## DESIGN AND FABRICATION OF ELECTROSPUN NANOFIBER CATALYST SUPPORT FOR POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

by

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### Abstract

Progress in fuel cell technology is impeded by the lack of understanding of the fundamental design characteristics necessary to improve the performance. Current catalyst design suffers from challenges related to platinum utilization, triple phase boundary, mass transport, and durability. Little improvement has been made in novel fuel cell catalyst designs, in particularly, there is a lack of microstructural optimization. As a result, a relationship between the catalyst layer microstructure and fuel cell performance has not been established. This study addresses this crucial problem by finding connections between controlled microstructure and key fuel cell performance factors. Specifically, electrospun nanofibers as a catalyst support offered a number of controllable structural parameters including: porosity, fiber diameter, fiber alignment, and layer thickness. The material and structural properties of carbonized nanofibers were optimized by factorial design for incorporation into a fuel cell membrane electrode assembly. Validation of the structural and material properties of the carbon nanofiber catalyst support was analyzed by electrochemical, physiochemical, and microscopy methods.

Carbon nanofiber were integrated into membrane electrode assemblies and tested *in situ* to develop structure-property-performance relationships pertaining to Pt loading, ionomer loading, substrate electrical properties, and fiber mesh geometry. Performance was characterized by cyclic voltammetry, polarization, and electrochemical impedance spectroscopy. Results confirm not only ionomer thickness and loading, but more importantly ionomer distribution influenced polarization losses. 150  $\mu$ g cm<sup>-2</sup> and 250  $\mu$ g cm<sup>-2</sup> Pt loading achieved the same maximum current density, suggesting reduced loading maintained satisfactory Pt utilization, decreasing the amount of Pt. Although the influence of fiber orientation on fuel cell performance was inconclusive, fiber iii

electrical conductivity, ionomer thickness, and Pt distribution were found to be essential for the development of efficient low cost catalyst layers. In conclusion, carbon nanofiber catalyst support revealed enhanced surface area, durability, Pt utilization, and efficiencies due to the porous mesh structure.

### Lay Summary

Although fuel cells are considered an efficient means of converting chemical energy into renewable electrical energy, the technology faces challenges that prevent wide spread commercialization. The current Department of Energy goals propose a target cost of \$40 kW/hour by 2020. Recent research progressed steadily in this direction through reducing material costs and improving efficiencies. The catalyst layer in a fuel cell system, which consists of expensive Pt metal supported on carbon powder, is one chief area for improvement. By designing a catalyst layer with controllable geometry and microstructure, the fuel cell performance can be correlated to the specific material design parameters. Using electrospun carbon nanofibers (CNF), the catalyst showed enhanced surface area, electrical conductivity, and porosity—leading to improved designs in the future. The CNF catalyst achieved comparable power density to published results using alternative carbonaceous materials while using less Pt, validating the potential of CNFs as a support material.

### Preface

Unless otherwise stated below, the work presented in this thesis, including the literature review, research proposal preparation, experimental design and execution, data analysis and interpretation, and thesis preparation was completed by Sophia Shuk Kwan Chan, under the supervision of Dr. Frank Ko from the University of British Columbia and Dr. Jasna Jankovic from Automotive Fuel Cell Cooperation.

The publications arising from this work are listed:

- A version of Chapter 4 has been published. Chan, S., Jankovic, J., Madhu, S., Susac, D., Tam, M., Yang, H., Ko, F., Electrospun carbon nanofiber catalyst layers for polymer electrolyte membrane fuel cells: Fabrication and optimization, Journal of Materials Science. 53(16) (2018) 11633-11647. The author conducted all the testing and was responsible for preparation of the publication and its content.
- A version of Chapter 6 and 7 has been published. Chan, S., Jankovic, J., Madhu, S., Susac, D., Tam, M., Yang, H., Ko, F., Electrospun carbon nanofiber catalyst layers for polymer electrolyte membrane fuel cells: structure and performance, Journal of Power Sources. 392 (2018) 239-250. Dr. Madhu Saha and Dr. Jasna Jankovic operated the XRF for the Pt loading measurements. AFCC fuel cell operator was responsible for obtaining the *in situ* performance data (EIS and polarization data). S/TEM images/maps were acquired with the assistance of Dr. Jankovic. ALD Pt deposition was conducted by Dr. Philip Kubik at SFU 4D Labs. H<sub>2</sub> furnace was operated by AFCC research staff. The author was responsible for all other testing and preparation of the publication and its content.

A remaining manuscript is in preparation regarding portions of Chapter 5 and 6: Chan, S., Susac, S., Jankovic, J., Madhu, S., Kremliakova, N., Yang, H., Ko, F., "Electrospun carbon nanofiber catalyst layers for polymer electrolyte membrane fuel cells: functionalization and surface chemistry analysis". A portion of the orthogonally aligned nanofiber mats were fabricated by a volunteer student, Nerine Law, under the author's direction. Dr. Darija Susac assisted the author with portions of the XPS data collection and interpretation. The author conducted all other measurements and is responsible for preparation of the publication and its content.

Research results from this thesis work have been presented by Sophia Chan at the following conferences:

- Chan, S., Jankovic, J., Susac, D., Saha, M.S., Tam, M., Yang, H., Ko, F "Electrospun Carbon Nanofiber Based Catalyst Support for Proton Exchange Membrane Fuel Cell," in: Pacific Centre for Advanced Materials and Microstructures, December 10, 2016, Vancouver, BC, Canada (*poster*)
- Chan, S., Jankovic, J., Susac, D., Saha, M.S., Tam, M., Choi. J., Yang, H., Ko, F. 2016.
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Chan, S., Yip. G., Yang, H., & Ko, F. 2014. "Fabrication and characterization of electrospun poly(acrylonitrile) single nanofibers," in: SAMPE 2014, June 2-5 (Seattle, Washington, USA), Society for the Advancement of Material and Process Engineering.

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slope can be used to determine R <sub>ionic</sub>

# List of Symbols

Greek symbols				
Symbol	Description	Unit		
З	Dielectric constant			
$\eta_{Carnot}$	Efficiency of Carnot engine	%		
$\eta$ Electrochem,max	Efficiency of electrochemical cell	%		
$\eta_{s,a}$	Anodic activation overpotential	V		
$\eta_{s,c}$	Cathodic activation overpotential	V		
$\eta_{d,a}$	Anodic concentration overpotential	V		
$\eta_{d,c,}$	Cathodic concentration overpotential	V		
σ	Electrical conductivity	S cm <sup>-1</sup>		
R	Electrical resistance	Ω		
l	Length between the electrical contacts	cm		
A	Cross sectional area of the specimen	$\mathrm{cm}^2$		
ρ	Electrical resistivity	$\Omega$ cm		
η	Intrinsic viscosity	dL g <sup>-1</sup>		
γ	Surface tension	N m <sup>-1</sup>		
$ ho_c$	Density of bulk carbon fiber	g cm <sup>-2</sup>		
	Roman symbols			
Wout	Work output	J		
$Q_{in}$	Heat input	J		
Q	Flow rate	$m^3 s^{-1}$		
$Q_M$	Charge associated with the formation of a monolayer	mC cm <sup>-2</sup>		
$T_L$	System's low temperature	°K		
$T_H$	System's high temperature	°K		
$E_a$	Electrical potential at the anode	V		
$E_c$	Electrical potential at the cathode	V		
$E^{\circ}_{cell}$	Equilibrium cell potential at standard conditions	V		
$E_{cell}$	Equilibrium cell potential, non-standard conditions	V		

$E_{OC}$	Open circuit voltage (OCV)	V
F	Faradays constant	$\rm C \ mol^{-1}$
n	Number of moles of electrons	
$\Delta G_{rxn}$	Change in Gibbs free energy	J mol <sup>-1</sup>
$\Delta H_{rxn}$	Change in Enthalpy	J mol <sup>-1</sup>
R	Universal gas constant	J mol <sup>-1</sup> K <sup>-1</sup>
$p_{H_2}$	Partial pressure of hydrogen gas	Pa
$p_{O_2}$	Partial pressure of oxygen gas	Pa
$\Delta V_{ohm}$	Ohmic overpotential	V
i	Total current density	A cm <sup>-2</sup>
$i_{lim}$	Limiting current density	A cm <sup>-2</sup>
$i_0$	Exchange current density	A cm <sup>-2</sup>
d	Fiber diameter	nm
Ι	Current carried by the nanofiber	А
X	Ratio of the initial jet length to the nozzle diameter	
V <sub>tot</sub>	Total bulk volume including pore volume	m <sup>3</sup>
Vsolid	Volume of solids, minus pore volume	m <sup>3</sup>
<i>MCNF</i>	Mass of CNF fibers	g
LCNF	Geometrical length of CNF mat	cm
W <sub>CNF</sub>	Geometrical width of CNF mat	cm
$ au_{CNF}$	Geometrical thickness of CNF mat	cm
<i>M</i> <sub>dry</sub>	Mass of dry fiber mat	g
M <sub>wet</sub>	Mass of wet fiber after submersion	g
Msub	Mass of fiber during submersion	g
$A_{Pt}$	Electrochemically active surface area	$m^2 g_{Pt}^{-1}$
$R_{PI}$	Pressure independent resistance	s m <sup>-1</sup>
$R_{MT}$	Total mass transport resistance	s m <sup>-1</sup>
Rohm	Total ohmic resistance of the MEA	$m\Omega{\cdot}cm^2$
Rionic	Proton resistance of the catalyst layer	$m\Omega \cdot cm^2$
$C_d$	Double layer capacitance	F

### List of Abbreviations

- AFCC = Automotive Fuel Cell Cooperation
- ALD = Atomic layer deposition
- CAT = In-house test cell with larger active area (5 cm<sup>2</sup>)
- CB = Carbon Black
- CCM = Catalyst coated membrane
- CF = Carbon fiber
- CL = Catalyst layer
- CNF = Carbon nanofiber
- CNT = Carbon nanotube
- CV = Cyclic voltammetry
- CVD = Chemical vapour deposition
- DoE = Department of Energy
- DOE = Design of Experiments
- DMF = N,N'-Dimethylformamide
- ECSA = Electrochemically active surface area
- EPSA = Effective platinum surface area
- EDX = Energy-dispersive X-ray spectroscopy
- EIS = Electrochemical impedance spectroscopy
- FC = Fuel cells
- FFP = Flow field plate
- GDL = Gas diffusion layer
- HOT = Cell temperature is 85 °C and the inlet RH's are at 50%

- HOR = Hydrogen oxidation reaction
- I/C = Ratio between ionomer and carbon mass
- iLim = Limiting current density
- MAT = In-house test cell with small active area  $(1.13 \text{ cm}^2)$  for performance screening
- MEA = Membrane electrode assembly
- MPL = Microporous layer
- MWCNT = Multiwall carbon nanotube
- NOC = Normal operating conditions cell temperature is 68 °C and the inlet RH's are at 105%
- OAN = Orthogonally aligned nanofiber layer
- OCV = Open circuit voltage
- ORR = Oxygen reduction reaction
- PAN = Poly(acrylonitrile)
- PAN-Co-MA = Poly(acrylonitrile-co-methyl acrylate)
- PEMFC = Polymer electrolyte (Proton exchange) membrane fuel cell
- PTFE = Polytetrafluoroethylene
- PVP = Polyvinylpyrrolidone
- RH = Relative humidity
- RHE = Reversible hydrogen electrode
- RNL = Random nanofiber layer
- RSM = Response surface method
- SEM = Scanning electron microscopy
- SHE = Standard Hydrogen Electrode
- STP = Standard temperature and pressure

- TEM = Transmission electron microscopy
- TGA = Thermogravimetric analysis
- TPB = Triple phase boundary
- XPS = X-ray photoelectron spectroscopy
- XRD = X-ray powder diffraction
- XRF = X-ray fluorescence

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#### **1** Introduction and Background

#### 1.1 Motivation

One of the most well-known Nobel laureates of our time, Richard Smalley, predicted ten of humanity's most pressing problems for the next 50 years. Of the issues he listed, energy and environment placed first and fourth, respectively. Presently, 85% of world energy consumption comes from fossil fuels, a non-renewable source [1]. Because of the worldwide population and economic growth, demand for fossil fuels is rapidly increasing. Not only is the increasing demand for energy depleting oil reserves, fossil fuels emit large amounts of greenhouse gases into the environment, affecting global climate patterns. Of the total U.S. emissions in 2016 (6,511 Million Metric tons), transportation and electricity account for 28% each [2]. For this reason, there is a global effort in commercializing low carbon and renewable energy technologies such as: biomass, solar cells, batteries, nuclear, and fuel cells (FC). Of particular interest are fuel cells for large scale applications, such as transport vehicles, back-up generators, or stationary power generators [3]. In fact, commercialization of fuel cells is already underway. Globally, several countries have demonstration projects utilizing fuel cells in space vehicles, city buses, cars, and submarines. With global fuel cell investments totaling 355 million dollars from 2014 - 2016, fuel cells are gradually becoming an attractive option for green energy. Specifically, Polymer Electrolyte Membrane Fuel Cells (PEMFC) have enormous potential in reducing CO<sub>2</sub> emissions from portable and transportation applications. The low operating temperature and compact design make this type of fuel cell more attractive, gaining earnest attention in research and academia. In addition to eliminating toxic emissions, fuel cell technology is two to three times more efficient than internal combustion engines because electricity is produced via electrochemical reactions. PEMFC also

offer the advantage of minimal maintenance since there are no moving parts in the fuel cell stack compared to combustion engines. Moreover, unlike battery powered vehicles which require several hours to fully charge, the fuelling process for fuel cells is similar to that of gasoline engines [4]. Although PEMFC has numerous advantages it remains challenging to commercialize. In order to reach wide spread commercialization, substantial research progress has been made in developing inexpensive catalysts, porous structures, hydrogen storage solutions, and hydrogen extraction methods. Moreover, significant effort has been made in building the infrastructure to accommodate fuel cell vehicles. The infrastructure and cost challenges are thoroughly discussed in the literature and demonstrates the complexity of scaling-up [5–9]. While there are several areas for research and development, many studies aim to reduce the cost of PEMFC by targeting the most expensive component – the catalyst layer (CL) which consists of precious metals [10–16]. A breakdown of the total manufacturing cost of the fuel cell components reveal that the catalyst layer accounts for 43% of the overall cost (Figure 1-1) [17]. Figure 1-2 illustrates the current status of the Department of Energy (DoE) fuel cell goals. As shown in Figure 1-2, the fuel cell cost and durability are the two targets the industry has yet to reach [3]. To meet the goals of \$40/kW and 5000 operational hours by 2020, a more collaborative effort to develop the membrane electrode assembly (MEA), particularly, the catalyst layer is paramount.



Figure 1-1: Breakdown of the 2016 projected fuel cell stack cost at 500,000 units per year



**Figure 1-2: Fuel cell performance targets for year 2020 issued by U.S. Department of Energy [3]** <sup>*a*</sup> *Ratio of direct current output energy to lower heating value of hydrogen* 

<sup>b</sup> Target includes fuel cell stack, BOP, and thermal system, and excludes hydrogen storage, battery, electric drive, and power electronics

<sup>c</sup> Based on Pt cost of \$1,550/troy ounce and cost projected to high-volume production (500,000 fuel cell stacks per year)

The catalyst layer's main function include: catalysis of the anode and cathode reactions, transport of fuels to reactant sites, conduction of protons and electrons, and water and heat removal [18]. In a PEMFC, the cathode oxygen reduction reaction (ORR) ( $\frac{1}{2}O_2 + 2H + 2e^- \rightarrow H_2O$ ) is torpid under the typical operating conditions, thus Pt catalyst is necessary to improve the kinetics of the cathode reaction. Much of the current research is related to developing new catalyst materials or metal alloys [10,13,19,20]. However, in addition to the cost of catalyst, there are several issues with the current catalyst layer including: catalyst activity, corrosion, lack of triple phase boundary, durability, and water removal. Research has shown that these challenges could be resolved by developing novel catalyst support structures that exhibit higher surface area, porosity, and conductivity [14,16,21–24].
Efficiency, performance, and durability of a PEMFC MEA depend largely on the microstructure and composition of the anode and cathode catalyst layers. A conventional PEMFC electrode catalyst layer comprises of catalyst Pt nanoparticles dispersed on an electrically conductive carbon black (CB) support arranged in connected agglomerated domains [25]. The porous CB structure, coated with a layer of ionomer (such as Nafion), provides a percolation path for electron and proton transport. The CB microstructure is irregular and often non-homogeneous, with highly tortuous transport paths for electrons, protons, and gas. Because of the inherent properties of CB, conductivity and gas diffusivity are insufficient, and portions of the Pt catalyst are buried within the agglomerate which becomes inaccessible for the reaction. The triple-phase boundary (TPB) is often not continuous and unavailable because of the agglomeration due to corrosion under operating conditions, reducing catalyst activity [26–28]. The concept of TPB is widely investigated in literature and states that ORR can only occur when proton conductive electrolyte, gas, and electrically connected catalyst are in contact with one another [29,30]. At high current densities cathode flooding (blocked pores) is an issue because product water does not quickly diffuse out of the MEA and causes reduction of gas diffusion. Furthermore, fabrication of these catalyst layers is not a fully controllable process; hence the properties of the layers and fuel cell performance cannot be easily refined. Due to the irregularity of the catalyst layer and inability to control the manufacturing process and layer parameters, there is a lack of understanding of the complex electrode structure and the factors that influence the catalyst activity and durability. Due to the disadvantages of carbon blacks, several studies focused on developing advanced materials with high surface area as the catalyst support material [31]. Recent research revealed the advantage of organized catalyst support structures and suggests that the geometry of macropores improved water management and mass transport [24,32,33]. Additionally, several types of carbon based

catalyst supports have shown promising results, including CNT and CNF [31,34]. Although studies have demonstrated performance improvement using novel catalyst structures, systematic research on the effect of geometry and organized microstructure on key fuel cell performance factors has been scarce. As a result correlations between microstructure and performance have not been established.

Realizing the challenges associated with the current catalyst supports, this thesis addresses the research opportunity regarding catalyst supports in the scope of material processing and fabrication. The development of highly controlled structures, coupled with full characterization of the material and structural properties, enables understanding of the relationships between fuel cell catalyst layer microstructure and its performance, knowledge crucial for further fuel cell technology development. Investigating the design of the catalyst support layer microstructure allows for fine tuning of key fuel cell performance factors, increasing fuel cell efficiency and reducing costs. This will lead to more compact devices, less materials usage, and more efficient manufacturing of MEA, hence lowering the cost of industrial production.

This thesis research aims to develop CNF based catalyst layers with optimized material and structural properties (porosity, electrical conductivity, fiber diameter, and mechanical strength) to investigate key fuel cell design parameters, such as support geometry, Platinum (Pt) loading, ionomer loading and distribution, Pt deposition methods, and substrate electrical conductivity. The study involves developing methods and techniques to optimize the fiber properties, Pt deposition, and ionomer morphology. This will enable understanding of the catalyst support layer and effect of various design parameters on fuel cell properties and performance. Although prior work has shown promising results using alternative carbonaceous materials in the catalyst, few have discussed the relationship between key fabrication parameters, material properties, and fuel cell

performance [22,35–41]. The current goal of the study is to compare the effect of orthogonally aligned and randomly oriented fibers on fuel cell polarization losses. Gaining a fundamental understanding of the catalyst structure could potentially improve Pt utilization, durability, water management, and mass transport, further improving fuel cell performance. Research in this unexplored area may improve current fuel cell designs, addressing DoE economic goals which lead to commercialization.

#### 1.2 Fuel cells

#### **1.2.1** Introduction and history of fuel cells

Since the discovery of fuel cells in the early 1800s, several types of fuel cells are currently in different stages of development. Fuel cells are often categorized by the type of electrolyte used. The types of fuel cells include: alkaline fuel cell (AFC), direct methanol fuel cell (DMFC), solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC), and polymer electrolyte membrane fuel cell (PEMFC) [3]. PEMFC is considered a promising candidate for next generation automobiles due to its high power density and lower operating temperature. PEMFC, the focus of this research, is a zero emission energy device that can reduce greenhouse gas emissions if commercialized.

The first demonstration of fuel cells was in 1839 by Sir William Robert Grove. However, the modern day fuel cell concept was not developed until the 1950s and 1960s. The first ever PEMFC was used in NASAs 1965 Gemini space flights as an auxiliary power source [42]. During the NASA Gemini program, the polymeric membrane was a type of polystyrene with low durability and conductivity. General Electric also used fuel cells to provide drinking water for the crew during space missions. In 1968, DuPont developed proton conducting electrolyte called Nafion and tested the first Nafion based PEMFC in 1969 [43]. General Electric developed PEMFC

for submarines used in the U.S. Navy from 1974 – 1976 using the same ion exchange membrane developed by DuPont for the Gemini 5 mission [42]. Siemens also developed PEMFC for submarines which were used by the German Navy in 2002 [42]. In 1993, Ballard presented the first fuel cell powered bus and in 1997 Daimler-Benz and Toyota launched prototype fuel cell cars [42,44]. Ballard deployed 30 fuel cell buses in 10 European cities [45]. In 2017, Ballard becomes the first fuel cell company to power buses for more than 10 million cumulative kilometers of revenue service [45]. Several fuel cells were later developed for backup power, stationary power generators, and fork lifts [42]. Since then, an increasing number of research has focused on hydrogen storage and extraction, fuel infrastructure, and improving fuel cell vehicles in collaboration with auto manufacturers.

According to the DoE, 62,000 fuel cells were shipped worldwide in 2016 [46]. There are three main markets for fuel cell technology: stationary power, transportation, portable power. The impressive 65% growth from 2014 to 2015 was largely attributed to a growth in the stationary and transportation sector. In the stationary sector, utilities in Korea and the U.S. are installing large-scale fuel cell power parks, contributing to a large portion of the 20% growth in fuel cell shipments. The gradual growth in light duty vehicles in California, Europe, and Japan also account for the increase in shipments in the transportation sector. Electric vehicle sales from Hyundai and Toyota, along with stationary fuel cells from Korea and Japan, increased Asian shipments by double from 2014 to 2015 [42]. In 2016, China emerged as a leading customer for fuel cell buses, with more than 30 deployed [46]. Furthermore, in addition to government research support, private investors globally have invested \$355.8 million into fuel cell companies between 2014 – 2016 [46]. As the potential for fuel cells is realized, governments will continue to support programs and create new policies and initiatives to encourage global development and commercialization of fuel cells.

Improving fuel cell technology could have a significant impact on the society and alleviate the dependency on oil, creating a more sustainable future.

## **1.2.2** Electrochemistry and basic principle

In order to understand how the fuel cell and its components operate, a brief discussion about thermodynamics and electrochemistry is presented. There are two main pathways of converting chemical energy into useful work – heat engines and electrochemical devices. Heat engines typically burn gasoline, coal, or oil, converting heat energy into mechanical work. Based on the second law of thermodynamics, the efficiency of a Carnot engine is defined by:

$$\eta_{Carnot} = \frac{W_{out}}{Q_{in}} = 1 - \frac{T_L}{T_H}$$
(1.1)

Where  $\eta_{carnot}$  is Carnot efficiency,  $W_{out}$  is work output,  $Q_{in}$  is heat input,  $T_L$  is the system's absolute low temperature, and  $T_H$  is the heat engines absolute high temperature. This means, to achieve maximum efficiency,  $T_H$  should be as high as possible, restricted by flame temperature and material properties (Figure 1-4). Carnot engine could never reach 100% efficiency because of the presence of wasted heat.



Figure 1-3: Example of basic electrochemical cell, current travels from anode to cathode

In comparison, electrochemical devices like batteries or fuel cells directly convert chemical energy into electrical energy, avoiding conversion losses present in heat engines (Figure 1-3). An electrochemical cell, such as a battery, consists of two half-cells. As shown in Figure 1-3, each half-cell consists of an electrolyte and electrode. A spontaneous redox reaction, where one half-cell loses electrons (oxidation) and one half-cell gains electrons (reduction) from their electrode, generates an electric current which is carried by an external circuit. This constant flow of electrons from the electrode produces a direct current which can be used to do work. One way to define electrochemical efficiency is through maximum thermodynamic efficiency, given by:

$$\eta_{electrochem,max} = \frac{\Delta G_{rxn}}{\Delta H_{rxn}} = -\frac{nFE_{cell}}{\Delta H_{rxn}} \times 100\%$$
(1.2)

Where  $\Delta H_{rxn}$  (J mol<sup>-1</sup>) is the change in enthalpy,  $\Delta G_{rxn}$  (J mol<sup>-1</sup>) is the change in Gibbs free energy, *n* is the number of moles of electrons, *F* is Faraday's constant, and E<sub>cell</sub> is the electrical potential. Actual efficiency is calculated based on operating cell voltage, rather than ideal equilibrium cell voltage. Fuel cells are often compared to efficiencies of Carnot heat engines. Below is an illustration comparing the two device's theoretical efficiency with regards to operating temperature (Figure 1-4). The graph clearly shows the advantages of fuel cells at lower operating temperatures compared to heat engines. Although the graph represents theoretical values, the difference in energy output at low temperatures is quite substantial. This means that fuel cells can operate at a much lower temperature while maintaining high efficiencies, ideal for automotive applications.



Figure 1-4: Comparison of the theoretical reversible work as a function of operating temperature for heat engine and fuel cells [44] (reproduced with permission)

$$E^{\circ}_{cell} = E^{\circ}_{c} - E^{\circ}_{a}$$
(1.3)

$$2H_2 \rightarrow 4H^+ + 4e^ E^\circ = 0 V vs. SHE$$
 (1.4)

$$0_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
  $E^\circ = 1.23 \text{ V vs. SHE}$  (1.5)

$$0_2 + 2H_2 \rightarrow 2H_20$$
  $E^\circ = 1.23 V$  (1.6)

$$E_{cell} = E_{cell}^{\circ} - \frac{RT}{nF} ln \left(\frac{1}{p_{H_2} p_{O_2}^{1/2}}\right)$$
 Nernst Equation (1.7)

In the case of standard temperature and pressure (STP), theoretical cell potential is given as the difference between the standard half-cell potential of the cathode and anode (1.3). Thus, given the half-cell potentials for the  $H_2/O_2$  redox reaction,  $E^{\circ}_{cell}$  of a PEMFC is 1.23 V (1.6). However when the cell is operating at non-standard conditions, the equilibrium cell potential is calculated from the Nernst equation. The Nernst equation can be expressed in several ways, a general expression for a  $H_2/O_2$  fuel cell is shown in (1.7). This expression gives the equilibrium cell potential when no current is flowing, or open circuit voltage (OCV). However, in reality, the OCV is much less than theoretical values. In addition, the voltage falls when more current is drawn from the fuel cell. A typical performance diagram for fuel cells is shown in Figure 1-5. The shape of the graph can be explained by four major irreversibilities (overpotential): (1) activation losses, (2) fuel crossover and internal currents, (3) ohmic losses, and (4) mass transport or concentration losses. Activation loss is caused by the slow kinetics of the reaction at the electrode surface. The transfer of electrons to or from the electrode uses a portion of the generated voltage. Fuel crossover is energy loss in fuel passing through the electrolyte, affecting the OCV of low-temperature cells. Ohmic losses occur because of various resistances associated with interconnects and materials inside the MEA, as well as resistance to the flow of ions through the electrolyte. The voltage drop is linear, proportional to current density. Concentration loss occurs when insufficient fuel is transported to the electrode surface. Because mass transport is responsible for the reduction of fuel concentration at the electrode surface, it is also termed mass transport loss. Therefore, the actual fuel cell voltage can be expressed by subtracting all the irreversibilities:

$$E = E_{OC} - |\eta_{s,a}| - |\eta_{s,c}| - |\eta_{d,a}| - |\eta_{d,c}| - \Delta V_{ohm}$$
(1.8)

Where E is actual cell voltage,  $E_{OC}$  is open circuit voltage (OCV),  $\eta_{s,a}$  is anodic activation (surface) overpotential,  $\eta_{s,c}$  is cathodic activation overpotential,  $\eta_{d,a}$  is anodic concentration (diffusion) overpotential,  $\eta_{d,c}$  is cathodic concentration overpotential, and  $\Delta V_{ohm} = iR$  is the ohmic overpotential (*i* is current density, *R* is area-specific resistance). The mathematical expressions for each overpotential has been defined and detailed in literature and cited text (appendix) [18,44].



Figure 1-5: Sources of overpotential and the resulting polarization curve [47] (reproduced with permission)

Considering the sources of overpotential, there are a number of ways to improve the performance or decrease the losses. Since activation loss is governed by the  $i_0$  exchange current density (i.e. the constant forwards and backwards flow of electrons to and from electrode at equilibrium). The current density is important to fuel cell performance and it is crucial to make this current density as high as possible. Some suggested ways to improve exchange current density include: using effective catalyst, increasing electrode surface roughness, increasing reactant concentration, and increasing input gas pressure [44]. The advantage of using an effective catalyst is clearly shown in Table 1-1, where Pt and Pd display the highest  $i_0$ . Generally, Pt is more suitable in acidic media and Pd in alkaline media due to instability and corrosion [15,19]. Additionally, increasing roughness of the electrode increases the available surface area per geometric area, thus allowing available surface for the catalyzed reaction to occur. Similarly, methods to decrease ohmic resistance within the stack include employing: electrodes with higher conductivity, thinner electrolytes, and appropriate materials and design. To decrease concentration losses, fuel cell design should be wary of partial pressure drops due to the consumption of the fuel at the surface

and electrode flooding. Insufficient water removal can plug the pores and slow down reactant gas diffusion [44].

Metal	<i>i</i> ₀ (Acm <sup>-2</sup> )
Pb	2.5 x 10 <sup>-13</sup>
Zn	3 x 10 <sup>-11</sup>
Ag	4 x 10 <sup>-7</sup>
Ni	6 x 10 <sup>-6</sup>
Pt	5 x 10 <sup>-4</sup>
Pd	4 x 10 <sup>-3</sup>

Table 1-1: Exchange current density (*i*<sub>0</sub>) for various metals in acid media [44]

### **1.2.3** Fuel cell design and components

## **1.2.3.1** The fuel cell assembly

A typical fuel cell stack contains a crucial arrangement called the Membrane Electrode Assembly (MEA). This is the core of the fuel cell, where redox reactions take place to generate electricity. The basic components of the MEA include: gas diffusion layers with microporous layer, cathode and anode catalyst layers, and a proton conductive electrolyte membrane (Figure 1-6). Typically, the anode or cathode will be no more than 10  $\mu$ m thick while the ionomer membrane ranges from 10 - 25  $\mu$ m [48]. The redox reactions occur at the electrodes and they depend on the type of the fuel cell. In a PEMFC, the hydrogen oxidation reaction (HOR) occurs at the anode, releasing electrons and protons (H<sup>+</sup>), as shown in (1.4). Protons are conducted through a proton conductive electrolyte membrane to the cathode, where the oxygen reduction reaction (ORR) occurs (1.5). The overall reaction is given by (1.6). Electrons released at the anode flow to the cathode through an external circuit to generate direct current.



Figure 1-6: Schematic of membrane electrode assembly components [18] (reproduced with permission) The MEA assembly is about a few hundred microns in thickness and can generate power densities up to about 1 W cm<sup>-2</sup> of electrode area when supplied with air and hydrogen [18]. As mentioned above, the PEMFC operates at a comparatively lower temperature than other fuel cells because it is limited by the necessity to humidify the electrolyte to effectively transport protons. The following sections describe the structure and function of each component in the MEA.

## **1.2.3.2** Gas diffusion layers

In a fuel cell, membrane and the two catalyst layers are sandwiched between two gas diffusion layers (GDL), usually ~200  $\mu$ m thick. Beside mechanical support, GDL provides an electrically conductive pathway for current collection between the flow field plate (FFP) and the electrode and enables reactant gas transport to the electrodes and liquid waste water removal. Figure 1-7 shows the supply of reactant gas through the gas channels on the FFP. The gas diffuses through the GDL uniformly, contacting the entire catalyzed surface area. The reaction is initiated by the catalyst and the electrons are released generating a current (1.4). Only the landing areas can conduct electric current, therefore the GDL transports the current laterally to the contact points [18]. It is typically

fabricated using carbon cloth or paper for its porous properties (Figure 1-8) [18]. The GDL has a number of functions and roles in the MEA: (i) it must be both thermally and electrically conductive through-plane and in-plane to transport electrons to the FFP, (ii) it must be sufficiently porous to allow waste water removal and transport of reactant gas, and (iii) it must provide structural support while maintaining ample flexibility to ensure adequate electrical contacts. Since the flux through the GDL is in both directions, it is important to ensure that the small carbon particles from the conventional catalyst layer do not migrate through; thus small pores (20 - 300 nm) are required to eliminate this concern [49,50]. This is usually addressed by the use of a Micro Porous Layer (MPL), a non-catalytic layer consisting of carbon particles and a hydrophobic binder, Polytetrafluoroethylene (PTFE). Because MPL plays a critical role in the MEA, substantial research has been done to understand and improve the interfacial properties with regards to material design [51,52]. The MPL and PTFE ensures better electrical contact to the electrodes while maintaining moisture levels in the membrane, essential for achieving high proton conductivity [49]. GDL layers are fabricated to possess hydrophobicity to avoid flooding and enable rapid gas diffusion [18,49]. Traditionally, MEAs are manufactured by stacking the catalyst layer onto the GDL, then hot-pressing the GDL to the polymer membrane [49].



Figure 1-7: Cross section of MEA components [18] (reproduced with permission)



Figure 1-8: Micrographs of commercial carbon fiber paper and carbon cloths (a: Toray Industries, b: SGL, and c: E-Tek) [18] (reproduced with permission)

## 1.2.3.3 Catalyst layers

The efficiency and performance of a membrane electrode assembly (MEA) depends largely on the composition and microstructure of the two catalyst layers, especially the cathode, where the kinetically slow reaction of oxygen reduction takes place. The conventional material used for commercial applications consists of agglomerated domains of carbon blacks which form an



electronically conductive structure by providing a percolation path for electron transfer. Typically, a thin catalyst layer of less than 0.5 mg<sub>Pt</sub> cm<sup>-2</sup> is desirable to maintain efficiency while keeping costs low [25]. The catalyst layer consists of dispersed nanoparticles of noble Pt catalyst (2 - 4 nm) on the carbon

Figure 1-9: Schematic of agglomerate based microstructure and Triple Phase Boundary (TPB)

support and a coating of ionomer (such as Nafion) as the proton conducting network [27]. Together, the proximity of these three materials form an interface called the triple-phase boundary (TPB). This is where the electronic and protonic conductive phases and gas come into contact with the catalyst (Figure 1-9) [29]. One of the challenges in conventional fuel cell is attributed to the mesoporous carbon structure since carbon degrades during start up and shut down procedures. This leads to carbon agglomeration and buried Pt particles which limit the TPB availability [53].

The degradation of carbon support and Pt are exacerbated by the presence of one another. Generally, the presence of Pt catalyzes the oxidation of carbon (1.9), while the oxidation of carbon accelerates Pt sintering/agglomeration. The agglomerated or large Pt particles end up having lower surface area and limited access to the gas, reducing the catalyst activity and ultimately the fuel cell efficiency. Cathode flooding is also a concern since the gas cannot diffuse through the pores flooded with the product water at the cathode. Additionally, carbon monoxide (CO) concentrations as low as 10 ppm can significantly decrease the performance. CO poisoning occurs because CO adsorbs strongly to Pt surface causing the active catalyst surface area to decrease [25]. This thin layer of CO prevents the adsorption of H<sub>2</sub> onto the Pt surface, therefore the reaction cannot take place, reducing the fuel cell efficiency. Similarly, CO<sub>2</sub> can produce CO by the reverse water-shift reaction, leading to the same CO poisoning effect (1.9). With the diverse issues associated with catalyst active surface area, it is essential to gain a fundamental understanding of the catalyst layer.

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$
  

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$E^\circ = 0.207 \text{ V vs. RHE}$$
(1.9)

A number of studies have been focused on improving the catalyst layer by introducing advanced materials that offer high surface area and stability. Several groups constructed novel supports to improve the Pt deposition and loading challenges [16,22,31,39,54,55]. Some groups manufactured nanowires, platinum coated whiskers, ordered carbon supports, and carbon nanotube supports with promising results [19,38,56–58]. Unfortunately, none of the studies show a significant reduction in catalyst loading while maintaining high level of fuel cell performance and satisfactory durability. To remain economically viable, much research is needed to improve the stability and efficiency of PEMFCs. In this study we will investigate the relationship between the catalyst layer's material properties and the overall fuel cell performance.

#### 1.2.3.4 **Proton conductive membrane and ionomers**

According to the chemical reactions happening at the anode catalyst layer shown in (1.4), the hydrogen is split into protons and thus need to be transported across the proton conducting



electrolyte membrane and recombine with oxygen to produce water at the cathode (1.5). In addition, a proton conductive network of ionomer must be present in the



electrodes in order to carry the protons required for the redox reaction. Kreuer and Grotthuss proposed two main mechanisms for proton migration through the membrane and the ionomer network: (1) proton diffuses through the electrolyte medium as a "vehicle," in this case as  $H_3O^+$ ; and (2) "proton-hopping", wherein protons are transferred from one vehicle to the next by simultaneous reorganization and reorientation of the species [59,60].

The first types of polymer used as a membrane material were perfluroinated polymers; however it was not feasible for prolonged usage because the durability was poor under oxidizing environments. Soon after, the industry discovered perfluorinated sulfonic acid (Nafion) membranes and ionomers, consisting of a polymerized tetrafluoroethylene (PTFE) backbone, giving it reliable chemical inertness. The cation exchange is realized by the sulfonic acid side chain groups  $-SO_3H$ . The acidity or exchange capacity of this polymer is measured by equivalent weight (EW)—lower EW denotes higher conductivity [18]. Nafion is currently the preferred ionomer membrane for fuel cell applications [18]. One limitation to Nafion, is that it is strongly dependent on the level of moisture. Beyond 100 °C there is insufficient hydration in the membrane and the conductivity drops dramatically.

## 1.3 Current catalyst layer materials

Conventional support material will be discussed in detail to highlight key challenges and disadvantages in catalyst performance. Because of current material challenges, an increasing number of research is focused on developing the support material to improve performance and durability in the fuel cell. Development of new carbon based catalyst support structures show advantages in terms of durability and catalyst activity compared to conventional materials. The fabrication and characteristic of the new carbon materials will be discussed.

#### **1.3.1** Conventional carbon supports

The catalyst support has a crucial function to the fuel cell performance. The support must have high surface area, porosity, electrical conductivity, and corrosion resistance. Thus, low cost carbon materials are traditionally used as the Pt support in low temperature PEMFC. Carbon black, typically produced by pyrolysis of hydrocarbons such as natural gas or oil fractions from petroleum processing, are widely used as catalyst support in PEMFC. Carbon black is a polycrystalline or amorphous form of carbon consisting of spherical particles of graphite below 50 nm in diameter and up to 250 nm when coalesced into aggregates [34]. The morphology and particle size distribution varies depending on the raw material and the thermal decomposition process. One example of an oil-furnace carbon black is Vulcan XC-72. This low cost and abundant material is produced by burning raw materials at about 1400 °C. The surface area of the support material is of utmost importance since it is related to Pt active surface area. Typically, the surface area of Vulcan material is about 250 m<sup>2</sup> g<sup>-1</sup>, however with additional activation steps, the BET surface area could increase up to  $800 - 1200 \text{ m}^2 \text{ g}^{-1}$  depending on the degree of activation [34]. CB can be activated by chemical (oxidative treatment) or physical activation (thermal treatment). Some known chemical activation methods include: addition of ZnCl<sub>2</sub> or H<sub>3</sub>PO<sub>4</sub> to the carbon precursor

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or oxidative treatments using HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub> or O<sub>3</sub> [22,34]. Activation of CB increases the microporosity (pores < 2 nm), thereby improving Pt dispersion and utilization [22]. Thermal treatment involves heating the carbon under inert atmosphere up to 800 - 1100 °C or in air/steam at 400 - 500 °C. The process removes surface impurities, thereby increasing the active surface area as shown by an increase in capacitive current during CV measurements [22].

Because PEMFC operates in extreme conditions, high humidity, low pH (< 1), and strongly reducing or oxidizing atmospheres (at the anode and cathode), there are often issues with catalyst and carbon stability. In addition, the path for electron, proton, and gas transport is erratic and sluggish because the microstructure is irregular and non-homogenous. Some other persistent problems associated with CBs include: (i) presence of trace organic sulphur compounds residual from petroleum (raw material) [16] and (ii) deep depressions that submerge the catalyst nanoparticles making them inaccessible to reactants leading to poor catalytic activity [16]. Additionally, CB is electrochemically unstable under certain fuel cell conditions, causing corrosion and thinning of the catalyst layer, which leads to the loss of active surface area and performance of the fuel cell [16]. Pt active surface area decreases because carbon degradation causes Pt particles to coalesce and form large aggregates or dissolve into the ionomer phase.

#### **1.3.2** Advanced material supports

There are several types of carbon structures that were studied for fuel cell applications. Antolini gives a comprehensive review of new carbon materials for the application of fuel cells and their performance and attributes compared to traditional materials [22]. Some of the mentioned carbon structures include mesoporous carbons, carbon nanotubes, carbon nanohorns and nanocoils, activated graphite fibers, and activated carbon nanofibers.

Because of the complex structure of conventional catalyst layers and the lack of knowledge about the factors that influence the catalyst layer efficiency, alternative structures such as carbon nanofibers and carbon nanotubes were investigated to improve catalyst efficiency and increase electrochemical surface area (ECSA) [35,41,54,56,61–64]. Owing to its large aspect ratio, Pt can be thinly distributed over the fiber surface; thus reducing costs and maintaining high efficiency. The continuous network of fibers provides high porosity improving fuel diffusivity and electrical conductivity by having an organized and straightforward path. The most traditional methods of fabricating CNFs are catalytic chemical vapor deposition or chemical vapor deposition with variants like thermal and plasma-assistance. The first CNFs were produced by decomposition of hydrocarbons over metal particles. Unlike CNT that are generally few tens of nanometers in diameter and few micrometers in length, CNF may go up to 500 nm in diameter and span several millimeters in length. The main differences between CNF and CNT are their size, morphology, processing technique, and price. Additionally, CNFs can be fabricated in several ways resulting in different structures and dimensions. In general, CNF can be categorized into three types: (i) ribbon like CNF, (ii) platelet CNF, and (iii) herringbone (or stacked-cup) CNF [44]. Each have their own unique set of properties and characteristics, however, herringbone is considered to be a balance between ribbon and platelet types, yielding higher catalytic activity than ribbon and better durability than platelet forms [16]. Since CNF have a peculiar structure, they generally do not need to be pre-treated for functionalization. CNF prepared in this manner can achieve a surface area of up to 120 m<sup>2</sup> g<sup>-1</sup>, diameter of about 100 – 150 nm and length of about 5 – 50 um [65]. Overall, CNF produced by chemical vapor deposition (CVD) improved catalytic activity in the fuel cell and obtained comparable ECSA to CNT at a fraction of the cost [66].

One of the earliest studies of CNF as catalyst support was reported by Rodriguez et al. for the support of Fe-Cu particles [67]. Since then, CNF has become a popular research topic as fuel cell catalyst support materials [68]. The CNF were generally fabricated by CVD techniques. Much of the reported uses of CNF are related to applications associated with direct methanol fuel cell (DMFC). Although the reports found positive and promising results, the DMFC assembly is beyond the scope of this project [69-72]. Of the CNFs reported for use in PEMFC, Li et al. prepared Pt nanoparticles (2 - 4 nm) supported on stacked-cup (SC) CNFs using polyol process. The Pt/SC-CNFs combination MEA displayed higher PEMFC performance than conventional CB supports (from 750 to 900 mW cm<sup>-2</sup>). According to the study, the high aspect ratio CNF formed a continuous conductive network within the Nafion matrix which attributed to improved fuel cell performance [63]. Zheng et al. also reported the effects of CNF microstructure on oxygen reduction reaction (ORR) activity [73-75]. They fabricated platelet (p-CNF), tubular (t-CNF), and fish bone (f-CNF) type CNF and conducted cyclic voltammetry analysis. The findings suggest that the ORR process on p-CNF, f-CNF and graphite are controlled by diffusion, whereas ORR on t-CNF is mutually controlled by surface reaction and diffusion [73,74]. Álvarez et al. synthesized CNF by decomposition of methane and deposited Pt by formic acid method. Single cell performance was conducted for CNF/Pt, Pt/f-CNF (functionalized), and Pt/CB. The ORR results found that CNF/Pt performed 1.5 times higher than Pt/CB at 600 mV [76]. The authors conclude that functionalization of the CNF surface negatively impacted the fuel cell performance because of the hydrophilic surface. The CNF was shown to be more resistant against electrochemical corrosion than CB under experimental conditions, possibly due to the difference in microstructure. The study suggests that improvement in ORR performance is attributed to the difference in textural properties and smaller number of micropores in the CNF support, thus increasing electroactive surface area and mass

transport compared to CB [76]. A brief table of notable CNF and CNT catalyst layers synthesized by different methods is presented in the appendix for further reading (Table A-1).

### **1.3.3** Geometry of catalyst support

Traditional CB have a non-homogenous and irregular microstructure that lack controllable parameters. Some research has been done to fabricate organized and ordered catalyst structures to improve the Pt utilization and mass transport. One study used aligned CNT (5 - 20 nm diameter)and 10 µm length) prepared by chemical vapor deposition as a cathode catalyst substrate. The aligned CNT decorated with nano Pt was synthesized with tunable nanopore diameter and structure, providing efficient channel for gas transport between individual CNTs [56]. Compared to commercial ink based MEA (470 mW cm<sup>-2</sup>), the aligned CNT achieved a peak power density of 860 mW cm<sup>-2</sup> at 0.4 V in oxygen atmosphere. The authors concluded that the substantial improvement in power density is due to better mass transfer of fuel and conductance between MEA and current collector by having aligned CNT structure and uniformly ordered nanopores [56]. A few studies have also fabricated ordered mesoporous carbon as electrocatalysts for fuel cells [32,55,77,78]. Kim et al. reported a novel platinum electrocatalyst for PEMFC application [24]. The unique 3D ordered macroporous inverse opal structure exhibited large porosity and low tortuosity with interconnected macropore network. The Pt (wall thickness 10 - 15 nm) electrode thickness was  $1.5 - 2 \mu m$  thick, decreasing diffusion distance and increased conductivity of reactants and ions. The 3D ordered structure achieved a current density of 440 mA cm<sup>-2</sup> at 0.6 V under fully humidified operating conditions [24]. Polarization results revealed enhanced mass transfer and water management compared to ink based catalyst layers in the high limiting current region because of the desirable 3D ordered geometry. The study concluded that 3D macroporous inverse opal structures had superior mass transport and water management as a result of the large

effective porosity and interconnected macropores, yielding short diffusion pathways and low tortuosity [24]. Xia et al. created a bio inspired hierarchical nanoarray decorated with Pt nanoparticles as a cathode layer [58]. The highly oriented nanowire array provided smooth mass transport channels facilitating fast charge and mass transport. The well-defined microstructure surpassed DoE goals achieving peak power density of 0.778 W cm<sup>-2</sup> with a low Pt loading of 0.065 mg cm<sup>-2</sup>. When compared to conventional catalyst with higher Pt loading (198 µg cm<sup>-2</sup>), the nanoarray demonstrated excellent Pt utilization and ECSA, achieving similar OCV [58]. Overall, the authors concluded the threefold power density improvement compared to conventional CB is due to the finely oriented nanowire arrays that provide smooth mass transport channels, enhancing Pt utilization and eventually reducing fuel cell costs [58]. The current literature establishes the remarkable improvements in PEMFC using ordered catalyst structures, addressing issues such as water management, mass transport loss, and Pt utilization.

## **1.3.4** Electrospinning in fuel cell applications

More recently, electrospinning has become a popular way to produce continuous CNFs due to the relative simplicity of the fabrication technique and controllable fiber properties [79]. Because of the relatively low fabrication cost and tailorable processing parameters, there is a growing number of research utilizing electrospun nanofibers as electrode materials [80–84]. The fabrication process involves electrospinning a precursor material (Polyacrylonitrile, Lignin, Polyacrylic Acid) which is later carbonized at elevated temperatures to produce carbon fibers (Chapter 1.5). CNFs made by electrospinning are beneficial because the fibers are continuous and the dimensions and porosity can be tailored [85–91]. Fiber diameter will vary depending on the precursor material and electrospinning conditions used. According to the review by Cavaliere, CNF diameters for catalyst support layers are typically between 50 – 700 nm. Electrospun CNFs

have been tested in DMFC and PEMFC fuel cells using Pt, PtRu, Pd, and PtRh catalysts [84]. Typical methods of depositing catalyst onto the CNF layer include electrospinning a suspension of Pt powder, electroless plating, electrodeposited, wet impregnation, magnetron sputtering, and spraying Pt powder onto the carbon layer [75,84,92].

One of the pioneer work conducted by Mathew et al., demonstrated the use of electrospinning to fabricate electrodes using three commercial catalysts [93]. Nanofiber mats were fabricated using a spinning dope consisting of a commercial catalyst (Vulcan and Ketjen Black), Nafion solution, and Poly(acrylic acid). The Poly(acrylic acid) was used as a carrier polymer to prevent droplets and form continuous Nafion fibers [93]. The study found nanofiber electrode based MEAs achieved power densities of up to 470 mW cm<sup>-2</sup> at 0.65 V under moderate operating conditions. The study also concluded that the performance of the MEA was insensitive to changes in the fiber ionomer content and did not change significantly with average fiber diameter in the range 200 - 500 nm [93]. Another two studies published by the same group showed the performance was improved because of the nanofiber morphology allowing lower Pt loadings and rapid expulsion of water [94,95]. In another study, Polyacrylonitrile (PAN) based electrospun CNF sprayed with 20 wt% Pt slurry was characterized in PEMFC [35]. The results showed that the surface area before Pt deposited and after deposition on electrospun CNF did not change ( $\sim 300 \text{ m}^2$  $g^{-1}$ ). This is an important observation because it demonstrates that the Pt is unable to penetrate through the shallow pores on the fiber surface, maintaining the large surface area. Furthermore, electrospun CNF was shown to possess much higher Pt utilization than Vulcan XC-72R (carbon black), 69% compared to 35% [35]. In a similar study, Pt nanoparticles were deposited onto PAN CNF for MEA testing[96]. The results demonstrated that functionalized CNF showed maximum Pt utilization when compared to other Vulcan and other variations of CNF. The *in situ* fuel cell

tests revealed decent maximum power density of 294.7 mW cm<sup>-2</sup> for functionalized CNF [96]. Instead of electrospinning a support layer, Sung et al. electrospun Pt nanowires and mixed them with commercial Pt/C catalyst to form the cathode electrode [97]. The authors report the Pt nanowires catalyst blend may have improved the fuel cell performance due to the increase in exchange current density [97]. The results also demonstrated the importance of Nafion concentration as it relates to the catalyst utilization and fuel cell performance. The authors also mentioned future investigations should focus on the ionomer distribution and whether ionomer preferentially bonds to Pt nanowires or Pt/C [97]. Another study demonstrated that Pt nanowires could be deposited onto electrospun CNF derived from Polyvinylpyrrolidone (PVP). Pt nanowires (2 - 5 nm diameter and 100 nm length) on CNF created a hierarchal structure, credited for improving the electrochemical properties [57]. The authors concluded that the flexible carbon fiber film demonstrated high surface area (33.5 m<sup>2</sup>  $g_{Pt}^{-1}$ ), good gas diffusion, and electron transport compared to carbon black catalyst [57]. Zamani et al. fabricated Iron-Polyaniline-Polyacrylonitrile nanofibers as non-precious metal catalysts for ORR. The study demonstrated the most active nonprecious ORR nanofiber catalyst prepared by electrospinning to date. Using graphene doped PAN/Polyvinylident fluoride to fabricate an electrospun catalyst layer, Wei et al. demonstrated an improvement in ECSA as a result of the porous nanofiber structure. The unique electrode structure achieved higher peak power density (0.88 W cm<sup>-2</sup> for Pt loading of 0.2 mg cm<sup>-2</sup>) compared to conventional electrodes (0.73 W cm<sup>-2</sup> for Pt loading of 0.4 mg cm<sup>-2</sup>) [98].

Instead of using CNF as a catalyst layer, Duan et al. successfully produced CNF microporous layer by electrospinning PAN and has achieved excellent three dimensional porosities, improved gas diffusion and exhibited excellent hydrophobicity. In his work, Pt/C (0.4  $mg_{Pt}$  cm<sup>-2</sup>) was sprayed onto a Nafion membrane and hot pressed onto a CNF gas diffusion layer

[99]. Overall it was shown that CNF is a feasible material for fuel cell applications owing to the enhanced electrical conductivity compared to commercial Vulcan XC-72R (> 10 S cm<sup>-1</sup> for CNF) [35,79,83,94,99,100]. Another attractive aspect of electrospun nanofibers is the potential to fabricate highly aligned and precise patterned nanofibers mats [101]. Nanofibrous polymer electrolytes have also been widely published in the literature [102–108]. The polymer membranes are usually fabricated as electrospun composite nanofibers containing Nafion and a carrier or uncharged polymer [102,103,109]. The electrospinning method offers higher network ion exchange capability, which is crucial for proton transport [109]. Evidently, considerable interest is shown in fabricating electrospun CNF for the application of fuel cell electrodes and catalyst support layers.

Currently, electrospun fibers are gradually becoming attractive for various fuel cell components. Electrospinning also has the ability to form different mesh structures. Electrospinning allows simple tailoring of key characteristics such as porosity, fiber diameter, layer thickness, mechanical, and electrical properties. Improvement in mechanical or electrical properties could also be fulfilled by incorporation of nanofillers in the spinning dope, such as CNT [110]. More importantly, fiber orientation and geometry can be controlled using electrospinning. For example, aligned fiber bundles, twisted yarns, unidirectional, orthogonally aligned, and coaxial fibers have been reported in literature [101,111–113]. Since geometry has the potential to improve mass transport and overall fuel cell performance (Chapter 1.3.3), electrospinning is a strong candidate to address the current catalyst layer challenges. The literature review suggests that a systematic study to tailor the fabrication process and design parameters for electrospun CNF has not been thoroughly studied for the application of catalyst support layers. For example, the effect of fiber

orientation on fuel cell performance, which is a unique contribution of this thesis, has not been explored in the literature.

## 1.4 **The electrospinning process**

Electrospinning is a simple process that can produce polymeric fibers in the nanometer to micrometer range by using an electric field. Ultrafine fibers can be produced by applying high voltage to the polymer solution. The process involves applying a sufficiently large voltage to a small droplet of polymer. The droplet becomes charged under the electric field and undergoes electrostatic repulsion. When the electrostatic repulsion becomes large enough to overcome the surface tension of the polymer solution, the droplet stretches, and at a critical point a jet of polymer erupts from the surface creating a Taylor cone [114]. While traveling from the spinneret nozzle to the ground collector, the polymer solution jet undergoes a continuous whipping motion caused by the electrostatic repulsion initiated at small bends in the polymer jet. Within this instability region where whipping and elongation occur, the solvents are evaporated leaving solidified nanofibers on the collector plate (Figure 1-11). The process of whipping, thereby elongating the fiber, is the key factor in the formation of continuous and uniform nanoscale polymer fibers [114].



Figure 1-11: Schematic illustration of electrospinning process

Electrospinning is an attractive method because the processing parameters which directly affect the fiber morphology can be controlled. For example, fiber diameter can be sufficiently controlled by varying polymer concentration, molecular weight of the polymer, spinning distance, voltage, and orientation or speed of the collector plate. Typically, smaller diameters can be achieved by decreasing the polymer concentration in the mixture, and vice versa for fabricating fibers with large diameters. The electrospinning process produces semi-crystalline nanofibers where some polymer chains form crystalline lamellae and others form an amorphous phase. The amount of lamellar structure determines the crystallinity of the fibers [110]. The shear force during the electrospinning process aligns the polymer chains along the fiber length. The resulting nanofiber deposits onto a collector plate creating a randomly deposited non-woven fabric membrane.

The electrospinning process is governed by a variety of forces which include Coulomb force between the charge particles on the jet surface, viscoelastic force due to the viscosity of the solution, the electrostatic force due to the external electric field, surface tension force, gravity force, and drag force due to air friction [114]. The different stages of electrospinning have been investigated extensively through modeling and theoretical analysis [115,116]. Because the electrospinning process parameters are a function of fluid properties, the relationship between spinnability and polymer molecular structure is critical. The convoluted interplay of these processing parameters make it impractical to establish a universal formula to include all polymersolvent systems. An approximation was created, called the Berry number (Be), which combines concentration and viscosity parameters [117]. Developed to determine spinnability and predict fiber diameter, the dimensionless number is defined as the product of the polymer concentration (c) and the solution intrinsic viscosity ( $[\eta]$ ) (1.10) [87,88]. The fiber diameter can be expressed as a power law equation where  $\alpha$  and  $\beta$  are experimental coefficients (1.11) [87]. The coefficient  $\alpha$ is correlated to molecular weight, radius of gyration of molecular chains, and entanglement of the molecular chains. Whereas coefficient  $\beta$  is related to crystallinity. The relationship shows that diameter is influenced by molecular conformation, molecular weight, and concentration of the polymer. As a result, fiber diameter increases as polymer concentration increases and the rate of increase is greater at higher molecular weights. A Berry number between 1 and 2.7 predicts a fiber diameter in the range of 100 - 500 nm with sufficient molecular entanglement to form continuous fibers [87].

$$Be = c[\eta] \tag{1.10}$$

$$d = \alpha (Be)^{\beta} \tag{1.11}$$

$$d = \left[\frac{\gamma \varepsilon Q^2}{I^2} \frac{2}{\pi (2 \ln \chi - 3)}\right]^{1/3}$$
(1.12)

Another set of parameters that control electrospinning parameters include: spinning distance, flow rate, applied voltage, and spinneret diameter. According to Rutledge et al. [118],

the diameter of electrospun fibers is governed by equation (1.12), where *d* is fiber diameter,  $\gamma$  the surface tension,  $\varepsilon$  the dielectric constant, *Q* the flow rate, *I* the current carried by the fiber, and  $\chi$  the ratio of the initial jet length to the nozzle diameter. In essence, these physical parameters relate back to the forces acting on the polymer droplet during the formation of the Taylor cone. Because of the accessibility to process a wide range of polymers, electrospinning has become a popular method to synthesize nanofiber based materials for various applications including filters, batteries, and medical scaffolds.

### 1.5 **Carbon fiber fabrication**

Carbon fiber (CF) are synthesized from precursor material such as rayon, petroleum pitch, and PAN. Generally, the precursor fiber is subjected to three stages of heat treatments—stabilization, carbonization, and graphitization. The first stage involves stretching the fiber in an oxidizing atmosphere at 200 - 300 °C under tension. During this step, the thermoplastic is converted into a non-plastic ladder structure. During carbonization, the fibers undergo another transformation at about 1000 °C in inert atmosphere. To improve the degree of graphitization, the fibers are further heated at 1500 - 3000 °C. The entire process is a complex series of chemical reactions detailed in literature [119]. There are a number of parameters which affect the final material properties, including: precursor material, ramp rate, heating temperature, and heating duration. Since 90% of CFs are produced by PAN precursor, a brief review of the heat treatment process and resulting material properties is provided [119].



Figure 1-12: Evolution of PAN chemical structure during the 3 steps of stabilization and carbonization (Top to bottom) [reproduced with permission] [120–122]

The mechanical properties of CF highly depend on the successful execution of the thermal treatment. Among the three processes mentioned, stabilization is the most complex and crucial stage as it sets the structure of the formation of CF. It is proposed that the stabilization process involves cyclization, dehydrogenation, aromatization, oxidation and crosslinking, eventually forming the ladder structure [123,124]. Optimal stabilization temperature is important because incomplete reaction will produce carbon fibers with poor properties. Generally, it has been argued that the optimal stabilization temperature for PAN is either 270 °C, 300 °C, or above 400 °C [119]. The two chemical changes during stabilization are dehydrogenation and cyclization which occur

in oxidizing atmosphere. Dehydrogenation forms double bonds by oxidation and elimination of water, as shown in Figure 1-12. This reaction is beneficial because the double bond increases the thermal stability of the polymer and reduces chain scission during carbonization [125]. Next, the most important reaction involves rearrangement of nitrile groups with adjacent groups to form a stable ladder structure. The formation of ladder structure holds the molecules together and increases stiffness [126]. Cyclization involves conversion of triple bond to double bond (C=N to C=N) in oxidizing or inert atmosphere, resulting in three hexagons laterally bound by nitrogen atom. Carbonization typically occurs between 800 – 1000 °C [127], where lower temperatures of ~1000 °C produce low modulus type fibers and 1500 °C produces intermediate modulus type fibers [128]. The process occurs in either nitrogen or argon rich atmosphere at a heating rate of 5  $^{\circ}$ C /min because of PAN structure instability. Higher heating rate causes a large amount of shrinkage, therefore it is beneficial to stretch and apply tension to the fibers beyond 600 °C in order to preserve orientation and overall mechanical properties [129,130]. Very high modulus type fibers can be produced by further graphitization beyond 3000 °C, achieving 99% carbon conversion from PAN [131].

Typically carbon nanofibers with higher Young's modulus can be achieved with an optimized stabilization temperature compared to fibers that have not been well stabilized [128]. A significant study by Yamashita et al. demonstrated that the fiber diameter of electrospun Poly(acrylonitrile-co-methyl acrylate) (PAN-co-MA) decreases after heat treatment [132]. They further observed that the stabilized fiber mats achieve higher Young's Modulus with increasing stabilization temperature. Consistent with Ko's results and other published results for PAN based CNF, the surface electrical resistance decreases as heat treatment temperature increases [132,133]. In Yamashita's study, FT-IR results demonstrated that the ladder structure for PAN-co-MA was

achieved at 300 °C [132]. However, it was also dependent on retention time and heating rate. Yamashita noted that beyond 280 °C, the fiber morphology started to fuse and change shape. It was also believed that the color change, from white to yellow to black, during this stage is due to the formation of the ladder ring structures [134]. Several groups have formed yarns or twisted bundles of CNF to improve the mechanical properties [82,85]. One study electrospun PAN onto a rapid rotating disc to form aligned fiber bundles. Tensile and electrical properties were analyzed for a series of heat treatment temperatures. Zhou et al. revealed CNF bundles carbonized at 1000 °C achieved 325 MPa and 40 GPa for tensile strength and Young's Modulus, respectively [135]. For fibers carbonized at 2200 °C, tensile strength and Young's Modulus was 542 MPa and 58 GPa, respectively [135]. Similarly, electrical conductivity for CNF carbonized at 1000 °C was 180 S cm<sup>-1</sup> in the parallel direction, while fibers carbonized at 2000 °C achieved 840 S cm<sup>-1</sup>. The authors concluded the improvement in electrical and tensile property is due to the high degree of graphitization and orientation [135]. The authors also mention improved properties which could be achieved by using PAN copolymer because the sudden evolution of heat during stabilization of PAN homopolymer may cause chain scission, making final CNF mechanically weak [135,136]. Not only do comonomers prevent thermal shock, they also act as plasticizer to break up the structure and allow polymer to be easily dissolved in the spinning solvent, improving the quality of spinning and fiber morphology [136]. Additionally, the applied tension should be optimized during heat treatment to achieve high degree of orientation [135].

### 1.6 **Research objectives**

This thesis is a contribution to the field of fuel cell development, specifically it addresses the fabrication and optimization of a novel catalyst support material for PEMFCs. The predominant purpose of this work was to develop a catalyst support, with predictable microstructure and

material properties, through a tailorable fabrication process to establish the relationship between the material and geometrical properties and overall fuel cell performance. The hypothesis of this work was that geometrically orientated CNF produced by electrospinning would provide an ideal microstructure to improve mass transport, proton transport, durability, and Pt utilization. The effect of Pt loading, Pt deposition method, ionomer distribution, fiber orientation, and fiber electrical conductivity on fuel cell polarization was explored. To evaluate the advantages of tailorable CNF as catalyst support material, full characterization using electrochemical and physicochemical methods was proposed.

Specifically, the predominant objectives of this thesis was to understand the fuel cell's performance in the context of the following material and architectural characteristics:

- I. Effect of fiber orientation (random vs. orthogonal),
- II. Effect of fiber electrical conductivity,
- III. Effect of Pt deposition method and Pt loading, and
- IV. Effect of ionomer loading and distribution

Upon completion of this project, information about the catalyst support microstructure and properties would assist in the future design of optimized MEAs that could significantly improve fuel cell cost and efficiencies. This research may potentially stimulate new fuel cell designs and uncover a new research field in advanced materials. If successful, this research may lead to revolutionary designs not only in fuel cells, but also in filtration devices, supercapacitors, and lithium ion battery electrodes and separators.

In order to establish these structure-property correlations, a systematic approach was proposed as follows:

- Select a polymer precursor and develop fabrication method to produce nanoporous carbon fiber mesh structure with controllable geometry and material properties. Optimize the fabrication process to achieve electrode target criteria such as high electrical conductivity, robust mechanical properties, small fiber diameter, and large porosity (Chapter 3 and 4).
- 2. Investigate a simple one step catalyst deposition method to achieve platinization of CNF for catalyst layer formation (Chapter 5).
- 3. Improve Pt and ionomer deposition by functionalization of CNF surface. Techniques include incorporation of surfactant polymers and acid treatment (Chapter 5)
- 4. Characterize microstructure, measure *ex situ* properties and *in situ* performance of CNF based fuel cell catalyst layers. Variables of interest are: ionomer and Pt loading, Pt deposition method, fiber orientation, and fiber electrical conductivity (Chapter 6).

Figure 1-13 provides an overview of the organization of this thesis. The research tasks are divided into three distinct phases that correspond to the research approach listed above. The flowchart illustrates the validation of each fabrication step to ensure the material properties sufficiently meet the design requirements.



Figure 1-13: Diagram of experimental approach illustrating the progression of experiments; tasks were divided into three key experimental phases: Fabrication optimization, deposition of Pt and ionomer, and MEA in-situ testing

# 2 Materials and Experimental Methods

The materials, experimental methods, and characterization methods presented in this thesis are described in their respective sub sections.

## 2.1 Materials

An electrospinning dope was prepared by mixing Poly-acrylonitrile-co-methyl acrylate (PAN-Co-MA) and dimethylformamide (DMF). PAN-Co-MA with average Mw of 100,000, was purchased from Scientific Polymer Products. 7 wt% and 10 wt% PAN-Co-MA solution was made by dissolving the polymer powder in DMF (Sigma-Aldrich) solvent. Carboxyl functionalized MWCNT (COOH-MWCNT) purchased from Cheap Tubes Inc. with  $10 - 30 \mu m$  length and < 8 nm diameter was used as received. The electroless plating solution for platinum deposition on nanofiber mats consists of Hydrogen hexachloroplatinate (IV) hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>, 99.9 %, Alfa Aesar), formic acid (CH<sub>2</sub>O<sub>2</sub>, >95.0 %, Sigma-Aldrich), deionized water, and Polyvinylpyrrolidone PVP ((C<sub>6</sub>H<sub>9</sub>NO)<sub>n</sub>, Sigma-Aldrich). Aquivion® D79-25BS, Solvay Specialty Polymers) was diluted to 5 wt% and 10 wt% by a 3:1 volume ratio of N-Propanol and deionized water for the ionomer deposition solution. Electrolyte membrane, GDL, and anode CL was supplied by AFCC and used as is.

#### 2.2 **Preparation of random and orthogonally aligned nanofibers**

The electrospinning process (NEU, Kato-Tech Co. Ltd.) was used to fabricate the as-spun nanofiber mat. PAN-Co-Ma was dissolved in DMF by weight percent. 7 wt% and 10 wt% PAN-Co-MA was dissolved in DMF and mechanically stirred on a hot plate at 85 °C for 12 hours. For spinning dopes requiring MWCNT, 1 wt% of the original polymer weight was measured and dispersed in the DMF first. The DMF and CNT suspension were bath sonicated for 30 minutes to encourage sufficient dispersion. PAN-co-MA was subsequently added to the suspension and 38 stirred in the same manner for 12 hours. Once the polymer solution was cooled to room temperature, it was transferred to a 10 mL plastic syringe with an 18G needle (0.838 mm diameter). A schematic drawing of the electrospinning apparatus is shown in Figure 2-1. The electrospinning parameters are listed in Table 2-1. The random fiber mat was collected on a rotating collector drum at ambient temperature with the relative humidity adjusted to roughly 30%. After spinning, the mat was stored in the oven (70 °C) to fully evaporate the solvent before further post processing.

	Random	Orthogonal
Spinning Distance	15 cm	10 cm
Voltage	17 kV	17 kV
Pump speed	0.80 mm/min	0.80 mm/min
Rotation speed	1 m/min	N/A
Traverse speed	10 cm/min	N/A

Table 2-1: Electrospinning parameters for RNL and OAN

Using the prepared polymer dope, orthogonally aligned fiber mat was fabricated using a parallel electrode method as described in the literature [137]. The ground wire was mounted to one pair of parallel plates and the distance between the parallel copper plates was maintained at a distance of about 7 cm. As shown in Figure 2-2, the orthogonal fibers were fabricated on a desktop set-up with the collector and syringe needle horizontally parallel to each other. A 10 mL plastic syringe with an 18G needle (0.838 mm diameter) was used. The voltage was held at 17 kV, with a spinning distance of 10 cm. Relative humidity (RH) was maintained at 30% at ambient temperature. By alternating the repulsion voltage between the two orthogonal directions after every 30 minutes a substantial mat was collected on the copper plates. The fibers were transferred onto a stainless steel frame and set aside in the 70 °C oven for drying before further heat treatment.


Figure 2-1: Conventional electrospinning apparatus



#### 2.3 Heat treatment

The heat treatment process consists of a series of intricate chemical reactions in oxidative and inert atmospheres to produce graphitic carbon. The first stage was to oxidize/stabilize the polymer to form a stable structure that does not degrade during higher temperature treatment. Samples were restrained between two square stainless steel frames to reduce fiber shrinkage and wrinkling (Figure 2-3). The samples were placed on a graphite boat and inserted into the high temperature furnace for two hours at 230 °C or 260 °C in air according to the experimental design (Figure 2-4). The temperature ramp rate was set at 1°C min<sup>-1</sup> as higher rates appear to produce mats that were prone to cracks due to severe shrinkage. Subsequently, the samples were taken out of the furnace and the frames were removed for the carbonization step. Since the carbonization step induces significant fiber and mat shrinkage (~30% reduction), applying tension on the sample causes cracks and defects. Instead, the stabilized fibers were sandwiched between carbon paper and restrained by a metal mesh to keep the mat flat and wrinkle free. The samples underwent a one hour heat treatment in argon at 850 °C or 1100 °C, according to the design of experiments (Chapter 3.3). The ramp rate again was kept at 3 °C min<sup>-1</sup> to prevent shrinkage and damage to the sample. Figure 2-5 illustrates the transition between as-spun, stabilized, and carbonized sample. The furnace was allowed to cool down to ambient temperature without a pre-set cooling rate. Carbonized fiber mat was then cut to the desired dimensions for Pt deposition.



Figure 2-3: Stainless steel frame for applying tension to as-spun mat during heat treatment



Figure 2-4: Tube furnace supplied with Air/Argon gas for carbonization procedure (left); graphite sample holder plate for keeping CNF flat during heat treatment



Figure 2-5: Transition between (A) as-spun, (B) stabilized, and (C) carbonized fiber mat

### 2.4 **Platinum deposition**

Several deposition methods discussed in literature were explored. In this study the different deposition methods are expected to yield unique morphology and dispersion, thus investigating the simplest and repeatable deposition method was necessary. Common deposition methods were evaluated including: Atomic Layer Deposition (ALD), hydrogen reduction, acetic acid reduction, and formic acid reduction. ALD deposition was performed in the 4D labs at SFU using the Cambridge NanoTech Fiji F200. The film was deposited under a pressure of about 5 x  $10^{-3}$  mbar. MeCpPtMe<sub>3</sub> was used as a Pt precursor with the pulse time of 20 s and the air pulse time of 20 s. Purge times used in the experiment were 3 seconds. Oxygen was pulsed into the reactor with a flow rate of 30 standard cubic centimeters per minute (sccm). Thin film was deposited at 270 °C under 188 cycles.

Sputter coater was used to deposit a thin layer of Pt onto one side of the CNF mesh. Samples were mounted on 15 mm aluminum stubs with adhesive carbon tabs (Ted Pella) and the edges and sides of the glass were painted with colloidal silver to ensure electrical connection between the edge of the sample and the stub. The region of interest was sputter coated with a 20 nm layer of Pt (EM MED 020 fitted with a quartz thickness monitor, Leica Microsystems, Concord, ON, Canada)

For the Pt deposition using wet chemistry, several pre-treatment methods were investigated to identify the most suitable method for CNF material. With a few exceptions, the methods closely

followed literature with reduced submersion time because CNF surface is less inert compared to CNT [138]. One variation, the carbon nanofibers were pre-treated in methanol for 30 minutes before submerging in plating solution [139]. Second variation, CNF were submerged in a mixture of 0.1 M citric acid for 1 hour and subsequently in a solution mixture of 1 mL (3-Aminopropyl) triethoxysilane and 50 mL ethanol for 30 minutes and dried in the fume hood [140]. Pre-treated and dried CNF were then submerged in Pt plating bath solutions described below.

In the first method, CNF were submerged into an acetone solution containing H<sub>2</sub>PtCl<sub>6</sub> and evaporated completely in the fume hood. The amount of dissolved H<sub>2</sub>PtCl<sub>6</sub> was calculated based on the desired Pt loading and estimated surface area. For example, the surface area of a 25 cm<sup>2</sup> CNF is estimated to be 5000 cm<sup>2</sup> cm<sup>-2</sup><sub>MEA</sub> (based on the calculations shown in chapter 2.7.6). To achieve 0.15 mg cm<sup>-2</sup><sub>MEA</sub>, the amount of Pt needed would be 750 mg. Following the stoichiometric conversions for molar mass of H<sub>2</sub>PtCl<sub>6</sub> and elemental Pt, a rough estimate of 1.6 g of H<sub>2</sub>PtCl<sub>6</sub> should be dissolved in 40 mL acetone. The dried sample was reduced at 350 °C in 10% Hydrogen/Argon atmosphere furnace for 1 hour at a ramp rate of 10 °C min<sup>-1</sup>.

In the second approach, reduction by acetic acid was performed according to method proposed by Kamavaram et al. [138]. 25 mL acetone was used to dissolve 45 mg of Platinum (II) Acetylacetonate (Pt(II)acac). Using a condenser under the fume hood, the solution was heated in an oil bath at ~100 °C for 2 hours. 10 mL glacial acetic acid was slowly added to the solution to reduce the  $Pt^{2+}$  ions. The solution was heated for another hour using a condenser, then allowed to fully evaporate overnight. The solution changes color from yellow to dark brown and finally black upon complete evaporation of the solvent.



Figure 2-6: Plastic frame holding CNF, used during Pt deposition

Table 2-2: Platinum plating bath chemical composition and concentrations

No.	Components	Amount		
1	H <sub>2</sub> PtCl <sub>6</sub>	25, 30, and 40 mg		
2	Polyvinylpyrrolidone	2 mg		
3	Deionized water	20 mL		
4	CH <sub>2</sub> O <sub>2</sub>	1 mL		
Plating temperature		20-25 °C		
Time for plating		72 hours		

 $H_2PtCl_6 + 2HCOOH \rightarrow Pt + 6Cl^- + 6H^+ + 2CO_2 \uparrow$  (2.1)

In the third approach, reduction of Chloroplatinic acid by formic acid was performed according to the method outlined by Sun et al. [141]. Since CNF were thin and delicate, a plastic frame was used to add support during Pt deposition and subsequent steps (Figure 2-6). Because of the extremely sensitive reduction technique, it is crucial to have clean tools and glassware for successful deposition onto the CNF. Therefore, thorough cleaning with 1:1 mixture of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> is recommended. The concentrations of the plating bath are shown in Table 2-2. Chloroplatinic acid and PVP was dissolved in 20 mL of DI water into a mixing beaker. The mixed solution was bath sonicated for 20 minutes and transferred to petri-dishes for plating. The CNF

mats were placed in the petri-dish and submerged completely in the plating bath solution. The petri-dish was wrapped with para-film and undisturbed for 72 hours at room temperature. The mechanism of Pt reduction is shown in Equation (2.1). The solution becomes dark after plating, indicating metallic Pt was formed. Once the plating is complete, the samples were carefully rinsed with deionized water. The resulting CNF/Pt mat was dried in an oven at 100 °C and stored in a desiccator for later use.

## 2.5 **Ionomer deposition**



Figure 2-7: Ionomer deposition set-up

Ionomer (Aquivion® D79-25BS, Solvay Specialty Polymers) was diluted to 5 wt% and 10 wt% by a 3:1 volume ratio of N-Propanol and deionized water. The solution was stirred slowly on the mechanical stir plate for < 4 hours to enhance deposition viscosity. The stirred solution was then poured through a funnel and filter paper using a vacuum pump. The set-up, shown in Figure 2-7, allows the ionomer to evenly deposit through the fiber mat without blocking the pores. Another method, dip coating, was used to compare the dispersion of the ionomer and study the effect of concentration on pore blockage, but proved to give less desirable results. The coated fiber mat was annealed in a convection oven at 140 °C for 15 minutes.

## 2.6 MEA assembly

Plastic frames from the previous fabrication step were removed by cutting with scissors or razor blade. Anode half catalyst coated membrane (CCM) (Pt loading 0.05 mg cm<sup>-2</sup>) with NRE-211 membrane was hot pressed onto the CNF sample and trimmed to the desired size for FC testing. The heat press was activated for 2.5 minutes under 9.8 kN at 150 °C. The GDL for cathode (Freudenberg, H23C10) and anode (Freudenberg, H14C10) were attached using an adhesive thermoset sheet and heat pressed together for an additional three minutes (Figure 2-8). The completed MEA has an active area of 5 cm<sup>2</sup> (CAT cell, Figure 2-9) and 1.13 cm<sup>2</sup> (MAT cell, Figure 2-10), suitable for small scale fuel cell test station.



Figure 2-8: Exploded view of the MEA (CAT cell) components for hot pressing



Figure 2-9: Completed MEA for CAT cell testing



Baseline CCM (V50) was prepared by AFCC staff using a conventional decal method. In the conventional decal method, the catalyst ink slurry was made by dispersing catalyst (50 wt% Pt on Vulcan XC-72 carbon black) with a mixture of 5 wt% Nafion ionomer solution, isopropyl alcohol, and DI water. The weight ratio of the ionomer (dry basis) to carbon (I/C) was maintained at 1.1. The catalyst inks were coated on polytetrafluoroethylene (PTFE) sheets that subsequently served as the decal substrates using metering bars (Meyer bars) under a motorized draw down table. Target Pt loadings for the cathode and the anode were 0.15 and 0.05 mg<sub>Pt</sub> cm<sup>-2</sup>, respectively and were measured on dry decal by XRF for at least 2 locations per coating to gauge uniformity. Freshly coated decals were dried on a hot plate set at 70 °C in the fume hood (to reduce cracks). After annealing at 150 °C in convection oven for 30 minutes, the catalyst layers were transferred onto the membrane (NRE-211) by hot-pressing to form the CCM. The GDL (Freudenberg) was identical to the ones used in the CNF MEA.

#### 2.7 Characterization and analysis methods

## 2.7.1 Thermal profile of PAN-co-MA

To determine the range of suitable heat treatment temperatures for PAN-co-MA, TGA was conducted to observe the onset of oxidation. The nanofiber mat was dried in 70 °C oven overnight

to ensure all moisture is evaporated. The specimen was rolled into a ball and placed in a clean Pt TGA pan. The data was collected from room temperature to 600 °C at a ramp rate of 5 °C min<sup>-1</sup> in air atmosphere. Comparing the onset of oxidation between PAN and PAN-co-MA can give information about suitable thermal stabilization temperatures.

## 2.7.2 SEM and TEM dimensional measurements

Nanofiber diameter and morphology were observed by Hitachi S-3500N and FEI Helios NanoLab 650 scanning electron microscope (SEM). As-spun and stabilized samples required sputtering to provide a conductive surface, which reduces charging and improves image quality. A thin coating of Au was sputter coated on the sample surface for 60 seconds at 40 amps using Edwards S150A sputter coater. Images were taken in several quadrants of the fiber mat and 100 diameter measurements were averaged using Image J software (U.S. National Institutes of Health). Fiber cross section, Pt particle size and ionomer distribution and morphology was observed using FEI Helios. The Pt particle size was measured using Image J and averaged over 30 measurements. Fiber mat cross sectional thickness was also measured using Image J and later confirmed using digital thickness gauge.

Samples post-fuel cell testing were embedded in resin and polished to a mirror finish for cross sectional imaging in SEM. Transmission electron microscope (TEM) and energy dispersive X-ray (EDX) maps of the samples were collected in order to observe Pt and ionomer distribution and film thickness. The ionomer thickness (including bridges) was measured using Image J and averaged over 200 measurements. Cross sections of the samples for TEM imaging were prepared by embedding small pieces of tested MEAs (with GDL removed) in TTE resin (trimethylolpropane triglycidyl ether and 4,4'- methylenebis (2-methylcyclohexylamine)). Thin (~100-200 nm) TEM slices were microtomed using a Leica Ultracut UCT ultramicrotome (Leica Mikrosystem, Wien,

Austria), and deposited on 100-mesh TEM copper grids. STEM/EDX imaging was performed on FEI Tecnai Osiris (Scanning) Transmission Electron Microscope, with 200 kV accelerating beam voltage.

#### 2.7.3 Mechanical testing



Figure 2-11: 2 cm gauge tensile test specimen

Mechanical tensile testing of nanofiber mats were conducted using the KES-G1 Kawabata microtensile testing system at the elongation rate of 0.01 cm s<sup>-1</sup>. For random nanofiber mats, sample strips of 3 cm x 0.5 cm were glued on a paper frame and tested. The gauge length for tensile test is 2 cm (Figure 2-11). The measured load in grams was converted to specific stress (g tex<sup>-1</sup>) via the formula in Equation (2.2). Areal density represents the weight of the specimen divided by the area, in m<sup>2</sup> (length x width). The specific stress in g tex<sup>-1</sup> was then converted to N tex<sup>-1</sup> by multiplying by 9.81 m s<sup>-2</sup> and further to MPa by multiplying the bulk density of carbon.

Stress 
$$(g/\text{tex}) = \frac{Force(g)}{Width(mm) \times Areal Density(\frac{g}{sg\cdot m})}$$
 (2.2)

## 2.7.4 In-plane and through-plane electrical properties

The random and orthogonally aligned CNF samples were characterized for electrical conductivity. The specimen were cut into small squares or strips and glued onto a glass slide using silver paint. Using a narrow brush, a thin and even layer was applied to the two edges that were 49

used to contact the electrical probes (Figure 2-12). The specimen dimension were measured with a micrometer and digital calipers to compute the conductivity per length. It was crucial that the specimen lays flat on the glass slide because any wrinkling would cause error in the calculations. Electrical resistance was measured with a two probe multi-meter (Agilent U1272A). Equation (2.3) was used for computing the resistivity and conductivity of the samples.  $\rho$  is the electrical resistivity measured in ohm-centimeter, A is the cross sectional area, l is the length between the silver paint and R is the electrical resistance in ohms. Conductivity ( $\sigma$ ), measured in S cm<sup>-1</sup>, was found by reciprocation of the resistivity  $(\rho)$ . At least 4 replicates were prepared and measured for each sample and the results were reported as an average with one standard deviation. An in-house apparatus for measuring through-plane resistance, mat thickness, and compression strength was used to mimic operational FC conditions (Figure 2-13). The measurements were recorded over a 25 s dwell at each pressure while fixing the current at 1 A. A series of electrical resistivity ( $\Omega$ cm) were recorded at pressures ranging from 500 kPa to 3000 kPa. The final through-plane conductivity (S cm<sup>-1</sup>) was calculated by reciprocating the resistivity at 1500 kPa (roughly FC operational pressure).



Figure 2-12: Conventional multi-meter and specimen preparation with silver paint



Figure 2-13: Through-plane electrical resistivity tool, measures resistivity as a function of pressure and thickness

$$\rho = R \frac{A}{\ell}, \qquad \sigma = \frac{1}{\rho}.$$
(2.3)

## 2.7.5 Chemical characterization

CNF were cut into small squares and mounted on a quartz single crystal holder using clear double sided tape. The chemical phase composition and crystal structure was confirmed by X-ray diffraction (XRD, Rigaku Multiflex, Japan) using Cu K $\alpha$  radiation at 40 kV and 20 mA. Diffraction data were collected from  $2\theta = 30^{\circ}$  to  $90^{\circ}$  with a step size of  $0.5^{\circ}$ . Pt loading was examined by X-ray fluorescence (XRF) (Thermo Scientific, Niton XL3t). Fiber surface chemistry was examined by X-ray photoelectron spectroscopy (XPS) (Axis Ultra DLD, Kratos Analytical) using monochromatic Al K $\alpha$  radiation at a power of 150 W. The pass energy was set at 20 eV, and the C 1s line at 284.6 eV was used as a reference. Because nanofiber sample tends to outgas, samples were cut into small squares and adhered onto the sample holder using minimal carbon tape. It is crucial to keep the sample dry and clean to avoid detecting contamination on the surface.

#### 2.7.6 **Porosity measurement and calculations**

Porosity was calculated by estimating the fiber spacing and amount of fibers in a given volume based on measured weight and density of carbon. The equation below was used to approximate the % porosity in the fiber mats. Porosity of the fiber mats was calculated based on their mass (m<sub>CNF</sub>), carbon bulk density  $\rho = 1.9$  g cm<sup>-3</sup> and measured fiber mats dimensions, length (L<sub>CNF</sub>), width (W<sub>CNF</sub>) and thickness ( $\tau_{CNF}$ ) (2.4). The calculated porosity was later confirmed by physical measurement methods.

$$Mesh \ porosity \ (\%) = \frac{V_{tot} - V_{solid}}{V_{tot}} = \frac{L_{CNF} \cdot W_{CNF} \cdot \tau_{CNF} - m_{CNF} \cdot \rho_{C}}{L_{CNF} \cdot W_{CNF} \cdot \tau_{CNF}}$$
(2.4)

Porosity of fiber mat was measured by using Archimedes principle in Equation (2.5). A rig was installed onto the digital balance to measure the mass of the fibers submerged in water or ethanol. It was crucial to use a wetting agent that can fully wet the carbon nanofibers, thus ethanol

was chosen. The dry mass of the fiber was measured before submersion, denoted  $M_{dry}$ . The mass after submersion with excess solution gently patted dry was measured, denoted  $M_{wet}$ . The mass of the sample fully submerged is denoted  $M_{sub}$ . The % porosity was calculated by the following equation:

$$Mesh \ porosity \ (\%) = \frac{M_{wet} - M_{dry}}{M_{wet} - M_{sub}}$$
(2.5)

## 2.7.7 X-Ray fluorescence

Pt loading was validated by X-ray fluorescence calibrated to a standardized platinum block. The average Pt loading was measured across the CNF sample in 3 locations. The measured area was 1 cm<sup>2</sup>. Front side and back side of the CNF sample was measured to ensure Pt deposited evenly through-thickness.

#### 2.7.8 *Ex situ* cyclic voltammetry

Cyclic voltammetry measurements were conducted at room temperature in a threecompartment electrochemical cell. The electrolyte was 0.09M H<sub>2</sub>SO<sub>4</sub>, the working electrode was a circular piece of CNF/Pt sample impregnated onto the mirror finish glassy carbon disk electrode (area =  $0.196 \text{ cm}^2$ ) by adding a 5 µL drop of diluted Nafion solution (water/5% Nafion ratio was 100:1) on it and dried under a heat lamp. Princeton Applied Research model 263A potentiostat/galvanostat was used, together with the CorrWare and CView system software for data acquisition and analysis. The electrolyte solution was deaerated by bubbling Nitrogen through it for 30 minutes prior to electrochemical measurements. The electrode was activated by cycling the potential between 0.025 and 1.2 V vs. Standard Hydrogen Electrode (SHE) at a scan rate of 20 mV s<sup>-1</sup>. The potential limits were chosen to be near the H<sub>2</sub> and O<sub>2</sub> evolution potentials, respectively. Three cycles were performed to reduce instabilities, the last cycle which was the most stable voltammogram was recorded for analysis.



Figure 2-14: CNF impregnated onto glassy carbon electrode for cyclic voltammetry (CNF geometric area was normalized for comparison)

## 2.7.9 In situ electrochemistry

Performance testing of the CNF and baseline MEAs was done using an AFCC in-house design rapid screening test apparatus (MAT cell), which utilizes straight channel cathode flow and radial anode flow with adjustable compression and no gasket sealing. For performance evaluation, the samples were tested in NOC (Normal Operating Condition) and HOT (High Operating Temperature) operating condition under voltage control mode with 100% H<sub>2</sub> on the anode, air on the cathode, and 2.5 bara balanced inlet pressures. For NOC, the cell temperature was 68 °C and both fuel and oxidant inlet RHs were at 105%. For HOT, the cell temperature was 85 °C and the inlet RH's were at 50%. Following the standard protocols used by AFCC, the overall performance was assessed by current density measured at 650 mV in NOC and 600 mV in HOT, while kinetic performance was assessed at 825 mV for both conditions, and oxygen transport assessment was done via the limiting current measured at 0.1 V in NOC. All performance measurements were repeated at least three times for each sample to ensure data quality.

For the full polarization analysis, the MEAs were tested in a single-cell hardware (CAT cell) with straight channels, and operated at 10.2 stoic (anode and cathode) to achieve iso-

conditions in the cell. Prior to obtaining current–voltage (IV) polarization data, the cell was conditioned at 68 °C and 100% RH in the potential range between 0.9 and 0.3 V in 0.05 V steps for 10 hours. Polarization data were collected by scanning the cell voltage from open circuit voltage (OCV) to 0.2 V in 0.05 V steps (3 minutes at each potential point). The HOT and NOC operating conditions were identical as the MAT cell measurements. Scans were repeated two times to ensure reproducibility within each MEA.

#### 2.7.10 Electrochemical impedance spectroscopy

	Parameter	Units	Value
	Temperature	°C	68, 85
Cathode			
	Pressure	bara	2.00
	Flow rate per cell	SLPM	4.00
	Composition	%	100% N <sub>2</sub>
	RH	%	40, 50, 65, 80, and 100
Anode			
	Pressure	bara	2.00
	Flow rate per cell	SLPM	1.00
	Composition	%	100% H <sub>2</sub>
	RH	%	40, 50, 65, 80, and 100

Table 2-3: Test station set-up and EIS testing protocols

The impedance spectra were obtained by applying an AC voltage of 10.0 mV over the frequency range from 1 Hz to 50 kHz with the CAT fuel cell test statio. EIS data were analyzed using a Randles equivalent circuit and fitted using ZView software (version 3.1c Scribner Associates, Inc.). Initially, cells were conditioned in H<sub>2</sub>/Air at 100 % RH and 1.5 A cm<sup>-2</sup> for 2 hours. Then the RH was brought to 20% until equilibrium was reached (~ 1 hour); after that the MEA was conditioned at the desired RH for another 20 minutes in H<sub>2</sub>/N<sub>2</sub>. All EIS measurements were recorded under H<sub>2</sub>/N<sub>2</sub> atmosphere and in the order of lowest to highest RH (Table 2-3). Once the measurements were completed for one condition, the RH was increased and the sequence repeated.

# **3 Optimization of Randomly Oriented CNF Layers**

#### 3.1 Introduction

In order to study the factors affecting structure and properties of electrospun CNF, a factorial experiment was designed. The processing parameters were optimized by way of the response surface method (RSM). PAN-co-MA was selected as a suitable precursor polymer because the thermal profile indicated a steady and controlled stabilization reaction, improving the formation of ladder structures. Preliminary experiments were conducted to approximate the appropriate range for the independent variables (factors). The four factors in the experiment were: polymer concentration, CNT concentration, stabilization temperature, and carbonization temperature. The systematic approach demonstrated the main effects, in addition to which fabrication parameters played a significant role on the four responses (fiber diameter, porosity, Young's modulus, and electrical conductivity). The factorial design indicated the most significant factors and interaction terms which was used to navigate the response surface. Contrary to the hypothesis and literature, addition of CNT in the polymer dope did not improve electrical properties and was removed from the process. There appears to be discrepancy between the validation experiments and the predicted model values; however, the trends were applicable as a starting point for the fabrication of catalyst layers with sufficient properties. The challenges and errors in the model are explained and discussed; suggestions are also made for future work. Overall, the RSM predictions generated a set of fabrication parameters which produced fibers that met the design criteria of a catalyst support layer.

#### 3.2 **Preliminary process screening**

From the TGA spectra shown in Figure 3-1, it can be seen that both PAN and PAN-co-MA experience a rapid weight loss around 300 °C. Onset temperature was measured at the inflection

point, indicating the initiation of decomposition. PAN-co-MA revealed a decomposition temperature of 274 °C, whereas pure PAN had a decomposition temperature of 280 °C (Figure 3-1). It was previously reported that increasing the amount of the comonomer decreases the decomposition temperature [142,143]. The onset of rapid weight loss can also indicate the initiation of cyclization, a component of the stabilization reaction. Aside from TGA indications, DSC is also thoroughly reported for the stabilization of PAN copolymers. It is widely accepted that pure PAN is not a suitable candidate for the synthesis of carbon fiber because of the sudden and rapid evolution of heat [132,136,142,144,145]. As described in earlier chapters, the thermal shock can result in chain scission, yielding poor properties in the carbon fiber [136]. Comparing the DSC spectra of PAN and PAN-Co-MA, it is clear that the onset of cyclization occurs at a lower temperature, along with a slow and steady release of heat [145]. The authors proved that PAN-co-MA released less heat and underwent two distinct reactions, as opposed to pure PAN, where a large amount of heat is suddenly released rapidly (Figure 3-2) [145]. The gradual release of heat helps to maintain good chain structure during cyclization. The similarity of the TGA behaviour of the polymer used in this study and the reported literature suggests the polymer would behave similarly under heat treatment processing. It is necessary to choose an appropriate temperature range to optimize the heat treatment because the stabilization reaction occurs over a range of temperatures. Gupta proposed the stabilization temperature range for the PAN-Co-MA in his experiment occurs from 230 – 267 °C [145]. Gupta suggests that stabilization initiates from the amorphous phase at lower temperatures and goes to completion at higher temperatures in the crystalline phase. Because fabrication of nanofibers by electrospinning alters the crystallinity of the polymer, the amount of amorphous and crystalline phases vary [146]. Using these temperatures

as a starting point, a factorial design of experiments can be conducted to narrow down the optimal stabilization temperature.



Figure 3-1: TGA spectra of PAN-co-MA (top) and pure PAN (bottom) in air (5 °C min<sup>-1</sup>)



Figure 3-2: DSC curves on heating PAN-co-MA and homopolymer PAN in air at 1  $^{\circ}C$  min  $^{1}$  [145]

Electrospinning Parameters				
Spinning Distance	15 cm			
Needle gauge	18G			
Voltage	17.5 kV			
Pump speed	0.80 mm min <sup>-1</sup>			
Collector rotation speed 1 m min <sup>-1</sup>				

Table 3-1: Electrospinning parameters used for spinning 12 wt% PAN-co-MA

The preliminary results about the fiber diameter and electrospinning conditions can be used as a marker towards building a suitable factorial design. The conventional electrospinning apparatus for randomly oriented nanofiber layers was used for the following experiments. Using the electrospinning parameters shown in Table 3-1, 12 wt% PAN-co-MA was used to produce fiber mats. The fiber mats were stabilized and carbonized at various temperatures to determine the relationship between electrical properties and degree of graphitization. Fiber diameter after each stage of the heat treatment is shown in Table 3-2.



#### Figure 3-3: Fiber shrinkage after each stage of heat treatment (as-spun, stabilized, and carbonized)

From the diameters measured by Image J, the average diameter decreases after carbonization step. The bulk fiber mat also shows shrinkage after carbonization (Figure 3-3). Because of the non-uniform shrinkage, a metallic frame was used to sandwich the fiber mat which applied tension to the sample during heat treatment. The frame kept the sample flat and applied enough tension to prevent deformation. Applying tension or stretching during heat treatment also improves crystallinity and mechanical properties [119]. From the SEM images, it is clear that the electrospinning produced uniform continuous nanofibers without defect or beading. This reveals that the spinning parameters used are suitable for fabricating continuous nanofibers.

Additionally, in-plane electrical conductivity was measured after carbonization to investigate the effect of increasing carbonization temperature. The stabilization temperature was kept constant for all samples while carbonization temperature ranged from 700 °C, 750 °C, 800 °C, to 900 °C. Electrical resistivity was measured for the strip samples using a multi-meter (Agilent U1272A). As can be seen in Table 3-3, the resistivity decreased dramatically at 900 °C. Electrical conductivity was calculated from Equation (2.3) as described in previous sections. The results reveal that the minimum temperature needed to produce satisfactory electrical conductivity (> 5 S cm<sup>-1</sup>) is around 900 °C. Above 900 °C, CNF conductivity will improve proportionally. The mechanical strength is also expected to improve at higher carbonization temperatures due to the formation of graphitic structures. However, increasing the Young's modulus causes the CNF  $_{60}$ 

samples to become brittle and fragile to handle. Drawing from the preliminary results, clearly a set of experiments should be conducted to determine the optimized processing conditions to meet all design targets. Comparing the target design criterion to the preliminary results, it appears that the fiber diameter is too large while the electrical and mechanical properties needs improvement.

Table 3-2: 12 wt% PAN-co-MA average fiber diameter after heat treatment process, fiber shrinkage of 30%

(um)	As spun	Stabilized	Carbonized	% change (As spun to Carbonized)
Mean	0.458	0.355	0.309	32.53%
SD	0.036	0.069	0.039	
Min	0.412	0.236	0.256	37.86%
Max	0.529	0.459	0.39	26.28%



Figure 3-4: SEM micrograph of As-spun 12 wt% PAN-co-MA fiber mat (5 kV; 3Kx left, 10Kx right)



Figure 3-5: SEM micrograph of stabilized 12 wt% PAN-co-MA fiber mat (5 kV; 3Kx left, 10Kx right)



Figure 3-6: SEM micrograph of carbonized 12 wt% PAN-co-MA fiber mat (5 kV; 3Kx left, 10Kx right)

Carbonization Temperature (°C)	Resistivity (Ωmm)	Conductivity (S cm <sup>-1</sup> )	
700	320	0.034	
750	25	0.40	
800	6.3	1.6	
900	0.58	17	

 Table 3-3: Relationship between fiber in-plane electrical conductivity and carbonization temperature

## 3.3 **Two-level factorial design**

A set of experiments was designed to optimize the fabrication process and produce fibers that meet design targets (Table 3-4). Fiber diameter, porosity, and layer thickness are essential parameters to control and observe. In addition to studying the microstructure, the catalyst support layer must have the basic functionalities such as being mechanically robust and electrically conductive to transport electrons.

A factorial experiment was designed using four factors to systematically develop an optimized fabrication process. The design aims to control the material properties essential in achieving a high efficiency catalyst layer. The surface area, porosity, electrical properties and mechanical robustness are of significant importance in the catalyst support design. The factors chosen for the experiment: (1) polymer precursor concentration, (2) fiber stabilization temperature,

(3) fiber carbonization temperature, and (4) concentration of the conductive filler material, were shown in prior studies to directly influence these criteria. It is well known that polymer concentration has a great influence on fiber diameter and spinnability [88], which would affect the final product surface area and porosity. Heat treatment temperature influences the electrical conductivity and mechanical integrity of the porous structure [82,119,147]. Addition of conductive filler material such as carbon nanotubes (CNT) is also shown to improve electrical properties of composite structures [140]. The two-level DOE produced 16 experimental runs as shown in Table C-1. Low and high level of polymer concentration was 7 and 10 wt%. Fiber diameters measured at 12 wt% already had fairly large diameters (Table 3-2), thus a much lower concentration was chosen as the low level to produce fibers with smaller diameter. CNT concentration of 0 and 1 wt% was chosen for the low and high level because higher concentrations would present challenges in dispersion [140]. Stabilization temperature was 230 °C and 260 °C for low and high level based on current TGA data and published results [145]. Ramp rate and durations were also found through the exploratory work. Ramping too fast caused fiber mats to crack and shrink, in addition to fiber fusion. Selecting a rate of 1°C min<sup>-1</sup> ensured fibers experienced less shrinkage stress and maintained the fibrous structure. For complete stabilization, fibers should be calcined for at least one hour, some authors found two hours to be sufficient [132,144,145]. Carbonization temperature was 850 °C and 1100 °C for low and high levels based on the electrical properties seen in the exploratory work. Beyond 800 °C the electrical conductivity increased dramatically, reaching 17 S cm<sup>-1</sup> at a carbonization temperature of 900 °C (Table 3-3). Experiments were carried out in standard order to reduce block effect and other environmental variations.

The 16 experimental results were inputted into the Design-Expert software for statistical analysis. Each factor was fitted to a regression model and verified for statistical significance by

ANOVA. The graphical representation of the factors and responses was used to identify the presence of factor interaction. Contour plots illustrate predicted values, not experimental values, from the design. Summary of the regression analysis and model constraints can be found in the appendix (Table C-2).

Parameter	Target	Unit
Mechanical strength (compression without breaking)	> 700 (4.8)	psi (MPa)
In-plane electrical conductivity	> 5	S cm <sup>-1</sup>
Through-plane electrical conductivity	> 0.05 @ 218 psi ( 1.5 MPa) compression at 10 µm	S cm <sup>-1</sup>
Catalyst layer thickness	< 10	μm
Geometrical surface area	> 50	cm <sup>2</sup> cm <sup>-2</sup> geom.
Fiber diameter	< 200	nm
Mesh porosity	> 40	%
Area weight	< 1.15	mg cm <sup>-2</sup>

 Table 3-4: CNF design targets for MEA application based on recommendations from AFCC and industry standards

#### 3.3.1 Effect of process parameters on fiber diameter

Using the Design-Expert software for model fitting, the main effects were computed. Verifying the model using ANOVA method, it was found that the significant coded model terms were A, C, AD, BC, and ABC. This means that fiber diameter was influenced by a combination of the main effects polymer concentration and carbonization temperature. And was also influenced by the interaction between polymer concentration/CNT concentration, stabilization/carbonization temperature, and polymer concentration/stabilization/carbonization temperature.

The results obtained from the model are consistent with published work which discuss that nanofiber diameter is directly related to polymer concentration. The diameter was also affected by carbonization temperature since the nanofiber experienced shrinkage during the heat treatment process. In fact, the fiber shrunk up to ~30% after carbonization (Table 3-2). Because of the

complex interaction terms, it is impossible to find the optimal fabrication parameters by simply looking at the design factors cube. For example in Figure 3-7, the cube shows the results for 0% CNT and 1 wt % CNT. The cube demonstrates that there was an interaction between polymer/CNT concentrations, since some vertices show a decrease of fiber diameter with decreasing CNT concentration, while others do not. When this counteracting trend is observed, there is a strong interaction between two factors. Therefore, a prediction of the optimal process conditions is useful for responses that involve multiple main effects and interaction terms. Chapter 3.3.5 explains the model fitting and optimization of the factors based on RSM.

The fiber diameters from the experiment ranged from 159 nm to 372 nm. A graphical representation of the fiber diameter and distribution can be found in the appendix (Figure C-1 and Figure C-2). The fiber diameters were normally distributed and showed narrow standard deviation.



Figure 3-7: Factorial cube for fiber diameter recorded at 0 and 1 wt% CNT, red and blue circle indicates interaction

## **3.3.2** Effect of process parameters on fiber electrical conductivity

The main effects of fiber electrical conductivity were computed using the Design-Expert software. Verifying the model using ANOVA method, it was found that the significant coded model terms were C and D. Therefore, the electrical conductivity of the sample was simply related to carbonization temperature and CNT concentration. This result appears to be consistent with the previously cited literature. In general, the designs factor cube and interactions curve revealed that there were no interactions. A strong interaction occurs when the response is different depending on the settings of two factors. When interaction curves intersect, it indicates that the effect of one factor depends on the level of the other. The interaction curve shows that D-1 and D+1 never crosses, this is a clear indication that interactions were not involved and the only main effects were carbonization temperature and CNT concentration.

A graphical representation of the electrical conductivities for each sample can be found in the appendix (Figure C-3). Contrary to the original hypothesis and published literature, the electrical conductivity was not improved by addition of CNT. The discrepancy can be attributed to the lack of dispersion in the spinning dope. During mixing, CNT could form agglomerates and become non-homogenously distributed in the fiber. Thus, there was no significant enhancement seen when CNT was added. The agglomerates obstruct the electric current from travelling through the fiber, the electrons must jump between CNT agglomerates instead of smoothly across a streamlined and straight connected network. Several studies have mentioned that the electrical properties depend greatly on dispersion and percolation limit [140,148]. Increasing the carbonization temperature from 850 °C to 1100 °C led to an order of magnitude increase in inplane conductivity, from 3.2 to 43.3 S cm<sup>-1</sup>. Because the in-plane electrical conductivity surpassed the minimal requirement desired for the current design, the addition of CNT was not a necessary step for the optimized fabrication process.



Figure 3-8: Design factor cube and interactions graph for electrical conductivity, interaction recorded at polymer concentration = 10 wt% and stabilization temperature = 230 °C

## 3.3.3 Effect of process parameters on fiber mesh porosity

The main effects of mesh porosity were computed using the Design-Expert software. Verifying the model using ANOVA method, it was found that the significant coded model terms were D and interaction BC. This means the main effect was CNT concentration and there was an interaction between stabilization/carbonization temperatures. As can be seen in the design factor cube, the porosity was increased with increasing CNT concentration (Figure 3-9). Interactions curve demonstrates that there was a strong interaction between BC because the C-1 and C+1 intersects. Again, this signifies that the two effects were co-dependent. The observed trend, related to CNT concentration, may be explained by the electrospinning process theory. The electrospinning process is governed by a variety of forces (viscoelastic and electrostatic force) [44]. The addition of CNT increases both the solution viscosity and electrical conductivity. The increase in solution electrical conductivity was shown to decrease fiber diameter and improve spinnability [45]. Moreover, increasing the electrical conductivity of the solution has an effect on the formation of the Taylor cone and straight jet length [45]. Decreasing the length of the straight jet portion allows for increased instability portion, which is responsible for the whipping and reduction of fiber diameter. Thus, altering the surface charge and the tangential electric field along the fluid surface resulted in lower fiber diameters leading to higher mat porosity. In summary, the porosity met the design targets for catalyst support layer. However, the porosity used in this model was estimated by calculating the surface area, a physical characterization method was used later to verify the assumptions (Chapter 4.2). A graphical representation of the porosity can be found in the appendix (Figure C-4).



Figure 3-9: Design factor cube recorded at 10 wt% polymer and interactions graph for % porosity; carbonization temperature setting: black square = 850 °C and red triangle = 1100 °C

## 3.3.4 Effect of process parameters on fiber young's modulus

Main effects related to Young's modulus was determined using Design-Expert software. Verifying the model using ANOVA method, it was found that the significant coded model terms were A, D, AB, and BCD. Thus, the main effects were polymer and CNT concentration. The response was also influenced by the interaction between polymer concentration/stabilization temperature and stabilization temperature/carbonization temperature/CNT concentration. Interactions curve demonstrates that there was a strong interaction between AB since the B-1 and B+1 intersects. Again, this means that the effect of one factor depends on the level of the other. From the graphical representation of the Young's moduli recorded for the experiments, the range was very broad, from approximately 16 GPa to 3 GPa (appendix Figure C-5). Although clear trends cannot be observed in the data set, it appears that modulus increased with decreasing polymer concentration while increasing CNT decreased the modulus. This observation might be explained by the poor CNT dispersion in the nanofiber, as previously mentioned. It was observed in prior work that poor electrical properties caused by insufficient dispersion of CNT, also led to poor mechanical properties [148]. Essentially, the agglomerated CNT forms stress concentrations inside the fiber causing it to break prematurely. Because lower polymer concentration typically produces smaller diameter fibers, it was expected that the fibers would have enhanced mechanical properties [88]. Briefly, the classical Weibull size effect theory explains the probability of having a small defect would decrease with decreasing cross sectional area [149]. Because the defects are smaller and fewer, fracture propagation caused by stress concentration decreases, yielding enhanced mechanical properties. To conclude, the modulus achieved for most of the samples were satisfactory for the current application, revealing that CNF is a mechanically robust and suitable material for this application.



Figure 3-10: Design factor cube recorded at 10 wt% polymer and interactions graph for elastic modulus; stabilization temperature setting: black square = 230 °C and red triangle = 260 °

#### 3.3.5 Development and validation of factor models

To model and predict the optimal processing parameters for fabrication of CNF, the experimental responses were developed into a first order function. The response equation is a function of the main effects and interactions, as mentioned in previous sections Equation (3.1). Representing the equation in terms of coded factors instead of actual values simply shows the

magnitude of each effect. To verify the significance of the model, key statistical values were studied. P-value, which measures the models statistical significance, should be less than the significance level of 0.05. As shown in Table 3-5, the P-value for all 4 responses satisfied this requirement, validating adequacy of these models.  $R^2$  is a measure of the percent of the responses being represented by the variables. Table 3-5 shows  $R^2$  and adjusted  $R^2$  for the four responses. Although higher values would be desirable, the models show adequate signal as measured by the signal to noise ratio – adequate precision. All modeled equations demonstrate a ratio greater than 4, the desired minimum ratio. The model predicts variabilities (adjusted  $R^2$ ) of 82%, 91%, 66% and 82% in new data for diameter, conductivity, porosity, and modulus, respectively. Ideally, the difference between predicted  $R^2$  and adjusted  $R^2$  should be less than 0.2 [150]. Larger differences, shown in the diameter and modulus models, may indicate a large block effect or issues with the input data and/or model (Table 3-5). Additional statistical fit parameters are presented in the appendix (Table C-2).

$$y_D = 242 + 18A + 3B - 16.75C + 10.12D + 3AB - 3.25AC + 27.63AD + 25BC + 22ABC$$

$$\ln y_C = 2.3 + 0.96C - 0.37D$$

$$y_P = 80.94 + 0.31B + 0.19C + 4.19D - 2.19BC$$

$$ln y_M = 1.75 - 0.22A - 0.13B + 0.046C - 0.14D + 0.22AB - 0.13BC - 0.13BD - 0.020CD + 0.26BCD$$
(3.1)

Response polynomial equation in coded factors, for *y<sub>D</sub>* diameter, *y<sub>C</sub>* conductivity, *y<sub>P</sub>* porosity, and *y<sub>M</sub>* Young's modulus

 Table 3-5: Significance probability (P-value) and correlation coefficient of linear regression for response surface equations

			Surrace equation		
Response	P-value	R <sup>2</sup>	Adjusted R <sup>2</sup>	Predicted R <sup>2</sup>	Adequate Precision
Diameter	0.0085	0.9273	0.8181	0.4827	11.345
Conductivity	< 0.0001	0.9260	0.9146	0.8878	19.036
Porosity	0.0023	0.7532	0.6635	0.4779	7.315
Modulus	0.0086	0.9270	0.8175	0.2016	10.173

Since the model equations show statistical significance, it is suitable for navigating the design space. To find the optimal processing parameters for this set of equations, a set of targets

and constraints on the variables were implemented. The highest priority was to minimize the fiber diameter, the experimental results showed a range between 159 and 372 nm. Modulus and conductivity were medium priority thus, achieving a value between 5 and 52 S cm<sup>-1</sup> was set as the target. Young's modulus was optimized in the same manner, targeting a modulus between 5 - 16 GPa. Lastly, since nanofiber mats are well known for large porosities, the optimization for porosity was set as the lowest priority [151]. The target was to maximize the porosity, which was between 71 and 95% from experimental results. A summary of the values and constraint used for optimization is presented in Table 3-6.

A list of solutions were generated by the software with the best solution having a desirability factor of 0.883. A table showing all possible solutions is presented in the appendix (Table C-3). From the list of predictions, the best possible fabrication process is shown in Table 3-7. From the results, the prediction removes agglomerated CNT from the process. This is plausible since non-uniformly dispersed CNT caused negative effects, such as decreased mechanical strength and electrical properties. As expected, the model predicts a high carbonization temperature (1100 °C) since this was the main effect for electrical conductivity. An example of the contour plots for predicted diameter is illustrated in Figure 3-11. Although the plot indicates that smaller diameter could be achieved in the blue region, it is not a feasible solution since stabilization occurs at higher temperatures. Sufficient stabilization is necessary to ensure the chemical structure is well aligned in preparation for carbonization step [119]. The red labels on the plot show the design points which were part of the 16 experiments. Lastly, the optimal predicted solution, producing a diameter of 149 nm, was revealed to be 10 wt% PAN-co-MA, 230 °C stabilization, 1100 °C carbonization, and no addition of CNT. Using the optimized fabrication parameters, CNF were prepared and characterized again to verify the RSM solution (Figure 3-12).

Name	Goal	Limit	Limit	Weight	Weight	Importance
A:Polymer concentration	is in range	7	10	1	1	3
B:Stabilization T	is in range	230	260	1	1	3
C:Carbonization T	is in range	850	1100	1	1	3
D:CNT concentration	minimize	0	1	1	1	3
Diameter	minimize	159	372	1	1	5
Conductivity	is in range	5	52.28	1	1	3
Porosity	maximize	71	95	1	1	1
Modulus	is in range	5	16.558	1	1	3

Table 3-6: Optimization targets and constraints for each response and factor



Polymer Concentration (wt %)	10.00
Stabilization T (°C)	230
Carbonization T (°C)	1100
CNT Concentration (wt %)	0.00
Diameter (nm)	149.25
In-plane conductivity (S cm <sup>-1</sup> )	37.96
Porosity (%)	78.81
Modulus (GPa)	6.79
Desirability	0.88



A: Polymer (wt%)

Figure 3-11: Contour plot of predicted values for fiber diameter; optimal solution of 149 nm at carbonization temperature of 1100 °C and 0 wt% CNT
Table 3-8: Material properties of CNF fabricated using predicted optimal parameters

Fiber diameter (nm)	333 ± 26
In-plane conductivity (S cm <sup>-1</sup> )	31.94 ± 2.95
Porosity (%) (measured)	79.82
Elastic modulus (GPa)	18.76 ± 1.22
Ultimate Tensile Strength (MPa)	72.69 ± 6.67
Through-plane conductivity (S cm <sup>-1</sup> )	0.37 ± 0.86
Compression strength (MPa)	> 3MPa





Although the validation experimental results reported in Table 3-8 differed from predicted model, the majority of the design targets were met. The assumption is that the trends and effects predicted by the RSM model are valid and can be taken as guidance for future investigation of CNF fabrication. It is important to note that process optimization by RSM is an iterative procedure [152]. To reduce variance and improve confidence levels, the DOE should be repeated using the predicted values from the initial optimization. Moreover, in the current study there were no repeats for each run, one sample was fabricated and tested for each of the 16 experiments. To improve the dataset, an average of three samples per run is recommended for future optimizations. Deviation from the model may be due to some outliers in the data or a block effect. Blocking essentially

happens when a variability cannot be overcome (e.g. needing two batches of raw material to produce one container of a chemical). Some of the variation in the data may be due to different batch spinning dopes or variations in the environment over several days. It is unclear whether temperature and relative humidity affects the electrospinning process [153]. The samples were prepared on separate occasions with maintenance on the tube furnace, thus the reproducibility of the data may be affected. Initially, tensile specimen were cut into strips after the carbonization step, this may have induce defects as the specimen are brittle after carbonization. The handleability may explain the large deviation between the 16 specimens. Subsequent tensile specimen, the optimized batch, were cut before the carbonization step to minimize the amount of defects, lowering the SD and increasing modulus (Table 3-8). Significant effort was made to perfect the sample preparation process, however variation between each specimen over the course of the 16 runs is plausible and probable. Outliers were discarded, however, the reported standard deviations across the samples should be considered (see appendix).

Variability in the results may also arise from the measurement methods used. For instance, the variance was relatively large for fiber diameter measurements (Figure C-2). The deviation was mostly a result of manually measuring the diameter using visual methods and Image J. Mechanical properties of the fibers also showed large deviations due to the nature of sample preparation. Because CNF were brittle and formed micro defects during sample preparation, the measured modulus and ultimate tensile strength revealed significant variance (Figure C-5). Experimental error caused by inaccurate measurement systems would decrease the significance of the predictors. As a result, the variability and errors from the experimental runs were transmitted to the RSM model. Ultimately, the predicted trend from the model was still applicable and satisfied design criteria. Except for fiber diameter, all responses showed accurate prediction within the

experimental error. In order to improve future models, reiteration of the optimization using additional sets of data would be required to refine the predictions and narrow the deviation. Presently, it is sufficient to demonstrate that the electrospinning and heat treatment process can produce CNF that possesses the material properties desired for MEA fabrication. Assembly of the MEA with the optimized CNF is discussed in Chapter 6.

## 3.4 Summary

Electrospinning method was used to fabricate non-woven nanofibrous layers for the application of fuel cells. As fuel cell catalyst supports require high surface area, porosity, durability, and electrical conductivity, a factorial design was implemented to optimize the material properties. Because of the requirement for high electrical conductivity, PAN and PAN-co-MA precursor were selected as possible candidates to produce carbon nanofiber. TGA result suggested that PAN-co-MA was favorable for high temperature carbonization and was selected for the factorial design. A factorial design using four factors and four responses was conducted to optimize the fabrication of carbon nanofibers. The four factors selected (polymer concentration, CNT concentration, stabilization temperature, and carbonization temperature) were previously shown to influence key fiber properties, such as, fiber diameter, porosity, electrical conductivity, and mechanical strength. From the 16 experiments conducted, a polynomial model was fitted to predict the most desirable fabrication parameters. The optimized variables were: 10 wt% PAN-co-MA, 0 wt% CNT, 230 °C stabilization temperature, and 1100 °C carbonization temperature. The predicted responses for this model were: ~150 nm diameter, ~38 S cm<sup>-1</sup> in-plane conductivity, ~78% porosity, and ~6.8 GPa Young's modulus. However, in validation experimental results, the properties deviated from the model, although still satisfying the overall design criteria of the CNF

layer. The current study has demonstrated the feasibility of using electrospinning to fabricate catalyst supports that met industry design targets.

# 4 Comparison Between RNL and OAN Properties

### 4.1 Introduction

The conventional electrospinning method was modified to spin unidirectional fibers with the same optimized processing parameters established in the previous chapter. The electrospinning method used two pairs of copper plates and two high voltage power sources. A schematic of the modified electrospinning apparatus is shown in Figure 2-2. OAN were fully characterized to investigate the effect of orientation on fiber diameter, layer thickness, porosity, electrical conductivity, and surface chemistry. Material properties were evaluated and compared against RNL to ensure design criteria were satisfactorily met. Surface chemistry was verified to demonstrate carbon content and surface groups were the same as RNL post-heat treatment. The majority of design targets were met, however OAN had inherent weaknesses due to the modified electrospinning process.

# 4.2 Structural and mechanical properties

The optimized parameters generated from the RSM were used to fabricate RNL and OAN samples. For the remainder of the research work RNL and OAN carbonization temperature was lowered to 900 °C instead of 1100 °C because samples carbonized at 900 °C showed better handleability while maintaining sufficient electrical properties. RNL was fabricated using traditional electrospinning method, while OAN was fabricated using modified electrospinning setup. Since the electrospinning method was modified, the fibers were characterized to ensure they satisfy the design targets for MEA application. Fiber diameter distribution is shown in Figure 4-1 and Figure 4-2 for RNL and OAN CNF, respectively. The average fiber diameter for RNL after carbonization was  $333 \pm 26$  nm. Although the fiber diameter did not meet the target requirement of > 200 nm, the RNL diameter was deemed appropriate for the application because CB agglomerates may span up to 5  $\mu$ m depending on the mixture and processing of the catalyst. Conversely, OAN met the design target, achieving a fiber diameter of 248 ± 46 nm after carbonization. The parallel electrode set-up may have induced additional thinning because the fibers were suspended across a 7 cm gap [154]. Although negligible, OAN fibers may sag under its own weight compared to RNL fibers which were collected on an aluminum foil. More probable, the OAN fibers may experience more fiber shrinkage compared to RNL because of the more fragmented structure. Because RNL fibers were entangled and formed a cohesive and well-packed non-woven fabric, the random network may have prevented further shrinkage. In OAN, the fibers are separated and aligned in one direction, thus the applied tension would cause stretching in one direction resulting in further reduced diameter (Figure 4-3). Furthermore, OAN and RNL likely consist of different crystal lamellar structure because of the modified electrospinning method and solvent evaporation process. As a result, OAN and RNL would behave differently during heat treatment.



Figure 4-1: RNL fiber diameter distribution using optimized fabrication process (CNF)



Figure 4-2: OAN fiber diameter distribution using optimized fabrication process (CNF)

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							G
	H	H					
	H	H	H	H	H	-	
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Figure 4-3: Schematic of OAN fiber organization and through pores

 Table 4-1: Porosity measurement by densometry of random and aligned CNF after Platinum and Ionomer deposition

Random CNF (%)	79.82
Pt Random CNF	87.39
Ionomer/Pt Random CNF	74.29
Orthogonal	73.19
Pt Orthogonal	67.40
Ionomer/Pt Orthogonal	64.27

It was hypothesized that OAN would have higher porosity since the fiber alignment should produce through pores with large spacing (Figure 4-3). The porosity measurements were made using a densometer which utilizes Archimedes principle. The porosity of random nanofibers after Pt and ionomer deposition were roughly 74% porous, while the orthogonally aligned fibers were 64% porous. Though the porosity decreased, it still remains comparable to the porosity of carbon black based catalyst layers. The conventional agglomerated catalyst layer is between 30 - 60%porosity [155–157]. The porosity did not change significantly with the application of ionomer and Pt because the coating was very thin and did not block secondary pores (Table 4-1). The decrease in porosity for OAN may be explained by the overlapping and adhesion between unidirectional fibers shown in Figure 4-4. It is also possible that the submersion liquid did not thoroughly permeate the deeper pores during the densometry measurements because of lower wettability, resulting in lower porosity values. In comparison, the calculated % porosity using Equation (2.4), was  $80\% \pm 5.05\%$  for RNL, revealing reasonable agreement to the densometry porosity values. Although previous studies have shown well organized orthogonal structures, the fiber diameter (1  $\mu$ m) and pore spacing (10  $\mu$ m) were much larger than the present work [158]. Moreover, the fiber mat geometrical area in prior work is typically very small (2-3 cm wide) because of the limitations of the parallel electrodes and fiber sagging across larger distances [112,113]. The main challenge for orthogonal nanofiber mats is maintaining the degree of perpendicularity due to the weakened electrical field with increasing gap distance and layer thickness [159,160].

OAN mats were electrospun until a suitable thickness was achieved, this involved stacking orthogonal layers manually ~40 times to reach a desired thickness. To the extent of the author's knowledge, the mat thickness achieved in this study has not been realized in prior work. Fiber mesh thickness was measured by SEM to ensure consistency and uniformity. Carbonized layer thickness was measured by micrometer as a first approximation. To verify the values from physical method, MEA were embedded into resin for cross sectional imaging. The cross section image shows the CNF thickness, roughly  $9.0 \pm 0.9 \ \mu m$  and  $\sim 9.7 \pm 1.2 \ \mu m$  for OAN and RNL samples respectively (Figure 4-5). It was important to maintain low and consistent thickness during

fabrication because it is related to the diffusivity which plays a key role in water management and fuel transport. A summary of the structural properties for OAN and RNL is presented in Table 4-2.



Figure 4-4: Orthogonally aligned carbon nanofiber mat fabricated by modified electrospinning method (SEM: 5 kV Secondary electron mode)

Carbonized OAN and RNL samples were tested on the KES-G1 Kawabata microtensile testing system to evaluate the mechanical strength. Because OAN was carbonized at 900 °C, an additional set of RNL carbonized at the same temperature was tested to have direct comparison. The mechanical properties averaged over five samples is illustrated in Figure 4-6. The ultimate tensile strength ( $3.77 \pm 1.71$  MPa) was significantly lower compared to RNL ( $67.15 \pm 5.16$  MPa) samples. The same trend can be seen for the Young's modulus where OAN and RNL achieved  $1.16 \pm 0.65$  GPa and  $16.18 \pm 1.88$  GPa, respectively. The OAN results reveal some scatter because of the inherent structure and fabrication method of the orthogonal fibers. The poor mechanical properties of the OAN were largely due to the orientation of the fibers. Since they were organized

in an orthogonal manner, approximately half of the fibers carried the load in the tensile axis. This drastically lowers the calculated tensile strength because the orthogonal fibers contribute to the cross sectional area as well. Another factor was the delamination during sample preparation. As explained in a prior section, because the orthogonal fiber layers were stacked consecutively instead of continuously drawn, the fibers lack cohesion through thickness. The residual static charge on the fibers caused the layers to peel off or wrinkle on the surface, causing variability in the measurements. Nevertheless, OAN showed reliable mechanical properties in compression, which is the main mechanical loading in a fuel cell stack. OAN did not crack or rip during the resistance under compression measurements (> 4 MPa).



Figure 4-5: Orthogonally aligned (A and C) and random nanofiber (B and D) cross sectional thickness (15 kV, secondary electron mode)

Table 4-2: Summary of OAN and RNL structural dimensions measured by SEM and densometry

	Layer thickness (µm)	Diameter (nm)	Porosity (%)	Porosity after I/Pt (%)
Orthogonally aligned nanofiber	$9.0 \pm 0.9$	248 ± 46	73	64
Random nanofiber	9.7 ± 1.2	333 ± 26	79	74



Figure 4-6: Ultimate tensile strength (left) and Young's modulus (right) for OAN and RNL (average of 5 samples carbonized at 900 °C)

# 4.3 Through-plane and in-plane electrical properties

Sample	In-plane conductivity (S cm <sup>-1</sup> )	Through-plane conductivity (S cm <sup>-1</sup> )
Target	> 5	> 0.05
RNL (1100 °C)	31.94 ± 2.95	0.453 ± 0.193
RNL (900 °C)	6.734 ± 0.320	$0.266 \pm 0.040$
OAN (900 °C)	1.535 ± 0.140	0.13 ± 4.20 x 10 <sup>-3</sup>
RNL (700 °C)	0.202 ± 0.021	4.41 x 10 <sup>-3</sup> ± 2.18 x 10 <sup>-3</sup>

Table 4-3: Summary of electrical properties for OAN vs. RNL

Electrical properties for OAN were measured by the same method as previously discussed.

The in-plane and through-plane resistance were measured at increasing carbonization temperatures for both OAN and RNL samples (Table 4-3). The effect of graphitization and carbonization temperature can be seen in both in-plane and through-plane measurements. RNL carbonized at 1100 °C achieved an in-plane electrical conductivity of 32 S cm<sup>-1</sup>. Samples carbonized at 700 °C

did not achieve the minimum target requirement of > 5 S cm<sup>-1</sup>. Similarly for through-plane resistance, the RNL sample carbonized at 700 °C did not meet the target requirement of > 0.05 S cm<sup>-1</sup>. OAN in-plane electrical conductivity was measured at 0° to the fiber axis. OAN showed weak electrical properties (1.5 S cm<sup>-1</sup> and 0.13 S cm<sup>-1</sup>) compared to RNL. A reason for this could be because the contact resistance between each fiber layer. Since the RNL was fabricated continuously, the fibers were deposited overlapping each other and allowed to dry in a compressed state. OAN, on the other hand, were electrospun as separate orthogonal layers. The layers underneath had time to dry and was not easily adhering to the next layer being deposited. Therefore, there was a lot of resistance between each stacked layer, resulting in higher throughplane resistance (threefold increase between 900 °C RNL and OAN) (Table 4-3). In-plane conductivity was also significantly poorer than RNL because only the fibers parallel to the measurement direction was conducting electrical current. It should also be noted that the OAN fiber mat was delaminating in some areas, thus increasing contact resistance throughout the layers. Although OAN samples met the design requirement for through-plane resistance, the effect of orientation and spinning method is apparent in the present results.

### 4.4 Surface carbon content via x-ray photoelectron spectroscopy

The analysis of the surface chemistry was performed by XPS to determine the possible functional groups. Functional groups are often used as nucleation sites for Pt deposition. It is also a good indication of what types of carbon are on the surface; amorphous or graphitic. From the C 1s scan, the peak was calibrated at a binding energy of 284 eV. The convoluted peaks are resolved using XPS Peak software. The deconvoluted peaks revealed the presence of graphitic and disordered carbon (Table 4-4). Furthermore, the  $\pi$ - $\pi$  satellite signal represents the graphitic carbon, demonstrating adequate amount of graphitic carbon on the fiber surface [161]. Other carbon

species include: C-OH, C-O-C, C-N, C=O, and COOH. These maybe residual species remaining after heat treatment or contaminants absorbed from the atmosphere. Calculating the area under the peaks, the atomic % of each species is found. The results reveal CNF carbonized at 1100 °C possess ~70% graphitic carbon and 12% disordered carbon on the surface. This corresponds to a graphitic to disordered ratio of 5.8. XPS results suggest that abundant graphitic structures were present, indicating the chosen heat treatment procedure was sufficient. Considering the carbonization temperature used was not particularly high compared to other published results or industry standards, the graphitic yield is encouraging. Since the graphitic portion is responsible for high electrical conductivity and mechanical stability, it is desirable for the CNF support. CNF carbonized at 900 °C was also examined to compare the effect of carbonization temperature on graphitic content. As expected, ratio between graphitic to disordered carbon decrease to 3.2 for samples carbonized at 900 °C (Table 4-5). However, the results also reveal there is little oxygen containing functional groups which would assist Pt deposition. Nonetheless, it is possible for atomic size defects, such as graphene edges, to act as nucleation sites during Pt deposition [162]. Subsequently, surface chemistry will be analyzed after chemical functionalization and Pt deposition to observe chemical bonding and chemical state of Pt in Chapter 5.2.2. Because samples carbonized at 1100 °C showed higher graphitic content, it was considered more inert to chemical treatments or Pt deposition. Hence, the carbonization temperature was lowered to 900 °C for results presented in Chapter 5 and 6.

Peak	RNL 1100 °C	Position (eV)	Area	Component %
0	C1: C=C graphitic	284.45	11656.02	71.22
1	C2: C-C aliphatic/dis-ordered	285	2026.402	12.38
2	C3: C-OH + C-O-C + C-N species	286.5	787.223	4.81
3	C4: C=O	287.7	563.494	3.44
4	C5: COOH	289.2	241.638	1.48
5	C6: π-π* shake up	290.7	1092.438	6.67
	sum		16367.22	100

Table 4-4: 1100 °C carbonized 10 wt% PAN-co-MA deconvoluted XPS peaks for C 1s, pass energy 20 eV

Table 4-5: 900 °C carbonized 10 wt% PAN-co-MA deconvoluted XPS peaks for C 1s, pass energy 20 eV

Peak	RNL 900 °C	Position (eV)	Area	Component %
0	C1: C=C graphitic	284.5	23116.53	63.79
1	C2: C-C aliphatic/dis-ordered	285.05	7306.078	20.16
2	C3: C-OH + C-O-C + C-N species	286.5	2261.594	6.24
3	C4: C=O	287.6	1374.142	3.79
4	C5: COOH	289.2	782.566	2.16
5	C6: π-π * shake up	290.7	1396.677	3.85
	sum		36237.59	100

Since OAN was fabricated using a modified electrospinning set-up the chemical structure and composition may be altered. XPS was conducted to evaluate the chemical bonding and graphitization of OAN samples carbonized at 900 °C. Although the OAN was heat treated under the same conditions, XPS revealed differing results from RNL. Figure 4-7 shows the composition of the carbon species from the deconvoluted Carbon 1s peaks. Similar to the RNL peaks, there were 6 components detected. Again, the characteristic  $\pi$  – $\pi$ \* satellites indicate the presence of sp<sup>2</sup> aromatic carbon. The individual carbon species on the OAN surface are labeled in the graphic, with the most notable results being the C=C and C-C components. Compared to the RNL samples, OAN comprises of notably less graphitic carbon (Figure 4-8). The graphitic to disordered carbon ratio is 1.33 and 3.16 for the OAN and RNL, respectively. It is plausible that the decrease in graphitic content is due to the electrospinning method rather than the carbonization process, since both samples are heat treated under the same conditions. Because OAN is electrospun using a desk top set-up, the humidity and environment cannot be readily controlled [163]. Relative humidity levels has been shown to affect the nanofiber morphology, roughness, and porosity [163]. The difference between the two electrospinning methods may be the reason for dissimilar surface groups. The drying time and solvent evaporation is different in the OAN samples as a result of having to manually stack the fiber layers in an orthogonal pattern.



Figure 4-7: Example of deconvoluted C 1s XPS spectrum for OAN (10 wt% PAN-co-MA carbonized at 900 °C), calibrated at 284.6 eV, pass energy: 20 eV

The RNL method can continuously deposit fiber and form a cohesive non-woven layer while the solvent is evaporating. RNL also experiences whipping motion during deposition whereas OAN experience little whipping and are aligned across two copper plates. The whipping motion from electrospinning results in thinner fibers and macromolecular chain alignment within the fiber [164–166]. Additionally, the quality of carbon fibers reportedly increased by stretching (molecular alignment), which improved the formation of the ladder structure during stabilization [167]. Thus, the crystallinity and molecular alignment was possibly the reason for OAN and RNL disparity. Because of the lower graphitic content, the electrical properties in OAN would also be deficient. Although there was a large variance between the amount of disordered and graphitic carbon in the OAN and RNL samples, the remaining carbon-oxygen groups appear to be similar.



Figure 4-8: OAN and RNL (carbonized at 900 °C) surface chemistry by deconvoluted C 1s XPS spectrum, pass energy 20 eV

# 4.5 Summary

Novel orthogonally aligned carbon nanofibers were successfully fabricated using a modified electrospinning method. Following the same post processing method as RNL, the OAN were fully characterized to ensure similar properties were obtained. Fiber diameter, porosity, layer thickness, surface chemistry, through-plane electrical resistance, and in-plane electrical conductivity were compared to RNL. OAN CNF were carbonized at a lower temperature of 900 °C, following RNL fabrication, to ensure good compromise between mechanical and electrical properties. The measured fiber diameter was  $248 \pm 46$  nm, compared to  $333 \pm 26$  for RNL. Porosity for the OAN layer was 73% and 64% before and after L/Pt deposition, respectively. The porosity

for RNL was slightly higher than OAN, 79% and 74% porosity, respectively. Although OAN was expected to have through-thickness pores and organized structure, the electrospinning process caused some fibers to adhere together rather than spreading out. The layer thickness for OAN and RNL were largely similar, approximately 9 µm. This is comparable to conventional catalyst supports using carbon black [168]. Therefore, all structural and dimensional requirements for the catalyst design were met. Tensile test revealed that RNL ( $67 \pm 5$  MPa) possessed significantly higher tensile strength compared to OAN ( $3.77 \pm 1.71$  MPa). The lower strength in OAN was largely due to less fibers in the loading axis direction—unable to carry the load. The inherent stacking of the OAN resulted in higher electrical resistances through-plane compared to RNL samples. The same challenge was observed in the in-plane direction because fibers perpendicular to the probing axis carry little current or have large resistances because of the inefficient path. Although the in-plane conductivity and through-plane conductivity for OAN was 1.5 S cm<sup>-1</sup> and 0.13 S cm<sup>-1</sup>, respectively, the electrical properties remain adequate for the current catalyst support design. Surface chemistry analysis by XPS also confirmed the decrease in graphitic content and increase in disordered carbon, leading to less conductive fibers. Although the graphitic to disordered ratio decreased, the OAN possessed similar amount of remaining carbon-oxygen species to those of RNL samples. The deconvoluted XPS results for RNL demonstrated higher graphitic content in 1100 °C carbonized sample compared to 900 °C carbonized sample. The higher graphitic content is beneficial for mechanical and electrical properties, however the graphitic structure may also inhibit Pt deposition. In Chapter 5.2.2, XPS reveals whether Pt preferentially bonds to functionalized CNF or original CNF. Ultimately, material characterization revealed that OAN met the key design criterion. Based on the material evaluations discussed, it appears RNL is a more suitable candidate for MEA application because of the superior electrical

properties and ease of controlling microstructure. The study concludes RNL and OAN processing parameters cannot be directly translated due to the difference in electrospinning method which yields dissimilar as-spun fiber properties (crystallinity, cohesion, porosity, etc.). The next chapter discusses the Pt plating and ionomer deposition process used for both OAN and RNL.

# 5 Platinum and Ionomer Deposition on CNF

### 5.1 Introduction

Using the optimized parameters discussed in Chapter 4, the CNF were prepared for Pt deposition. Several deposition methods were explored to determine the simplest and effective process. Because CNF is not traditionally used as a catalyst support, not much information has been reported about Pt deposition methods. The main challenge was selecting a deposition process that yields a homogeneous Pt coating with small particle size and reduces the handling to prevent the thin CNF layers from tearing. Because Pt is the most expensive component of the MEA, it is important to utilize a method that would deposit a thin layer, adequate for achieving high catalytic surface area. Some of the deposition results discussed here include atomic layer deposition, electrodeposition methods using different reducing agents, and hydrogen reduction. Most of the methods were deemed unfeasible because samples were too delicate or the Pt was not uniformly distributed on the fiber surface. Electroless plating using formic acid as reducing agent was favorable because it was a facile method and produced nanowire-like clusters which exhibit high surface area. Pt loading was controlled and different particle size was also observed by changing concentration of the plating bath. Chemical analysis revealed the deposited Pt's chemical state, which was consistent with Pt 4f XPS patterns reported in the literature. Next, ex situ electrochemical characterization via cyclic voltammetry (CV) was conducted to determine the effective platinum surface area (ECSA). The CV results reveal that the ECSA does not follow a linear relationship with increasing Pt concentration. Additionally, the ex situ testing revealed the presence of catalytically active facets which were consistent with the literature. Ionomer was also deposited to determine how the Pt would interact with ionomer. From the cross sectional STEM/EDX maps, it appears that the ionomer adhered well to CNF/Pt and formed a thin layer

around the entire fiber. The ionomer was shown to form a connected network between fibers, allowing the protons to travel efficiently through-plane. Optimization of the Pt loading and ionomer loading was necessary to obtain feasible catalyst supports for MEA fabrication and *in situ* FC testing.

### 5.2 Evaluation of Pt deposition process

#### Hydrogen Reduction

Different types of pre-treatment were investigated to form functional groups on the CNF surface as described in Chapter 2.4. After soaking in the Pt bath overnight, the bath solution completely evaporated and the dried sample was reduced in hydrogen furnace using the conditions explained in Chapter 2.4. Figure 5-1A shows small Pt particles were deposited on the CNF surface. The Pt formed a homogenous dense layer around the fiber and was distributed across the surface of the mat. Although the size of the Pt particle was desirable and the Pt loading was 115  $\mu$ g cm<sup>-2</sup>, the Pt was not consistently distributed within the thickness. SEM images of early samples revealed that the morphology was inconsistent and often does not produce the desired Pt loading. From Figure 5-1A, The CNF was pre-treated in citric acid and (3-Aminopropyl) triethoxysilane, soaked in a H<sub>2</sub>PtCl<sub>6</sub> acetone bath, and reduced in H<sub>2</sub> furnace. The method formed a thick coating with little or no exposed CNF, this may create a challenge for the formation of a TPB.



Figure 5-1: Pt deposition by various methods (5 and 10 kV, secondary electron mode)

### Acetic Acid Method

Because the acetic method requires solution to be constantly stirring or boiling, the delicate CNF could easily crack, therefore stabilized fibers were also explored. The stabilized fiber achieved higher Pt loading than the CNF,  $45 \ \mu g \ cm^{-2}$  and  $3 \ \mu g \ cm^{-2}$  respectively (Figure 5-1C and D). However, the acetic acid method proved to be ineffective and cumbersome since stabilized fibers would still need to be carbonized at a later step to increase the electrical conductivity.

## ALD Pt deposition

SEM images of CNF coated with ALD revealed poor deposition. The Pt was either too thin, depositing on an atomic level, or the CNF surface was overly inert for this method (Figure 5-1B). XPS of this sample also did not reveal Pt species on the surface. ALD may have deposited an atomic layer of Pt which is not enough for the fuel cell to function effectively. To achieve a thicker layer of Pt using ALD, the deposition cycles would need to be increased significantly, causing the process to be economically unfeasible.

# Formic Acid method

Pre-treating the CNF with methanol (MeOH) and depositing Pt using formic acid method, the Pt particle were evenly distributed on the fiber surface and dispersed evenly to create small islands Figure 5-1E. The morphology shown was promising and desirable, however, the MeOH treatment was not effective and produced inconsistent Pt loading. Similarly, Figure 5-1F reveals large nanowire clusters formed from the formic acid method. The Pt did not distribute homogenously on the fiber surface using MeOH and (3-Aminopropyl) triethoxysilane pretreatment, large regions were bare.

Lastly, Triton X and PVP surfactant was added to promote nanowire growth in one direction and to also prevent precipitation in solution [169]. In Figure 5-1G, a good dispersion of

small Pt particles were obtained using the formic acid method with addition of 0.1 mL Triton X. The method yielded 130  $\mu$ g cm<sup>-2</sup>, which is near the targeted Pt loading. The addition of a pretreatment step did not improve the Pt morphology or yielding, in fact, the 0.5 mL Triton X was extremely difficult to remove and can be seen as thick layers in the SEM images (Figure 5-1H). Figure 5-1I shows a similar sample using 0.1 mL Triton X with inconsistent coating. Fibers beneath the surface had uneven or sparse coating of Pt. Because surfactants would be considered impurity in the MEA and can hinder the performance, a small amount of PVP was used for later optimized samples. Evaluating all the methods and challenges associated with each, the final procedure for Pt deposition includes: pre-treatment in 3M HNO<sub>3</sub>, followed by formic acid reduction method with addition of 2 mg of PVP in the plating bath. Results of the developed plating method can be seen in Figure 5-2. Nanowire were grown in small circular clusters with homogenous distribution and controllable Pt loading.

## 5.2.1 SEM/TEM evaluation of Pt nanowire coating

Low, medium, and high Pt loading samples were examined in SEM. As can be seen from the SEM images, the Pt clusters were evenly and homogeneously distributed through the thickness of the CNF layer (Figure 5-2). The particles were densely dispersed along the fiber, yielding numerous catalyst reaction sites. Increasing the Pt concentration yielded larger clusters and more densely packed Pt. High magnification images reveal that the particles appear to be a nanowire like structure arranged into a sphere (Figure 5-3 and Figure 5-4). This is advantageous since the nanowire structure increases the specific surface area, ultimately improving the catalyst reaction sites. The average cluster size measured by Image J was roughly 10, 25, and 70 nm, for low, medium, and high concentration, respectively.



Figure 5-2: SEM micrograph of electroless plated Pt on CNF (top to bottom: low, medium, and high concentration Pt precursor) (1 kV, secondary electron mode)



Figure 5-3: SEM image showing dense Pt nanowire clusters on CNF surface (120kx, 1 kV, secondary electron mode)

TEM observation confirmed the presence of Pt nanowires with a preferential growth direction. Nanowire length and diameter is roughly 10 - 15 nm and 3 - 5 nm, as observed from

TEM micrographs (Figure 5-4). The nanowires protrude randomly from spherical clusters on the CNF surface. The crystallographic spacing shown in the TEM reveals a d-spacing of 0.23 nm which corresponds to a single crystal direction of <111> as seen in XRD peaks [141]. Comparable Pt nanowire morphology is obtained by Shangfeng et al. following the same Pt growth methodology [170]. Cross sectional EDX elemental mapping also revealed an even Pt coating around the fibers (Figure 5-4). The thickness of the Pt layer was uniform across all fiber cross sections. The 1D architecture of the Pt nanowire is expected to enhance mass transport by improving the oxygen diffusion to the Pt surface. Therefore, desired efficiency could be achieved with reduced Pt loading as a result of the higher Pt utilization. The applied electroless plating was found to be suitable for fabrication of CNF/Pt mats for fuel cell assembly and testing. Although challenges were met in exact Pt loading control, with careful handling, using as strict as possible deposition conditions, satisfactory control was achieved.



Figure 5-4: TEM of Pt Nanowire crystal structure (left) and cross sectional STEM EDX map of Pt around each fiber (right) (STEM/EDX, 200 kV)

# 5.2.2 Chemical composition by XRD and XPS

Surface chemistry analysis was conducted to compare the OAN and RNL before and after chemical functionalization and Pt deposition. Because OAN had much lower graphitic content 100

than RNL, the goal was to determine whether the Pt deposition would be more favorable for OAN layers. The effect of lower graphitic content was also investigated for RNL samples carbonized at 700 °C for comparison. The influence of chemical functionalization treatment was analyzed for OAN and RNL with regards to changes in nitrogen and carbon species. Lastly, XPS and XRD data validated the quality of the Pt coating by measuring  $Pt^0/Pt^{n+}$  ratio and crystal structure.

### 5.2.2.1 Functionalization analysis

Chemical treatment using HNO<sub>3</sub> was used to encourage even distribution of Pt during electroless plating. Acid treatment on CNT and CNF has been shown to introduce oxygen functional groups which assist in the deposition of Pt [61,171,172]. To verify the production of functional groups from acid treatment, the surface chemistry was analyzed by XPS. Figure 5-5 illustrates the nitrogen species before and after HNO<sub>3</sub> treatment for RNL carbonized at various temperatures. Left over nitrates were seen in all three samples, with 900 °C and 1100 °C carbonized samples exhibiting higher amounts. From the non-treated samples, it appears that pyridinic nitrogen decreased with increasing carbonization temperature, while substitutional and pyridine nitrogen experienced the opposite trend. The nitrogen trends were consistent with literature regarding the heat treatment for PAN carbon fibers [167]. After HNO<sub>3</sub> treatment, RNL carbonized at 1100 °C appear to exhibit unchanged ratio between nitrogen species. This suggests that acid treatment did not have large effect on this sample, possibly due to the higher content of graphitic carbon – which is typically inert and stable (Figure 5-6). Contrary, RNL 900 °C showed the largest change in nitrogen species, converting from predominately substitutional nitrogen before treatment to pyrrolic after treatment. Also, a large drop in pyridinic nitrogen was observed after acid treatment. These changes indicate the HNO<sub>3</sub> treatment was very effective on RNL 900 °C samples. Interestingly, although RNL 700 °C had the least graphitic carbon, the acid treatment did not appear to affect the chemical structure. Except for the increased nitrate amount, the remaining nitrogen species appear unchanged before and after treatment (Figure 5-5). It is not clear from observation of C and N species the reason for the large impact of treatment on RNL 900 °C samples. However, the overall atomic % composition of the sample reveals that the amount of nitrogen increased significantly after treatment (0.8% to 3.11%) (Table 5-1). Contrary, atomic % of nitrogen was relatively stable before and after treatment in RNL 700 °C (11.53% to 11.51%) and 1100 °C (1.39% to 1.37%) samples. This may be a result of left over nitrates by incomplete washing after treatment because RNL 900 °C retained the highest amount of nitrates.



Figure 5-5: Comparison of nitrogen species before (left) and after (right) HNO3 chemical treatment for RNL carbonized at 700 °C, 900 °C, and 1100 °C

Following the same procedure, the effect of geometrical structure and spinning method on surface chemistry was investigated. In Figure 5-7, OAN and RNL carbonized at 900 °C was measured by XPS before and after HNO<sub>3</sub> treatment. From the N 1s deconvoluted curves, the OAN appears to have dominant substitutional and pyridinic species. The percent composition of each species was significantly different from RNL samples, although they were carbonized at the same temperature. According to Laffont's study, at a transition temperature of ~500 °C, pyridinic structure partially changes to form substitutional nitrogen [167]. With increasing carbonization temperature, Watt proposed N atoms located at graphene edges link together and are eliminated as gaseous N<sub>2</sub>, leading to the formation of graphene structure [173]. As shown in Figure 5-7, RNL had a larger amount of substitutional nitrogen, suggesting the successful formation of substitutional nitrogen from pyridinic. Moreover, atomic % composition indicated only 0.8% nitrogen in RNL, while OAN 900 °C had 4% (Table 5-1). This observation may explain the discrepancy in chemical composition and surface properties of the OAN fibers. Because OAN was fabricated using modified electrospinning method, it is possible the alignment and geometrical structure of the assembly affected the carbonization process. As discussed previously, the whipping motion in electrospinning influences the molecular chain alignment, possibly inducing favorable gas diffusion and steric situation [167]. Moreover, the arrangement and elimination of atoms was further enhanced by applied tension during heat treatment [167]. Although moderate tension was applied, OAN experienced larger shrinkage than RNL. As a result, the chemical structure and the material properties differed because of the nature of OAN fibers.

Because of the inherent nature of the OAN fibers, it was expected that the composition of nitrogen before and after treatment would not follow the same trend as RNL. As shown in Figure 5-7, the OAN fibers showed a more balanced composition of nitrogen, with the addition of nitrates. Instead of experiencing a large increase in pyrrolic nitrogen, the OAN samples had a small decrease in pyridinic and substitutional. Based on the virtually identical nitrogen groups after treatment, it appears that the HNO<sub>3</sub> treatment did not have a large influence on the surface chemistry. Again, the majority of nitrates detected are likely residual from incomplete sample washing. After HNO<sub>3</sub> treatment, nitrogen content increased from 0.8% to 3.11% and 4% to 6.13% for RNL and OAN, respectively. Similarly, the HNO<sub>3</sub> treatment did not seem to affect C

composition. With RNL samples, carbon content decreased after treatment, however in OAN samples the carbon content remained constant. Interestingly, oxygen atomic % is the highest for both treated and non-treated OAN sample (Table 5-1). It is possible that oxygen groups provided functionality for the Pt plating, thus increasing the  $Pt^0$  content [11].



Figure 5-6: Comparison of carbon species before (left) and after (right) HNO<sub>3</sub> chemical treatment for RNL carbonized at 700 °C, 900 °C, and 1100 °C



Figure 5-7: Comparison of nitrogen species before (left) and after (right) HNO<sub>3</sub> chemical treatment for OAN carbonized at 900 °C

Sampla ID	Atomic %					
Sample ID	С	0	Ν	Na	Pt	
RNL 900	96.53	2.64	0.83	0.00	0.00	
RNL 900 HNO3	84.54	12.34	3.11	0.00	0.00	
RNL 900 Pt	58.85	16.40	5.25	0.00	19.50	
RNL 900 HNO₃ Pt	59.55	16.26	8.53	0.00	15.66	
RNL 700	86.26	2.21	11.53	0.00	0.00	
RNL 700 HNO3	80.60	7.89	11.51	0.00	0.00	
RNL 700 Pt	72.17	12.83	8.72	0.00	6.28	
RNL 700 HNO₃ Pt	71.74	10.43	10.84	0.00	6.99	
RNL 1100	94.85	3.76	1.39	0.00	0.00	
<b>RNL 1100 HNO</b> 3	91.60	7.03	1.37	0.00	0.00	
RNL 1100 Pt	55.47	17.54	6.70	0.00	20.29	
RNL 1100 HNO <sub>3</sub> Pt	85.33	8.45	3.68	0.00	2.54	
OAN 900	78.49	15.87	4.00	1.64	0.00	
<b>OAN 900 HNO</b> 3	78.94	14.93	6.13	0.00	0.00	
OAN 900 Pt	64.16	16.09	5.18	0.00	14.57	
OAN 900 HNO₃ Pt	70.72	19.26	2.46	0.00	7.56	

Table 5-1: Surface chemical composition denoted in atomic percentages

# 5.2.2.2 Chemical composition of platinized CNF



Figure 5-8: Relationship between degree of graphitization and metallic Pt to oxidized Pt ratio

XPS analysis was conducted on samples after Pt deposition to observe the effect of  $HNO_3$ treatment. The results shown in Figure 5-8 reveal there is an increasing trend between carbonization temperature and the ratio Pt<sup>0</sup>/Pt<sup>n+</sup>. Interestingly, higher metallic content was achieved across all samples without HNO<sub>3</sub> treatment. It is well known that higher degree of graphitization results in a more stable sp<sup>2</sup> carbon structure, this generally means less number of nucleation sites for Pt reduction [174,175]. Although XPS results indicated lower metallic content for lower carbonization temperatures, it is not representative of the Pt distribution and coverage. Since XPS is a surface method and it scans a small area ( $20 \,\mu m^2$ ), it cannot give information about Pt yield or thickness of Pt coating throughout the CNF layer. From SEM observations, HNO3 treatment assisted with Pt deposition by yielding a denser Pt coating with homogenous distribution throughout the fibrous layer. The effect of the treatment was most clearly seen in 900 °C carbonized RNL samples. This observation may be explained by the Pt coverage and reduction process (Figure 5-9). It is assumed that Pt deposition is initiated by heterogeneous nucleation at an anchoring site (defect or functional group) and continues to deposit by crystal growth [176]. The slow reduction process allows for the formation of nanowires by anisotropic growth [141]. Thus, samples exposed to acid treatment possessed more anchoring sites for nucleation-leading to denser nanowire growth on the CNF surface. This led to homogenous distribution of nanowires with high surface area (Figure 5-10). Since the resulting Pt nanowire coating exhibited high surface area, it was more prone to developing a thin oxide layer when exposed to air [177]. This phenomena explains the reason samples treated with acid retains lower ratio of metallic to oxidized Pt content (Figure 5-11). The metallic ratio is higher for highly graphitized samples for the same reason-the Pt surface area is much lower with less nucleation sites. This thin oxide layer is present on all Pt coatings and would be removed during potential cycling before MEA testing. Overall,

the current method of acid treatment allows for dense and homogenous deposition of Pt nanowires with large surface area. It should be noted that CNF produced for the remainder of the thesis was carbonized at 900 °C instead of the original optimized 1100 °C because more uniform Pt was achieved. Since samples carbonized at 900 °C showed surface groups that would be beneficial for Pt deposition, higher Pt yield and stronger bonding may exist. It was not critical to carbonize at higher temperatures since carbonization at 900 °C already provides sufficient electrical and mechanical properties.



Figure 5-9: SEM images of CNF/Pt without HNO<sub>3</sub> treatment (left) and with treatment (right); Pt surface area is higher after treatment



Figure 5-10: Nanowire growth on CNF surface with (left) limited anchoring sites and (right) many anchoring sites [176]

Platinum electroless plated RNL was analyzed by XRD and shown in Figure 5-12. The diffraction shows strong characteristic peaks for crystalline platinum. The three major peaks detected here correspond to (111), (200), and (222) at  $2\theta = 39.77^{\circ}$ , 45.99°, and 83.70°, which indicates that the deposited Pt is face centered cubic (FCC) structure (JCPDS Card 04-0802). The presence of (111) plane normally indicates high catalytic activity, since the adsorption/desorption

occurs on this facet [20,178–181]. From the sharp and high intensity of the diffraction peak, it appears the catalyst layer contains an abundant amount of Pt(111) which would improve the catalytic activity of the FC and potentially decrease amount of Pt required.



Figure 5-11: Comparison of metallic to oxidized Pt ratio for RNL with and without HNO3 treatment



Figure 5-12: X-ray diffraction diagram for Pt electroless plated CNF layers

## 5.3 Ex situ CV and effective platinum surface area



Figure 5-13: EPSA was calculated based on the area under the H<sub>ad</sub> oxidation curve

Although there are a number of studies using perchloric acid as the electrolyte solution to avoid adsorption of sulfate anions onto the Pt surface, prior work has shown that ECSA does not appear to be affected by the supporting electrolyte [182]. Moreover, H<sub>2</sub>SO<sub>4</sub> electrolyte can mimic the anion–electrode interaction between Pt surface and surrounding nafion sulfonic groups [183– 185]. To gain a preliminary understanding of how the catalyst layer will perform in fuel cell, *ex situ* CV was conducted to measure the electrochemical surface area. From the integrated charge in the hydrogen adsorption/desorption peak areas (Figure 5-13) in the CV curves and the Pt polycrystallite hydrogen adsorptions constant 0.21 mC cm<sup>-2</sup> Pt, the effective platinum surface area (EPSA, cm<sup>2</sup><sub>Pt</sub> cm<sup>-2</sup>) and the specific Pt surface area ( $A_{Pt}$ , m<sup>2</sup> gpt<sup>-1</sup>) were calculated according to the following equations; where  $Q_M$  is the charge associated with the formation of a monolayer of hydrogen [186]:

$$EPSA (cm2Pt cm-2) = Q_{M} (mC cm-2)/0.21 mC cm-2$$
(5.1)

$$A_{\rm Pt} (m^2 g_{\rm Pt}^{-1}) = EPSA (cm^{2}_{\rm Pt} cm^{-2})/Pt \text{ loading } (mg cm^{-2})^* 0.1$$
(5.2)

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$$Pt \% Utilization = EPSA\left(\frac{cm^2}{cm^2}\right) \times \frac{1}{A_{Pt}}\left(\frac{g_{Pt}}{m^2}\right) \times \frac{1}{Pt \ loading}\left(\frac{m^2}{g_{Pt}}\right) \times 100\%$$
(5.3)

EPSA is related to platinum utilization shown in Equation (5.3), therefore improving the EPSA would contribute to enhancing the fuel cell efficiency or decreasing the amount of Pt deposited on the catalyst layers. The voltammetric profiles of CNF/Pt membrane (Figure 5-14) displays the characteristic features with an H-sorption potential region (0.0 - 0.4 V), a double layer potential region (0.4 - 0.7 V) and an O-sorption potential region (0.7 - 1.0 V). From the cyclic voltammogram, the EPSA was calculated by hydrogen desorption region. The hydrogen desorption potential region of the curve also revealed small humps that are characteristic of different Pt crystallographic planes that exists [187]. This is consistent with the XRD results presented earlier.



Figure 5-14: Cyclic voltammogram of CNF/Pt catalysts with 3 different Pt loadings at 25 °C in N<sub>2</sub>-saturated 0.09M H<sub>2</sub>SO<sub>4</sub>, scan rate: 20 mV s<sup>-1</sup> (1.25, 1.5, and 2.0 g L<sup>-1</sup> precursor), normalized to geometric surface area of electrode

#### 5.3.1 Electrochemical surface area of RNL

Low, medium, and high concentration (~1.25, 1.5, and 2 g  $L^{-1}$ ) of Pt precursor was used to investigate the yielding of electroless plated Pt. The results suggest that the yielding is generally

presented by a linear relationship as seen in Figure 5-15, although not completely linear. However, further increasing the Pt loading would not be desirable since the Pt formed agglomerates and decreased the available active surface area. As seen from prior SEM images, the high concentration sample revealed large clusters that were densely packed. This dense morphology likely delays fuel diffusion and reduces the Pt utilization since the area beneath the surface is not easily accessible. Thus, it appears the ECSA trend was slowly plateauing as the loading increased. This demonstrated a diminishing return between Pt loading and active surface area, which is undesirable since the intention is to reduce Pt cost by reducing the amount deposited. The current method appears to be a promising deposition method for applying a thin layer of Pt on carbon nanofibers. Previous studies using other methods of Pt deposition obtained electrochemical area ( $A_{Pt}$ ) of about 50 – 100 m<sup>2</sup> gpt<sup>-1</sup>, while the current study achieved 66.5 m<sup>2</sup> gpt<sup>-1</sup>. This method attained comparable electrochemical areas to industry and literature but has room for improvement [138,186,188–190].



Figure 5-15: Relationship between Pt precursor concentration, ECSA and Pt loading
# 5.3.2 Electrochemical surface area of OAN

To evaluate the electrochemical performance of OAN sample, ECSA was evaluated by CV using the same method as mentioned in prior sections. As shown in Table 5-2, OAN follows the same trend as RNL sample with similar Pt loading. The results suggest that Pt deposition method was consistent between OAN and RNL samples. Additionally, the Pt nanowire morphology was preserved. Thus, OAN samples show comparable ECSA to RNL, suggesting orientation of the fiber does not have an effect for *ex situ* electrochemical performance. Because *ex situ* CV is performed in liquid electrolyte cell, the fibers would be completely wetted and in contact with reactants. The reaction *in situ* is slightly different since reactants are in gas phase, thus diffusion through the pores and efficient water management play a significant role. It is important to note that *ex situ* CV gives an indication of the available Pt surface area, however the *in situ* performance depends on multiple variables and operating conditions.

Table 5-2. ECSA for various KIVL and OATV samples	Table 5-2: ECSA for various RNL and OAN samples	
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Sample description	Pt loading (µg cm <sup>-2</sup> )	ECSA ex situ (m <sup>2</sup> g <sub>pt</sub> <sup>-1</sup> )
RNL, med I/C	157	36.87
RNL, high I/C	141	26.02
OAN, med I/C	140	23.54
RNL, med I/C, 700°C	283	38.79
RNL, med I/C	279	45.60
RNL sputtered, med I/C	81	82.83

Table 5-3: H2 cross over current and shorting resistance for RNL and OAN samples tested in CAT cell at105% and 50% RH for 68 °C and 85 °C, respectively (\*V50 was tested in 68 °C for both RH)

ID	68	°C	85	°C
	<i>i<sub>x</sub></i> (mA cm <sup>-2</sup> )	$R_{\rm s}$ ( $\Omega$ cm <sup>-2</sup> )	<i>i<sub>x</sub></i> (mA cm <sup>-2</sup> )	$R_s$ ( $\Omega$ cm <sup>-2</sup> )
RNL 150 µg cm <sup>-2</sup> , med I/C	2.923	1992.74	1.953	127.471
RNL 150 µg cm², low I/C	4.065	2856.125	0.379	123.981
RNL 150 µg cm², high I/C	4.26	6658.567	0.359	193.262
RNL 250 µg cm <sup>-2</sup> , med I/C	5.078	376.871	0.83	103.874
OAN 150 μg cm <sup>-2</sup> , med I/C	1.559	38.676	0.46	29.213
V50 150 μg cm <sup>-2</sup> , 1.1 I/C	6.702	141.4	5.084*	86.1*

H<sub>2</sub> crossover current ( $i_x$ ) and shorting resistance (Rs) was estimated by linear sweep voltammetry [191]. Comparing the crossover current, it appears all the RNL samples have comparable crossover to the baseline V50 (Table 5-3). The OAN sample experienced an  $i_x$  of 1.56 mA cm<sup>-2</sup>, the lowest of the MEAs. Comparing the OAN and RNL geometry, it appears that OAN has lower  $i_x$  possibly due to the difference in fiber orientation and porosity. As shown in prior chapters, the OAN orientation revealed lower porosity compared to RNL because the fibers were densely adhered together. In relation to ECSA and Pt loading, the  $i_x$  does not appear to show correlations between the samples. The results indicate that all RNL regardless of I/C and ECSA have similar  $i_x$ . V50 baseline showed slightly higher  $i_x$  likely due to the unoptimized fabrication of the catalyst layer, creating non-homogenous distribution of the carbon and ionomer. Compared to the conventional catalysts reported in the literature, CNF appears to have higher crossover current density due to the large open porous architecture [191–193].

#### 5.4 **Ionomer deposition and morphology**

Preliminary ionomer deposition was achieved by using vacuum pump and funnel method as described in Chapter 2.5. The loading and distribution of the ionomer was controlled by diluting the ionomer solution to achieve lower loading. Using the funnel and pump efficiently distributed the ionomer and did not induce blocked pores. The ionomer was thinly coated on each fiber and throughout the thickness. Loading was measured by weighing the sample before and after deposition and dividing by geometric surface area. Ionomer to carbon weight ratio, I/C, was calculated from the measured ionomer loading and measured Pt loading (5.4).

$$\frac{I}{C} = \frac{\text{ionomer loading}\left(\frac{mg}{cm^2}\right)}{Pt \text{ mass per area}\left(\frac{mg}{cm^2}\right) - Pt \text{ loading}\left(\frac{mg}{cm^2}\right)}$$
(5.4)

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The SEM images suggest that no pores were blocked and a thin layer was distributed on each fiber (Figure 5-16). High magnification micrographs prominently show a thin layer of ionomer surrounding the Pt nanowire clusters. Cross sectional TEM images were obtained to observe the ionomer and Pt coating dispersion and thickness. The EDX chemical composition maps reveal a homogenous thin layer of Pt deposited around each fiber. Since ionomer is responsible for transporting H<sup>+</sup> ions across the membrane, it is important to have a connected network in the catalyst support layer to improve the mass transport properties. From the EDX fluorine mapping images, there were thin strands connected across the fibers throughout the cross section. Because the fiber mat is porous, it is crucial that ionomer is dispersed through the thickness and connected between fibers to form a continuous network for proton transport. In the combined map, the ionomer uniformly surrounds the Pt layer creating a possible triple phase boundary region (Figure 5-17). Thickness measured from TEM images reveal that the ionomer coating was 29.46  $\pm$  21.38, 63.08  $\pm$  60.47, and 102.65  $\pm$  84.90 nm thick, for low, medium, and high I/C, respectively. Depositing 5 wt% and 10 wt% ionomer solution resulted in I/C of 0.11 and 0.285 respectively (Table 5-4). Medium loading I/C was achieved by annealing at 140 °C after the first deposition and repeating with 5 wt% ionomer again. The standard deviation for the ionomer thickness was large because ionomer was stretched between fibers, forming bridge structures (Figure 5-17 and Figure 5-18). The ionomer adhering onto the CNF/Pt was fairly thin and consistent throughout the regions. From the distributions graphs, there is a clear trend showing ionomer thickness increases with increasing I/C (Table 5-4 and Figure 5-19). Thus, the results confirm that ionomer loading and thickness was tailored by using the current deposition method with satisfactory distribution. Further control of the ionomer distribution and coating thickness would require thorough future work.

Previous ionomer study has shown that increasing I/C increases oxygen transport resistance. The authors also revealed that lower pressure-independent oxygen transport resistance was attributed to homogenous distribution of ionomer [194]. Decreasing I/C improved the oxygen transport resistance while increasing protonic resistance. It was recently reported in literature that effective ionomer thickness is an important parameter. The authors found optimal ionomer distribution and protonic conductivity with I/C of 0.4 and effective ionomer thickness of 1.6 nm [194]. Although not directly comparable because of using CNF, the current results agree with the conclusions by Orfanidi et al. which suggests that oxygen mass transport was largely affected by ionomer distribution and thickness [194]. *In situ* results presented in Chapter 6.3.2 discusses the effect of I/C on fuel cell performance and oxygen transport resistance.



Figure 5-16: Ionomer distribution between the pores and all around CNF/Pt surface

Table 5-4: Ionomer loading and I/C for CNF with similar Pt loading

Pt loading (mg cm <sup>-2</sup> )	I/C	lonomer loading (mg cm <sup>-2</sup> )
0.138	0.110	0.057
0.164	0.156	0.080
0.141	0.285	0.178



Figure 5-17: TEM/EDX mapping of ionomer by fluorine signal (left), combined map showing Pt, carbon and ionomer (right)



Figure 5-18: TEM/EDX maps of combined Platinum (red) and Fluorine in ionomer (green) distribution (A-D) and only ionomer distribution (E-F): Low I/C sample (A and E), medium I/C with a part of NRE membrane shown (B and F), high I/C (C and G), and high I/C OAN revealing ionomer pockets (D and H).





Surface wettability demonstrated a shift from hydrophilic to hydrophobic surface upon deposition of ionomer. Figure 5-20A reveals low contact angle for water wettability for CNF/Pt, meaning the platinized fibrous layer was moderately hydrophilic. Figure 5-20B, however, illustrates the contact angle after a thin layer of ionomer was coated on the fiber surface. The 125° contact angle suggests that the catalyst layer was hydrophobic. The results are promising since it is consistent with literature regarding ionomer chain alignment [30]. The hydrophilic CNF/Pt substrate encourages the hydrophilic side chains of ionomer to be preferentially oriented towards the CNF/Pt surface. The orientation allows for the formation of an intermediate water layer as shown in Figure 5-21 [30]. The hydrophobic backbone facing away from the CNF/Pt also improves water management by keeping water out of secondary pores [30]. This continuous water layer enhances the proton conductivity and electrocatalytic activity because the oriented hydrophilic ionomer group donates protons to this intermediate water film. In the practical scenario where ionomer is not in contact with all active Pt surface, a continuity of water channels can maintain the

proton conduction network [30]. Therefore, retaining the intermediate water layer in close contact with Pt is highly desirable for the proton conductivity and overall electrocatalytic activity.



Figure 5-20: Wettability of catalyst layer before and after ionomer deposition; contact angle of 50° and 125° (A and B)



Figure 5-21: Orientation of ionomer side chains towards hydrophilic Pt particles

## 5.5 Summary

To obtain the ideal Pt layer on the optimized CNF, several deposition methods were investigated. However, many challenges were encountered, proving some methods were unfeasible and inconsistent. The electroless plating method was the most suitable for CNF, producing well dispersed low Pt loading nanowires. The Pt nanowires were characterized in XPS, XRD, *ex situ* CV, and SEM to determine the Pt surface area and morphology. XPS revealed that more nucleation sites led to the formation of more oxidized Pt because of exposed surface area. XRD confirmed the presence of FCC Pt structure and the (111) crystal plane. This crystal plane is 118

desirable because literature suggests this is a catalytically active plane for ORR. Visual inspection by SEM indicated that increasing concentration of the Pt precursor increased the Pt loading and produced larger Pt clusters. Additionally, ex situ CV determined the optimal Pt precursor concentration to obtain highest active surface area. ECSA results were in agreement with SEM images, suggesting that the medium concentration (1.5 g  $L^{-1}$  Pt precursor) sample attained sufficient Pt surface area with a homogenous distribution. Trends from ECSA calculation suggests that lower Pt loading was more favorable because less Pt could be used while maintaining adequate active surface area. Lastly, the OAN ex situ properties were comparable to RNL, revealing similar ECSA at a given Pt loading. The consistency of the ECSA between RNL and OAN suggests Pt nanowires were of reasonable quality and repeatability, indicating the success of the Pt plating process and post processing. The funnel technique used to deposit the ionomer successfully formed a uniform and connected network without blocking pores throughout the catalyst layer thickness. Different concentrations of ionomer were deposited to determine the ideal I/C ratio for the CNF layers. SEM inspection revealed that ionomer was thoroughly coated on CNF and did not cover any pores. Ionomer thickness was measured by STEM/EDX mapping and revealed an increase in thickness with increasing ionomer concentration. Ionomer coating thickness was  $29.46 \pm 21.38$ ,  $63.08 \pm 60.47$ , and  $102.65 \pm 84.90$  nm thick, for low, medium, and high I/C, respectively. Additionally, ionomer bridges were formed between fibers for medium and high I/C samples. The bridges were expected to be beneficial since a homogenous network of ionomer would be formed throughout the CNF thickness, thereby facilitating a continuous TPB. Fuel cell performance is highly dependent on ionomer distribution and effective thickness, therefore it is crucial to compare the quality of the ionomer layer through visual techniques as well as in situ fuel cell measurements (Chapter 6.3).

# 6 In situ Evaluation of CNF Based MEA

## 6.1 Introduction

To understand and evaluate the feasibility of CNF catalyst support layers, the membrane electrode assembly (MEA) was fabricated for *in situ* fuel cell testing. A modified process for assembling the MEA was developed specifically for the CNF layers. Because the CNF was a standalone layer, conventional methods of assembly did not apply. Two types of MEA were fabricated, one for pre-screening and one for full scale fuel cell performance evaluation. The screening MEA had a small active area of 1.13 cm<sup>2</sup> and was tested in HOT and NOC conditions at specific potentials. The obtained results provided insights into the optimal CNF designs. Next, the top five performing samples from the MAT cell were fabricated into MEAs for full in-depth fuel cell testing. Polarization curves and Nyquist plots were collected for each sample. Maximum power density, ohmic resistance, ionic resistance, and oxygen transport resistance were evaluated and compared to unoptimized V50 CB. Particularly, the performance results were interpreted in the context of Pt loading and morphology, ionomer loading and distribution, fiber orientation, and fiber electrical properties. The results of the pre-screening and full fuel cell test emphasized the effect of material variables on fuel cell polarization losses. Ultimately, ionomer distribution appeared to be correlated with the fiber orientation, Pt loading, and ionomer loading. Lastly, characterization of the MEA after fuel cell testing was performed to verify the integrity of the CNF catalyst.

## 6.2 In situ MAT cell performance (pre-screening of CNF)

Following the testing procedure described in Chapter 2.7.9, *in situ* testing only under specific conditions and voltages were used to provide indications to the regions of polarization losses (Figure 6-1). Sample IDs and several variables of interest are listed in Table 6-2. Each 120

sample was run three to five times and the average of those runs are reported. For the RNL MEAs, the effects of ionomer loading, Pt loading, and carbonization temperature (CNF support conductivity) were explored. Three different I/C was analyzed to determine the ideal range for ionomer deposition on CNF structures. The I/C was lower compared to the baseline samples (1.1) because higher I/C would cause pore blockages and poor distribution in the CNF structure. Two Pt loadings, 150 and 250 µg cm<sup>-2</sup>, for CNF were fabricated in order to directly compare with the baseline loadings. The effect of carbonization temperature was analyzed to investigate the effect of electrical conductivity and surface chemistry. Since XPS revealed varying chemical compositions, the resulting Pt growth and properties could have an effect on overall in situ performance. All MEAs were compared to the two baseline samples with Pt loading of 150 µg cm<sup>-</sup>  $^{2}$  and 250 µg cm<sup>-2</sup> (described in Chapter 2.6). Vulcan catalyst was used as a baseline comparison because the Pt is distributed on the surface of the spherical carbon support, similarly to surface deposition of Pt on nanofibers. The difference is agglomerated structure in Vulcan catalyst layers, as opposed to aligned fibrous structure in CNF based MEAs, as well as diameter of the carbon support and porosity. A regional morphology comparison between CNF based catalyst layer with V50 CB is shown in Figure 6-2D and E. The V50 baseline used in this study was prepared using a Meyer bar method and has been previously measured and reported by Shukla et al. [195]. The current baseline was not optimized, however the porosity and characteristics reported in the literature provides an estimate of the properties. At an I/C of 1.1, the V50 is expected to have a porosity of roughly 40%, similar to the literature [195]. Table 6-3 compares testing results for all samples measured at 825 mV which is the activation region. The performance in this region is related to activation energy barrier between reacting species and is expected to be primarily affected by the electrode properties, such as ECSA, electrical properties of the electrode, and

ionomer contact with the active sites [44]. Also, overall pressure, temperature and reactant concentration play a role in this region [44]. The results demonstrate that all the CNF based MEAs outperformed the V50 baselines, in some cases even a 5x enhancement. Although V50 and CNF sample consist of the same Pt loading, CNF demonstrated superior performance owing to its highly porous structure and favorable Pt distribution. The very porous structure of CNF ensured uniform (high) concentration of the reactant gases throughout the layer, which was not the case with a dense unoptimized V50 catalyst layer. It is believed that TPB was more optimized since Pt was evenly distributed on CNF surface, as evident in the TEM images (Figure 5-18). Moreover, V50 showed poor performance in the activation region, indicating poor Pt utilization compared to CNF with Pt nanowire. The results suggest that the large surface area and high porosity of CNF contributed to the improved catalyst performance.

Table 6-1: Operating conditions of single cell performance tests performed in MAT cell hardware

	, , , , , , , , , , , , , , , , , , ,	
Temperature (°C)	68	85
Inlet relative humidity (%)	105	50
Balanced inlet pressure (bara)	2.	5
Stoic (both H <sub>2</sub> and Air)	> 1	0
Anode	100%	6 H <sub>2</sub>
Cathode	Ai	r
FFP aeometrv	Cathode: straight channel,	Anode: radial, no gasket

Normal condition (NOC)

sealing

Hot condition (HOT)

Sample ID	Pt loading (µg cm <sup>-2</sup> )	I/C	Alignment	Carbonization T (°C)
R150L	138	0.110	Random	900
R150M	157	0.158	Random	900
R150H	141	0.285	Random	900
R250M	279	0.156	Random	900
S80M	81	0.132	Random	900
V50-0.15	150	1.000	Baseline	NA
V50-0.25	250	1.000	Baseline	NA
O150H	140	0.238	Orthogonal	900
R250-T2	283	0.207	Random	700
R250-T1	246	0.177	Random	900

Table 6-2: Summary of in situ MAT cell samples and their properties



Figure 6-1: Regions of polarization losses in typical fuel cell. Voltages at which measurements were performed in this study are marked on the graph

At 825 mV, the RNL samples R250M and R250-T1 had the highest current (Table 6-3) which indicates fast kinetics at the Pt surface. This is plausible since R250M and R250-T1 both have higher Pt loading (250  $\mu$ g cm<sup>-2</sup>), improving the reaction kinetics (activation). It is worth to mention that both RNLs have I/C in the mid-range level. The next best performing sample was RNL R250-T2 with the same high Pt loading, medium I/C, but carbonized at 700°C. The CNF support in this sample had lower electrical conductivity due to the lower carbonization

temperature. This result verifies that electrical properties of the electrode support play an important role in the kinetic region as well.



Figure 6-2: High resolution STEM/EDX images of CNF/Pt and V50. (A) Electroless plating: nanowires showing (111) crystal planes (insert); (B) Cross section of CNF/Pt; (C) Pt sputter coated on fibers close to membrane; (D and E) STEM-EDX maps comparing carbon black V50 catalyst layer (0.25 mg<sub>Pt</sub> cm<sup>-2</sup>), white rectangle selects a region visually comparable in morphology to the CNF region; (F) EDX map of Pt distribution (red) on fibers; Pt layer illustrates 0.25 mg cm<sup>-2</sup> loading. Green color denotes Fluorine signal from ionomer, blue color denotes Carbon particles or fiber cross section, and red denotes Pt.

Ionomer thickness or I/C ratio also played a critical role in this region. Comparing 900 °C carbonized RNLs with similar Pt loading, but different I/C, R150L (low I/C), R150M (mid I/C) and R150H (high I/C), the highest performance was obtained with R150M (mid I/C). Low I/C RNL, as shown in (Figure 5-18), had a very thin layer of ionomer surrounding CNF/Pt fibers, but no connecting bridges to provide path for proton transport. Medium I/C sample contained a number of bridges and medium thickness of the ionomer film, enabling more efficient transport of protons without inhibiting oxygen access to active sites too much. High I/C sample contained more 124

connecting ionomer bridges, but the thickness of ionomer on the fibers was too high, hence inhibiting oxygen transport to Pt. Comparing the geometry, orthogonally oriented (O150H) CNF achieved lower current density compared to randomly oriented (R150H) CNF in the activation region. This was possibly due to the lower electrical conductivity of the OAN sample, which affected the activation energy barrier for electron transport. Generally, the trend in the kinetic region reveals that CNF samples performed better in NOC conditions compared to HOT conditions in the activation region. This was expected since humid and colder NOC conditions enhance proton conductivity due to the presence of condensed water, while dry and warmer HOT conditions increased proton resistance [196].

The effects of parameters in the **ohmic region** were investigated under NOC operation at 650 mV and HOT operation at 600 mV. Ohmic losses in a fuel cell are typically caused by resistance to the electron transport through the electrodes and external circuit, by contact resistances between flow-field plates/gas diffusion layer/electrodes/membrane, as well as resistances to the ionic transport through the ionomer in electrodes and the membrane [197]. Assuming that all external electrical resistances, and membrane ionic resistance are similar for all samples, the effect of Pt loading and distribution, ionomer loading, CNF electrical conductivity, and fiber alignment on the performance was evaluated. Figure 6-3 (red bars) compares performance of the samples with varying Pt loading, while I/C and carbonization temperature are kept constant. As expected, Pt loading does not have a large impact on ohmic resistance in CNF samples under both HOT or NOC conditions. However, CNF sample R150M with Pt loading of 0.15 mg cm<sup>-2</sup> showed more than two times higher performance compared to the same loading baseline V50 sample, indicating lower ohmic resistance (Figure 6-3 green bar). For this CNF sample, an in-plane conductivity of 6.73 S cm<sup>-1</sup> was measured (Table 4-3), which is higher than 4

S cm<sup>-1</sup> for CB in V50 [22]. In addition, a thin, almost continuous film of Pt on the surface of the fibers is providing additional conductivity to the R150M CNF layer, as through-plane conductivity increases from 0.266  $\pm$  0.040 S cm<sup>-1</sup> before Pt deposition to 0.388  $\pm$  0.0289 S cm<sup>-1</sup> after Pt deposition. When compared to the S80M sputtered sample (conductivity of 0.219 S cm<sup>-1</sup> at 34  $\mu$  g<sub>Pt</sub> cm<sup>-2</sup>), which has Pt only on one side of CNF mat and a very low loading, the sputtered CNF sample performed much lower than the electroless plated sample and comparable to the V50 sample (Figure 6-3 green bar). Although sputtered sample had lower Pt loading, V50 and sputtered sample achieved comparable NOC performance. This comparison shows that Pt distribution matters and could provide additional conductivity for the catalyst layer. Although the electrical conductivities did not differ significantly, it is worthwhile to report the through-plane properties because the catalyst layer electrical properties are not well-understood or accurately measured in the current literature [198–200]. Understanding the through-plane properties is beneficial for managing the local thermal variations which is linked to degradation and stability issues [199,201]. Pt distributed on the surface of the carbon support was beneficial to lower the ohmic resistance. In addition to carbon support conductivity and Pt distribution effect, ionomer loading and distribution also played a role. Ohmic resistance of V50 catalyst layer could be high due to the fact that ionomer coated Pt/C agglomerates have less electrical contact points, hence increasing overall electrical resistance. The effect of ionomer in the ohmic region was also seen when comparing the performance in HOT and NOC conditions (Figure 6-3 green bar). The performance of CNF samples in HOT compared to the NOC condition was lower due to the increased resistance of the ionomer film under higher operating temperatures and dry conditions. Even when ionomer bridges are present, the distance between the ionomer coated fibers are large, hence making proton conductivity a major challenge for the CNF based samples. In the dry HOT conditions, this effect

was especially enhanced. V50 catalyst layer, however, performed better in HOT than in NOC conditions. Due to the unoptimized deposition of the catalyst ink and the nonhomogeneous film of ionomer (Figure 6-2E), it is possible that NOC conditions caused flooding of the catalyst layer even in the ohmic region, causing drop in performance. Thick and connected ionomer in V50 catalyst layer provided satisfactory protonic conductivity in HOT conditions, hence retained higher performance (Figure 6-3 green bar).

Figure 6-3 (blue bars) reveals the effect of ionomer loading (or I/C ratio) on performance of CNF samples in the ohmic region. The results follow the same trend as in the kinetic region, with the mid I/C being the optimal design. Low I/C had only a thin layer of ionomer film coating the Pt (Pt + ionomer film thickness ~ 30 nm), which does not contain ionomer bridges to provide protonic path. NOC performance was satisfactory but HOT performance suffered a significant drop due to drying of ionomer. High I/C sample had the lowest performance. This is possibly not so much the ohmic effect, but the fact that fibers are covered in a thick (103 nm) ionomer film, inhibiting oxygen transport to the active Pt sites, lowering the overall performance. Mid I/C sample, with moderately thick ionomer film and a number of ionomer bridges, provided the best performance.

Effect of electrical conductivity of the CNF support on the performance in the ohmic region is given in Figure 6-3 (purple bars). As expected, in agreement with *ex situ* electrical measurements, the CNF carbonized at lower temperature of 700°C showed lower performance due to lower CNF support conductivity. Figure 6-3 (yellow bars) compares performance of CNF samples with randomly aligned fibers and orthogonally aligned fibers. As the *ex situ* conductivity data revealed, RNL samples had higher electrical conductivity, hence improved performance. Although the expectation was that orthogonally aligned CNF samples would improve overall performance, it seems that aligned fibers did not contain enough electrical contact points between

the fibers, which was manifested in increased ohmic resistance.

ent Carbonization T (°C)	Curren 825 m	Current Density at 825 mV (A cm <sup>-2</sup> )		ensity at 100 (A cm <sup>-2</sup> )
	NOC	HOT	NOC	HOT
dom 900	0.0361	0.0056	3.4410	3.0048
dom 900	0.0852	0.0509	3.8579	3.2762
dom 900	0.0572	0.0128	3.1850	2.0863
dom 900	0.1426	0.0676	3.6235	2.6889
dom 900	0	0	2.2786	1.9766
eline NA	0.0306	0.0435	0.8142	1.7973
eline NA	0.0120	0.0509	0.7653	1.5950
onal 900	0.0454	0.0250	3.0011	2.7621
dom 900	0.1228	0.0550	3.3001	2.6693
dom 700	0.0954	0.0963	3.3938	3.0928
	ent Carbonization T (°C) dom 900 dom 900	entCarbonization $T (^{\circ}C)$ Curren 825 mNOCdom9000.0361dom9000.0852dom9000.0572dom9000.1426dom9000elineNA0.0306elineNA0.0306elineNA0.0120onal9000.1228dom7000.0954	entCarbonization $T (^{\circ}C)$ Current Density at 825 mV (A cm^2)NOCHOTdom9000.03610.0056dom9000.08520.0509dom9000.05720.0128dom90000dom9000.03060.0435elineNA0.01200.0509onal9000.01280.0550dom7000.09540.0963	Carbonization T (°C)         Current Density at 825 mV (A cm <sup>-2</sup> )         Limiting D mV (A cm <sup>-2</sup> )           NOC         HOT         NOC           dom         900         0.0361         0.0056         3.4410           dom         900         0.0852         0.0509         3.8579           dom         900         0.0572         0.0128         3.1850           dom         900         0.1426         0.0676         3.6235           dom         900         0         0         2.2786           eline         NA         0.0306         0.0435         0.8142           eline         NA         0.0120         0.0509         0.7653           onal         900         0.1228         0.0550         3.3001           dom         700         0.0954         0.0963         3.3938

Table 6-3: Summary of current densities at 825 and 100 mV for all samples measured in the MAT cell; 68 °C105% RH and 85 °C 50% RH for NOC and HOT, respectively

transport loss) region measured at 100 mV. In this region the rate of fuel consumption is equal to its maximum supply speed [44]. Thus, the current density cannot rise because the fuel cannot be supplied at a greater rate. Generally, higher current density results in lower surface concentration

Finally, Table 6-3 compares the performance of all samples in the limiting current (or mass

of reactant species. In this region, the surface concentration of reactants reaches zero, thus the current is limited [197]. When compared to CNF samples, the baseline V50 samples performed very poorly. The lower porosity carbon black structure flooded in the NOC conditions, thus inhibiting reactant oxygen transport to the reaction sites. Nevertheless, the HOT performance in V50 samples was almost two times higher compared to NOC, as condensed water was no longer present and the dense network of ionomer still provides satisfactory transport of oxygen and protons for the reaction. Most CNF samples performed well in this region, especially in NOC conditions. The open structure of CNF cathode provided an easy path for oxygen diffusion and 128

although water was produced, it did not block the pores. The best performance was achieved for sample R150M, ~160  $\mu$ g cm<sup>-2</sup> Pt loading, followed by R250M, ~280  $\mu$ g cm<sup>-2</sup> Pt loading, both with mid I/C level. Comparing Pt loading effect (including R250-T1, 250  $\mu$ g cm<sup>-2</sup>), the results confirm already reported trend that catalyst layers with the same thickness, but lower Pt loading (lower Pt/C ratio), provide lower mass transport resistance [202]. Even the sputtered sample S80M with only 81  $\mu$ g cm<sup>-2</sup> Pt showed decent performance in this region, confirming the trend, although its overall performance was lower compared to other CNF samples due to high activation and ohmic overpotential.

Effect of I/C ratio, represented by samples R150H (high I/C), R150M (mid I/C) and R150L (low I/C), reveals that the sample with high I/C had the lowest performance in the mass transport region. That is because the thick ionomer film increases resistance to the oxygen transport. The effect was even more pronounced in HOT conditions. Sample with the low I/C performed moderately, as thin ionomer films provided lower oxygen transport resistance, but its overall performance was still low due to proton transport limitations. Mid I/C ratio again proved to be the optimal design. When comparing CNF samples with different carbonization temperatures (R250-T1 and R250-T2), it is evident that electrical conductivity of the support does not play a significant role in the mass transport region, as expected. Alignment of the fibers was expected to improve the mass transport due to the aligned pores. However, our results show that the performance of the aligned CNF sample (O150H) was lower than that of samples with randomly oriented fibers (R150H). This is in agreement with the densometry results, where OAN porosity was lower compared to RNL. TEM-EDX maps (Figure 6-4) reveal that the aligned CNF cathode contained pockets of ionomer in the contact points of the fibers. These pockets reduced the total porosity of the cathode affecting oxygen diffusion and increased oxygen transport resistance through the

ionomer film in these areas, reducing the performance in the mass transport region. Optimization of ionomer deposition is required to improve the aligned design.

Overall, the results indicate that CNF catalyst support demonstrated promising performance in the current fuel cell operating conditions. The effect of the large porosity and interconnected fiber network was evident in the *in situ* results in comparison to traditional CB catalysts. For comparison, a commercial CB catalyst can achieve a current density of roughly 1.5 A cm<sup>-2</sup> at 0.6 V, which is notably higher than that of the CNF MEAs [203,204]. Overall, the effect of ionomer distribution and concentration is paramount and can be clearly seen in activation, ohmic and mass transport overpotential regions. The mid-level ionomer concentration performed best in all three regions because it displayed a good balance between ionomer thickness and distribution. The ionomer bridges provided sufficient proton transport paths while remaining openly porous to support oxygen transport. The effect on oxygen transport resistance can be seen when ionomer loading was too high, producing a thick layer surrounding the fibers (> 100 nm), as shown in R150H RNL in the mass transport region. As evident from the various performance results, the performance improvement using CNF as catalyst support is encouraging.



Figure 6-3: Comparison between CNF samples in the ohmic loss region (85 °C, 50% RH, 600 mV and 68 °C, 105% RH, 650 mV conditions): high and low Pt loading; Pt deposition methods; low, medium, and high I/C; carbonization temperature; and orthogonal and random fiber mat.



Figure 6-4: STEM/EDX mapping of OAN catalyst layer with Pt loading of 0.15 mg cm<sup>-2</sup> (red: platinum, green: ionomer)

# 6.3 In situ CAT cell performance (full evaluation of CNF)

From the screening *in situ* test, the highest performing samples were evaluated in a larger sized (5 cm<sup>2</sup>CAT cell) fuel cell. The tested samples are listed in Table 6-4. The subsequent analysis involved recording EIS, CV, and polarization curves. The results were analyzed and compared to *ex situ* observations to determine structural property and performance correlations.

Sample Name	Orientation	Pt loading (µg cm <sup>-2</sup> )	I/C
RNL 150, med I/C	RNL	170	0.149
RNL 150, low I/C	RNL	166	0.109
RNL 150, high I/C	RNL	149	0.271
RNL 250, med I/C	RNL	250	0.203
OAN 150, med I/C	OAN	150	0.179

Table 6-4: Summary of CNF sample properties tested in CAT cell for polarization analysis

# 6.3.1 Current and power density analysis

Samples were tested under the same HOT and NOC conditions and polarization curves were plotted against V50 baseline sample (Table 6-5). The collected data were iR-corrected and appeared to have the same general trend as pre-screening results. The exception is the high I/C

RNL (150 µg cm<sup>-2</sup>) sample which performed better than low I/C. The OAN and low I/C RNL appears to achieve very similar current densities. Still, all RNL samples attained higher current densities than the V50 baseline. As shown in Figure 6-6, power density plot reveals a clearer trend and maximum power density achievable for CNF catalyst. As expected, NOC samples achieved higher maximum power densities because of the higher RH and low operating temperatures allowing sufficient proton conduction. The high I/C RNL (150 µg cm<sup>-2</sup>) achieved the highest maximum power density of roughly 1.0 W cm<sup>-2</sup>. Comparing the effect of geometry under NOC conditions, OAN power density was ~30% less than that of RNL with the same I/C and Pt loading. The negative effect of high Pt loading can be clearly seen in Figure 6-6. Maximum power density dropped nearly 50% when Pt loading was increased from 150  $\mu$ g cm<sup>-2</sup> to 250  $\mu$ g cm<sup>-2</sup> (Figure 6-6). The poor performance was largely due to the decreased electrochemical surface area because of the much larger particle size. As a result, Pt utilization was low and the catalyst remains costly with poor performance. In the interest of preserving parameters used in the CNF system, when preparing the V50 catalyst layer, the reported V50 may not be of optimal structure and performance. Thus, the current power density results for V50 are subpar compared to industrial performance standards. Nonetheless, the reported trends are helpful in determining MEA manufacturing variables to control and optimize. Furthermore, the present results are encouraging and comparable to published results using nanofibers as catalyst supports. At the same voltage (0.6 V), Park et al. reported a max current density of 900 mA cm<sup>-2</sup> for Pt/e-CNF slurry coated on carbon paper by spray method [35]. The pioneer work by Pintauro et al., using Nafion catalyst ink and Polyacrylic acid (PAA) as the electrospinning carrier polymer, revealed a current density of 873 mA cm<sup>-2</sup> at 0.6 V with Pt loading of 0.1 mg cm<sup>-2</sup> [94,95]. Electrospinning using graphene doped PAN/PVDF (Polyvinylidene fluoride) with 0.1 mg cm<sup>-2</sup> Pt loading also revealed similar results,

achieving roughly 1.4 A cm<sup>-2</sup> at 0.6 V [98]. More recently, a porous CNF Pt support (0.4 mg cm<sup>-2</sup>) achieved a current density of 200 mA cm<sup>-2</sup> at 0.6 V [39]. Additionally, the present study revealed a significant performance improvement compared to a recently reported freestanding electrospun CNF catalyst with similar fiber diameter and layer thickness [205]. Kayarkatte et al. reported a current density of roughly 400 mA cm<sup>-2</sup> at 0.6 V for Pt loading of 0.3 mg<sub>Pt</sub> cm<sup>-2</sup>, while the present study achieved ~1.0 A cm<sup>-2</sup> with half the Pt loading [205]. Therefore, the benefits of the large porosity and interconnected fiber network is evident from the *in situ* results in comparison to traditional CB catalysts and published work.

	Normal condition (NOC)	Hot condition (HOT)
Temperature (°C)	68	85
Inlet relative humidity (%)	105	50
Balanced inlet pressure (bara)	2.5	
Stoic (both $H_2$ and Air)	10.2	
Anode	100%	H <sub>2</sub>
Cathode	Air	
FFP geometry	Straight ch	annels

 Table 6-5: Operating conditions of single cell performance tests performed in CAT cell hardware



Figure 6-5: Polarization characteristics of the MEAs fabricated with RNL and OAN cathode catalyst (0.15 and 0.25 mg<sub>Pt</sub> cm<sup>-2</sup>) for H<sub>2</sub>/Air at 68 °C and 85 °C, Nafion 211 membrane, 2.5bara balanced anode and cathode inlet pressure. Dotted lines indicate iR-corrected data for comparison



Figure 6-6: Power density characteristics of the MEAs fabricated with RNL and OAN cathode catalyst (0.15 and 0.25 mg<sub>Pt</sub> cm<sup>-2</sup>) for H<sub>2</sub>/Air at 68 °C and 85 °C, Nafion 211 membrane, 2.5 bara balanced anode and cathode inlet pressure

ID	68	<b>O</b> °	85	<b>O</b> °
	<i>i<sub>x</sub></i> (mA cm <sup>-2</sup> )	$R_{\rm s}$ ( $\Omega$ cm <sup>-2</sup> )	<i>i<sub>x</sub></i> (mA cm <sup>-2</sup> )	$R_{\rm s}$ ( $\Omega$ cm <sup>-2</sup> )
RNL 150 µg cm², med I/C	2.923	1992.74	1.953	127.471
RNL 150 µg cm², low I/C	4.065	2856.125	0.379	123.981
RNL 150 µg cm², high I/C	4.26	6658.567	0.359	193.262
RNL 250 µg cm <sup>-2</sup> , med I/C	5.078	376.871	0.83	103.874
OAN 150 μg cm <sup>-2</sup> , med I/C	1.559	38.676	0.46	29.213
V50 150 μg cm <sup>-2</sup> , 1.1 I/C	6.702	141.4	5.084*	86.1*

Table 6-6: The shorting resistance and the H<sub>2</sub> cross-over currents measured with H<sub>2</sub>/N<sub>2</sub> at 2.5 bara balanced inlet, 105% RH 68 °C and 50% RH 85 °C operating conditions; \*measured at 68 °C 50% RH

## 6.3.2 Impedance and transport analysis

To understand the performance and effect of the material properties, EIS was used to determine the ohmic and ionic resistances of the catalyst layer. Oxygen transport resistance was measured to determine the pressure dependant and pressure independent resistance. Equivalent circuit using a modified Randles and Warburg element circuit was used to fit the impedance data. Oxygen transport resistance was determined following the technique described in Baker's publication [206]. The pressure dependent  $(R_{PD})$  portion accounts for the Fickian intermolecular diffusion through large pores (> 100 nm). Pressure independent resistance ( $R_{PI}$ ) consists of Knudsen diffusion through small pores (< 100 nm) and the ionomer layer surrounding Pt particles. Because the CNF layer is a very open structure with large pores, the majority of the calculated pressure independent resistance was caused by the diffusion through the thin ionomer layer. From the measured R<sub>PI</sub> shown in Table 6-7, the highest oxygen transport resistance was observed in sample with medium I/C and 250 µg cm<sup>-2</sup>. The trend clearly shows that increasing the I/C ratio increases R<sub>PI</sub> from 38.1 to 64.5 s m<sup>-1</sup>. The experimental results are plausible since TEM ionomer measurements reveal a thickness of 29.46  $\pm$  21.38 and 102.65  $\pm$  84.90 nm for samples with low and high I/C, respectively. Certainly, diffusion through thicker ionomer films would be slower; even so, 250  $\mu$ g cm<sup>-2</sup> sample revealed significantly slower diffusion compared to all 150  $\mu$ g cm<sup>-2</sup>

samples. This could be attributed to poorer distribution of ionomer and Pt since it was observed that larger clusters formed at high Pt loadings. The larger clusters may cause the ionomer to coat non-uniformly throughout the CNF layer creating a more tortuous path for oxygen transport. Similar results were obtained for OAN sample. R<sub>PI</sub> was higher in OAN sample, likely because the ionomer was poorly distributed and concentrated in the junctions, as seen in TEM images (Figure 5-18). The ionomer pockets in the OAN samples would drastically increase the oxygen resistance and create a more tortuous path for oxygen transport Table 6-7. Total mass transport resistance (R<sub>MT</sub>) also reveal consistent trends with small fluctuations between samples. Since the total mass transport resistance includes transport through other components of the fuel cell, it can be assumed that the resistance in other components is consistent across all samples. Thus, only the catalyst layer transport resistance is considered. Subtracting the RPI from RMT gives the estimated RPD, assuming all samples have comparable  $R_{PI}$  through respective components. Since CNF were fabricated by the same method, they should have similar porosity and hence similar transport resistance through intermolecular pores. The R<sub>MT</sub> results appear to be consistent across all samples, although OAN and low I/C RNL appear to have slightly higher R<sub>PD</sub>. R<sub>PD</sub> appears to be higher in OAN sample possibly because of the lower porosity caused by CNF adhering together and forming bundles. The structure of the OAN and ionomer pockets in and around the pores would cause RPD and R<sub>MT</sub> to increase (Table 6-7). Additionally, water trapped in the pores, causes flooding which prevents oxygen gas transport to the active sites. OAN may have challenges with water management since it displayed overall higher RMT compared to other samples. Same observations appeared in RNL 250 µg cm<sup>-2</sup> medium I/C sample. The poor distribution of ionomer may induce flooding, hence lowering oxygen transport. Overall, the oxygen transport resistance proved that thin ionomer films improve the mass transport and ionomer distribution is an important parameter.

Table 6-7: Total mass transport resistance and pressure independent transport resistance in CAT samples

	RNL,	RNL,	RNL,	RNL,	OAN,
	150µg/cm²,	150µg/cm²,	150µg/cm²,	250µg/cm²,	150µg/cm²,
	I/C Med	I/C Low	I/C High	I/C Med	I/C Med
R <sub>PI</sub> s/m	46.3	38.1	64.5	122.9	105.9
R <sub>MT</sub> (2.6bara)s/m	109.8	136.5	116.9	174.8	177.5

Table 6-8: Ohmic and ionic resistance measured by EIS for CAT samples under NOC and HOT operating

	Operating condition	RNL, 150µg/cm², I/C Med	RNL, 150µg/cm², I/C Low	RNL, 150µg/cm², I/C High	RNL, 250µg/cm², I/C Med	OAN, 150µg/cm², I/C Med
	68 °C, 30% RH	0.0653	0.0706	0.0718	0.0813	0.0683
$R_{ohm}, \Omega cm^2$	68 °C, 100% RH	0.0125	0.0132	0.0126	0.0133	0.0120
Rionic Course 1/2	68 °C, 30% RH	2.48820	3.05540	0.9656	4.3135	4.6508
$\sqrt{\frac{c_{d}}{c_{d}}}, \Omega C m^{2} S^{2} m^{2}$	68 °C, 100% RH	0.8637	0.7044	0.245	0.8718	2.6544
$R_{ohm,} \Omega cm^2$	85 °C, 50% RH	0.0285	0.0268	0.0289	0.0288	0.0264
$\sqrt{\frac{R_{ionic}}{c_d}}, \Omega cm^2 s^{-1/2}$	85 °C, 50% RH	1.2641	0.9710	0.3990	1.7856	3.2437



Figure 6-7: Nyquist plot of CAT samples in NOC conditions under H<sub>2</sub>/N<sub>2</sub> conditions (right: zoom in of x-intercepts)



Figure 6-8: Equivalent Circuit used to fit Nyquist plot for CAT samples



Figure 6-9: |Z| as a function of  $\omega^{-1/2}$  for the cell in NOC conditions, slope represents a relationship for R<sub>ionic</sub>

Total ohmic and ionic resistances were measured by EIS for all CAT samples. EIS using H<sub>2</sub>/N<sub>2</sub> method was recorded under HOT and NOC conditions, same as the polarization curves. Nyquist plots are shown in Figure 6-7 in the high frequency region with a close-up of the intercept. The curves were fit using a modified Randles circuit shown in Figure 6-8. The x-axis intercept of the Nyquist plot was determined as the ohmic resistance, which is largely the membrane resistance, of the MEA [207]. The ionic resistance (R<sub>ionic</sub>) was determined by following the method described in Hou's work [208]. According to Hou's method, the results from the Bode plots could be used to determine the R<sub>ionic</sub> by plotting the magnitude (|Z|) against the frequency ( $\omega$ ). From the |Z| vs  $\omega^{-1/2}$  plot in Figure 6-9, the R<sub>ionic</sub> was determined by fitting a linear trend line and calculating the slope, which equates to  $\sqrt{\frac{R_{ionic}}{C_d}}$ . The presented capacitance in the equivalent circuit is a combination of the interfacial capacitances which were expected to be similar across all samples.

Since double layer capacitance (C<sub>d</sub>) is not readily deconvoluted from the chosen equivalent circuit, it is assumed to be a constant value. Thus, comparing the slopes reveals the Rionic of the MEA system, mainly contribution from catalyst layer. Total R<sub>ohm</sub> represents the (a) resistance to ion migration within the electrolyte, (b) resistance to electron transport within the cell components (electrodes, gas diffusion layer, and flow field/current collectors), and (c) contact resistances. Although typically, R<sub>ionic</sub> dominates the resistance contribution since ionic transport is more difficult than electronic charge transport at low frequency. Ohmic (Rohm) and Rionic was measured at 30% and 100% RH at 68 °C. Comparisons between all samples reveal that R<sub>ohm</sub> was lower at 100% RH and was virtually identical across all samples (Table 6-8). At 30% RH, Rohm across all samples was roughly 0.07  $\Omega$ cm<sup>2</sup>, which is an order of magnitude less than R<sub>ionic</sub>. The difference between the OAN and RNL R<sub>ohm</sub> does not appear to be significant, 0.0120  $\Omega$ cm<sup>2</sup> and 0.0125  $\Omega$ cm<sup>2</sup> respectively (Table 6-8). The low Rohm was consistent with the CNF ex situ through-plane resistance presented in Chapter 4.2. The trend was consistent with polarization results where RNL150 µg cm<sup>-2</sup> with Med I/C obtained the lowest R<sub>ohm</sub> at both 30% and 100% RH, hence higher performance. For the same sample in HOT conditions (85 °C and 50% RH), Rohm was slightly higher, 0.0285  $\Omega$ cm<sup>2</sup> and 0.0125  $\Omega$ cm<sup>2</sup> for HOT and NOC conditions, respectively. Comparison of 30%, 50%, and 100% RH reveals that Rohm decreases with increasing RH, since water is a good conductor and also hydrates the proton membrane. The results suggest R<sub>ohm</sub> was generally consistent owing to a highly conductive stable CNF structure. Similarly, under NOC conditions Rionic was lower at 100% RH compared to 30% RH. At 100% RH, RNL 150 µg cm<sup>-2</sup> with high I/C achieved the lowest R<sub>ionic</sub> (Table 6-8). Since high I/C results in thick ionomer coating on the fibers, it may have improved bonding with the electrolyte membrane. As a result, the mobility of the protons was increased due to a well-connected ionomer network for efficient transport. OAN

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sample possessed the highest Rionic at both RHs, indicating the ionomer was not well distributed and was not well-bonded with the membrane. Because the OAN had pockets of ionomer trapped at the fiber junctions, the TPB was not continuous, resulting in a slower path for proton transport. At 68 °C under 30% and 100% RH,  $R_{ionic}$  increased as follows: 150 µg cm<sup>-2</sup> high I/C < 150 µg cm<sup>-2</sup> <sup>2</sup> medium/low I/C and 250  $\mu$ g cm<sup>-2</sup> medium I/C < OAN 150  $\mu$ g cm<sup>-2</sup> medium I/C. The same trend was observed for HOT conditions (85 °C under 50% RH). Again, lower Rionic was seen in the 150 µg cm<sup>-2</sup> high I/C sample since the thicker ionomer coating allows for proton transport even in dryer environments. OAN possessed the highest Rionic because of the ionomer pockets and lack of ionomer bridges connecting the fibers through-plane (Table 6-8). In summary, the 150  $\mu$ g cm<sup>-2</sup> high I/C sample showed the highest performance as a result of low ohmic and ionic resistances in both NOC and HOT conditions. However, 150 µg cm<sup>-2</sup> medium I/C showed higher oxygen mass transport because of the thinner ionomer layer and better water management at high current densities, allowing efficient diffusion through the ionomer. As a result, both 150  $\mu$ g cm<sup>-2</sup> medium and high I/C have sufficient TPB, translating to improved peak power density compared to traditional V50 CB.

# 6.4 **Degradation post fuel cell test**

Stability and durability is a major concern for PEMFCs which is outlined by the DoE as an industry goal for 2020. So far, CNF has been favorable as a catalyst layer, therefore it was important to verify the integrity and microstructure post-fuel cell testing. Visual methods via SEM were used to evaluate the condition of the catalyst post fuel cell testing.

## 6.4.1 Fiber and Pt distribution evaluation

A common issue with conventional carbon black catalyst is the agglomeration of Pt and carbon corrosion during start-up and shut down procedures [209]. It is detrimental to the fuel cell

performance because degradation will lead to decreased Pt surface area and lower the reaction kinetics. Therefore, a support material with high electrical conductivity and chemical stability is desirable for maintaining performance. Herein, the fiber and Pt morphology were examined in the SEM before and after fuel cell testing to determine signs of degradation (Figure 6-10, Figure 6-11, and Figure 6-12). From the images shown, CNF has maintained its integrity after fuel cell testing, the fibers did not shatter or change in morphology. As shown, the post-tested CNF layer consists of an interconnected network providing optimal electrical conductivity. The images suggest that CNF were mechanically robust and may be feasibly utilized as a support material without suffering degradation or defects. On the other hand, Pt shows variable amount of corrosion or instability. In Figure 6-10 and Figure 6-12 there were notable changes in the Pt coating. There were regions where Pt was stripped off the CNF support revealing bare CNF underneath. The Pt also became sparse and formed channels where Pt was stripped off or coalesced. The mechanism of Pt degradation and loss of surface area is widely detailed in the literature. Generally, researchers have found that loss of Pt surface area is caused by increased potentials and voltage cycling [210]. For instance, Pt dissolution can occur at voltages higher than 0.8 V vs. RHE by a process similar to Ostwald ripening. Ostwald ripening happens when the Pt dissolution occurs on small nanoparticles and is transported to larger nanoparticles where reduction (redepositon) occurs [210]. The reduction of small Pt nanoparticles is driven by the reduction of surface energy, so nanoparticles with high surface energy are dissolved and redeposited onto larger Pt particles to lower the surface energy [210]. As a result, coarsening of Pt nanoparticles reduces the available active surface area. Moreover, research has found that Pt in solution may diffuse into the proton membrane at higher cathode potentials and exit the cell via waste water on the cathode side [211]. The rate at which Pt coarsening occurs increases with voltage cycling between 0.87 V and 1.20 V. Since the MEA were

cycled prior to recording stable polarization curves, it is possible that the CNF/Pt experienced some coarsening and loss of active surface area. It was shown that Pt nanoparticles grew from ~2-3 nm to ~6 nm on CNF after MEA cycling. Because of the nanowire cluster structure, it was challenging to precisely measure the size of individual wires and its' growth. At most, cluster size was measured but is not a reliable indication of whether Ostwald ripening occurred or not. The average cluster size measured in the long axis is ~22.5 ± 5.47 nm (60 points) and a distribution of the Pt cluster size for RNL sample with 167  $\mu$ g<sub>Pt</sub> cm<sup>-2</sup> is shown in Figure 6-13. Chapter 5.2.1 reported an average cluster size of ~25 nm for similar Pt loading. The manual measurement of cluster size did not show significant increase, however any increment would likely be within the standard deviation.



Figure 6-10: Before and after fuel cell testing; RNL with Pt loading of 167 µg cm<sup>-2</sup> (left before, right after) (2 kV, secondary electron mode)



Figure 6-11: Before and after fuel cell testing; RNL with Pt loading of 148 µg cm<sup>-2</sup> (left before, right after) (2 kV, secondary electron mode)



Figure 6-12: Before and after fuel cell testing; R150M with Pt loading of 157 µg cm<sup>-2</sup> (left before, right after) (2 kV, secondary electron mode)



Figure 6-13: Distribution of Pt particle cluster size measured in the long axis post fuel cell testing

# 6.4.2 Cross sectional evaluation



Figure 6-14: Cross sectional evaluation post fuel cell testing: Pt shown on fibers (15 kV, secondary electron mode)



Figure 6-15: Cross sectional evaluation post fuel cell testing: R150H cross section, Pt shown on fibers (15 kV, secondary electron mode)



Figure 6-16: O150H OAN cross section post MAT FC testing (15 kV, secondary electron mode)



Figure 6-17: Post fuel cell testing with sufficient Pt distribution and adhesion (left OAN O150H, right RNL R150M) (STEM EDX, 200 kV)



Figure 6-18: Cross section of R150H (left) and R250-T1 (right) showing regions of delamination (15 kV, secondary electron mode)



Figure 6-19: Cross sectional evaluation post fuel cell testing: O150H OAN (left) R150H RNL (right) (15 kV, secondary electron mode)

MAT (small fuel cell) tested samples were embedded into resin and imaged in SEM and

TEM for cross sectional analysis. The cross section revealed that Pt was securely adhered onto the 147
fiber surface and remained homogenously distributed throughout the thickness (Figure 6-14 and Figure 6-15). OAN cross section also revealed the orientation of fibers remained intact (Figure 6-16). The Pt appears to be homogenously adhered to OAN and did not show signs of degradation and defects (Figure 6-17). Although the Pt and CNF morphology did not change post fuel cell testing, some regions experienced delamination. Selected SEM shown in Figure 6-18 reveal CNF delaminating from the membrane. Although this was only a small section from the overall active surface area, the regions of delamination from the membrane possibly led to increased ohmic overpotentials in R150H and R250-T1. It is possible that R150H (high I/C) performed worse in the MAT testing compared to CAT testing because of delamination and poor contact, resulting in high ohmic resistances. Although delamination was found in the cross sections, it is possible the delamination occurred during sample preparation and embedding into the resin. Delamination likely occurred because the proton membrane shrinks and deforms when the water fully evaporates after testing. During testing, the CNF catalyst should be sufficiently attached to membrane because the cell operates under compression. Certainly, ohmic resistance may be mitigated by improving interfacial properties as discussed by Leeuwner [51]. Generally, the majority of CNF samples did not have delamination issues, with OAN adhering remarkably well (Figure 6-19).

#### 6.5 **Summary**

MEA were fabricated using a modified technique to sandwich the standalone CNF into the assembly. The hot pressed MEA were then prepared for pre-screening *in situ* fuel cell testing. The pre-screening experiment involved running small (1.13 cm<sup>2</sup>) MEA in key overpotential regions such as: kinetic, ohmic, and mass transport loss overpotential regions. The effect of material properties were obtained by analyzing the current density achieved in the key potential ranges. Material and design parameters that were tested include: Pt loading, I/C ratio, substrate electrical

conductivity, fiber geometry, and Pt deposition method. Polarization curves were recorded for CAT samples under NOC and HOT conditions and evaluated for peak current density and power density. The performance was evaluated by determining the oxygen transport, ionic, and ohmic resistance in the cell through EIS measurements. From the power density plots, the two best performing (~1 W cm<sup>-2</sup>) samples were 150  $\mu$ g cm<sup>-2</sup> with high and medium I/C. Although, 150  $\mu$ g cm<sup>-2</sup> with medium I/C showed slightly higher R<sub>ionic</sub> and R<sub>ohmic</sub>, it had lower R<sub>MT</sub> and R<sub>PI</sub> which allowed for efficient oxygen transport at high current densities. Vice versa, 150 µg cm<sup>-2</sup> with high I/C possessed low R<sub>ionic</sub> and R<sub>ohmic</sub>, signifying good electrical contact and efficient charge transfer, but high R<sub>MT</sub> and R<sub>PI</sub> because of the thick ionomer film reducing oxygen diffusion. Through the EIS and polarization data, ionomer distribution and thickness appeared to be the greatest factors in optimizing the fuel cell performance. RNL performed significantly better than the unoptimized V50 because of the open pore structure and large surface area for catalyst reaction sites. Additionally, the large open pore structure in RNL improved water management, allowing sufficient oxygen transport at high current density (mass transport loss overpotential region). The RNL structure established a continuous TPB by addressing the key issues with traditional catalyst layers: decreased Pt surface area, tortuous path, non-homogenous microstructure and distribution, and water management. The performance results indicate RNL performed better than OAN largely because of having a non-optimized OAN fabrication method. Porosity and ionomer distribution was challenging for OAN because of the tendency for fibers to adhere forming large ionomer pockets between layers at the junctions. Therefore, TPB was likely lacking, resulting in high resistances in the cell. Overall, RNL with Pt loading of 150 µg cm<sup>-2</sup> showed the highest performance, meaning high Pt utilization and potential to decrease catalyst costs. The current results demonstrated the importance of having a balance between R<sub>MT</sub> and R<sub>ionic</sub> and with further understanding and enhanced ionomer deposition methods, the ionomer thickness could be optimized to yield low  $R_{MT}$  and  $R_{ionic}$  in the MEA.

#### 7 **Conclusions and Recommendations**

Although fuel cells have been identified as a viable solution for sustainable energy and reduction of greenhouse emissions, the technology has yet to become successfully commercialized due to cost and durability challenges. The carbon black catalyst layer, one of the most expensive components of the fuel cell, has many shortcomings and issues due to the unpredictable microstructure. The random structure leads to inhomogeneous TPB (catalyst, carbon, and ionomer junction), which decreases the efficiency because of having a limited number of reactions sites. Several studies have developed new support materials to improve the catalyst surface area, stability, and TPB [21,22,24,31,64,212]. Although materials such as nanotubes, nanowires, and novel nanoporous structures have shown notable performance enhancements, there remains a lack of understanding between the material and structural properties and the influence it has on the fuel cell's performance.

Therefore, the objective of this thesis was to design a novel catalyst support with predictable and controllable architecture and material properties to understand the *in situ* performance differences in the context of certain material properties. In order to understand the effect of organized and random (analogous to CB) microstructure, electrospinning was selected as a method to produce tailorable fiber orientation with high surface area and porosity. In addition, the CL fabrication process involved controlled deposition of Pt and ionomer, yielding predictable morphology and loading. Thus, through this controlled fabrication method, the CL was fully characterized at every stage of the process. By coupling the characterization results with *in situ* fuel cell testing at NOC and HOT conditions, performance differences were interpreted with greater insight and understood in the context of fiber orientation, fiber electrical conductivity, Pt loading, Pt deposition method, and ionomer loading. Understanding the relationship between fuel cell

performance and material properties and architecture could vastly improve the technology by reducing instability, Pt usage, and costs.

#### 7.1 **Development of nanofiber based catalyst layer**

In order to investigate the *in situ* performance of this novel catalyst support, a bottom-up processing approach to optimize the CNF was employed. First, fabrication of the randomly deposited and orthogonally aligned nanofiber mats were developed through systematic experimental optimization and modelling via response surface method (Chapter 3.3.5). Refinement and validation of this process led to material and structural properties that satisfied industry design targets (Chapter 4). Secondly, the optimized CNF support was successively coated with Pt and ionomer to complete the CL in preparation for MEA assembly. The ex situ characterization of the Pt and ionomer layer revealed controllable Pt distribution, Pt loading, ionomer thickness, and ionomer loading (Chapter 5). Finally, the freestanding CNF catalyst layer was embedded into the MEA for in situ testing (Chapter 6). The effect of fiber geometry, Pt loading, ionomer concentration, Pt deposition method, and support electrical conductivity on fuel cell polarization losses were analyzed from SEM/TEM, CV, EIS, and polarization data. In Chapter 6.3, relationships between microstructure and fuel cell performance were established, fulfilling the research objectives in this study. This fabrication approach led to a systematic method to compare the effect of distinct material and structural characteristics on fuel cell performance metrics. Researching the feasibility and material properties of CNF catalyst supports gave insight into how future catalyst layers may be redesigned to target specific structural or material characteristics for increased efficiency. With regards to process and material design, the outcomes from this study could be applicable to other porous membrane systems including electrolysers, batteries, supercapacitors, and filtration devices.

#### 7.2 **Research outcomes and contributions**

The goal of the research was to determine the relationship between the catalyst's material and geometrical properties and the influence it has on the fuel cell's polarization losses. Properties of interest include: fiber orientation, support electrical conductivity, Pt loading, Pt deposition method, and ionomer distribution. The conclusions and contributions are presented according to the main objectives of this study (Chapter 1.6), which are summarized in the following sections.

#### 7.2.1 Effect of fiber orientation

To understand the role of geometry and structure of the support, randomly oriented and orthogonally aligned CNF were fabricated and tested in situ. EIS and polarization curves were analyzed to determine the performance associated with fiber orientation. It was found that both geometries had similar total R<sub>ohm</sub>, suggesting that the OAN was relatively conductive under operating conditions despite subpar ex situ conductivity. Compared to RNL, the ~30% drop in maximum power density was likely the result of the threefold increase in Rionic. Rionic was caused by the poor distribution of the ionomer coating resulting in slow proton transport. Moreover, limited current analysis between OAN and RNL showed OAN achieved slightly lower current density, 3.0 compared to 3.19 A cm<sup>-2</sup>, suggesting the challenges of flooding and lack of porosity for expelling water. The lower porosity, permeability, and poor ionomer distribution caused the R<sub>MT</sub> and R<sub>PI</sub> to increase significantly. It was found that the OAN structure did not enable homogenous distribution nor ionomer bridges between fibers leading to accumulation of ionomer in the junctions and pores. This again confirms the importance of ionomer distribution and coating thickness as it affects both oxygen transport and protonic resistances. Compared to CB baseline, the OAN design achieved an order of magnitude increase in maximum current density as a result of the advantageous CNF architecture and large pores. The study concludes that the geometry and

structure greatly influenced the ionomer distribution and hence fuel cell performance in the ohmic and mass transport overpotential regions. Specifically, the lower OAN performance was caused by the increased protonic and oxygen transport resistance as a result of unoptimized mesh porosity and permeability leading to inhomogeneous ionomer distribution – inconsistent TPB. Finally, contrary to our initial hypothesis, the results suggest that the organized OAN structure did not show improved fuel cell performance. However, it is believed that OAN performance may be improved by controlling the pore spacing and optimizing the ionomer deposition method to improve ionomer distribution.

#### 7.2.2 Effect of fiber electrical conductivity

To understand the role and effect of the carbon support, CNF graphitic content was varied by carbonizing at 700 °C and 900 °C. Characterization involved observation by SEM and electrical conductivity measurements. SEM micrographs revealed visually identical and homogenous Pt distribution on both sets of CNF. *Ex situ* measurements revealed electrical conductivity of RNL is far greater than V50 structure due to the interconnected network of the thin CNF layer. From *ex situ* results, in-plane and through-plane electrical conductivity measurements confirmed that higher carbonization temperature increased electrical conductivity by nearly two orders of magnitude. The results are also in agreement with XPS, where carbonization at 700 °C and 900 °C achieved a graphitic to amorphous carbon ratio of 1.6 and 3.2, respectively. As expected, samples carbonized at 900 °C achieved higher maximum current density *in situ* because high electrical conductivity is crucial for charge transfer and decreasing the ohmic overpotential. The prescreening *in situ* tests demonstrated that graphitic content and electrical conductivity did not have a significant impact on activation overpotential and mass transport overpotential. However, in the ohmic overpotential region, 700 °C and 900 °C carbonized MEA achieved current density of 0.7 and 1.0 A cm<sup>-2</sup>, respectively. Nonetheless, the CNF (700 °C) MEA outperformed the unoptimized V50 with the same Pt loading by nearly 3.5 times even with lower electrical conductivity. This observation suggests that the CNF, as a catalyst support material, consists of an efficient microstructure compared to CB. Finally the study demonstrated that samples carbonized at 700 °C and 900 °C showed notable performance difference in the ohmic overpotential region. The performance may be further improved by increasing electrical conductivity (carbonization temperature) and reducing interfacial resistances between the individual components of the fuel cell.

#### 7.2.3 Effect of Pt deposition and loading

To understand the role of Pt on the fuel cell performance, two different deposition methods were evaluated with varying Pt loadings. Results indicated that electroless plated RNL achieved five times higher maximum current density than V50 with the same amount of Pt. Moreover, sputter coated RNL with half the Pt loading achieved almost identical maximum current density to V50, revealing the superiority of CNF porous structure even when Pt and ionomer were poorly distributed. Although MAT test evaluation of the Pt loading revealed that 150 and 250  $\mu$ g cm<sup>-2</sup> loadings achieved the same current density (~1 A cm<sup>-2</sup> at 650 mV), the CAT cell tests revealed a different trend. In the CAT cell, the maximum power density dropped by 50% when Pt loading was increased to 250  $\mu$ g cm<sup>-2</sup>. This observation was unexpected because higher ECSA and activation current density was achieved with higher Pt loadings. This observation indicated that the polarization losses were mostly caused by the ohmic and mass transport losses. The R<sub>ionic</sub> was particularly high under dryer (30% RH) conditions, suggesting the lack of ionomer bridges and a connected ionomer network. Moreover, RNL sample with 250  $\mu$ g cm<sup>-2</sup> Pt loading exhibited the lowest limiting current out of all the RNL samples, suggesting poor oxygen transport or water

management. Since the higher Pt loading sample exhibits more surface area and denser coatings, the deposited ionomer loading may not have been sufficient to form the TPB. Therefore, the results suggest that the ratio between I/Pt might be more critical than I/C ratio. This imbalanced ratio between ionomer and Pt resulted in higher  $R_{ionic}$ ,  $R_{MT}$ , and  $R_{PI}$  decreasing the overall fuel cell performance. Therefore, this study furthermore shows that properties such as ECSA or Pt loading cannot be considered in isolation when investigating the performance. In this study, RNL with 150 µg cm<sup>-2</sup> Pt loading demonstrated exceptional power density performance which means less Pt could be used to achieve satisfactory performances. Nonetheless, the complex combination of TPB and the material's porous structure are of utmost importance and should be further optimized to reduce Pt usage and costs.

#### 7.2.4 Effect of ionomer distribution and loading

To understand the effect of ionomer loading and distribution on fuel cell performance, three different I/C loadings were tested *in situ*. Both sets of *in situ* testing confirmed that as concentration was further increased, power density showed a diminishing return. Ionomer concentration affects ohmic overpotential and mass transport overpotential regions because of increased oxygen transport resistance and R<sub>ohm</sub>. Low ionomer concentration showed a significant disadvantage in power density (30% drop) when compared to medium concentration (1 W cm<sup>-2</sup>). When ionomer was insufficient, the R<sub>ionic</sub> increased due to poor proton transport. However, very thick ionomer coatings increased the oxygen transport resistance. Hence, the EIS and polarization results were in agreement and confirmed that fuel cell performance was highly influenced by ionomer distribution and thickness. The study concludes, medium and high I/C achieved the highest performance, up to 5x higher maximum power density than conventional V50 CB. The main challenge was utilizing the appropriate amount of ionomer to encourage TPB while maintaining free and direct pathways

for gas transport. Although the current results provided insight into the importance of ionomer distribution and thickness, rigorous optimization of the deposition process would be necessary to achieve an efficient balance between oxygen transport resistance and protonic resistance. Finally, the study concludes ionomer distribution has significant influence on fuel cell performance and was a factor of carbon support geometry, Pt loading, and Pt/ionomer ratio. The optimization of ionomer in the CNF based MEA would balance R<sub>MT</sub>, R<sub>ohmic</sub>, and R<sub>ionic</sub>, ultimately reducing potential losses in the ohmic and mass transport overpotential regions – improving fuel cell efficiency and reducing material usage and costs.

Ultimately, based on the aforementioned conclusions, ionomer distribution and loading had the greatest influence on fuel cell performance. Regarding optimization of CNF layers, the connected ionomer network should be optimized to achieve a balance between  $R_{ohm}$ ,  $R_{ionic}$ , and  $R_{MT}$  to reduce polarization losses in the ohmic and mass transport regions. Compared to the unoptimized baseline CB, the results demonstrated that CNF catalyst support increased maximum power density even without an optimized TPB due to having a well-connected network and porous structure. With regards to material and structural properties, the established relationships provide a guideline for enhancing future catalyst designs to improve durability and lower costs.

#### 7.3 Health and safety concerns

During the progression of this research, safety and health concerns were raised by AFCC regarding the handling of nanomaterials. Industry laboratories often have serious procedures and protocols to ensure a safe and standardized working environment. For this reason, new materials introduced to the AFCC laboratories must pass health and safety requirements. Unlike CBs, which

have well-documented hazard prevention procedures, CNFs have not been previously used in the AFCC laboratories, therefore new procedures were developed to decrease risks and exposure. It is well known that nanostructures raise occupational health concerns because it is not well documented how the nanomaterials would interact with human bodies. Particularly, carbon is considered a carcinogen since it has been shown to cause lung cancer in animals [213]. Because of the health risks involved, manufacturers implement strict safety procedures to reduce exposure to airborne particles. The National Institute for Occupational Safety and Health (NIOSH) outlined a recommended airborne exposure limit (REL) of 3.5 mg m<sup>-3</sup> averaged over 10 hours for carbon black [214]. Electrospun CNF, on the other hand, has not been rated by NIOSH. The most comparable material would be CNT and CVD CNF (5-30 µm length). For CNF, NIOSH recommends an exposure of below 1 µg m<sup>-3</sup> for an 8 hour Time Weighted Average (TWA), respirable fraction (elemental carbon) during a 40 hour work week [215]. Because this is for short CNFs, it is not representative of electrospun fibers. Electrospinning forms fibers that are several centimetres long. In the case of electrospun CNF, the fibers are in a cohesive non-woven fabric structure with virtually zero fallout. The perceived risk of exposure during the processing of MEA is when the CNF layer is cut with scissors. To reduce exposure in the current study, CNF samples were cut and handled under a fume hood or well ventilated area. It was estimated that the current experiment and procedure produces 0.53  $\mu$ g m<sup>-3</sup> per 8 hour of airborne substance. Compared to carbon black, which is an easily airborne powder, electrospun CNF is safer and has a much lower risk of airborne particle exposure. Therefore, following the developed working procedures, it was found that CNFs were relatively safe and met AFCC safety standards. For these reasons, it is worthwhile to consider replacing carbon black catalysts with electrospun CNF to lower occupational health risks in the future.

#### 7.4 **Recommendations for future work**

From this study, CNF was demonstrated as a feasible catalyst support with controllable structural and material properties. To build upon this work, there are several opportunities for further research to improve performance and applicability in this area.

#### • Geometrical effect

Although OAN was expected to improve mass transport and aid with water management, the current results are inconclusive. Because the OAN structure was fabricated using a different electrospinning apparatus which displays an altered electrospinning electric field, the process parameters should be optimized separately from RNL electrospinning. Additional properties of interest include fiber spacing and pore size. It is plausible that the OAN did not achieve high porosity and mass transport because the fibers did not have optimal pore spacing. As a result, future work should focus on developing a fabrication method which deposits orthogonal fibers simultaneously with controllable fiber diameter, pore size, and pore spacing. Prior work has primarily demonstrated feasibility of controlling alignment direction, however the results are limited to small areas (2 cm<sup>2</sup>) and minimal layer thickness [90,112,216,217]. The orthogonal layer should be cohesively deposited to reduce delamination and contact resistance between layers. In addition, the study could determine the effect of the degree of alignment and pore size/spacing on diffusivity and mass transport. The optimized orthogonal structure may show improved ionomer distribution leading to higher power densities. Optimized RNL showed significant improvement in maximum power density compared to V50. It is apparent that geometrical effect is a factor. Whether OAN or RNL achieves higher power density requires further development of the orthogonal deposition technique and systematic optimization of the process parameters. The effect of oriented fibers as it relates to the performance of the catalyst samples in hydrogen fuel cells warrants further scrutiny in a future study.

#### • Protonic conductivity

In addition to *ex situ* electrical conductivity, an apparatus may be designed to measure protonic conductivity. Since ionomer plays a critical role in the catalyst design, it is necessary to create a method to characterize the protonic conductivity *ex situ*. The standardised *ex situ* measurement would assess the quality of the ionomer coating without destroying the sample. Current methods involve measuring the entire MEA and separating the ionic response from the EIS data [218,219]. Measuring the entire MEA as a screening method to understand ionomer deposition is a costly and destructive technique. Another method measures the in-plane protonic conductivity of the polymer membrane using a four point probe humidity controlled apparatus [220]. This may be an applicable method, however, the method has been primarily used for polymer membranes rather than catalyst layers. Additionally, electronic and protonic conductivities should be separated in the raw data. As a first approximation in-plane measurements could be useful however, through-plane is a more accurate representation of the fuel cell operating conditions. Measuring the protonic conductivity would allow for quick evaluation of the ionomer layer when investigating advanced deposition methods.

#### • Durability and stability testing

Fuel cell operating conditions should be optimized for CNF MEAs because the microstructure is vastly different from traditional catalyst layers. Applying CNF MEAs to fuel cell stacks optimized for CB may not give an accurate representation of the CNFs potential. In addition to evaluating the CNF catalyst *in situ*, the experiment should include stability and durability testing. Durability and stability is a major problem in the current catalyst supports because of carbon agglomeration and Pt dissolution. To confirm the feasibility of CNF as catalyst supports, *in situ* fuel cell testing should be scanned over 10,000 cycles to evaluate the durability and stability [221,222]. From the current results, post-fuel cell testing Pt and fiber morphology did not reveal visible degradation or changes. However, the SEM images indicated some delamination from the membrane which may have been caused by sample preparation or the harsh fuel cell environment. Therefore, to have a deeper understanding of the CNF and Pt material properties *in situ*, stability testing should be performed. Additional tests could be conducted to evaluate the effect of surface treatment or post processing on durability.

#### • Imaging technique

Although the obtained STEM micrographs displayed presence of ionomer film around the fibers, it was a challenging method for imaging due to electron beam sensitivity. As a result, some ionomer samples were melted and destroyed during high resolution imaging. Refining operation parameters and imaging regions quickly may reduce melting; however other methods should be included for accurate representation. Cryogenic SEM may reduce ionomer melting as it is often used for samples with beam sensitivity or instability issues. Additional imaging techniques could include atomic force microscope infrared-spectroscopy (AFM-IR), which can give spatial resolution down to < 10 nm. A standardized procedure should be implemented for cross sectioning to ensure preservation of the imaging surface. However, it may be difficult to observe a large cross sectional area with these techniques. The ideal technique would allow for *in situ* or hydrated environment imaging because ionomer swells in humid conditions. Understanding the ionomer distribution and thickness is necessary to develop improved catalyst structures in the future.

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# A Appendix

Appendix A provides a supplementary literature review summary, some which were not mentioned in the discussion.

Material	Application	Catalyst Deposition	Parameters (catalyst loading, porosity, thickness, etc.)	Performance	Advantages	Challenges	Ref.
Twisted CNFs	Study effect of twist on electrical conductivity	N/A	Diameter of single fiber: 280 nm Yarn diameter: 25 mm	Electrical Conductivity increase with increasing porosity (~1 S/m at 90% porosity) Higher porosity with lower twist (90% porosity at 300 tpm)	Increase in conductivity due to permanent junctions between fibers, forming alternate paths	Fiber breakage during twisting, decreases conductivity	[85]
Stacked-cup CNFs	Catalyst layer, performance compared to CB	Modified ethylene Glycol synthesis method 2-3 nm Pt particles	SC-CNF diameter: 75- 100 nm	Higher performance than CB, different Pt loadings were tested	Can maintain continuous electrical conduction path, not easily cut down by Nafion micelles	Agglomeration observed for 30wt% Pt/SC- CNFs	[63]
CNT on carbon paper	<i>In situ</i> CNT on carbon paper, combined GDL and catalyst layer (Cathode)	Sputter coat 2-3 nm Pt Nanodots	Loading: 0.04mg/cm (cathode) Pore size: <100 nm MWCNT OD: 30nm ID: 10nm	Max power Density: 595mW/cm²	Significantly higher power density compared to Pt/Vulcan XC72R with equal Pt loading	Requires acid treatment, limiting the effectiveness of CNT as catalyst support Optimization needed to control particles	[212]

Table A-1: Summary of prior research related to CNF/CNT as catalyst supports in FC

						size and dispersion	
Electrospun Random CNF	Catalyst layer improve morphology	Pt slurry spray method	Diameter: 250 nm Pore size: 2.36 nm Loading: 0.5 mg/cm <sup>2</sup> (anode and cathode)	Electrical conductivity: 9.9 S/cm Current density: 900mA/cm <sup>2</sup> compared to 450mA/cm <sup>2</sup> for Pt/XC-72R	Pt/XC-72R: 4.5 S/cm Pt utilization 69% compared to 35% on Pt/XC-72R	Difficult for Pt particles to penetrate the well-developed shallow pores	[35]
CNF mats using PAN	Catalyst support layer, study Pt loading and performance	Pt clusters electrodeposited	Pt size: (50 – 200 nm) Fiber diameter: 150 nm Mat thickness: ~50 μm Loading: 0.21mg/cm <sup>2</sup> Specific surface area: ~7 m <sup>2</sup> /g	Peak current density: 117.5 mA/cm <sup>2</sup> electrical conductivity of mats: ~50 S/cm	90mA/cm <sup>2</sup> compared to 39mA/cm <sup>2</sup> for Pt/CFM and commercial Pt/C electrodes Use less Pt loading Pt/C electrode electrical conductivity only ~42 S/cm	Performance of Pt/CFM superior to Pt/C in both stability and activity, although dispersivity and size of Pt particles on CFM are inferior to Pt/C	[83]
CNT@SnO₂	catalyst support, invested core- sheath nanocomposite structure	Precursor H₂PtCl₀ and EG as solvent	SnO <sub>2</sub> sheath pore size: 2-5 nm SnO <sub>2</sub> particle size: 4.7 nm MWCNT D: 40 – 60 nm MWCNT L: 5 – 15 μm	Current densities for CNT@SnO <sub>2</sub> higher than that for Pt/CNT	Long term stability of Pt/(CNT@SnO <sub>2</sub> ) significantly higher than that of Pt/CNT SnO <sub>2</sub> is sufficiently steady at high potentials, high corrosion resistance Mesopores formed by SnO <sub>2</sub> mitigate the Pt migration or aggregation	N/A	[62]

Platelet, tubular, and fishbone CNF	Conducted voltammetric analysis, effect of microstructure on ORR activity	Catalyst powder suspension, dispersed by ultrasonic in Nafion solution	Pd NP size: 3 – 8 nm f-CNF: 60 nm Diameter, 0.3cm <sup>3</sup> /g pore volume, 86.6m <sup>2</sup> /g specific surface area p-CNF: 100 nm Diameter, 0.35cm <sup>3</sup> /g pore volume, 204.7 m <sup>2</sup> /g specific surface area	No ORR peak found on Pd/AC,ORR of Pd/f-CNF is diffusion controlled and ORR of Pd/p- CNF controlled jointly by surface reaction and diffusion	High active surface area of Pd/p-CNF (0.9m²/g), much higher than Pd/AC and Pd/f-CNF (0.37m²/g; 0.21m²/g) high active surface area reduce over- potential of electrochemical reaction	N/A	[73]
Pt-PANI/CNT	PANI introduced to bridge Pt NP and CNTs, catalyst support layer	Pt colloidal NP, narrow size distribution	Pt loading: 20% Pt NP size: 2 - 4 nm ECA: Pt/PANI/CNT 64.5 m <sup>2</sup> /g	Pt-PANI/CNT has 3 times longer durability than Pt/C and 1.5 times longer than Pt/CNT, 40% as benchmark under same ADT conditions	ECA increase 28% compared to Pt/C Pt/C durability is much lower than Pt/CNT PANI-Pt/CNT experiences 4500 cycles before ECA drops to 40% Pt NP tightly anchored onto surface of CNT by covalent bonding with N atoms in PANI	N/A	[223]
Pt/CNT	Catalyst support layer, evaluate effect of different oxidation treatments on CNT	Electroless plating of Pt	Synthesized CNT	Functionalized and sensitized C/Pt: 1.34E-4 mA/cm <sup>2</sup>	Pt/CNT electrocatalyst contained 67% Pt(0) and 32.7% Pt(IV) Showed high electrocatalytic	N/A	[61]

					activity in PEM stack		
Hybrid MWCNT/SWCNT	Catalyst support layer, optimized SWNT-MWNT hybrid structure and high mass activity at high power output	Reduction of Pt salts with EG	SWCNT thickness: $0.3 - 1.4 \ \mu m$ Pt Loading: $20 - 100 \ \mu g/cm^2$ optimum blend: 20-30 $\mu g_{Pt}/cm^2$ on SWNT and 5 $- 10 \ \mu g_{Pt}/cm^2$ on MWNT	<b>Peak power density:</b> ~700 mW/cm²	Porosity of MWNT and proton conductivity of Pt- SWNT achieve very active catalyst layer	N/A	[41]
Vertically aligned nitrogen doped carbon nano tubes	Investigate ORR rate/activity, for catalyst support layer	Metal-free catalyst system, use only CNT	NCNT length: 7.5 μm NCNT width: ~50 nm ECSA: 0.29 cm <sup>2</sup>	Current density: 2.62E- 3 A/cm <sup>2</sup> ORR rate constant: 5.38E-3 cm/s	ORR rate compares favorably with those obtained on Pt-based 62% higher performance than benchmark accepted for ORR catalysts	N/A	[64]
Electrospun Pt/C	Fabricate electrospun Pt/C onto carbon paper	Pt in spinning dope	Nanofiber D: ~800 nm Pt Loading: either 0.4 mg/cm <sup>2</sup> or 0.2 mg/cm <sup>2</sup>	Max power density: 705 mW/cm <sup>2</sup> Current density: 1080 mA/cm <sup>2</sup>	28% improvement in FC performance compared to MEA with decal cathode/anode	N/A	[224]

## **B** Appendix

Appendix B provides further discussion and theory about irreversible losses in the fuel cell.

### **Polarization losses**

Polarization loss refers to the decrease in electrode potential from ideal equilibrium values due to the irreversible losses in the electrochemical system. The losses are represented in performance (polarization) curves which display the electrical potential as a function of current density. As mentioned in Chapter 1.2.2, the four irreversible losses which are briefly described here are: OCV loss kinetic loss, ohmic loss, and concentration loss.

#### **OCV loss**

The OCV represents the cell voltage when zero current is discharged. In practice, the OCV is always lower than the theoretical equilibrium cell voltage because of inherent fuel crossover. Fuel crossover describes the  $H_2$  that crosses through the proton conducting membrane to the cathode side to react with  $O_2$  directly. Other factors related to OCV loss include short circuits and impurities.

#### **Kinetic loss**

Kinetic loss refers to the energy incurred to overcome the activation barrier to drive the reaction forward. This loss occurs in the low current density region of the polarization curve and is estimated by the Butler-Volmer formula Equation (B.1); where *i* is the current density,  $i_0$  is the exchange current density,  $\alpha$  is the kinetic transfer coefficient and  $\eta_{kin}$  is the activation overpotential. The two factors that determine the sluggishness of the reaction are the transfer coefficient and exchange current density. The transfer coefficient refers to the experimental coefficients for the forward and backward reactions at the electrode (reduction and oxidation). It is the proportion of electrical energy applied that is harnessed in changing the rate of an 182 electrochemical reaction. Exchange current density refers to the back and forth flow of electrons from and to the electrolyte. If the  $i_0$  is high, the more active the surface of the electrode is and more likely the current is to flow in one direction.

$$i = i_0 \left[ e^{\left(\frac{\alpha_a F}{RT} \eta_{kin}\right)} - e^{\left(-\frac{\alpha_c F}{RT} \eta_{kin}\right)} \right]$$
(B.1)

$$\Delta Vohm = iR_i \tag{B.2}$$

$$R_{i} = R_{i,i} + R_{i,e} + R_{i,c}$$
(B.3)

$$\Delta V_{trans} = -\frac{RT}{nF} \ln\left(1 - \frac{i}{i_{lim}}\right) \tag{B.4}$$

#### **Ohmic loss**

The linear portion of the polarization curve is dominated by ohmic loss. Ohmic loss refers to the cell resistance and includes bulk resistances of the components, interfacial resistances, protonic and electronic resistances. These losses can be expressed by Ohm's law (B.2); where  $R_i$  is the total cell resistance. Total  $R_i$  is shown in Equation (B.3); where  $R_{i,i}$  is the ionic resistance,  $R_{i,e}$  is the electronic resistance, and  $R_{i,c}$  is the contact resistance.

#### Mass transport loss

Mass transport (concentration) polarization refers to the concentration gradient caused by rapid consumption of the fuel at the electrode. The reactant concentration decreases with increasing current density. Thus, the surface concentration reaches zero when the rate of consumption exceeds the diffusion rate. The current at this stage is called the ( $i_{lim}$ ) limiting current density (B.4). A fuel cell cannot produce more than the limiting current because there are no reactants at the catalyst surface. Mass transport loss is more prominent in the cathode side because if water is not removed efficiently, excess water accumulates in the pores causing flooding which hinders the diffusion of oxygen to the reaction sites.
# **C** Appendix

Appendix C provides raw data for the factorial design, regression modeling statistics, and theory of response surface method.

# C.1 Raw data for factorial design experiments

<u> </u>								
		Factor 1	Factor 2	Factor 3	Factor 4			
Std	Run	A:Concentration	<b>B:Stabilization Temp</b>	C:CNT loading	D:Carbonization Temperatur			
		wt%	°C	wt%	°C			
1	5	7	230	0	850			
2	2	10	230	0	850			
3	4	7	260	0	850			
4	8	10	260	0	850			
5	6	7	230	1	850			
6	11	10	230	1	850			
7	1	7	260	1	850			
8	12	10	260	1	850			
9	9	7	230	0	1100			
10	14	10	230	0	1100			
11	15	7	260	0	1100			
12	13	10	260	0	1100			
13	7	7	230	1	1100			
14	3	10	230	1	1100			
15	10	7	260	1	1100			
16	16	10	260	1	1100			

Table C-1: Summary of 4 factor 2 level factorial design



Figure C-1: Histogram of average fiber diameter of Sample #10 (nm)



Figure C-3: Fiber mat factorial design in-plane electrical conductivity (S cm<sup>-1</sup>)



Figure C-5: Fiber mat factorial design results for elastic modulus (GPa)



Figure C-2: Fiber mat factorial design average fiber diameter (nm)



Figure C-4: Fiber mat factorial design % porosity



Figure C-6: Fiber mat factorial design through-plane electrical resistance  $(m\Omega \cdot cm^2)$ 

# C.2 Regression modelling for process optimization

Source	Sum of Squares		Mean Square	F Value	p-value Prob > F	
Model (Diameter)	41724.50	9	4636.06	8.50	0.0085	
A-Polymer Concentration	5184.00	1	5184.00	9.50	0.0216	
B-Stab Temperature	144.00	1	144.00	0.26	0.6258	
C-Carb Temperature	4489.00	1	4489.00	8.23	0.0285	
D-CNT Concentration	1640.25	1	1640.25	3.01	0.1336	
AB	144.00	1	144.00	0.26	0.6258	
AC	169.00	1	169.00	0.31	0.5980	
AD	12210.25	1	12210.25	22.38	0.0032	
BC	10000.00	1	10000.00	18.33	0.0052	
ABC	7744.00	1	7744.00	14.19	0.0093	
Residual	3273.50	6	545.58			
Corrected Total	44998.00	15				
Model (Porosity)	359.25	4	89.81	8.39	0.0023	
B-Stab Temperature	1.56	1	1.56	0.15	0.7096	
C-Carb Temperature	0.56	1	0.56	0.05	0.8228	
D-CNT Concentration	280.56	1	280.56	26.22	0.0003	
BC	76.56	1	76.56	7.16	0.0216	
Residual	117.69	11	10.70			
Corrected Total	476.94	15				
Model (Conductivity)	16.97	2	8.48	81.28	< 0.0001	
C-Carb Temperature	14.77	1	14.77	141.50	< 0.0001	
D-CNT Concentration	2.20	1	2.20	21.07	0.0005	
Residual	1.36	13	0.10			
Corrected Total	18.33	15				
Model (Modulus)	205.10	9	22.79	5.27	0.0280	
A-Polymer Concentration	35.62	1	35.62	8.24	0.0284	
B-Stab Temperature	18.59	1	18.59	4.30	0.0834	
C-Carb Temperature	1.08	1	1.08	0.25	0.6357	
D-CNT Concentration	14.49	1	14.49	3.35	0.1168	
AB	50.89	1	50.89	11.77	0.0140	
BC	20.17	1	20.17	4.67	0.0741	
BD	6.33	1	6.33	1.46	0.2717	
CD	2.63	1	2.63	0.61	0.4652	
BCD	55.30	1	55.30	12.79	0.0117	
Residual	25.94	6	4.32			
Corrected Total	231.04	15				

 Table C-2: ANOVA analysis for diameter, porosity, electrical conductivity, and young's modulus regression models

Number	Polymer Concentration	Stab Temp	Carb Temp	CNT	Diameter	Conductivity	Porosity	Modulus	Desirability
				concentration					
1	10.00	230.00	1100.00	0.00	149.25	37.96	78.81	6.79	0.88
2	9.64	230.00	1099.99	0.00	158.26	37.9545	78.8122	7.53704	0.882754
3	9.90	230.01	1099.16	0.00	152.127	37.7131	78.7952	6.95798	0.882541
4	9.67	230.42	1100.00	0.00	158.967	37.9557	78.7598	7.43480	0.882095
5	9.82	230.00	1089.96	0.00	158.998	35.1341	78.6223	6.90035	0.880323
6	10.00	232.06	1099.93	0.00	156.566	37.9345	78.5538	6.61754	0.879461
7	10.00	233.15	1100.00	0.00	160.391	37.9560	78.4184	6.53089	0.874506
8	10.00	230.00	1100.00	0.08	155.272	35.7879	79.4765	6.47390	0.866599
9	9.30	230.00	1099.85	0.00	166.905	37.9042	78.8124	8.32109	0.864310
10	10.00	230.00	1070.31	0.00	165.169	30.2104	78.2489	6.08202	0.861251
11	10.00	234.59	1099.96	0.00	165.482	37.9445	78.2383	6.41608	0.860404
12	10.00	232.32	1067.17	0.00	173.136	29.4910	77.9876	5.93799	0.839244
13	10.00	231.49	1058.50	0.00	175.198	27.5906	77.9103	5.79191	0.833368
14	8.50	230.34	1100.00	0.00	187.817	37.9560	78.7703	10.45610	0.813782
15	8.41	230.00	1099.99	0.00	189.378	37.9524	78.8123	10.82220	0.810429

Table C-3: Response surface function predicted optimized solutions ranked by desirability

### C.3 Response surface methodology principles

Factorial experiments can be designed in various ways depending on the number of factors and levels. The specific case used for the optimization of CNF properties was a  $2^k$  factorial design, i.e. two levels (high and low level) for each factor. Typically,  $2^k$  designs are useful at the start of a response surface study where screening experiments are performed to identify the important system variables. The  $2^k$  design is also used to fit a first-order response surface model to generate factor effect estimates. Using Design-expert software, the design was analyzed to determine interactions and main effects for each response. For example, the software uses visual methods to assist in choosing the significant main effects. In a half-normal plot, significant effects lie far away from the "error" linear line, any effect lying on the line near zero is considered insignificant (Figure C-7). Additionally, the Pareto graph illustrates the magnitude of the effect's t-value. Effects below the "t-value limit" (black line) are considered insignificant and should be deselected for the model (Figure C-8).



|Standardized Effect|

Figure C-7: Example of half-normal plot in Design-Expert, here C and D are main effects as they fall far

from the linear line



Rank

Figure C-8: Pareto graph displaying the magnitude of the chosen effects, effects below the lower limit are

insignificant



#### **Run Number**

Figure C-9: Residuals vs. run number; diagnostic method to validate the model

In DOE, the "*main effect* is defined as the change in response produced by a change in the level on that factor averaged over the levels of the other factor" [152]. By convention, *A* refers to the effect of factor *A*, *B* refers to the effect of factor *B*, and *AB* refers to the *AB* interaction, etc. For instance, mathematically, the main effect of factor *A* is represented in (C.1). Here,  $y_{A+}$  represents the average response at the points where *A* is at the high level and  $y_{A-}$  is the average response at low level; *a*, *b*, *ab*, and (1) represents the response totals of all replicates (*n*) taken at the points in the design. Similarly, for main effect of *B* shown in Equation (C.2). The interaction between AB is expressed in Equation (C.3).

$$A = \bar{y}_{A+} - \bar{y}_{A-}$$
  
=  $\frac{1}{2n} [ab + a - b - (1)]$  (C.1)

$$B = \bar{y}_{B+} - \bar{y}_{B-}$$
(C.2)

$$= \frac{1}{2n} [ab + b - a - (1)]$$

$$AB = \frac{1}{2n} [ab + (1) - a - b]$$
(C.3)

To determine the significant variables in the process, ANOVA (analysis of variance) is used to examine the magnitude and direction of the effects. The analysis involves calculating sum of squares, mean squares,  $F_{0}$ , and P-value for the factors *A*,*B*, *AB*, and etc. For example, sum of squares for *A*, *B*, and *AB* is expressed in Equation (C.4), (C.5), and (C.6). The total sum of squares and error sum of squares is expressed in Equations (C.7) and (C.8).

$$SS_A = \frac{[ab + a - b - (1)]^2}{n \times 4}$$
(C.4)

$$SS_B = \frac{[ab+b-a-(1)]^2}{n \times 4}$$
(C.5)

$$SS_{AB} = \frac{[ab + (1) - a - b]^2}{n \times 4}$$
(C.6)

$$SS_T = \sum_{i=1}^{2} \sum_{j=1}^{2} \sum_{k=1}^{n} y_{ijk}^2 - \frac{y_{...}^2}{4n}$$
(C.7)

$$SS_E = SS_T - SS_A - SS_B - SS_{AB}$$
(C.8)



Figure C-10: Example contour plot for fiber diameter, factor B and C are fixed at 230 °C and 1100 °C, respectively

To verify which effects are statistically significant, an F-test is performed. The higher the F ratio, the more likely that the variance is significantly larger than random error. The F value is defined as the mean square divided by mean square of the error (C.9). If  $F_0 > F_{\alpha,k,n-k-1}$  the hypothesis is rejected and the effect is statistically significant. Alternatively, the hypothesis is rejected if the P-value is less than  $\alpha$ . A summary of all the ANOVA computations discussed are generated using Design-Expert and presented in Table C-2. Once the significant main effects and interaction terms are identified, a regression model is fitted to the data. The first-order regression model is shown in Equation (C.10); were *x* is the coded variables and  $\beta$  are the regression coefficients. This can be used to predict the response at any point in the space spanned by the factors in the design. To validate this model, Design-Expert offers a number of diagnostic tools such as normal plot of residuals, residuals versus predicted response, and residuals versus run plot. An example of residuals (difference between actual vs. predicted) versus run is presented in Figure

C-9, here the plot shows reasonable fluctuations about the zero line. If a point falls beyond the red lines (95% confidence controls) then it should be flagged as an outlier. Using the optimization function in Design-Expert, predicted solutions were generated according to input constraints shown in Table 3-6. An example of the software predictions are illustrated in contour and 3D plots, shown in Figure C-10. Generally, this first-order method is used to determine an appropriate direction of potential improvement [152]. A more formal method for the process optimization, method of steepest ascent, may be used to conduct additional experiments and refine the model.

$$F_{0} = \frac{SS_{R}/k}{SS_{E}/(n-k-1)} = \frac{MS_{R}}{MS_{E}}$$
(C.9)

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 \dots + C$$
 (C.10)

# **D** Appendix

Appendix D provides procedures for how oxygen transport, ohmic, and ionic resistances were extracted and interpreted from the polarization and EIS data sets. A brief description of EIS theory is included, a more in-depth discussion is detailed in the literature [207,225].



D.1 Resolving oxygen transport resistance from limiting current data

Figure D-1: Limiting current as a function of dry mole fraction of oxygen for four different total pressures in a cell

As mentioned in Chapter 6.3.2, oxygen transport resistance was determined using the method proposed by Baker et al. [206]. The method relates limiting current to oxygen transport resistance by Equation (D.1). Limiting currents were extracted from polarization curves measured at four different outlet pressures. The collected data should lie on a straight line passing through the origin as shown in Figure D-1. The slope of this line is proportional to the oxygen transport resistance R<sub>MT</sub>. This calculation was repeated for each cathode pressure. The result is a list of values of R<sub>MT</sub> for each cathode pressure tested. The computed R<sub>MT</sub> was plotted as a function of 195

outlet pressure in Figure D-2. The slope of the linear best fit line corresponds to the slope of  $R_{MT}$  with respect to total pressure *p*. The y-intercept from this plot represents  $R_{PI}$  (Figure D-2). Finally, the transport resistance can be further deconvoluted into pressure dependent resistance  $R_{PD}$  by Equation (D.2), where  $P_{cathode}$  is the cathode pressure.

$$R_{MT} = \frac{4Fx_o}{i_{lim}} \frac{p - p_w}{RT}$$
(D.1)

$$R_{MT} = R_{PI} + R_{PD}(P) = Intercept + Slope \cdot P_{cathode}$$
(D.2)



Figure D-2: Dry transport resistance as a function of total pressure in a cell. The line represents the best linear fit to the four data points

#### **D.2 Introduction to EIS theory**

EIS is widely used in research areas such as corrosion, electrode kinetics, membranes, batteries, and fuel cells. It is a non-destructive method used to characterize the electrochemical properties of a cell. Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and then measuring the current through the cell. For an ideal resistor,

the resistance may be calculated by Ohm's law (R = V/I). Ohm's law assumes resistance is independent of frequency and that AC currents and voltages through a resistor are in phase with each other. In the real world however, circuit elements exhibit much more complex behavior. As a result, the simple concept of resistance is replaced by a more general circuit parameter impedance. Unlike resistance, impedance is not limited by the aforementioned assumptions for ideal resistors. Applying a sinusoidal potential excitation results in an AC current signal which can be analyzed as a sum of sinusoidal functions. The electrochemical impedance is measured using a small excitation signal to observe the cell's response in the pseudo-linear range (Figure D-3). The response shown in Figure D-4, is a sinusoidal current at the same frequency but shifted in phase.



Figure D-3: Current versus Voltage curve showing pseudo-linearity[226]



Figure D-4: Presentation of an AC sinusoidal potential signal (E) with a resulting current response (I) [226]

The sinusoidal perturbation voltage applied to the system is expressed as a function of time shown in Equation (D.1), where  $E_t$  is the potential at time t,  $E_0$  is the amplitude of the voltage signal, and  $\omega$  (rad/sec) is the radial frequency. The relationship between radial frequency  $\omega$  and frequency f (hertz) is shown in Equation (D.4). In a linear system, the response signal,  $I_t$ , is shifted in phase ( $\Phi$ ) and has a different amplitude than  $I_0$ , as shown in Equation (D.5). The impedance of the system then can be expressed by Equation (D.6).

$$\mathbf{E}_{t} = \mathbf{E}_{0} \sin(\omega t) \tag{D.3}$$

$$\omega = 2\pi f \tag{D.4}$$

$$I_{t} = I_{0} \sin(\omega t + \phi)$$
 (D.5)

$$Z = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}$$
(D.6)

 $\exp(j\phi) = \cos\phi + j\sin\phi \tag{D.7}$ 

 $\mathbf{E}_{t} = \mathbf{E}_{0} \exp(\mathbf{j}\boldsymbol{\omega} \mathbf{t}) \tag{D.8}$ 

$$\mathbf{I}_{t} = \mathbf{I}_{0} \exp(\mathbf{j}\omega t - \boldsymbol{\phi}) \tag{D.9}$$

$$Z(\omega) = \frac{E}{I} = Z_0 \exp(j\phi) = Z_0(\cos\phi + j\sin\phi)$$
(D.10)

$$Z' = Re(Z) = |Z| \cos \phi \tag{D.11}$$

$$Z' = Im(Z) = |Z| \sin \phi \tag{D.12}$$

Because of the complex set of differential equations that is required to relate the electrochemical system properties to the voltage or current excitation responses, a simplified mathematical formula, Euler's relationship in Equation (D.7), is generally used to express the impedance as a complex function. With this relationship, the AC potential signal and current response can be expressed as Equation (D.8) and Equation (D.9); where j is the imaginary number ( $\sqrt{-1}$ ). The impedance is then represented as a complex number as expressed in Equation (D.10). The expression for Z is composed of a real and an imaginary part, and can be presented in a

complex impedance notation shown in Equation and Equation; where Z = Z' + jZ''. If the real part is plotted on the X-axis and the imaginary part is plotted on the Y-axis of a chart, we get a "Nyquist Plot" (Figure D-5). Notice that in this plot the Y-axis is negative and that each point on the Nyquist Plot is the impedance at one frequency. For example in Figure D-5, low frequency data are on the right side of the plot and higher frequencies are on the left. The frequencies cannot be plotted on the Nyquist plot, they are usually represented in the Bode plot. Thus, as shown in the figure, the cell impedance is expressed as Equation (D.13) and Equation (D.14). In the Bode plot, the impedance is plotted with log frequency on the X-axis and both the absolute values of the impedance ( $|Z|=Z_0$ ) and the phase-shift on the Y-axis.



Figure D-5: Nyquist Plot with Impedance Vector [226]

$$|Z| = (Z'^2 + Z''^2)^{1/2}$$
(D.13)

$$\tan\phi = \frac{Z''}{Z'} \tag{D.14}$$

An equivalent electrical circuit model is normally used to interpret the EIS data. The circuit model consists of common electrical elements such as resistors, capacitors, and inductors. It is important to use the elements that are based on the physical electrochemistry of the system. The method could be misleading since more than one circuit model could potentially fit the data. Therefore, it is important to understand the electrochemical system and fit the electrical elements

which are logically applicable to the actual system. Some example circuits and the corresponding Nyquist plot curve is shown in Figure D-7.



Figure D-6: Example of a Bode plot showing the relationship between log impedance, phase angle and applied frequency[226]



Figure D-7: Nyquist plots for (a) a capacitor, (b) a capacitor in series with a resistor, (c) a capacitor in parallel with a resistor, and (d) a resistor in series with a parallel RC-circuit (Reproduced from [227] with permission of The Royal Society of Chemistry)

#### **D.3 Procedure for analyzing EIS data**

EIS measurements in  $H_2/N_2$  consist of measuring amplitude and phase variations of the fuel cell voltage and current when an AC sinusoidal voltage perturbation is applied to the fuel cell. The measurement is repeated over a specified frequency range of 1 Hz – 50 kHz. MEAs were conditioned at the desired RH for at least 20 minutes along with three subsequent cleaning cycles to remove possible contaminants from the cathode surface. The EIS data was collected using CorrWare and analyzed by ZView software. The EIS data is presented as a Complex (Nyquist) plot and Bode plot shown in Figure D-8.



Figure D-8: Example of EIS data visualization in the ZView software, complex plot and bode plot are used to resolve impedances in the fuel cell components



Figure D-9: Screenshot of model fitting using Randles circuit in ZView



Figure D-10: Example plot of |Z| (magnitude) as the function of  $\omega^{-1/2}$  (frequency) for the cell; the slope can be used to determine  $R_{ionic}$ 

Model fitting using equivalent circuits gives results for  $R_{ohm}$  and  $R_{ionic}$ , which is the total ohmic resistance (resistance to ion migration within the electrolyte, resistance to electron transport within the cell components, and contact resistances) and catalyst protonic resistance, respectively. The particular equivalent circuit used for this data was a Randles circuit with Warburg element (Figure D-9). The  $R_{ohm}$  was simply found as the high frequency intercept while  $R_{ionic}$  was found

(D.15)

by following the computations proposed by Hou et al. [208]. According to Hou, the frequencydependent impedance is only determined by the ratio of  $R_{ionic}$  to  $C_d$  as shown in Equation (D.15) (Figure D-10). This step was repeated for all samples at the various operating conditions.