\text{in}}} \), to calculate the ratio of power the module can provide based on an expected or calculated amount of incident solar insolation. Historically, the efficiency improvements in modules have resulted in more than doubling of the amount of power per square meter each module can produce [26], [28]. Secondly, the installed PV cost is also heavily impacted by the size of the manufacturing infrastructure, an example of economies of scale. By capitalizing on these economies of scale, the PV industry has been able to increase the output of modules on an annual basis by more than several orders of magnitude [29], [30]. The third major factor in reducing PV \( S_w \) is the cost of the silicon material. While other materials are involved in the manufacturing of PV modules, such as glass, aluminum and ethyl-vinyl acetate (EVA), the active photovoltaic layers have the highest single impact on the overall installed cost per module, constituting between 30-50\% of the final Si module price [9], [26]. Part of the reason for the continued cost reduction of PV modules is due to lower amounts of silicon required for PV manufacturing as wafer thickness has been reduced from 500\( \mu \)m to 250\( \mu \)m.

Much of the silicon production for PV has used the Czochralski (Cz) single crystal growth process [31]. The Cz growth process refines silicon material obtained from fragments of highly pure silicon by melting it with induction heating inside a large quartz crucible. As the heat is applied, a seed crystal is inserted, rotated and slowly withdrawn. A diagram of the Cz growth process is shown in Figure 3-1 - Diagram of the Cz Growth Technique.
Silicon is considered an abundant material because surveys of the Earth’s crust through 16km show that the most prevalent material is silicon [32]. Because the production of metallurgical grade silicon is highly energy intensive, most of this process is done in nations with low cost electricity. Major silicon processing is done by Elkem and Pechiney in Europe, the USA, South Africa, Brazil and Australia at rates of 98.5% to 99.5% pure Si with a mean price of 1.5-2.5$/kg. Metallurgical grade of silicon is produced at a rate of roughly 1 million tonnes per year out of quartz through reduction with carbon electrodes. This silicon is used for a wide range of applications such as steel-deoxidation, aluminum alloying, silicones and electronic grade silicon [32].

To manufacture electronic grade silicon into metallurgical grade silicon, impurities must be reduced by a factor of at least 100,000. Reaching this level of purity requires even higher levels of energy inputs and the use of hydrochloric acid to produce trichlorosilane or silane which is decomposed after the process using hydrogen as a reductant through hot silicon rods or
a fluid-bed reactor process (FBR). These added energy and chemical inputs to the process increase the cost of electronics grade silicon by 1000% to 2000% to 30-45 $/kg. A common synthesis route for electronics grade silicon involves the following process: \( \text{Si} + \text{HCl} \rightarrow \text{SiHCl}_3 \) (Tricholorosilane) which is then decomposed with hydrogen on a silicon surface at 1100°C through the following reaction: \( 2\text{SiHCl}_3 + \text{H}_2 \rightarrow \text{Si} + 2\text{HCl} + \text{SiCl}_4 \). During this production process, up to 40% of the processed material will not achieve the necessary purity to be classified as electronic grade silicon. The most common feedstock for PV production is drawn from this “cast-off” material [32].

In the mid-1970s the large government programs for procuring PV modules led by SERI boosted the young industry. One of the first massive government purchases, known as US Government Block I in 1975-1976 was of modules with roughly 5% efficiency at a price of around $30/W in 1980 USD [28]. In 1976 through 1977, US Government Block II purchases of modules saw commercial efficiencies improve to the 6-7.4% range with costs decreasing to approximately $20/W in 1980 USD. As funding rapidly declined for PV purchases and technology development in the mid 1980s, the industry found itself with modules of efficiencies exceeding 10% [20]. During this era, the development of poly-crystalline silicon cells led to further reduced costs for manufacturing.
The vast majority of new Si devices are manufactured using screen-printing of metal contacts leading to a device as in Figure 3-2 - Standard Screen Printed Solar Cell [9]. Most of these devices are installed to serve market demand for grid connected or stand alone systems which deliver power directly to the grid by converting DC electricity into AC, or by supplying power directly to the home, often with storage in battery banks. Grid connected systems are pursued in the developed world while grid independent systems are commonly used in the developing world, especially in situations where a home or area is at the end of a distribution line which faces frequent blackouts.

The solar spectrum can be approximated by a black body of 5900K that leads to a very broad spectrum of photons including energies far outside the bandgap of Si. Like other semiconductor materials, silicon demonstrates the highest efficiency as a photovoltaic when converting photons with the same energy as the bandgap. Photons absorbed by silicon result in thermalization, meaning they are converted to heat instead of free electrons that can be harvested for purposes of power. For photovoltaic applications, silicon also has the consequence of being
an indirect semiconductor where the maximum of the valence band and the minimum of the valence band are not directly opposite each other. Thus, light absorption is much weaker than in a direct bandgap material such as Gallium Arsenide (GaAs). Quantitatively, this can be understood that for 90% light absorption, only 1µm of GaAs is needed whereas 100µm of silicon would be needed. The ideal material for converting the solar spectrum to electricity through a photovoltaic process would be have (1) a bandgap (E_g) of 1.1 eV and 1.7eV, (2) a direct band structure and (3) made of readily available and non-toxic materials.

Even though the technology for silicon materials are well understood and Si is an abundant material there are still significant reasons for concern over the continued reliance of the PV industry on Si. As detailed above, the PV industry relies on Si that is often the cast-off material from electronics grade manufacturing, meaning that PV manufacturing is deeply tied to the continued growth of an electronics industry which has tremendous ecological impacts [33]. Because the semiconductor industry has volatile cycles of boom and bust, the bleed over effects into the PV industry are dramatic and crippling, especially on start-up companies that have very low profit margins on their final product.

Limits of energy availability are not the concern: since an enormous amount of energy reaches the Earth from the Sun, an efficiency of only 1-2% is enough to run the photosynthesis processes that power the entirety of the biological interactions of the planet. If just .025% of this of this energy flow could be captured and converted to electricity, it would be enough to satisfy world electricity demand [34]. However, the manufacturing process of PV systems has a large systemic impacts [35]. With a wider analysis of the material flows involved, the holistic energy impact of PV technology can be analyzed. One of the metrics for determining the environmental
impact of PV technology is the energy returned on energy invested (EROEI) that quantifies the net energy of the technology. Net energy is the amount of energy produced by a bounded system after initial energy expenditures involved in manufacturing are considered. The range of various studies has found that the EROEI of silicon PV technologies range from 3.23:1 to 10:1, meaning that for every unit of energy in joules that are used to produce the photovoltaic system, between 3.23 and 10 times as much energy in the form of electricity is produced over the term of its useful life. A lower net energy will indicate a lower ratio of useful electricity generation to manufacturing impacts. Table 3-1 summarizes literature on the net energy of PV systems.

Table 3-1 - Net Energy from Literature of PV Technologies

<table>
<thead>
<tr>
<th>Study</th>
<th>Net Energy [36]</th>
<th>System</th>
<th>Technology</th>
<th>Life Cycle Boundaries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alsema et al. (2000)</td>
<td>3.75:1 to 10:1</td>
<td>Roof top and ground mounted systems connected to the grid</td>
<td>Polycrystalline Silicon and Amorphous Silicon</td>
<td>Does not include decommissioning or recycling, lifetime of 15-30 years</td>
</tr>
<tr>
<td>Meijer et al. (2003)</td>
<td>2.38:1 to 8.57:1</td>
<td>A single module</td>
<td>Polycrystalline Silicon</td>
<td>Does not include transport, maintenance or disposal, module lifetime assumed to be 15-30 years</td>
</tr>
<tr>
<td>Battisti et al. (2005)</td>
<td>3.75:1 to 10:1</td>
<td>Grid connected PV system,</td>
<td>Polycrystalline Silicon</td>
<td>Cradle to Grave</td>
</tr>
<tr>
<td>Study</td>
<td>Net Energy [36]</td>
<td>System</td>
<td>Technology</td>
<td>Life Cycle Boundaries</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-----------------</td>
<td>--------------------------------------------------</td>
<td>------------------------------</td>
<td>----------------------------------------</td>
</tr>
<tr>
<td>tilted and</td>
<td></td>
<td>A single</td>
<td>Polycrystalline Silicon</td>
<td>Cradle to Grave</td>
</tr>
<tr>
<td>fitted to a</td>
<td></td>
<td>module</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roof</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mohr et al.</td>
<td>7.14:1</td>
<td>Residential PV energy system</td>
<td>Polycrystalline Silicon</td>
<td>PV Module as main energy source,</td>
</tr>
<tr>
<td>(2009) [38]</td>
<td></td>
<td></td>
<td></td>
<td>incorporates lead acid battery and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>inverter</td>
</tr>
<tr>
<td>Celik et al.</td>
<td>3.23:1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2007) [39]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Because glass is a key portion of the PV manufacturing process that contributes to a lower EROEI, the development of a transparent conductor alternative to ITO hold the potential to remove glass from the PV manufacturing process, increasing the EROEI of the technology. Work from this study has the potential to replace glass with a nanofiber transparent conductive layer, thus removing the energy requirements of glass and increasing the energy payback time of the PV module itself. The energy requirements of glass and frame in a photovoltaic module are calculated as 200MJ/m³ of a 1st generation silicon PV module out of a total of 4600MJ/m³ to produce the entire module or 4.3% of the total PV module manufacturing [40].

Though the overall energy payback of PV modules are not calculated in this study, the energy payback time of a PV module as defined by Knapp et. al is provided here for reference in Equation (1) [41].
3.1.1 PV as a Scalable Technology

To have a significant impact on global electricity production, PV will need to have a tremendous increase in installed capacity. In 2011, the volume of newly grid-connected PV around the globe rose to almost 69 GW. Almost 21 GW or 30.4% of this capacity is in Europe [42]. Out of an approximate global installed electrical generating capacity of 5000 GW, solar PV accounts for roughly 1.38% of total global installed electricity generation capacity [8]. If electrical generation through solar PV was doubled over the next few years to more than 140 GW a particular concern is whether there would be material shortages with very large and rapid growth. If the industry were to increase by this factor, the material composition of the PV manufacturing process will need to be analyzed to ensure that the production rate of each input can meet these needs.

The increasing unaffordability of liquid fuels is driving a greater reliance on electricity generation and any acceleration in this process would accelerate demand for PV even faster. One study finds that 16kWh are consumed for each peak watt nameplate capacity (Wp) of Si PV that is manufactured [43]. Meaning that each GW of PV production requires roughly 16,000 GWh. If the current amount of globally installed PV was doubled to 140 GW, the additional 71 GW would require 1,360,000 GWh of electricity for manufacturing. While this might seem like a rather large number, it is only 247.27 hours of the currently installed global electricity capacity.
Though the entire global electricity infrastructure couldn’t focus on manufacturing PV for 10.3 consecutive days, the production of these PV modules would be spread out over time. Because of the high level of energy consumption in manufacturing PV, we can expect silicon PV to remain a relatively small contributor to global electricity generation over the next decade because it is tied to increasingly unaffordable energy prices.

In addition to energy consumption during manufacturing, another potential factor that could limit large-scale installations of silicon PV involves the use of silver as the front contact [44]. Though silicon is abundant, silver has a known reserve of only 400,000 metric tonnes. Tao et al. calculated the ability to use reserves of silver in manufacturing PV by looking at the extraction rate of silver and its ability to scale with silicon PV production. The annual production of silver is 21,400 metric tonnes, allowing a maximum production of 305 GW crystalline-Si solar cells with silver contacts each year. Because silver is a widely used material, optimistically, one-third of the available silver capacity could be used to produce PV modules, limiting production to 100GW per year. As noted by Tao, since the global production of silicon PV was 8.67 GW in 2009 with an annual growth rate of 51% it will take less than 17 years to reach the 100GW/year consumption rate of silver reserves [44]. This is only two years less than the current production rate of silver. The current global demand for silver reserves are on pace to face limits in less than 19 years.
3.1.2 Second Generation Solar PV - Amorphous Silicon

Due to the cost of producing monocrystalline (mc-Si) and polycrystalline (pc-Si) PV, the field has sought over the last few decades to minimize material used in creating efficient and high production PV modules and technologies. One way of minimizing material inputs to solar cells is through using amorphous silicon (a-Si). Though after decades of research, two main problems remain with a-Si: efficiency and degradation.

The potential of a-Si for use as a photovoltaic has been diminished because of the efficiency hit it takes in comparison to mc-Si and pc-Si. Also, the Staebler-Wronski effect causes light induced degradation of the material performance over time [46]. After the first publications that explained the concept behind amorphous silicon (a-Si) in the 1960s, commercial products appeared on the market only five years later [47], [48]. Now the module efficiencies of a-Si based solar cells exceed 7-9% and feature cell efficiencies have surpassed 13%.

The properties of a-Si are different from the Si involved in monocrystalline and polycrystalline cells because it is an alloy of silicon with hydrogen. The typical silicon lattice structure is disrupted by hydrogen, changing the distributions of bond length, angles and leads to
a change in bandgap from $E_g = 1.12\text{eV}$ to $E_g = 1.7\text{eV}$. The deposition process of a-Si is typically chemical vapor deposition (CVD) with a silane precursor at temperatures below 500°C. In the case of a-Si film deposition, the material performance is significantly impacted by the disorder within the crystalline structure, stability of an a-Si layer is related more to the hydrogen content and less on the processing parameters [31]. Most of the improvements in a-Si solar cell efficiencies are attributed to improvements in cell design rather than improved material properties. Recent explorations into hot-wire chemical vapor deposition (HWCVD) have not yielded notable efficiency improvements and it is generally thought that the efficiency capabilities of a-Si only have the potential for marginal efficiency gains [31].

![Figure 3-4 Diagram of an Si cell](image)

Because the mobility for charge carriers is low in a-Si, the generation of an electric current must be supported by an internal electric field. To create a field high enough, these cells must be thin, on the order of only a few hundred nanometers. Amorphous silicon cells can be deposited in one of two configurations: substrate and supersubstrate. Supersubstrate cells are
deposited on a transparent conductive oxide (TCO) material coated on a glass substrate. The TCO material can be patterned to allow the incorporation of a large number of cells on a single large area substrate [49]. Substrate cells can be deposited on polymer or flexible metal foils.

**3.1.3 Second Generation Solar PV - Copper Indium Diselenide**

Beginning with work done by Boeing in the late 1970s and further development by ARCO Solar, CuInSe₂ (CIS) cells were noted for their flexibility in processing parameters and ease of adaptation to photovoltaics [31], [50]. The development of CIS and CIGS cells is typically through one of two possible synthesis routes onto Mo coated soda lime glass substrates. The first synthesis route involves the deposition of precursor layers by sputtering with a subsequent treatment or annealing in the in H₂Se vapor, this can be done with readily available equipment and is primarily tailored to use low-bandgap, high-In content materials. The second approach is through co-evaporation: all of the In, Ga, Se and Cu are evaporated together onto a moving substrate, which is ideal for high throughput. Substrates are prepared at temperatures of greater than 500°C for the deposition of Mo. The heterojunction between the Mo coated substrate and the active layer is formed through the chemical deposition of a thin CdS layer through a Cd-ion solution using thiourea as a source of sulfur.
3.1.4 Second Generation Solar PV - Cadmium Telluride

Solar cells and modules based on Cadmium Telluride (CdTe) feature high efficiencies and low costs. CdTe cells are currently considered the most cost effective PV modules in $/w terms [24]. The initial work on CdTe cells was done on single crystals at RCA labs, where indium was alloyed into n-type crystals [31]. In 1963, the first solar cells made with an active layer of CdTe were reported [51]. For PV applications, CdTe is considered an ideal material in many ways: it has a bandgap close to the ideal, is very readily handled in large scale thin-film deposition, above temperatures of a few hundred degrees C it is self-stabilizing. The deposition of CdTe layers can be done at a temperature of 450°C-600°C at rates of >1µm/minute and can also be done through simplistic methods like electrodeposition and screen printing. High quality CdTe layers can be obtained through the process of closed space sublimation, an evaporation process with the substrate located very closely to the source. Active layers are deposited on a TCO coated substrate that is typically SnO₂ or indium-tin-oxide (ITO).

The CdTe crystalline structure is zinc blende, with a lattice constant of \( a_o = 0.6482 \text{nm} \). Because cadmium is more abundant than tellurium, the limiting material in the production process of CdTe PV is tellurium. The primary use of Te is as an additive for alloying in steel to improve its characteristics in machining. For copper alloys, Te is often added to improve its machinability without affecting the conductivity. Lead alloys use Te to improve their resistance to vibration. Tellurium is added to cast iron to help control the depth of chill. In the manufacture of rubber, Te is used to aid in the vulcanization of rubber. For the production of many synthetic fibers, tellurium is used. Vehicles with seat-cooling systems use bismuth-telluride thermoelectric...
cooling devices. Other uses of Te are in photoreceptor applications and thermoelectric electronic devices, as an ingredient in blasting caps, or as a pigment to produce various colors in glass and ceramics.

To estimate the amount of CdTe PV that can be manufactured, one study uses a best-case scenario assumption that CdTe modules are roughly $2 \mu m$ thick. [44] The atomic mass of tellurium is 128amu and can be used to calculate the potential production capacity based on the amount of available total reserves. With 48,000 metric tons of Te available at the time of the study, one estimate places the potential capacity of CdTe for manufacture at 816 GWp [44], [52]. Another study estimates the amount of CdTe capacity available for manufacture at 300GWp [53]. With updated numbers from the 2012 USGS Mineral Commodity survey, the reserve amount has been revised to 24,000 metric tons meaning that the lower bounded estimate is closer to realistic manufacturing numbers [52].

3.1.5 Third Generation Solar Cells - Organic Materials

Third generation solar cells are typically layers of transparent conductive oxides and organic polymer materials. Theoretical understandings of organic materials as photoreceptors in imaging systems were developed as early as the 1950s [54]. In the first few years of the 1960s, researchers discovered that dyes such as methylene blue had semi-conducting properties [55]. Dyes were then observed as the first materials that exhibited a photovoltaic effect [56]. Later development in the field of polymer PV devices included the observation of free electron generation in biological materials such as carotenes, porphyrins and chlorophylls. Organic semiconductor materials like polymer based solar cells offer the ability to produce electricity generated from the PV effect at a lower cost and potentially lower net life cycle energy because they avoid the use of complex and energy intensive mining process of raw commodities.
Organic PV devices typically use a planar structure that consist of an active layer between two electrodes, typically a TCO like ITO and a non-transparent highly conductive material such as aluminum, calcium, magnesium or gold. In an organic solar cell, light is absorbed which excited an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) which forms an exciton, an electron hole pair. For the solar cell to generate an electric current, the exciton must dissociate. Dissociation is when an electron reaches an electrode while the corresponding hole reaches the other electrode. To achieve this charge separation, an electric field is used which is created by the work functions of the electrodes through a process of rectification. Work functions of the two electrodes are chosen to optimize the exciton dissociation so that the electron is collected at the metal electrode (anode) and the hole is collected at the ITO electrode (cathode). The HOMO and LUMO of adjacent molecules can interact to form a conduction band and a valence band, such as in an inorganic semi-conducting material. The shape of the HOMO and LUMO bands are determined by the electrodes, the conductivity of the polymer and by the potential difference between the electrodes [57].
In organic polymers, the LUMOs and HOMOs of the molecules may not interact strongly enough to form a conduction band or valence band. Transport of charges in these materials occurs as they hop between localized states, opposed to moving within a band as in inorganic materials. Because of this, charge carrier mobility is quite low compared to inorganic materials, typically several orders of magnitude lower. A low dielectric constant ensures that charge separation is difficult in comparison to inorganic materials. Additionally, the absorption of a photon in an inorganic material produces a hole and a free electron, in the case of an organic material, the hole and electron are bound together. Because of this phenomena, the thickness of a dye or conjugated polymer solar cell is limited to typically less than 10 nm as exciton dissociation typically occurs at the electrode interface, though it can also happen in the crystal lattice or by contacting impurities or absorbed oxygen [58].
At the electrode interface, the conjugated polymer and the metal electrode form a junction as atoms diffuse into the polymer matrix and disrupt the conjugation as deep as several Å into the polymer [57]. This diffusion increases the barrier for electron injection at the interface. If the organic solar device has a thicker layer, exciton dissociation becomes unfeasible. As the transparent electrode, ITO is the common high-work function material. The uneven surface of ITO on glass leads to localized field variations that can degrade polymers at rapid rates. On the ITO cathode, atoms will react with the active layer and can lead to a reaction. In the case of PPV, oxygen can diffuse which can form aromatic aldehydes [59].

Conjugated polymers are receiving greater focus from the PV community as understandings of polymer science improve and roll-to-roll printing techniques have the potential to reduce the cost of PV production. Due to the understanding that polymers such as polyacetylene could have their conductivity dramatically increased due to the presence of dopants, polymer PV devices became even closer to an economically feasible reality [60]. In solar cells based on conjugated polymers, delocalized excitons known as polarons form, leading to a lower open-circuit voltage. These excitons relax the energetic gap which becomes smaller than the \( \pi-\pi^* \) gap [57]. Conjugated polymers that can be used in solar cells include polyvinylpyrrolidine (PPV) and PPV derivatives like MEH-PPV or HO-PPV, PEDOT and P3HT.

Much of the research into active layers for organic PV has focused on creating heterojunctions to aid in disassociating excitons. A heterojunction uses two materials with differing electron affinities and ionization potentials. In this case, the electron will be accepted by the material with the larger affinity for an electron and the hole will be accepted by the material with a lower potential for ionization. Heterojunction cells often include \( \text{C}_{60} \) because of
its electron conductance on the order $10^4$ S/cm. Since excitation dissociation is most effective at the interfaces in heterojunctions, the exciton diffusion lengths of roughly 10nm limits the thickness of the active layer. Because a thicker film is needed to aid in absorbing as much energy as possible from incoming photons, blended polymers of donors and acceptors, known as bulk heterojunctions can be implemented in solar cells to improve PCE and overall cell efficiency. Organic PV faces two major challenges in becoming a widely adopted technology: many of the polymers are sensitive to oxygen and cells often degrade significantly under light and heat.

### 3.2 Transparent Conductor Materials and Spectrophotometry

Transparent conductors are materials that show transparency for a limited, well-defined range of wavelengths in the visible spectrum from $0.4\mu m < \lambda < 0.7\mu m$, known as the luminous spectrum. Though traditionally these materials have been based on oxides, they can also be developed from non-oxide materials. Because of their transparency, they are useful in solar energy capture and energy efficiency measures. For highly conductive transparent conductor materials, the most important application is in collecting current for solar cells and for use as transparent electrodes for use in electrochromic smart windows. When solar energy reaches a material, a portion of that energy is transmitted, a portion is transmitted and a portion is absorbed. This can be expressed by equation (2), where $T$ is transmittance, $R$ is reflectance and $A$ is absorbance [61].

$$T(\lambda) + R(\lambda) + A(\lambda) = 1 \quad (2)$$

The portion of the electromagnetic spectrum of most interest in energy applications is covered by the wavelengths that constitute the ultraviolet band (UV), visual (vis) and infrared (IR) regions. Table 3-2 shows the various wavelengths for light in these bands,
### Table 3-2 – Wavelengths that Constitute UV, Vis and IR Bands

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>UV</td>
<td>Near</td>
<td>10-190nm</td>
</tr>
<tr>
<td></td>
<td>Far</td>
<td>190-380nm</td>
</tr>
<tr>
<td>Visible</td>
<td>Violet</td>
<td>380-430nm</td>
</tr>
<tr>
<td></td>
<td>Blue</td>
<td>430-490nm</td>
</tr>
<tr>
<td></td>
<td>Green</td>
<td>490-575nm</td>
</tr>
<tr>
<td></td>
<td>Yellow</td>
<td>575-590nm</td>
</tr>
<tr>
<td></td>
<td>Orange</td>
<td>590nm-650nm</td>
</tr>
<tr>
<td></td>
<td>Red</td>
<td>650-780nm</td>
</tr>
<tr>
<td>IR</td>
<td></td>
<td>.78-300um</td>
</tr>
</tbody>
</table>

Beer’s law and Lambert’s law are important to understand for studying TC performance. Lambert’s law states that: the proportion of the monochromatic light absorbed by a homogenous medium is independent of the intensity of the incident light and that each layer of equal thickness of the medium absorbs an equal fraction of the radiant energy that traverses it. Therefore it stands to say that if a material absorbs 30% of the incident light, 70% will emerge. Beer’s law states that the absorbance of a material is proportional to the concentration of the absorber and to the length of the path of radiant energy through the material or solution. Using Beer’s Law we can start with equation (3) for intensity (I) where,
\[ I = I_o 10^{-KL} \]  \hspace{1cm} (3)

In (3), K is the absorption coefficient, C is the concentration of a solute and L is the length of the path through the solution. We can solve this equation for absorbance through steps (4), (5) and (6) giving us:

\[ \log_{10} \frac{I}{I_o} = -KCL \]  \hspace{1cm} (4)

\[ -\log_{10} \frac{I}{I_o} = -KCL \]  \hspace{1cm} (5)

\[ \log_{10} \frac{I_o}{I} = KCL \]  \hspace{1cm} (6)

With this relationship established, the absorbance can be related to the transmittance \((I/I_o)\) of a material or solution by formula (7).

\[ \text{Absorbance} = \log_{10} \left( \frac{1}{I} \right) = 2 - \log_{10} (\%T) \]  \hspace{1cm} (7)

Transparent conductive films used in electrochromic and solar cell devices are typically thin films that range from a few nanometers to one micron [62]. Typically, sputter deposition is used to make a coating on polymers, glass or metals in a uniform fashion. Sputter deposition involves setting up plasma in a low-pressure environment that incorporates inert gases. The energized ions in the plasma act to dislodge materials from a cylinder or solid plate from the target that contains the raw material intended to be incorporated in the film. The substrate then receives the material on its surface. If evaporation is used to deposit a transparent conductive film, the film’s raw material is heated in a vacuum until it is evaporated and transferred to a
substrate in a vacuum [63]. Sputtering and evaporation can be referred to jointly as physical vapor deposition.

Deposition of films can take place by other methods such as sol-gel deposition which involves placing a substrate in a chemical solution and withdrawing it at a controllable rate and then subjecting it to heat treatment [64]. Chemical solutions can also be applied using spray coating. Another method of applying a chemical solution is through chemical vapor deposition (CVD). By using heat, a CVD process decomposes a precursor material into a vapor to deposit a thin film on a substrate.

Substrates for TC deposition are most often glass and typically float glass because it is widely available and standardized. When float glass is melted and solidified on the surface of liquid tin, it produces uniform and standard flatness. This is an ideal characteristic for using float glass in TC deposition because the flatness minimizes problems during the deposition process. Float glass has a maximum transmittance of $T < 92\%$. Polymers can also be used as a TC substrate, though their sensitivity to photodegradation and photooxidation leads to low performance under light and heat which limits their applications. Polyethylene terephthalate (PET) foil can be suspended inside glass panes for use in window constructions.

To improve the performance of solar energy devices, antireflection coatings can be incorporated to limit the amount of infrared energy entering a solar cell’s active layer. This is done through applying a layer that has a refractive index that is approximately the square root of the refractive index of the underlying material, roughly 1.23. An anti-reflective coating should correspond to a quarter wavelength for visible light that is approximately 100nm. It is possible to obtain transmittance across the luminous wavelengths of greater than 99\% using anti-reflective
coatings, such as silica based nanoparticle films. Additional anti-reflective coatings can include materials of nonporous organosilicates, magnesium diflouride and AlOₓFᵧ [65], [66].

While transparent conductor materials based on ITO or tungsten oxides can be useful in preventing IR spectra from entering a building and increasing the temperature of the thermal envelope in a ‘smart window’ application, the widest use of transparent conductors for energy are in solar cells. In solar cell applications, transparent conductors are located on the side of the solar cell exposed to incident photons to allow proper current collection. TCs for solar cell electrodes typically aid in the collection of holes. For solar cells with thin film active layers, the path length of photons is a critical consideration. In this case, cloudy TC layers can be of use for increasing the path length. For this purpose, textured aluminum zinc oxide films have been studied. [67] For potential use in other thin-film applications ZnO:B has been implemented in large-area devices. [68] In silicon based PV devices, for c-Si and p-Si metallic grids are used as the transparent conductive layer. For a-Si thin film devices, SnO₂ is commonly the TC layer.

The primary figure of merit for a transparent conductor material is the ratio of the electrical conductivity to the optical absorption coefficient of the film. Additional parameters of importance include the physical, thermal and chemical resilience, the material’s etchability, the conductivity, the plasma wavelength, the work function, thickness, deposition temperatures, uniformity, toxicity and cost. While TC materials are used in energy for solar cells and smart window applications, they can also be used in flat panel displays, automatically dimming rear view mirrors in cars and glass touch control panels like those on consumer electronic devices [69]. In general, transparent conductive materials can be made from a wide range of materials other than some of the TCOs mentioned previously: silver by chemical bath deposition, various
forms of SnO$_2$ by spray pyrolysis, TiN by CVD, Cd$_2$SnO$_4$ by sputtering, and ZnO:I, ZnO:Al, ZnO:B, ZnO:Ga, ZnO:Ga all by CVD or sputtering.

The key to optimizing the performance of a transparent conductor is in maximizing the ratio of conductivity to low absorption of visible light that can also be measured as high optical transparency. The equation for calculating the figure of merit for TC performance is done by equation (8).

\[
\frac{\sigma}{\alpha} = -[R_s \ln (T + R)]^{-1} \quad (8)
\]

\[
\alpha = \ln \left( \frac{I_o}{I_1} \right) \quad (9)
\]

\[
\sigma = \frac{1}{R_s} \left( \frac{L}{W T} \right) \quad (10)
\]

Absorbance can be calculated with equation (9) where $I_o$ represents the intensity of the light entering the material and $I_1$ being the intensity of the light leaving the material. Conductivity is represented by equation (10). $R_s$ represents the sheet resistance of the material, a measure commonly used to compare the conductive performance of thin films, and is calculated using equations (11) through (13).

\[
R = \rho \left( \frac{L}{A} \right) = \rho \left( \frac{L}{W t} \right) = \frac{\rho L}{t W} \quad (11)
\]

\[
R = R_s \frac{L}{W} \quad (12)
\]

\[
R_s = R \frac{W}{L} \quad (13)
\]
When (11) is applied to a material with a relatively uniform thickness it becomes (12). Then, $R_s$ can be calculated with (13) to obtain a result with units of $\Omega/\square$ or resistance per unit area. The absorption coefficient ($\alpha$), also known as the attenuation coefficient, describes how easily light, energy or matter can penetrate a material. The visible absorption coefficient can be used to calculate the intensity of the visible spectrum light emerging from a material with equation (14), where $I$ represents the intensity of the measured intensity of the transmitted light, $I_o$ is the initial measured intensity of the light and $x$ is the path length. To obtain the transmittance from this equation we can use (15).

$$I = I_o e^{-\alpha x} \quad (14)$$

$$T = \frac{I}{I_o} = e^{-\alpha x} \quad (15)$$

Sheet resistance values for films can range between several hundred $\Omega/\square$ depending on the transparency and conductivity of the film. Typical values for common transparent conductor materials are displayed in Table 3-3, using data points from lab measurements carried out by Gordon. [69]
Recently, nanomaterials such as aligned silver or other metallic nanoparticles or nanoscale carbon have been investigated as TCs either as a standalone material or as a composite in a polymer in order to improve the properties of polymer carriers that have typically been poor performers as TCs because of their inherent tendency to degrade over the time durations needed to improve the performance of solar cells.

### Table 3-4 - Non-Oxide Based TCs

<table>
<thead>
<tr>
<th>Material</th>
<th>Sheet Resistance (Ω/□)</th>
<th>Transmittance</th>
<th>Figure of Merit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene in Organic Solar Cell [75]</td>
<td>1000000</td>
<td>0.85</td>
<td>6.15313E-06</td>
</tr>
<tr>
<td>Silver Nanowire</td>
<td>250</td>
<td>0.88</td>
<td>0.031290734</td>
</tr>
<tr>
<td>SWNT [76]</td>
<td>300</td>
<td>0.82</td>
<td>0.016796763</td>
</tr>
<tr>
<td>SWNT [77]</td>
<td>920</td>
<td>0.867</td>
<td>0.007616204</td>
</tr>
</tbody>
</table>
We see when comparing Table 3-3 to Table 3-4, the performance of non-oxide based TCs materials are significantly lower than their ZnO and ITO based counterparts. ITO is also significantly less expensive in cost per gram than the nanomaterial based TCs. There is compelling room in applied science research for developing a TC that is low in cost while achieving performance aims in line with that of current nanomaterials.

Depending on the applications, the $R_s$ can vary widely in a range of as little as $10\Omega/\square$ to as high as $10^6 \Omega/\square$ [78]. Using a theoretical study on the ability for TCs to be used in thin film solar cells, Rowell and McGhee concluded the necessary performance for an ITO replacement was an $R_s$ of less than $10\Omega/\square$ and a transmittance of greater than 90% [79].

### 3.3 Electrospinning

In the developing field of applied nanotechnology, one of the most promising areas is in creating nanoscale fibers from polymer solutions through the process of electrospinning. Because of the large surface area to volume ratio of nanoscale fibers, they have the potential to be highly effective in electrical applications because of amount of surface area accessible to the flow of electrons. The surface area to volume ratio of nanofibers can be up to 1000 times larger than that of a micrometer diameter fiber or a human hair. Other than in electronics, applications for nanofibers are in many fields such as tissue scaffolds, filtration, protective clothing [80]. There are multiple processes that can create nanoscale fibers from polymers, that include synthesis through templates, self-assembly, phase separation, drawing of a polymer solution and electrospinning [81], [82]. The other methods listed previously show great promise for lab scale development of nanofibers but have significant limitations in approaching industrial scale production of nanofibers [83].
The process of electrospinning was originally developed over a century ago beginning with patents in 1902 [84], [85]. Beginning in 1995 at the University of Akron, the potential for electrospinning to create a high volume of nanoscale fibers was rediscovered and the modern field of electrospinning was born [86]. For experimentation, electrospinning has extremely minimal requirements of only a high voltage power supply, a uniformly flat-tipped needle, a collector and a syringe. One of the most attractive features of electrospinning is its ability to produce fibers from polymers, semiconductors, composites and ceramics [87], [88]. Currently the field is moving past the characterization of various materials and their ideal conditions for electrospinning into the production of various assemblies and placements of nanofibers towards the creation and development towards creating devices, such as placing a single nanofibers across an electrode.

Electrospinning uses electrostatic forces to stretch a viscoelastic solution along a uniaxial axis. The forces applied in electrospinning draw a continuous production of nanoscale fibers from a solution into an electrospinning jet. For the commonly known process of electrospinning, first the solution is drawn through a spinneret that is commonly in the form of a flat-tipped syringe needle. Then, a high voltage is applied to the solution so that the repulsive force within the charged solution is larger than that of its surface tension, this is known as the critical voltage. At the critical voltage, a jet burst forth from a constantly supplied drop of solution, typically delivered through a syringe pump [89]. At the critical voltage, the solution drop remains stable at the point where it contacts the tip of the spinneret and breaks down into an instability region as the solvent evaporates. To collect the nanofibers created through the stretching of the solution in the instability region, a grounded electrically conductive collector is used for capture. The fibers are distributed by this method in a nonwoven mesh. Parameters such as the flow rate of the
solution, the applied electric voltage, the distance of the spinneret from the collector, the solution viscosity, the solution conductivity and humidity can all be varied to change the diameter and other properties of the fibers. In a 50 nm diameter fiber, roughly 10,000 molecules cross any one section with molecules that stretch into the range of 1-100µm. Roughly 3% of the polymer molecules in a fiber of 50nm in diameter are on the surface of the fiber [90].

![Common Electrospinning Setup](image)

**Figure 3-7 - Common Electrospinning Setup**

During the electrospinning process, the solution jet breaks into three specific regions: the *cone-jet*, *stable jet* and *spiral jet*. At the base of the *cone-jet*, the polymer jet touches the tip of the charged needle. The jet’s geometry is a tapered cone, known as a Taylor cone, where the velocity of the liquid increases while the polymer is pulled by the electrostatic force. Depending on the surface tension of the solution, the base may have circular cross sections or it could be anchored to the lip of the flat tipped syringe needle. Once the electrostatic force exceeds that of the critical voltage, the formerly flat solution is pulled out into a *stable jet*. The *stable jet* region
is where the electrostatic force accelerates the stretching of the material. A solution with a higher conductivity can form a jet easier than a solution with lower conductivity. In the jet phase, the mass per unit time ratio remains constant along each point of the jet’s axis. The jet is continually driven by the high electrical potential that is applied between the solution and the collector. Each solution contains electrical charges, usually ions, that move as they respond to the electric field generated from the potential. The jet contains an intrinsic elongational viscosity that resists the applied electrical forces. As the jet is pulled towards the collector the solvent evaporates and the temperature of the liquid typically increases, dynamically shifting the viscoelastic parameters. The electrostatic forces pull the charges towards the collector, embedded in the direction of the electric field, moving the charge from the reservoir of the solution in the syringe and completing the electrical circuit between the charge and the ground.

When the radial forces generated by the electric charges carried by the jet are larger than the forces leading to the cohesion of the jet, a spiral jet forms, where a single jet of solution forms into a rapid whipping motion. As the single jet forms a spiral whip, the nanofibers reach their nanometer diameter. At the collector the spiral jet stops and the splay deposits a nonwoven mesh of nanofibers on a target [90]. The fiber from the material contained inside the solution remains after the solved evaporates. The collector can consist of many differing geometries and materials though it must be conductive. As the jet approaches the collector, because it is charged it can be repelled by the fibers already placed on the collector.

Even though the basics of electrodynamic effects on the excitation of dielectric liquids were understood in the late 1800s, it wasn’t until the 1930s that several different configurations were developed to create yarns out of electrospun fibers [91], [92]. Over eighteen patents were issued on electrospinning before 1976 [83]. Electrospinning has seen limited uptake in traditional
fiber production industries because of its low output at roughly 30 meters per minute, while
typical yarn fabrication takes place at a rate of 200-1500 meters per minute [93]. Over one
hundred fibers have been used in the electrospinning process to create nanoscale fibers, a
testament to the versatility of the process [94].

Because electrospinning has been demonstrated in its ability to create continuous fibers
from numerous materials, it is an ideal candidate for connecting the properties of nanoscale
materials to macroscale applications [16]. Devices such as the Nanofiber Electrospinning Unit by
Katotech and the Nanon manufactured by MECC are the first stages of scaling up nanofibers
production to higher throughput and quality control standards. These electrospinning units are
capable of providing industrial level control over processing and system parameters.

Figure 3-8 - Nanofiber Electrospinning Unit (left) and the Nanon (right)
In electrospinning, the parameters that affect the resulting fibers are divided into two major categories summarized in Figure 3-9, the system parameters and the processing parameters.

![Electrospinning Processing Parameters](image)

**Figure 3-9 - Electrospinning Processing Parameters [16]**

Surface tension is the property of the surface of a liquid that results in its resistance of an external force. A liquid obtains this property from the cohesion of molecules that face the surrounding atmosphere as the bulk liquid faces internally cohesive forces. Within a liquid, each of the molecules are pulled in equilibrium by the surrounding liquid molecules. Because molecules on the surface only have these forces pulling inwards, they form a surface and create
internal pressure as the liquid contracts to a minimal area. In electrospinning, as the solution is charged and overcomes its surface tension the critical voltage threshold is reached and a Taylor Cone will form. Depending on the balance of the surface tension, this can lead to the formation of beads on polymeric nanofibers. Because the surface tension decreases the surface area for each unit of fluid mass, low concentration solutions will agglomerate and will result in the formation of spherical beads. In solutions with higher concentrations of polymer, the interactions between the polymeric molecules and the solvent will result in the stretching of the solution, reducing the probability of the formation of beads [95]. The surface tension of the solution is a function of the composition of the solvent and the concentration of the polymer. If the surface tension is too low, droplets will form from the application of an electric field, turning what would typically be a jet into a spray [96]. If fiber beads are detected in electrospun fibers, this can be corrected through decreasing the applied voltage and increasing the spinning distance.

The viscosity of a solution is affected by the concentration of the polymer or material in the solvent and the molecular weight of the polymer [83]. Because of the significant role that the viscosity of the solution plays in determining the final characteristics of electrospun fibers, it is one of the most critical in determining the final fiber morphology. High viscosity solutions result in larger fiber diameters while lower viscosity solutions result in lower diameter fibers and potentially the lack of fiber formation when an electric field is applied to the solution spinning dope [90].

Because the electrospinning process relies on the application of an electric field to a solution, the conductivity of the solution and the dielectric properties of the solvent are also critical parameters. As detailed above, the stretchability of the solution results from the repulsion of charges within the fluid. With a highly conductive solution, a higher amount of charge will be
present across the electrospinning jet. If higher solution conductivity is desired, ions can be added when the spinning dope is prepared. When fiber uniformity is determined to be rather low, an increase in the solution conductivity results in more uniform fibers. As ions are added, the critical voltage for electrospinning is decreased [89]. The dielectric effect of the solvent increases the susceptibility of the solution to electric charges, increasing the rate at which the solution flows from the spinneret as an electric field is applied. In solutions with solvents of higher dielectric constants, bead formation is reduced [97].

The voltage applied during the electrospinning process is one of the key processing parameters. When the voltage is applied to the tip of the spinneret, an electric field is created between the fluid and the collector. Once the voltage increases beyond a critical threshold, it overcomes the surface tension in the solution and a jet is ejected from the surface of the solution. This leads to the charging of the liquid on the edge of the spinneret and the formation of a Taylor cone, an elongation of the surface of the liquid that results in a hemispherical surface. With a higher voltage, the electrostatic force becomes so great that the droplet falls inside the flat-tipped syringe or spinneret and the jet initiates within it. As the voltage is increased, the diameter of the electrospun fibers are reduced because of the increased stretching applied to the solution jet. Consequently, a lower voltage results in an increase in the time the solution is stretched and finer fibers. The voltage affects both the morphology and crystallinity of fibers [89].

As the jet slowly depletes the amount of solution present at the surface of the liquid, a constant feed rate is necessary to ensure a constant supply of spinning dope. A constant amount of solution can be provided by a syringe pump or constant applied pressure in an industrial electrospinning unit. With a higher feed rate the fiber diameter is typically increased whereas a lower feed rate will result in a smaller diameter fiber. The feed rate also has an effect on the size
of beads that form on the fibers with a higher feed rate resulting in larger beads and smaller beads with a lower flow rate [95]. Beads can also be formed with a smaller diameter spinneret as clogging of the solution can occur.

Electrospun fibers have a wide range of applications, especially because multi-functional fibers can be formed with composite materials present in the spinning dope [98]. Potential applications include: drug delivery, wound dressings, scaffolding for tissue engineering, filtration for liquids and gases, sensors, protective clothing and in electronic devices by enabling nano-devices, through providing shielding functionality and enhancing photovoltaic performance [89]. For electronic devices, nanofibers are desirable because of the large surface area, their porous structure and the ability to incorporate conductive composite materials.

Though nanofibers have been used in the fabrication of photovoltaic devices, the incorporation of electrospun nanofibers into devices has been limited. Much of the work that has been focused on nanofibers for photovoltaics has been on ZnO nanofibers produced through other methods. D.C. Olson et. al have reported the fabrication of ZnO nanofibers by a hydrothermal growing technique on an ITO template to produce a PCBM:P3HT PV device with an efficiency of 2.03% [99]. For use in a PV active layer, nanofibers of P3HT have been formed through exposure to several solvents such as 1,2,4-trichlorobenzenen, tetralin, p-xylene,trans-decalin and pinnae after slow-cooling at room temperature [100]. These P3HT devices have shown use in PV devices after combination with PCBM in solution to act as an acceptor material. Solar cells fabricated with P3HT:PCBM nanofibers have reached efficiencies of up to 3% given the proper solution processing parameters [101].
The incorporation of electrospun nanofibers into photovoltaics has mainly focused on using TiO$_2$ and ZnO. Peining et. al have reported photovoltaic properties of nanofibers electrospun from a solution of dispersed graphene in a solution of acetic acid and PVA. Once sintered at 450°C, these nanofibers have been shown to form a TiO$_2$-Graphene composite (TGC) material [102]. When incorporated as the active layer in dye-sensitized solar cells (DSC), this TGC demonstrates improved PV performance with an increase in short-circuit current and energy conversion efficiency improved by 33% over a solely TiO$_2$ based DSC fabricated as a control. S. Wu has fabricated hybrid PV devices with P3HT and an electrospun ZnO nanofibrous network [100]. In this process, ZnO nanofibers were developed using a zinc acetate and PVP gel which were sintered at 450°C for 5 minutes. After a ZnO film was spin coated on an ITO glass substrate using a sol-gel method, the ZnO nanofibers film was applied and spin coated with P3HT. Solar cells fabricated in this method of ZnO nanofibers and P3HT exhibited a PCE of 51% [100].

An additional approach for using electrospun materials to enhance to performance of photovoltaic devices includes the application of nanofibers optimized for use as transparent conductor electrodes in solar cells. Results presented in this thesis are focused on using multi-walled carbon nanotube and carbon nanofibers [103], there has been additional work on creating a nanofiber based TC layer for solar cells. By using electrospun copper acetate, metallic grids of nanofibers have been fabricated for use as a TC [104]. In this approach, first copper acetate is dissolved in a solution and PVA is incorporated as a spinning dope. Once these fibers are electrospun, they are calcined in air to obtain 100nm Cu nanofibers in a grid form that is highly conductive and transparent. The sheet resistance of the Cu nanofibers was measured at 200 Ω/□
and 96% transmittance. The limitation of this approach is that the Cu nanofibers oxidize rapidly in air.

The future of nanofibers may not include any electricity at all. With a new process known as Forcespinning™, solutions of solid materials that are either placed in a solvent or melt spun and extruded using centrifugal force through a rotational speed of as high as 5,000 RPM to make nanofibers of PEO, PLA, polystyrene and many more [105]. The advantage in forcespinning is that it may allow high volume production of nanofibers that exceeds what can currently be achieved by electrospinning without the complexity of multi-spinneret systems.

3.4 Carbon Nanofibers and Composites

For a material to be used in the fabrication of carbon based materials, it needs to be able to leave a carbon residue even after being subjected to high temperatures. The acrylic polymer of polyacrylonitrile (PAN) is one of the most widely used materials for the production of carbon fibers because of its high yield at temperatures of carbonization and in graphitization [106]. The structure of PAN is that of carbon, nitrogen and hydrogen which has been shown to be electrically conductive after pyrolysis [18].

![polyacrylonitrile](image)

Figure 3-10 - The structure of polyacrylonitrile transformed by heat into carbon fiber [107]
PAN solutions have been electrospun to create nanofibers have been used to fabricate carbon nanofibers [98], [108–111]. After dissolution of PAN in dimethylformamide (DMF), PAN is electrospun to create nanofibers which are then stabilized in air and carbonized in an inert atmosphere to create carbon nanofiber and carbon nanofibers composites. The process and solutions parameters for producing PAN nanofibers for carbonization have been studied to determine their effect on fibers for study and commercial applications. Fibers electrospun at voltages in the range of 4-8kV have been shown to have irregular shapes whereas at voltages higher than 12kV smoother fibers are observed [111]. Once the electrospinning voltage increases past 20kV, multiple jets form in a PAN/DMF solution that disrupts the electrospinning process by clogging the spinneret or by resulting in beaded fibers [112]. There have been discrepancies in the literature of the reported effects of voltage on the fiber diameter. While T. Wang and S. Kumar have reported no variation of fiber diameter with voltage [113], V.E. Kalayci et. al have noted that there is a decrease in the fiber diameter with an increased voltage [114].

For PAN nanofibers to be useful in applications that require high conductivity, after electrospinning subsequent stabilization and carbonization processes must be carried out. The stabilization process cyclizes the molecules in the carbon fiber chain at a temperature of 200-260°C in air for a duration of 30 minutes to several hours in air. As cyclization occurs, first a ladder structure form as the pendant nitrile groups crosslink. Then, oxygen is integrated into the ladder structure. While the heating also enables this process, it also shrinks the fibers leading to a smaller diameter. The nitrogen that remains in these carbon fibers chains are used to enable crosslinking and higher conductivity during the carbonization process.
Once the PAN chains are stabilized, a subsequent carbonization process is undertaken at temperatures of up to 1200°C in nitrogen or argon. As the temperature increases from the stabilization, at 450°C propionitrile, acrylonitrile, ammonia and water are released. Once 700°C is reached, nitrogen begins to be removed from the structure until 1000°C where 5.8wt% nitrogen remains. At this stage, graphitic ribbons are formed through dehydrogenation. As the temperature increases, the ribbon structure grows into a thin sheet which is fused together at higher temperatures, increasing the conductivity. Roughly half of the weights of the PAN fibers are removed during this stage. If the PAN fibers are graphitized at a temperature of 2500°C all of the nitrogen will be removed.
The conductivity of PAN nanofibers are determined by their basic structural unit which are a group of turbostratic layers that are randomly twisted and interlocked [115]. After stabilization, the basic structural units exhibit no conductivity but after exposure to higher temperatures an oriented structure forms from interlayer spacing, the growth of graphite crystallites and the population of voids [106]. After graphitization, the conductivity of carbon nanofibers formed from PAN nanofibers can increase up 490 S/cm [116]. The conductivity mechanism is due to \( \pi \) electrons inside the graphite layers. Conductivity is increased in these materials as the space between each graphitic layer decreases and the growth of these graphitic layers [116].

Because a goal of this study is in exploring a model that can reduce the energy requirements for manufacturing PV modules and devices, the energy consumed during carbonization and in developing carbon fiber composites are important to note. It was calculated that the material makes up 44\% of the overall cost, the process materials consume 6\% of the overall cost and energy consumes 15\% of the cost of carbonizing PAN. In using a cost of $5.83 per pound of carbon fiber material, energy ends up costing about $0.30 [117]. Another study found that carbon fiber materials require roughly 3.7 kWh/kg [118] to produce, a number within reasonable range of the estimate from the Cohn et al. study.
Chapter 4 Materials and Methods

4.1 Materials

The materials used in this study are Polyacrylonitrile (PAN), $M_w=150,000$ which was purchased from Scientific Polymer Products, Inc., N,N-Dimethylformamide (DMF) CAS 68-12-2 which was purchased from Fisher Scientific. Polyvinylpyrrolidone (PVP) $M_w=55,000$ which was purchased from Scientific Polymer Products, Inc., Polyacrylonitrile-co-Methyl Acrylate, (PAN-co-MA) 94% Acrylonitrile, $M_w=100,000$. COOH functionalized Multi-walled nanotubes (MWNT) were purchased from Cheaptubes.com with outer diameter (OD) = <8nm and inside diameter (ID) = 2-5nm, length = 10-30um and measured electrical conductivity >100 S/cm.

4.2 PAN and PAN-co-MA Solution Preparation

For each solution of PAN and PAN-co-MA that was made, each polymer was dissolved in DMF at concentrations of 7wt%, 8wt%, 9wt%, 10wt%, 11wt% and 12wt%. These solutions were prepared by adding the dry polymer at the proper concentration to a solution vial and then adding the solvent along with a magnetic stir-bar. These solution vials were placed on a hot plate for 4-8h at 80°C to prepare for electrospinning.

4.2.1 Polymer Solutions with Nanoparticles

To prepare each solution for the addition of nanoparticles, PVP was added to DMF and stirred for 1 minute using a vortex mixer to thoroughly dissolve the PVP. Multi-walled carbon nanotubes of various concentrations were added to each solution. Each PVP/DMF/MWCNT solution was cup sonicated for 24h at 33W with a pulse of 6 minutes on and 6 minutes off. PVP
was added to aid in the dispersion of nanotubes by wrapping which relies on interactions between the polymer and the tubes. This is thermodynamically driven by the elimination of a hydrophobic interface between the tubes and the aqueous medium. After sonication, PAN or PAN-co-MA was added at a 10wt% PAN/DMF ratio.

### 4.3 Nanofiber Fabrication

Each solution was added to 10mL syringes [BD Syringe REF #309604] with a needle of 18.5 gage. The syringes were placed in a Katotech Nanofiber Electrospinning Unit manufactured by KATO TECH CO. LTD. and a field of 17.0kV was applied, with 20cm between the needle tip and the target with syringe pump speed of .064mm/min.

For each solution that was electrospun for characterization as a transparent conductor material, square quartz slides [QSI, order number 2120] were used as a target, rotated on an arm moving at 60 rotations per minutes. Each slide was coated with electrospun PAN-co-MMA/MWCNT/PVP composite fibers with the thickness varying based on the amount of time each slide was left on the rotating arm.

For each solution that was used to test the solution properties of PAN and PAN-co-MA fiber membranes, the target was aluminum foil.

### 4.4 Carbonization Processing Parameters

Each fiber coated slide and fiber membrane was covered with a steel carbonization mask to provide necessary tension for carbonization and placed in a Thermolyne 79400 quartz tube furnace. The furnace was programmed to ramp up at a varying rate to a stabilization temperature in the range of 220-280°C in O2 for 120-150 minutes before the furnace was flushed with N2.
and ramped up at 5°C/min up to the final carbonization temperature of 700°C, 900°C or 1100°C. This temperature was varied to observe the effect on final conductivity.

![Figure 4-1 – Graphical Representation of Carbonization Process](image)

4.5 Characterization Methods

Colloidal Ag paste [Ted Pella # 16040-30] was applied to each slide and membrane with a paintbrush and allowed to dry to provide an electrode for measuring conductivity across the nanofiber mesh. These layers of carbon nanofibers were characterized using a Keithly Electronic Characterization System probe station and limited measurements with a multimeter to measure the resistance values for calculating the corresponding sheet resistance and membrane conductivity. The electrical conductivity was measured using the four-point probe method. Electrical conductivity, $\sigma$, was calculated by the expression, $\sigma$ (S/cm) = $L/(t \times R)$, where $R$ is
electrical resistance in Ω, t is thickness of the specimen in cm and L is distance the between electrodes in cm. The prepared composite carbon nanofibers were also subjected to Renishaw InVia Raman microscope, using He-Ne laser at 633nm excitation. A Therion UV spectrophotometer was used to characterize the optical transparency across the visible spectrum. Images were captured using a Hitachi 4200N Scanning Electron Microscope and Olympus LEXT OCS4000 Confocal Microscope.
Chapter 5  Results

5.1 PAN and PAN-co-MA Copolymer Membranes – Microstructural Observations

To analyze the fiber diameter and microstructure of each polymer membrane at each concentration, SEM images were undertaken before and after carbonization. Each fiber diameter was calculated after measuring one hundred fibers from corresponding SEM images. Additional SEM images are presented in Appendix A and diameter distributions were measured for each sample and presented in Appendix B.

5.1.1 Nanofibers Prior to Carbonization

SEM images were captured of PAN and PAN-co-MA before carbonization to determine the average diameters each concentration of each polymer could provide after electrospinning.

Table 5-1 presents the mean fiber diameters of each sample from 7wt% to 12wt% for PAN and PAN-co-MA. Uncarbonized fibers for 11wt% weren’t measured because 11wt% and 12wt% PAN fibers were too viscous for electrospinning membranes and the trend line for fiber diameters from 7wt%-12wt% for PAN-co-MA provides reasonable certainty that the mean fiber diameter for 11wt% PAN-co-MA will be approximately 530nm.

Table 5-1 – Mean Diameters of PAN and PAN-co-MA after electrospinning

<table>
<thead>
<tr>
<th>Mean Diameter</th>
<th>PAN</th>
<th>PAN-co-mA</th>
</tr>
</thead>
<tbody>
<tr>
<td>7wt%</td>
<td>210.7 ± 7.8nm</td>
<td>330.6 ± 9.4nm</td>
</tr>
<tr>
<td>8wt%</td>
<td>255.2 ± 6.1nm</td>
<td>335.6 ± 5.6nm</td>
</tr>
<tr>
<td>Mean Diameter</td>
<td>PAN</td>
<td>PAN-co-mA</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td>9wt%</td>
<td>382.5 ± 9.3nm</td>
<td>354.96 ± 7.8nm</td>
</tr>
<tr>
<td>10wt%</td>
<td>421.1 ± 9.4nm</td>
<td>514.2 ± 12.5nm</td>
</tr>
<tr>
<td>12wt%</td>
<td>Too Viscous</td>
<td>561.7 ± 10.6nm</td>
</tr>
</tbody>
</table>

For 7wt%-12wt% PAN-co-MA, mean fiber diameters ranged from 210.47nm to 561nm whereas for 7wt% PAN to 10wt% PAN fiber diameters ranged from 330.6nm to 514.6nm. For 7wt%-12wt% PAN-co-MA, mean fiber diameters ranged from 210.47nm to 561nm whereas for 7wt% PAN to 10wt% PAN fiber diameters ranged from 330.6nm to 514.6nm.

SEM images for Figures 5-1 through 5-5 show consistent fiber formation at all of the polymer concentrations with a limited number of beads present at 8wt% and 9wt% though these beads are not present at higher or lower concentrations.

Figure 5-1 - 7wt% PAN (left) and PAN-co-MA (right) at 5k magnification uncarbonized

Figure 5-1 shows 7wt% PAN and PAN-co-MA which both demonstrate beadless and consistent fibers for both homopolymer and co-polymer samples.
Figure 5-2 and Figure 5-3 show PAN and PAN-co-MA at 8wt% and 9wt% concentrations respectively. At concentrations of 8wt% and 9wt%, PAN shows evidence of beading while PAN-co-MA does not.

Figure 5-2 - 8wt% PAN (left) and PAN-co-MA (right) at x5k magnification

Figure 5-3 - 9wt% PAN (left) and PAN-co-MA (right) at x10k magnification
Figure 5-4 shows PAN and PAN-co-MA with a concentration of 10wt% at x20k magnification, both polymers exhibit smooth fibers. Above 10wt% concentration, homopolymer PAN would regularly clog the electrospinning needle. Concentrations of 11wt% for PAN and PAN-co-MA were electrospun but weren’t imaged for this study before carbonization. Figure 5-5 shows 12wt% PAN-co-MA which was the highest electrospun concentration of PAN-co-MA. Even at such a high concentration, the co-polymer performed well in creating smooth consistent fibers. Likely PAN-co-MA could be electrospun at even higher concentrations.
5.1.2 After Carbonization

After electrospinning, each PAN and PAN-co-MA sample was carbonized at 700°C, 900°C and 1100°C to create carbon fiber. The following SEM images were taken of each sample to determine the effect of carbonization on the fiber diameter and fiber morphology.

PAN After Carbonization

Table 5-2 presents the mean diameters of PAN nanofibers carbonized at 700°C, 900°C and 1100°C. Fiber diameters widely ranged from 236.8nm (7wt%) to 567.37nm (11wt%) at 700°C, from 143.8nm (7wt%) to 460.44nm (11wt%) at 900°C and 108.62nm (7wt%) to 432.9nm (11wt%) at 1100°C

Table 5-2 - Mean Diameter of PAN after Carbonization at 700°C, 900°C and 1100°C

<table>
<thead>
<tr>
<th>Mean Diameter</th>
<th>700°C</th>
<th>900°C</th>
<th>1100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>7wt%</td>
<td>236.8 ± 3.2nm</td>
<td>143.8 ± 3.7nm</td>
<td>108.62 ± 3.1nm</td>
</tr>
<tr>
<td>8wt%</td>
<td>282.9 ± 7.6nm</td>
<td>160.1 ± 3.3nm</td>
<td>124.2 ± 4.47nm</td>
</tr>
<tr>
<td>9wt%</td>
<td>262.50 ± 5.1nm</td>
<td>125.2 ± 2.1nm</td>
<td>127.5 ± 4.1nm</td>
</tr>
<tr>
<td>10wt%</td>
<td>404.4 ± 8.2 nm</td>
<td>387.7 ± 7.5nm</td>
<td>351.3 ± 3.1nm</td>
</tr>
<tr>
<td>11wt%</td>
<td>567.37 ± 9.6nm</td>
<td>460.44 ± 7.3nm</td>
<td>432.9 ± 4.25nm</td>
</tr>
</tbody>
</table>

As shown in Appendix A with SEM images of the fibers at these carbonization parameters, except for 7wt% PAN, each of the carbonized membranes produced consistent fibers that were resilient to breakage. In 7wt% PAN, SEM images showed broken fibers at 900°C and 1100°C.

PAN-co-MA After Carbonization

Table 5-3 presents the mean diameters of PAN-co-MA nanofibers carbonized at 700°C, 900°C and 1100°C. Fiber diameters ranged from 327.1(7wt%) to 568.1nm (11wt%) at 700°C,
from 235.4nm (7wt%) to 412.5nm (11wt%) at 900˚C and 107.3nm (7wt%) to 257.06 (10wt%) at 1100˚C before decreasing with 11wt% at 168.1nm.

**Table 5-3 – Mean Diameter of PAN-co-MA after Carbonization at 700˚C, 900˚C and 1100˚C**

<table>
<thead>
<tr>
<th>Mean Diameter</th>
<th>700˚C</th>
<th>900˚C</th>
<th>1100˚C</th>
</tr>
</thead>
<tbody>
<tr>
<td>7wt%</td>
<td>327.1 ± 4.6 nm</td>
<td>235.4 ± 7.8 nm</td>
<td>107.3 ± 2.3 nm</td>
</tr>
<tr>
<td>8wt%</td>
<td>224 ± 3.6 nm</td>
<td>223.3 ± 3.8 nm</td>
<td>192.1 ± 5.4 nm</td>
</tr>
<tr>
<td>9wt%</td>
<td>319 ± 5.5 nm</td>
<td>310.11 ± 4.7 nm</td>
<td>292.2 ± 4.9 nm</td>
</tr>
<tr>
<td>10wt%</td>
<td>332.7 ± 6.1 nm</td>
<td>317.66 ± 5.5 nm</td>
<td>257.06 ± 5.3 nm</td>
</tr>
<tr>
<td>11wt%</td>
<td>376.9 ± 5.52 nm</td>
<td>211.5 ± 3.2 nm</td>
<td>168.1 ± 4.1 nm</td>
</tr>
<tr>
<td>12wt%</td>
<td>568.1 ± 5.5 nm</td>
<td>412.5 ± 5.8 nm</td>
<td>N/A</td>
</tr>
</tbody>
</table>

As depicted in Appendix A, for carbonized concentrations of PAN-co-MA at 7wt% an analysis of the SEM images appears to show that nanofibers fused together at temperatures of 900˚C and 1100˚C. At 1100˚C for 7wt% the fibers also appear to be aligned, this could be due to an error in transferring the sample from the electrospun aluminum target for analysis by SEM though more exploration beyond the scope of this thesis is warranted.

**5.2 PAN and PAN-co-MA Copolymer Membranes – EDX, Raman Spectroscopy and Electrical Conductivity**

To further characterize the nanofibers produced by homopolymer PAN and the copolymer PAN-co-MA, EDX spectra were gathered along with Raman analysis and measurements of electrical conductivity.
5.2.1 EDX Measured Carbon Content

For determining the carbon content of the fibers that underwent pyrolysis, EDX analysis was carried out on each fiber membrane. This characterization process revealed helped to demonstrate the effectiveness of the temperature at converting the PAN or PAN-co-MA to carbon. Table 5-4 shows the carbon content of each polymer which varies greatly and shows no clear trend.

Table 5-4 – EDX Measured Carbon Content of PAN and PAN-co-MA fibers at 700°C

<table>
<thead>
<tr>
<th>Concentration (wt%)</th>
<th>Polymer</th>
<th>Tc (°C)</th>
<th>C (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>PAN-co-MA</td>
<td>700</td>
<td>58.74</td>
</tr>
<tr>
<td>10</td>
<td>PAN</td>
<td>700</td>
<td>58.98</td>
</tr>
<tr>
<td>12</td>
<td>PAN-co-MA</td>
<td>700</td>
<td>65.31</td>
</tr>
<tr>
<td>9</td>
<td>PAN-co-MA</td>
<td>700</td>
<td>65.84</td>
</tr>
<tr>
<td>12</td>
<td>PAN-co-MA</td>
<td>700</td>
<td>65.88</td>
</tr>
<tr>
<td>11</td>
<td>PAN-co-MA</td>
<td>700</td>
<td>67.57</td>
</tr>
<tr>
<td>10</td>
<td>PAN</td>
<td>700</td>
<td>68.48</td>
</tr>
<tr>
<td>7</td>
<td>PAN-co-MA</td>
<td>700</td>
<td>69.13</td>
</tr>
<tr>
<td>8</td>
<td>PAN</td>
<td>700</td>
<td>69.16</td>
</tr>
<tr>
<td>7</td>
<td>PAN</td>
<td>700</td>
<td>70.57</td>
</tr>
<tr>
<td>8</td>
<td>PAN-co-MA</td>
<td>700</td>
<td>70.7</td>
</tr>
<tr>
<td>7</td>
<td>PAN-co-MA</td>
<td>700</td>
<td>73.37</td>
</tr>
<tr>
<td>11</td>
<td>PAN</td>
<td>700</td>
<td>73.64</td>
</tr>
<tr>
<td>9</td>
<td>PAN</td>
<td>700</td>
<td>74.34</td>
</tr>
<tr>
<td>11</td>
<td>PAN-co-MA</td>
<td>700</td>
<td>85.61</td>
</tr>
<tr>
<td>10</td>
<td>PAN-co-MA</td>
<td>700</td>
<td>92.22</td>
</tr>
</tbody>
</table>

As referenced in Table 21, the carbon content in of each fiber has a wide range of variability in PAN and PAN-co-MA fibers. The average carbon content of measure PAN fibers at 700°C is 71.54 wt% and for PAN-co-MA fibers is 78.02 wt%.

At a temperature of 900°C the difference between the two polymers becomes more distinct as noted in Table 5-5.
Table 5-5 - Carbon Content of PAN and PAN-co-MA fibers at 900°C

<table>
<thead>
<tr>
<th>Concentration (wt%)</th>
<th>Polymer</th>
<th>Tc</th>
<th>C (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>PAN</td>
<td>900</td>
<td>73.27</td>
</tr>
<tr>
<td>7</td>
<td>PAN</td>
<td>900</td>
<td>73.47</td>
</tr>
<tr>
<td>10</td>
<td>PAN</td>
<td>900</td>
<td>75.24</td>
</tr>
<tr>
<td>9</td>
<td>PAN</td>
<td>900</td>
<td>76.44</td>
</tr>
<tr>
<td>11</td>
<td>PAN</td>
<td>900</td>
<td>84.23</td>
</tr>
<tr>
<td>7</td>
<td>PAN-co-MA</td>
<td>900</td>
<td>90.01</td>
</tr>
<tr>
<td>11</td>
<td>PAN-co-MA</td>
<td>900</td>
<td>90.9</td>
</tr>
<tr>
<td>11</td>
<td>PAN-co-MA</td>
<td>900</td>
<td>91.04</td>
</tr>
<tr>
<td>12</td>
<td>PAN-co-MA</td>
<td>900</td>
<td>91.29</td>
</tr>
<tr>
<td>10</td>
<td>PAN-co-MA</td>
<td>900</td>
<td>91.54</td>
</tr>
<tr>
<td>8</td>
<td>PAN-co-MA</td>
<td>900</td>
<td>92.04</td>
</tr>
<tr>
<td>12</td>
<td>PAN-co-MA</td>
<td>900</td>
<td>92.95</td>
</tr>
<tr>
<td>9</td>
<td>PAN-co-MA</td>
<td>900</td>
<td>93.96</td>
</tr>
</tbody>
</table>

At 900°C the average PAN carbon content is 76.53 wt% and for PAN-co-MA is 91.71wt%.

Table 5-6 - Carbon Content of PAN and PAN-co-MA fibers at 1100°C

<table>
<thead>
<tr>
<th>Concentration (wt%)</th>
<th>Polymer</th>
<th>Tc</th>
<th>C (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>PAN-co-MA</td>
<td>1100</td>
<td>89.86</td>
</tr>
<tr>
<td>8</td>
<td>PAN-co-MA</td>
<td>1100</td>
<td>90.06</td>
</tr>
<tr>
<td>8</td>
<td>PAN</td>
<td>1100</td>
<td>90.45</td>
</tr>
<tr>
<td>10</td>
<td>PAN-co-MA</td>
<td>1100</td>
<td>90.93</td>
</tr>
<tr>
<td>9</td>
<td>PAN</td>
<td>1100</td>
<td>91.3</td>
</tr>
<tr>
<td>11</td>
<td>PAN</td>
<td>1100</td>
<td>91.43</td>
</tr>
<tr>
<td>7</td>
<td>PAN</td>
<td>1100</td>
<td>92.15</td>
</tr>
<tr>
<td>10</td>
<td>PAN</td>
<td>1100</td>
<td>92.69</td>
</tr>
<tr>
<td>11</td>
<td>PAN-co-MA</td>
<td>1100</td>
<td>92.88</td>
</tr>
<tr>
<td>7</td>
<td>PAN-co-MA</td>
<td>1100</td>
<td>93.12</td>
</tr>
<tr>
<td>12</td>
<td>PAN-co-MA</td>
<td>1100</td>
<td>93.54</td>
</tr>
</tbody>
</table>

As displayed in Table 5-6, at 1100°C the average PAN carbon content is 91.60 wt% and for PAN-co-MA the average is 91.73wt%.
5.2.2 Raman spectroscopy

To determine the degree of graphitization of each polymer after carbonization, Raman spectroscopy analysis was carried out on the PAN and PAN-co-MA samples. By measuring the spectroscopy of each fiber membrane, the graphitic structure can be investigated. Under excitation with an infrared laser, carbon materials exhibit two peaks that allows characterization indicating the degree of graphitization. These two peaks represent the disordered graphitic structure ($I_D$) that is equal to $1350\text{cm}^{-1}$ and the disordered graphitic structure ($I_G$) that is equal to $1600\text{cm}^{-1}$. By measuring the intensity of these two peaks, the degree of graphitization can be observed when comparing their ratio, $R= I_G/I_D$. For each of the carbonization parameters for 7wt% PAN/PAN-co-MA through 9wt% PAN/PAN-co-MA, a Gaussian curve fit was applied to determine the relative intensity of the D and G bands. The R is a measure of the degree of graphitization. Detailed Raman spectroscopy plots 7wt%, 8wt% and 9wt% PAN and PAN-co-MA can be found in Appendix C.

![Figure 5-6 - Plotted Raman Ratio of PAN and PAN-co-MA samples](image-url)
In each of the samples, the ratio of the graphitic to the disordered peaks (R) increased as the carbonization temperature $T_c$ increased as demonstrated in Figure 5-6. Though with PAN membranes, R reached a peak and then leveled off at $T_c=1100^\circ$C. Values of each sample’s ratio are provided in Table 5-7.

**Table 5-7 - Raman Ratio - Note: R=I_g/I_d**

<table>
<thead>
<tr>
<th></th>
<th>PAN</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>700</td>
<td>900</td>
<td>1100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7wt%</td>
<td>0.5624</td>
<td>0.5715</td>
<td>0.5819</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8wt%</td>
<td>0.5352</td>
<td>0.5422365</td>
<td>0.6148</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9wt%</td>
<td>0.5156</td>
<td>0.57306</td>
<td>0.6389</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>PAN-co-MA</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>700</td>
<td>900</td>
<td>1100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7wt%</td>
<td>0.5519</td>
<td>0.6008</td>
<td>0.6434</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8wt%</td>
<td>0.5643</td>
<td>0.5739</td>
<td>0.6489</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9wt%</td>
<td>0.56007</td>
<td>0.6144</td>
<td>0.63009</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.2.3 Electrical Conductivity

For each nanofiber membrane sample, the electrical conductivity was measured using a multimeter with silver paint serving as the electrode. Two different samples were measured for each value. The conductivity increased with as higher concentrations of PAN were used shown in Figure 5-7 which displays the variation in conductivity values for each PAN sample. These values are presented in Table 5-8.

Figure 5-7 - Conductivity of PAN Membranes

<table>
<thead>
<tr>
<th>Electrical Conductivity for PAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>7wt%</td>
</tr>
<tr>
<td>8wt%</td>
</tr>
<tr>
<td>9wt%</td>
</tr>
<tr>
<td>10wt%</td>
</tr>
</tbody>
</table>
For nanofiber membrane samples made of PAN-co-MA, the conductivity increased dramatically from PAN samples, the highest conductivity for PAN was 10wt% PAN at $\sigma = 4.1542$ S/cm at 1100°C whereas 7wt% PAN-co-MA displayed conductivity of $\sigma = 31.5948$ S/cm which is a 650% increase in conductivity. These conductivity trends are demonstrated in Figure 5-8 and individual values are summarized in Table 5-9. Though possible explanations for this conductivity increase between PAN and PAN-co-MA will be covered in Chapter 6, these results follow from the Raman peak ratios that were identified. Samples with higher conductivity followed the trend of $I_g/I_d$ ratio above which points to higher graphitization among the PAN-co-MA samples.

![Figure 5-8 - Conductivity of PAN-co-MA Membranes](image-url)
Table 5-9 - Electrical Conductivity Values for PAN-co-MA in S/cm

<table>
<thead>
<tr>
<th></th>
<th>700</th>
<th>900</th>
<th>1100</th>
</tr>
</thead>
<tbody>
<tr>
<td>7wt%</td>
<td>.1699</td>
<td>1.9473</td>
<td>31.5948</td>
</tr>
<tr>
<td>8wt%</td>
<td>.0110</td>
<td>5.4554</td>
<td>15.3163</td>
</tr>
<tr>
<td>9wt%</td>
<td>.0046</td>
<td>2.5045</td>
<td>14.2857</td>
</tr>
<tr>
<td>10wt%</td>
<td>.0049</td>
<td>1.8181</td>
<td>13.8826</td>
</tr>
</tbody>
</table>

As based on two measurements for each sample

Figure 5-9 - Conductivity Values for PAN and PAN-co-MA Membranes

In Figure 5-9 we see values for PAN and PAN-co-MA overlayed with each other to clearly show the conductivity increase obtained with PAN-co-MA at lower concentrations of the polymer and smaller fiber diameters.
5.3 PAN Composite Nanofibers as a Transparent Conductor

Carbonized nanofibers were studied in thin layers for application as a model system for a transparent conductor, MWCNT composite nanofibers were electrospun and thin layers were deposited on quartz slides for characterization by studying the microstructure, the coverage of quartz slides, the carbonization performance, optical transparency, electrical conductivity and work function.

5.3.1 Microstructural observations

To study the microstructure of the MWCNT/PAN composites, confocal images were captured along with SEM images of various concentrations of MWCNT. For comparison with the detailed analysis of uncarbonized PAN and PAN-co-MA fiber properties above, MWCNT/PAN-co-MA concentrations of 16wt%, 19wt% and 22wt% were analyzed.

Uncarbonized Fiber Diameters

For the uncarbonized fiber samples and the carbonized fibers presented in the following section, MWNT agglomerations were clearly present because of the high concentrations of nanotubes. Agglomerations were more prominent after MWNT concentrations of MWNT/PAN ratios higher than 10wt%. Figure 5-10 through Figure 5-12 show SEM images and fiber distributions for electrospun composite fibers of 16wt%, 19wt% and 22wt% MWNT to PAN ratio.
Figure 5-10 - SEM image and Diameter Distribution of 16wt% MWCNT/PAN-co-MA Uncarbonized

Figure 5-11 - SEM image and Diameter Distribution of 19wt% PAN-co-MA Uncarbonized
As we can see in Table 5-10, with higher concentrations of nanotubes, high mean fiber diameters were displayed.

**Carbonized Fiber Diameters**

MWCNT/PAN-co-MA composite fibers were carbonized at 750°C and 850°C and their mean diameters were plotted to analyze the difference between uncarbonized and carbonized...
fibers showing a clear trend of diameter increase with higher MWNT concentrations as shown in
Figure 5-13 and detailed in Table 5-11 for 750°C and Table 5-12 for 850°C.

![Figure 5-13 - Mean Fiber Diameters of Carbonized Fibers](image)

**Table 5-11 - MWCNT Fiber Diameters at 750°C**

<table>
<thead>
<tr>
<th>MWCNT Concentration (wt%)</th>
<th>Carbonization Temp (°C)</th>
<th>Average Diameter (nm)</th>
<th>+- (nm)</th>
<th>Minimum (nm)</th>
<th>Maximum (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>750</td>
<td>344.91</td>
<td>5.6</td>
<td>245</td>
<td>461</td>
</tr>
<tr>
<td>19</td>
<td>750</td>
<td>356.9</td>
<td>13.8</td>
<td>277</td>
<td>720</td>
</tr>
<tr>
<td>22</td>
<td>750</td>
<td>432.39</td>
<td>12.17</td>
<td>239</td>
<td>821</td>
</tr>
<tr>
<td>25</td>
<td>750</td>
<td>456.55</td>
<td>10.5</td>
<td>207</td>
<td>580</td>
</tr>
</tbody>
</table>
Table 5-12 - MWCNT Fiber Diameters Carbonized at 850°C

<table>
<thead>
<tr>
<th>MWCNT Concentration (wt%)</th>
<th>Carbonization Temp (°C)</th>
<th>Average Diameter (nm)</th>
<th>+- (nm)</th>
<th>Minimum (nm)</th>
<th>Maximum (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>850</td>
<td>270.07</td>
<td>5.91</td>
<td>182</td>
<td>507</td>
</tr>
<tr>
<td>16</td>
<td>850</td>
<td>274.21</td>
<td>6.32</td>
<td>194</td>
<td>491</td>
</tr>
<tr>
<td>19</td>
<td>850</td>
<td>349.62</td>
<td>12.5</td>
<td>188</td>
<td>856</td>
</tr>
<tr>
<td>22</td>
<td>850</td>
<td>353.92</td>
<td>8.87</td>
<td>239</td>
<td>704</td>
</tr>
<tr>
<td>25</td>
<td>850</td>
<td>431.6</td>
<td>4.35</td>
<td>218</td>
<td>664</td>
</tr>
</tbody>
</table>

5.3.2 Coverage of slides

After selecting five representative samples of confocal images of the MWCNT/PAN-co-MA composites, image processing was applied in order to determine the coverage of each slide by nanofibers that resulted in images such as Figure 5-14 and Figure 5-15.

Figure 5-14 - 19wt% PAN/MWCNT loading after carbonization, image color inverted to count pixel colors
To determine the coverage of the slide, each representative image was first processed to find edges using ImageJ. Then, a color range selection was applied to select each of the fibers and to fill in the necessary area with mostly white pixels in order to contrast. Then, a fill layer was applied in order to ensure a proper level of contrast in the image. Last, the histogram was analyzed for the bright pixels to reveal the percent coverage of nanofibers in the covered area.

![Image](image.png)

**Figure 5-15 - 25wt% MWCNT loading after carbonization, image inverted to count pixel colors**

Once this analysis was applied to the representative images, the values in Table 5-13 were obtained which show a mean coverage of 36.51% but values as high as 48.19% in one of the samples.

<table>
<thead>
<tr>
<th>MWCNT/ PAN-co-MA Concentration</th>
<th>Slide Area</th>
<th>Coverage by Fibers</th>
<th>Coverage Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>25wt%</td>
<td>133.28µm²</td>
<td>43.88µm²</td>
<td>31.59%</td>
</tr>
<tr>
<td>22wt%</td>
<td>134.15µm²</td>
<td>42.10µm²</td>
<td>32.71%</td>
</tr>
</tbody>
</table>
### MWCNT/ PAN-co-MA Concentration

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Slide Area</th>
<th>Coverage by Fibers</th>
<th>Coverage Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>25wt%</td>
<td>132.70µm²</td>
<td>63.94µm²</td>
<td>48.19%</td>
</tr>
<tr>
<td>19wt%</td>
<td>132.37µm²</td>
<td>46.23µm²</td>
<td>34.93%</td>
</tr>
<tr>
<td>19wt%</td>
<td>133.56µm²</td>
<td>46.93µm²</td>
<td>35.14%</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td>36.51%</td>
</tr>
</tbody>
</table>

#### 5.3.3 Optical Transparency

For the evaluation of slide performance at a potential TC material, thin layers of nanofibers on quartz slides were analyzed for transparency (T%) under a visible spectrum of 200-800nm at MWCNT concentrations of 0wt%, 4wt%, 7wt%, 10wt%, 13wt%, 16wt%, 19wt%, 22wt% and 25wt%. Transparency plots are presented in this section with Figure 5-16 through Figure 5-19 for the NF TC layers in the visible spectrum. Plots of transparency for this material at MWNT concentrations of 4%, 7%, 10%, 13%, 19% and 22% are available in Appendix D.

![Figure 5-16 - Optical Transparency of NF TC at 0% Concentration of MWCNT](image-url)
For pure PAN-co-MA nanofibers with no nanotube loading, the transparency for these two samples ranged between 88% and 92%. The wide variation is due to the variation in coverage of each sample that is a function of duration of exposure to the electrospinning jet and random variation due to the fiber placement of the electrospinning process.

**Figure 5-17 - Optical Transparency of NF TC at 16% Concentration of MWCNT**

![Graph](image1)

**Figure 5-18 - Optical Transparency of NF TC at 25% Concentration of MWCNT**

![Graph](image2)
At 16wt% and 25wt% MWNT concentration, transparencies ranged from 94.5% to 99% and 90% to 96% respectively. Though the concentrations of nanotubes were increased in these samples, the transparency showed no dramatic decreases in the optical spectrum because of greater amounts of nanotubes. These characterizations did not consider the IR response of the nanotubes.

![Graph showing transparency vs. wavelength for different nanotube loadings.](image)

**Figure 5-19 – Composite of all NF TC Layers**

In Figure 5-19 a composite of all NF TC measurements are presented showing the full range of potential transparencies that can be achieved by the material with varying nanotube loadings. The transparency (T%) shows variation between 85% and above 96%; well within the range necessary to compete with ITO. Transparency values for plots above show little to no correlation with the amount of nanotube loading.
5.3.4 Electrical Conductivity of Nanofiber Thin Layers

Measuring quartz slides containing layers of nanofibers that are only a few fibers thick presents a unique set of challenges. For these conductivity measurements, carbonized slides of thin nanofibers layers were covered with silver paste and analyzed using a Keithly Probe Station.

![Sheet Resistance vs MWCNT Loading](image)

Figure 5-20 - Nanofiber TC Slide Sheet Resistance Performance

As can be seen from Figure 5-20, the percolation threshold occurs for this material between 1% MWCNT and 10% MWCNT loading. Each MWCNT loading was calculated per the final “dry fiber” weight ratio of MWCNT-to-PAN/PAN-co-MA, not the original electrospinning dope concentration. The material potential for a low sheet resistance is demonstrated as MWCNT concentrations above 22% reach towards the 1kΩ/□ point and surpass it, falling as low at 700Ω/□. Though this level of conductivity is not high enough to be functional in solar cell materials, achieving this level of conductivity shows a clear potential for further development.
Because of the variation in the sheet resistance performance of each MWCNT-NF TC sample, to show the performance potential of the material, Figure 5-21 highlights the best values for each MWCNT loading.

**Figure 5-21 - Best Values of MWCNT/PAN-co-MA Composite Thin Layers**

Each MWCNT-NF TC sample was carbonized at various temperatures between 800°C and 900°C the relationship of these temperatures is shown in Figure 5-22.
5.3.5 Work Function

Four membrane samples were evaluated for their work functions using a photoelectron spectrometer. Indium tin oxide has a work function on the range of 4.6-4.7eV [119]. Prior work on carbon nanotubes has found that their work function is on the range of 4.95–5.05 eV [120].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Work Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>10wt% PAN-co-MA 700°C</td>
<td>5 eV</td>
</tr>
<tr>
<td>10wt% PAN-co-MA 900°C</td>
<td>4.75eV</td>
</tr>
<tr>
<td>19wt% MWCNT/PAN-co-MA 700°C</td>
<td>4.91 eV</td>
</tr>
<tr>
<td>25wt% PAN 700°C</td>
<td>4.73eV</td>
</tr>
</tbody>
</table>
The NF-TC in this study were found to have work functions on the range of 4.73-5eV as shown in Table 5-14. With a higher work function than ITO, the work function will need to be decreased to serve as a straightforward ITO replacement.
Chapter 6  Discussion

6.1 PAN-co-MA For Electrical Applications

To compare the results obtained above for PAN-co-MA and PAN to literature, first the diameter of the electrospun are considered. PAN-co-MA fibers demonstrated a larger diameter than the PAN fibers before carbonization. The mean diameter ranged from 325nm to over 550nm for PAN-co-MA. For PAN fibers, the mean diameter showed less variance, ranging from 236nm to more than 350nm. These values are in line with published results, Gu et al. found in a study of electrospun PAN concentrations between 6wt% to 12wt% that mean diameters were at 200nm for 6wt%, 280nm for 8wt% and 390nm for 10wt% [121]. For Sutasinprompra et al. average fiber diameters were found to be slightly smaller at mean diameters of less than 180nm for 8wt% PAN nanofibers and 190nm for 10wt% PAN nanofibers[122]. No studies could be found of PAN-co-MA electrospun nanofibers values.
For carbonized fibers, the lowest diameter values were obtained for PAN at a concentration of 7wt% at temperatures of 700˚C to 236.8nm to 143.8nm at 900˚C and 108.62nm at 1100˚C. At 11wt% PAN, carbonized fibers were at 567.33nm at 700˚C, 460.44nm at 900˚C and 432.9nm at 1100˚C. For PAN-co-MA fibers, the smallest diameters were obtained from 7wt% concentration fibers at 327.1nm at 700˚C, 235.4nm at 900˚C and 107nm at 1100˚C. For 12wt% PAN-co-MA values, the mean fiber diameter was 568.1nm at 700˚C and 421.3nm at 900˚C and at 11wt% PAN-co-MA the fiber diameter was 168.4nm at a carbonization temperature of 1100˚C. Though specific results for an extensive study of carbonized PAN fiber diameters have yet to be published by other authors, Zhou et al. found that carbonized PAN nanofibers of a 10wt% solution were less than 200nm after pyrolysis at temperatures less than greater than 1000˚C [123]. Panapoy et al. found that carbonized PAN fibers from a spinning dope at a 9wt% concentration yielded fibers of a diameter of 275nm, 242nm and 208nm at 800˚C, 900˚C and
100°C respectively [124]. No previous studies have detailed the effect of PAN-co-MA during the process of carbonization heat treatments.

Figure 6-2 - Carbonized Fiber Diameters for PAN and PAN-co-MA at 700°C, 900°C and 1100°C

This diameter-concentration relationship was originally noticed as it was developed into the Berry Number, the relationship between fiber diameter and molecular conformation and has been developed further by Ko et al. [125].

In further comparing the use of PAN-co-MA to PAN in electrical applications for carbon nanofibers, the carbon content of fibers were studied using EDX analysis. The carbon content of carbonized fibers were compared at 700°C, 900°C and 1100°C in the following plots. At 700°C,
carbon contents for PAN and PAN-co-MA ranged from 58wt% to an extreme of 93% but most values ranged from 68wt% to 74wt% and showed little differentiation between the two polymers.

Figure 6-3 - EDX Carbon Content of Nanofibers at 700°C

At 900°C PAN and PAN-co-MA showed a very clear separation of carbon content, PAN demonstrated a carbon concentration of 73wt% to 85wt% while PAN-co-MA shows concentrations of 90-95wt%. In studying the stabilization phase of carbon fiber precursors, Fitzer et al. found that PAN copolymers containing methyl acrylate showed lower activation energies for cyclization, thus indicating the potential for higher rates of cyclization during the cyclization process leading to higher carbonization performance throughout the rest of the process [126]. These results would suggest that at higher rates of cyclization during stabilization, carbonization performance would increase and carbonization would occur at lower temperatures. In this study,
the presence of high carbon content for PAN-co-MA at 900°C reinforces the findings of Fitzner et al. and also demonstrates that their results have significance during the carbonization process.

Figure 6-4 - EDX Carbon Content of Nanofibers at 900°C

Though at 1100°C, the differentiation between the two polymers is no longer present because at this temperature enough energy is present to convert the material to the carbon at a desired concentration.
To compare the level of graphitization performance of PAN and PAN-co-MA nanofibers at concentrations of 7wt%, 8wt% and 9wt% were compared using data obtained using Raman spectroscopy and were reported previously in the results section. As the intensity of the graphitic and disordered peaks were compared, the ratio of the graphitic peak (Ig) to the disordered peak (Id) increased as the temperature of carbonization (Tc) was increased. At 700°C, 900°C and 1100°C PAN nanofibers at a concentration of 7wt% displayed an R (Ig/Id) of .5625, .5715 and .5819 respectively. PAN-co-MA nanofibers at a concentration of 7wt% demonstrated ratios of .5519, .6008 and .6434 at 700°C, 900°C and 1100°C respectively. For PAN-co-MA, the ratio of the graphitic to disordered peaks displayed a high ratio regardless of the concentration and demonstrated a higher ratio at lower temperatures, reinforcing the indication from EDX analysis that PAN-co-MA achieves a higher performance for electrical applications during carbonization. In carrying out a similar study, Kim et al. found that PAN displayed a increasing $R_{Ig/Id}$ at higher...
carbonization temperatures, increasing from .3663 to .7194 as $T_c$ was increased from 700°C to 1000°C [127].

Conductivity of PAN-co-MA nanofibers displayed an extensive increase in conductivity over PAN nanofibers. At 1100°C, PAN nanofibers of concentrations from 7wt% to 10wt% demonstrated conductivity of $0.6947 \text{ S/cm}$ to $4.15 \text{ S/cm}$ with a increasing conductivity as fiber concentration and diameter increased. PAN-co-MA nanofibers from 7wt% to 10wt% demonstrated results of $31.59 \text{ S/cm}$ to $13.5 \text{ S/cm}$ respectively, showing a marked increase over homopolymer PAN. Notably, the relationship of conductivity to polymer concentration was reversed for PAN-co-MA compared to PAN. The increase of 7x to 19.4x results from the increased cyclization in the nanofiber from the presence of methyl acrylate in the carbon matrix during the carbonization process as detailed above in EDX and Raman results. The results for the conductivity of PAN nanofibers are within the range of published results. Kim et al. found that carbonized PAN nanofibers ranged from $6.8 \times 10^{-3} \text{ S/cm}$ at 700°C to 1.96 S/cm at 1000°C [127]. Bayat et al. found the electrical conductivity of PAN nanofibers to range between .055S/cm to 2.6S/cm from 700°C to 900°C respectively [128]. Because detailed studies of PAN-co-MA nanofibers have typically overlooked conductivity, no references for PAN-co-MA nanofibers conductivity could be found. With the enhanced conductivity of PAN-co-MA membranes along with increased performance during carbonization, in electrical applications PAN-co-MA should be selected over PAN in applications where electrical conductivity is imperative.
6.2 PAN-co-MA Fibers as a Transparent Conductor

As a model system was developed for using thin layers of carbonized nanofibers in transparent conductor applications, special attention was given to the diameter effect of MWCNT concentrations on the diameter, the slide coverage, the transparency and the conductivity of this material. Because nanofibers had previously seen study in bundles or in membranes form, this is one of the first potential applications of nanofibers as a thin layer.

When comparing the electrical performance of the MWCNT composite material to the results of other MWCNT and SWCNT composites, the potential for MWCNT nanofibers is clear, even though conductivities of less than 1kΩ□ are competitive with many of the results of other SWNT composites. Single-walled carbon nanotubes are typically an order of magnitude higher in cost than MWNT. The samples plotted in Figure 6-6 use SWNT of high concentrations, of 25%-50% volume fraction, far higher than in the NF-TC samples in this study.

Reductions in nanoparticle density can be attributed to the high aspect ratio of nanofibers that constrains the nanoparticles in fewer dimensions than in a bulk polymer composite material. Additionally, the high surface area to volume ratio also reduces the amount of material needed to reach a useful level of conductivity. The transparency of the carbon nanofibers composite samples in a useful range of sheet resistance ranged from T%=89% to T%=92%.

In Figure 6-6, nanofiber and other carbon nanotube composite TC materials are also compared performance numbers for ITO. When compared to published performance numbers of ITO, the NF-TC doesn’t hold up against its performance of 100Ω□ and T% = .88. The NF-TC performs with a sheet resistance of 700 Ω□ to 1000 Ω□ and T% > 90%.
Figure 6-6 - Comparison of MWCNT Results to Publications on ITO and SWCNT Composites [76], [123], [129]

As a model system, this material also demonstrates the ability to further load nanofibers with MWCNT to achieve higher conductivities. The low correlation between the transmissivity (T%) and sheet resistance leaves open the possibility of higher concentrations of nanotubes. The high transparency of the NF TC layer is obtained primarily through a low need for coverage of the material by the fibers as demonstrated in Figure 6-7.

Figure 6-7 – Limited Relationship between T% to Sheet Resistance
In Figure 6-8 we see how each of the NF-TC layers are extremely thin: consisting of roughly 1-2 nanofibers in thickness. Carbonized fiber diameters ranged from mean diameters of 344.91nm to 456.55nm at MWCNT concentrations of 4% to 25% respectively at 750°C. If we hold the mean NF TC layer thickness 800nm and model it as a thin film, we can gain an insight into the conductivity in S/cm of NF TC performance in Figure 6-9. However, these numbers do not consider the NF TC as a fiber model nor do they consider contact resistance of measurement. Likely the conductivity is significantly higher. Modeling as a thin film, conductivities range from .259 S/cm at no concentration of MWCNT to 16.02 S/cm at 42wt% concentration of nanotubes. As the diameter of the fibers increased with the addition of nanotubes shown in the previous section, the conductivity also increased. Fiber diameters of MWCNT composite fibers increased from a mean diameter of 270.07nm to 431.6nm with 10wt% PAN-co-MA as MWCNT concentration increased from 4wt% to 25wt%.
In comparison to published results for the affect of MWCNT on the conductivity of PAN nanofibers in a composite Ra et al. found that electrical conductivity reached 4.5 S/cm at 800°C for 10 wt% MWCNT and results of anisotropy suggested that the percolation threshold wasn’t reached at 10 wt% of MWCNT concentration [130]. From analysis of the co-polymer comparison study, it is suggested higher performance for a NF-TC could be obtained by switching from 10wt% PAN-co-MA to 7wt% PAN-co-MA.

In considering carbonized nanofibers as a transparent conductor, special attention will need to be given to the contamination of the carbonization process. This study analyzed hundreds
of NF composite samples but a considerable number of these samples were lost in the tube furnace due to contaminations from other materials. Because of the sensitive nature of the cyclization process of polyacrylonitrile in oxygen, residues from other materials can present significant challenges.

Because these samples were placed in a tube furnace at high temperatures, removing the nanofiber sample from quartz substrates without disrupting the fiber network proved to be a difficult task. Therefore, mechanical testing was not an option with this process. Zhou et al. found that carbonized nanofibers bundles at 1000°C had a tensile strength of 325Mpa and Young’s modulus of 40Gpa and these properties were improved by 67% and 45% respectively after treatment at 2000°C [123]. Carbon nanofibers transparent conductor my samples have the potential to achieve the properties needed for flexible electronics if they can be removed from brittle and inflexible substrates.
Chapter 7 Conclusions and Recommendations

In this study, homopolymer PAN and PAN-co-MA were compared for their performance in producing carbonized fiber for electrical applications and carbonized fibers were developed as thin layers on a substrate in a model system for a transparent conductor material. By comparing PAN and PAN-co-MA electrospun carbonized nanofibers, it was determined that PAN-co-MA is a superior carbon fiber precursor for electrical applications because the presence of methyl acrylate catalyzes graphitic sheet formation in the carbon fiber structure. Nanofiber transparent conductor layers demonstrated the ability to achieve a sheet resistance as low as 700 Ω/□ and a transparency greater than 90%.

SEM images were used to analyze the microstructure of PAN and PAN-co-MA nanofibers before and after carbonization. After electrospinning solutions of both polymers at concentrations of 7wt%, 8wt%, 9wt%, 10wt%, 11wt% and 12wt% fiber diameters were measured with image analysis software. PAN nanofibers before carbonization ranged from 210.7nm to 421nm and PAN-co-MA fiber membranes displayed mean diameters of 330.6 to 561nm. After carbonization, mean fiber diameters decreased to 108nm to 351.3nm for PAN and 107.3 to 257.06nm for PAN-co-MA. Minimizing the thickness of an electrospun carbon fiber membrane is ideal because of the smaller carbonized fiber diameter.

PAN carbonized nanofibers demonstrated higher concentrations of carbon than PAN at 900°C under EDX suggesting that carbonization was occurring at lower temperatures. To investigate the degree of graphitization in the nanofiber samples, Raman spectra were measured to obtain the ratio between the graphitic and the disordered peaks of each sample between 7wt% and 9wt% for PAN-co-MA. Both polymers demonstrated the highest R ratio at 1100°C,
indicating higher degrees of graphitization at this temperature. PAN-co-MA at 7wt% and 8wt% demonstrated the highest graphitization ratio of any sample, providing a possible explanation for the high level of conductivity in these samples. Conductivity measurements of these samples determined that PAN ranged from .5 S/cm for low polymer concentrations and greater than 4 S/cm for higher polymer concentrations. PAN-co-MA demonstrated significantly higher levels of conductivity than PAN with 7wt% PAN reaching a conductivity of greater than 30 S/cm, more than seven times the conductivity of PAN. For electrical applications, carbon fiber from PAN-co-MA is recommended because of the high conductivity and low diameter after carbonization.

For the development of a nanofiber/MWCNT transparent conductor model system, carbon nanotubes were dispersed in polymer solutions, electropsun on quartz substrates and subsequently carbonized. Before carbonization, composite nanofibers demonstrated displayed an increasing diameter with higher concentrations of MWCNT. For samples of 16wt%, 19wt% and 22wt%, mean diameters increased from 380nm to 455.9nm. After carbonization, samples of 4wt% through 25wt% MWCNT were measured to have mean diameters of 344nm-456nm at 750°C to 270nm-431.6nm at 850°C. Quartz slide substrates showed coverage of surface area from 31.59% to 48.19%, demonstrating the potential to use significantly smaller amounts of costly nanoparticles than thin film samples. Transparencies from 88% to greater than 96% were achieved with the thin layers of carbonized nanofibers. Transparencies were reliant on the primary factor of slide coverage and not the level of nanoparticle loading. The measured sheet resistance of the material decreased with high MWCNT concentrations and the percolation threshold was achieved in the range of 1-10wt% MWCNT. A sheet resistance of less than 1\(k\Omega\) was reached for samples with greater than 30wt% MWCNT and a sample with greater than 40wt% MWCNT showed a sheet resistance of 700 1\(k\Omega\).
Table 7-1 compares transparent conductor criteria for ITO with the equivalent values for the NF TC. Specifications for a GE 150W CdTe module were used to calculate the rough proportion of ITO in each module based on the density, relative thickness of the TC layer and cost of ITO from Sigma Aldrich in bulk. Nanofiber transparent conductor values were calculated based on the amount of coverage provided during electrospinning per unit of time. As each sample in this study was coated for about 30 seconds, the 2.54 cm x 2.54 cm quartz slide was used as a determinant for the amount of material that would be needed to cover an equivalent area of CdTe PV modules to achieve a megawatt of PV capacity.

Table 7-1 - ITO vs. NF TC Properties

<table>
<thead>
<tr>
<th></th>
<th>ITO</th>
<th>Nanofiber Transparent Conductor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
<td>Indium (In) Tin (Sn)</td>
<td>Carbon (PAN/PAN-co-MA) + MWNT</td>
</tr>
<tr>
<td>Scarcity</td>
<td>Indium (Scarcie)</td>
<td>Propene (relatively abundant)</td>
</tr>
<tr>
<td>g/MW CdTe</td>
<td>14.25g ITO/MW</td>
<td>62.45g NFTC/MW</td>
</tr>
<tr>
<td>$/MW</td>
<td>$372.92</td>
<td>$282.44</td>
</tr>
<tr>
<td>Ω/□</td>
<td>&lt;100 Ω/□</td>
<td>&lt;1000 Ω/□</td>
</tr>
<tr>
<td>T%</td>
<td>&gt;85%</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>Work Function</td>
<td>4.7</td>
<td>4.9</td>
</tr>
<tr>
<td>Mechanical Durability</td>
<td>Low</td>
<td>High Potential</td>
</tr>
<tr>
<td>Thermal Stability</td>
<td>&lt; 300°C</td>
<td>&lt; 700°C</td>
</tr>
</tbody>
</table>

Though indium scarcity is not an immediate challenge to scaling up PV connecting grid capacity, reliance on ITO presents a challenge for the long-term viability for any solar cell structure that uses it as a transparent conductor. After this initial study, the properties of this model system are clearly not ready to replace ITO, however it does show significant potential as a pathway for development as the costs are significantly lower than any nanoparticle composite TC system that would use single walled carbon nanotubes. With high transparencies and a clear pathway to improving the sheet resistance with higher concentrations of carbon nanotubes, the ability for a nanofibers TC to meet the performance of ITO is a distinct possibility after further
research.

Would a nanofiber TC actually work in a solar cell structure? Nanofiber TC samples were coated on PEDOT and shown to maintain their integrity, demonstrating the potential for this material to serve in organic solar cell or thin film applications. Because this system also has the potential to eliminate the energy needs of glass (200MJ/m3) in the solar cell fabrication process, also improving the energy payback time of a solar PV system. Additionally this material has demonstrated potential to reduce the dependencies of PV technologies on scarce minerals with more abundant petrochemically derived polymers and renewable materials such as lignin through incorporation in future PAN composites. Polyactrolynitrile is produced by the free radical polymerization of acrylonitrile, a monomer derived from propene. Propene is a byproduct of oil refining and natural gas processing. Because of the tremendous amounts of fossil fuel energy used in the extraction of non-renewable resources, the material and energy chain is simplified with the use of oil and natural gas by-products directly, rather than indirectly through the extraction of resources. A further study of the life cycle analysis could details the impacts of this process.

7.1 Recommendations for Further Work

Further work in developing this NF TC model into a useable device will require higher levels of dispersion among nanoparticles so that higher concentrations of MWCNT can be achieved. With the relationship of high MWCNT loading to lower TC sheet resistance observed in this study, MWCNT concentrations of greater than 50% would likely achieve the level of performance necessary for a touch screen device.
Because of the strong mechanical properties of carbon nanotube composite carbonized nanofibers, this material holds a significant potential for use in flexible electronic devices. Removing the NF TC layer from an inflexible quartz substrate will be necessary to explore this pathway of development. Initial experiments were carried out to test this possibility that weren’t incorporated into this thesis. Loops of copper wire were held in the electropsinning jet and coated with layers of nanofibers that could be successfully carbonized. By removing the quartz from the procedure, this also opens a pathway for mechanical property testing of a NF TC membrane.

Through replacing the MWCNT in this study with single-walled nanotubes or higher quality MWCNT, significant increases in the conductive properties of this model system could be achieved. Additionally, a qualitative relationship was established between the thickness of the nanofiber membrane and the conductivity but was not of significant quantitative development to include in this thesis.

7.2 Maybe not for solar cells?

Though the context of this study was on developing a transparent conductor for use in solar cell applications, this NF TC model system shows significant potential for use in touchscreen applications. With the growing popularity of touchscreen phones, computers and displays that use ITO as a component, indium depletion is a concern for more reasons than just use in solar cells. Will we use all of our indium for consumer devices rather than for energy generation?

A transparent conductor alternative, like the NF TC developed in this study, could help to alleviate scarcity concerns. With lower conductivity and higher transparency requirements than solar cells, touchscreen devices could be a practical application of nanofibers as a transparent
conductor. Typically the sheet resistance for a TC material in a touch screen is on the range of 100-300 $\Omega/\square$ with a transparency of greater than 90% [131]. This is very close to the values already obtained by the NF TC in this study and could likely be achieved with additional development of the model presented in this work.
References


W. J. MORTON, WILLIAM JAMES MORTON. Google Patents, 1902.


[118] E. Fitzer, “Pan-based carbon fibers--present state and trend of the technology from the viewpoint of possibilities and limits to influence and to control the fiber properties by the process parameters,” *Carbon*, vol. 27, no. 5, pp. 621–645, 1989.


Appendices

Appendix A Nanofiber SEM Images Post-Carbonization

SEM images of PAN and PAN-co-MA fibers carbonized at several temperature are presented here, detailed analysis and commentary is available in Section 5.1.1 and 5.1.2 as well as Section 6.1.

Section 01 PAN carbonized at 700°C, 900°C and 1100°C

Figure A-1 - SEM images of PAN carbonized at 700 (left), 900 (middle), 1100°C (bottom)
Figure A-2 - 8wt% PAN 700°C (left), 900°C (middle) 1100°C (bottom)

Figure A-3 - 9wt% PAN 700°C (left), 900°C (middle), 1100°C (bottom)
Figure A-4 - 10wt% PAN 700°C (left), 900°C (middle), 1100°C (bottom)

Figure A-5 - 11wt% PAN 700°C (left), 900°C (middle), 1100°C (bottom)
Section 02  PAN-co-MA carbonized at 700°C, 900°C and 1100°C

Figure A-6 - 7wt% PAN-co-MA 700°C (left), 900°C (middle), 1100°C (bottom)

Figure A-7 - 8wt% PAN-co-MA 700°C (left), 900°C (middle), 1100°C (bottom)
Figure A-8 - 9wt% PAN-co-MA 700°C (left), 900°C (middle), 1100°C (bottom)

Figure A-9 - 10wt% PAN-co-MA 700°C (left), 900°C (middle), 1100°C (bottom)
Figure A-10 - 11wt% PAN-co-MA 700°C (left), 900°C (middle), 1100°C (bottom)

Figure A-11 - 12wt% PAN-co-MA 700°C (left), 900°C (middle), 1100°C (bottom)
Appendix B Nanofiber Diameter Distributions

To supplement fiber SEM images and measured diameters in Chapter 5.1, fiber diameter distributions are presented in the following sections.

Section 01 Nanofibers Prior to Carbonization

Figure B-1 - 7wt% PAN (top) and PAN-co-MA (bottom) fiber diameter distribution based on 100 fibers

Figure B-2 - 8wt% PAN (left) and PAN-co-MA (right) fiber diameter distribution based on 100 fibers

Figure B-3 - 9wt% PAN (left) and PAN-co-MA (right) fiber diameter distribution based on 100 fibers
Figure B-4 – 10wt% PAN (left) and PAN-co-MA (right) fiber diameter distribution based on 100 fibers

Figure B-5 – 12wt% PAN-co-MA fiber diameter distribution based on 100 fibers
Section 02  Nanofiber Diameter Distributions After Carbonization

7.2.1 PAN Nanofibers After Carbonization

Figure B-6 - 7wt% PAN 700, 900, 1100 Fiber Diameter Distributions

Figure B-7 - 8wt% PAN 700, 900, 1100 Fiber Diameter Distributions

PAN 700, 900, 1100 Fiber Diameter Distributions
Figure B-8 - 9wt% PAN 700, 900, 1100 Fiber Diameter Distributions
Figure B-9 - 10wt% PAN 700, 900, 1100 Fiber Diameter Distributions
7.2.2 PAN-co-MA Nanofibers After Carbonization

Figure B-11 - 7wt% PAN-co-MA 700, 900, 1100 Fiber Diameter Distributions
Figure B-12 - 8wt% PAN-co-MA 700, 900, 1100 Fiber Diameter Distributions
Figure B-13 - 9wt% PAN-co-MA 700, 900, 1100 Fiber Diameter Distributions

Figure B-14 - 10wt% PAN-co-MA 700, 900, 1100 Fiber Diameter Distributions
Figure B-15 - 11wt% PAN-co-MA 700, 900, 1100 Fiber Diameter Distributions
Figure B-16 - 12wt% PAN-co-MA 700 and 900 Fiber Diameter Distributions
Appendix C Raman Spectra Plots

Figure C-1 - 7wt% PAN Raman Spectra, 700C (top), 900C (middle), 1100C (bottom)
Figure C-2 - 8wt% PAN Raman Spectra, 700C (top), 900C (middle), 1100C (bottom)
Figure C-3 - 9wt% PAN Raman Spectra, 700°C (top), 900°C (middle), 1100°C (bottom)
Figure C-4 - 7wt% PAN-co-MA Raman Spectra, 700C (top), 900C (middle), 1100C (bottom)
Figure C-5 - 8wt% PAN-co-MA Raman Spectra, 700C (left), 900C (right), 1100C (bottom)
Figure C-6 - 9wt% PAN-co-MA Raman Spectra, 700C (left), 900C (right), 1100C (bottom)
Appendix D Nanofiber TC Transparency Plots

Figure D-1 - Optical Transparency of NF TC at 4% Concentration of MWCNT

Figure D-2 - Optical Transparency of NF TC at 7% Concentration of MWCNT
Figure D-3 - Optical Transparency of NF TC at 10% Concentration of MWCNT

Figure D-4 - Optical Transparency of NF TC at 13% Concentration of MWCNT
Figure D-5 - Optical Transparency of NF TC at 19% Concentration of MWCNT

Figure D-6 - Optical Transparency of NF TC at 22% Concentration of MWCNT
Appendix E Additional Images of Nanofiber TC

Figure B 1 - Confocal images of 25wt% MWCNT carbonized nanofiber mesh at (A) at 5x and (B) 100x magnification, 30º tilt of image rendered in 3D

Figure B 2 - Confocal images of 25wt% MWCNT carbonized nanofiber mesh at (A) at 5x and (B) 100x magnification, 30º tilt of image rendered in 3D
Appendix F Randomly Selected I-V Curves of Transparent Conductor Slides

Slide 1101-3 : 30wt% MWCNT/10wtPAN at 700°C

Slide 1101-5 : 15wt% MWCNT/9wtPAN at 700°C
Slide 1102-1: 15wt% MWCNT/10wt PAN at 900°C

Slide 1104-5: 15wt% MWCNT/9wt PAN at 800°C
Slide 1106-2: 30wt% MWCNT/9wt PAN at 800°C

Slide 1110-4: 30wt% MWCNT/9wt PAN at 800°C

Slide 1111-4: 23wt% MWCNT/10wt PAN at 850°C
Slide 1117-1: 7wt% MWCNT/10wt PAN at 850°C

Slide 1119-4: 23wt% MWCNT/10wt PAN at 800°C
Slide 1120-3: 23wt% MWCNT/10wt PAN at 900°C
Appendix G  
Select XRD and TGA Curves

Figure G-1 – XRD of Carbonized 4wt% MWCNT vs 16wt% MWCNT PAN

Figure G-2 - Raman Spectra of 19wt% MWNT PAN-co-MA Carbonized at 800C
Figure G-3 - TGA of PAN-co-MA in Oxygen