ELECTROSPUN REINFORCED POLYMER-POLYMER COMPOSITE MEMBRANES FOR APPLICATIONS IN PEM FUEL CELLS

by

David J. Wilson

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Degree in Major with Distinction

Spring 2015

Copyright © 2015 David J. Wilson All Rights Reserved

ELECTROSPUN REINFORCED POLYMER-POLYMER COMPOSITE MEMBRANES FOR APPLICATIONS IN PEM FUEL CELLS

by

David J. Wilson

Approved:	
11	Erik T. Thostenson, Ph.D.
	Professor in charge of thesis on behalf of the Advisory Committee
Approved:	
	Bingqing Wei, Ph.D.
	Committee member from the Department of Mechanical Engineering
Annound	
Approved.	Christopher I. Klovin. Ph.D.
	Committee member from the Board of Senior Thesis Readers
	committee member nom the board of Semor Thesis Readers
Approved:	
II	Michelle Provost-Craig, Ph.D.
	Chair of the University Committee on Student and Faculty Honors

ACKNOWLEDGMENTS

I must first acknowledge the Mechanical Engineering department of the University of Delaware for allowing me to pursue my research goals and providing appropriate funding and guidance for me to complete my thesis as an undergraduate. This research was supported by the National Science Foundation Nanotechnology Undergraduate Education (NUE) Program under Grant No. (1138182), Dr. Mary Poats, Program Director.

Secondly, I must acknowledge all those that have helped me individually throughout my course of research. Of those, I must specifically acknowledge Cedric A. Jacob for encouraging me to pursue my own personal interest in performing undergraduate research and helping me derive my topic of interest. I must also thank Andrew M. Baker for helping me understand the fuel cell side of my research, as well as encouraging and guiding my efforts to succeed. Without their constant guidance, my research would most likely have gone unsuccessful. Lastly, I would like to thank Sagar M. Doshi for offering his help in using testing equipment that I am not authorized or trained to use. His help in SEM imaging provided accurate results for proof of concept in this study.

TABLE OF CONTENTS

LIST LIST ABST	OF TA OF FI TRAC	ABLES IGURES T	vi . vii x
1	INT	RODUCTION	1
	1.1 1.2 1.3	Motivation and Scientific Objectives Scope of Research Thesis Organization	1 1 2
2	CUF	RRENT STATE-OF-THE-ART	4
	2.1 2.2 2.3 2.4	Introduction Electrospinning Polymer-Polymer Composites PEM Fuel Cells	4 5 6 7
3	SCI	ENTIFIC BASIS AND PRELIMINARY RESULTS	. 10
	3.1 3.2	Introduction PVDF Electrospinning	. 10 . 11 . 14
	3.3	PVDF Consolidated Polymer-Polymer Composites	. 18
		3.3.1 Experimental3.3.2 Testing3.3.3 Results	. 19 . 21 . 22
4	ELE	ECTROSPUN REINFORCEMENT PRODUCTION	. 24
	4.1 4.2 4.3 4.4 4.5	Materials Solution Preparation Electrospinning Parameters Nanofiber Results and Imaging Electrospinning Remarks	. 24 . 26 . 26 . 28 . 30

5	5 NANOFIBER CONSOLIDATION & MEMBRANE PRODUCTION				
	5.1	Materials	32		
	5.2	Solvent Degradation Rate (Reinforcement Degradation)	33		
	5.3	Solution Preparation	38		
	5.4	Nonwoven Nanofiber Mat Consolidation	38		
		5.4.1 μVO Method	40		
		5.4.2 µVARTM Method	43		
	5.5	Results	45		
	5.6	μVO & μVARTM Remarks	47		
6	CON	NCLUSIONS	49		
	6.1	Summary	49		
	6.2	Conclusions	49		
	6.3	Future Work/Path Forward	51		
REFE	RENG	CES	54		
А	PVI	DF-CNT ELECTROSPUN NANOCOMPOSITES	56		

LIST OF TABLES

Table 3.1	Processing conditions used for C. Jacob's research. They are the derived parameters for electrospinning at the different weight concentrations of PVDF needed for the study. Note the correlation between solution weight concentration and the solution flow rate into the system.	15
Table 4.1	The processing conditions used for electrospinning Polyvinylidene Fluoride and Polystyrene. Note the difference in solution concentration due to the difference in molecular weight of each polymer	27
Table 5.1	The testing method and parameters for analyzing the degradation rate for PVDF and PS respectively when subjected to DMAc, DMF, and methanol for a set time interval.	34
Table 5.2	The processing parameters for both the μ VO and μ VARTM consolidation techniques.	45
Table A.1	For the electrospinning of PVDF with a concentration of dispersed CNTs, only 15 wt% and 20 wt% PVDF solutions were used, since these weight concentrations yielded the best nanofibers of pure PVDF. With these solution concentrations, the CNT weight concentrations varied between 0.1% and 0.25%.	57

LIST OF FIGURES

Figure 3.1	(a) A diagram of the entire electrospinning setup with appropriate labelling.(b) Photographs of the electrospinning setup used for this research developed by Jacob (2015).13
Figure 3.2	The SEM imaging shows the nanofiber morphology for different solution concentrations of PVDF in DMF. (a) 20 wt%; (b) 15 wt%.; and, (c) 10 wt%. (d) A close up of the nanofibers that weren't re-dissolved after electrospinning and were produced from 10 wt% solution. They were the smallest nanofibers produced during the study, at under 20 nm in diameter
Figure 3.3	The composite formulation method is shown with appropriate labelling of components. These include aluminum tooling and caul plate to produce tooling-quality finish on the film, highly porous fabric connected to a vacuum line to alleviate the air and solvents, and a vacuum bag to ensure a proper seal. The layup is left under vacuum for 48 hours and, afterwards, left in ambient pressure for 24 hours to ensure complete solvent evaporation and flat film geometry
Figure 3.4	(a) shows a freeze fracture surface of the μ VARTM film, demonstrating the internal structure maintains the electrospun morphology while (b) shows the surface morphology showing a high degree of consolidation. 23
Figure 4.1	Electrospinning samples viewed under a laser microscope at 150x magnification for (a) PVDF and (c) PS. Also, (b) and (d) are the samples viewed under SEM imaging for PVDF and PS respectively. Notice the differences in morphology such as overall fiber size and bead formation. This could be a source of error at the end of research due to their morphological differences, in which case, future research will hold morphology of much higher regard

Figure 5.1	The preliminary test results for the μ VARTM technique using (a) PS and (b) PVDF consolidated using DMAc as the solution solvent, and (c) PS and (d) PVDF consolidated using DMF as the solution solvent. Both solution types were of 20wt% concentration Nafion. As can be seen from the images, the reinforcements are completely dissolved, leaving discontinuous surfaces of Nafion combined with dissolved PS and PVDF. 36
Figure 5.2	The improved composite processing layup, μ VO method, for creation of reinforced Nafion films (a) and (b). The new layup effectively removed all but the aluminum tooling surface and caul plate. The whole layup is placed in a sealed vacuum oven for either neat consolidation (non-heated) or heated consolidation of nanofiber mats at 60°C
Figure 5.3	Photos (a) and (b) show the μ VO technique in action within the vacuum oven. These tests were run with various caul plates and tooling surfaces of either glass, aluminum, or teflon. The images above show a glass tooling surface with an aluminum caul plate. Each test trial was set to 60-65°C and let to cast for a duration of 15-25 minutes for total evaporation. 41
Figure 5.4	(a) Image taken using a confocal laser microscope of a 20 wt% Nafion infused PS reinforcement. (b) An image of the same except with a PVDF reinforcement. As seen from both (a) and (b), the reinforcements remain completely intact. However, the surface structure of the composite seems not be present, it is assumed that the Nafion concentration was not high enough to completely diffuse through and cover the entire reinforcement
Figure 5.5	Image of the μ VARTM technique in progress. Here, the pyramid type structure on top of the aluminum tool surface is made of Teflon to help keep Nafion from bonding to the tool surface
Figure 5.6	 (a) Image of final membrane showing layers of diffusion and the brittle structure formed when the caul plate was removed. (b) Confocal laser microscope image of the composite structure at 150x magnification showing consolidation with no change in nanofiber structure. Images of (b) and (c) are very similar for different reinforcement material types, with PS being the reinforcement represented here.

Figure A.1	Electrospun morphology is nearly identical with or without carbon	
	nanotubes with fibers approximately 200nm, though some larger	
	fibers and beads also exist.	58

ABSTRACT

Polymer electrolyte membrane (PEM) ffuel cells are seen as the next generation of clean energy, sought to replace the likes of batteries. However, PEM fuel cells are limited by a mechanically unstable Nafion membrane that limits its lifespan. To combat this dilemma, it has been suggested that such membranes can be mechanically reinforced in a variety of ways, specifically through the consolidation of electrospun nanofiber mats. Previous research in the development of electro-active composites successfully derived the procedure for producing such hierarchically consolidated nanofiber composite films, called the μ VARTM method. Application of this technique towards the PEM fuel cell membrane dilemma, thus, could result in the next huge step in PEM fuel cell lifespans.

Therefore, as a proof-of-concept, polystyrene and polyvinylidene fluoride were chosen and dissolved in dimethyl formamide to be electrospun for the creation of the reinforcements for this study. Afterwards, degradation testing provided that the reinforcements should be consolidated within a Nafion solution dissolved in methanol and deionized water at a 4:1 ratio. Dimethyl acetamide was also a tested solvent to compare against Methanol, however, was shown to destroy the reinforcements. In consequence, the results that followed not only yielded a much more in depth understanding of the nanofiber consolidation process, or μ VARTM method, for producing composite membranes, but also sifted through the challenges of applying such a discovery towards PEM fuel cells to bring about the necessary procedure in producing accurate membranes in the future.

Х

Chapter 1

INTRODUCTION

1.1 Motivation and Scientific Objectives

Fuel cells are the next development in eventually reaching an appropriate alternative fuel source, consuming environmentally safe elements, like hydrogen and oxygen, as opposed to burning valuable fossil fuels and producing harmful byproducts, like carbon monoxide. Of the different types of fuel cells, polymer exchange membrane (PEM) fuel cells are most common, as they are currently being used for transportation applications such as cars and buses. These fuel cells are colloquially referred to as the batteries of the future, as they are predicted to eliminate such outdated technology. They are advantageous because of their low volume and weight, but are, however, not without certain disadvantages. This thesis aims to focus on fixing a particular disadvantage that these fuel cells possess – a short lifespan caused by a mechanically weakened membrane within the fuel cell. Thus, this thesis will studied a process aimed at creating a mechanically reinforced membrane, increasing the lifespan of fuel cells.

1.2 Scope of Research

All research that follows is a continuation of the collaborative research performed with Dr. Cedric Jacob on the formulation of consolidated electrospun nanofiber mats for electroactive composites. This thesis seeks to utilize and further the understanding of the process, later referred to as the µVARTM method, mutually

designed with Jacob. The experimental process, parameters, and analysis for creating and testing electrospun nanofiber reinforced membranes all comes from the aforementioned research.

In his research, Jacob suggested that by the formulation of a consolidated polyvinylidene fluoride (PVDF) nonwoven nanofiber mat, electroactive "smart" composites could be created exhibiting high piezoelectric qualities with the addition of carbon nanotubes (CNTs) [1]. During his research, a novel vacuum infusion based process was invented in order to consolidate these PVDF electrospun nanofiber mats while removing porosity of the sample simultaneously. This process also succeeded in forming hierarchically organized sub-micron polymer-polymer composites, in which the fiber phase can also be used as a carrier system for nanoparticles like CNTs. Thus, to continue off of this important discovery, the scope of this project has three main areas of focus: (1) to understand the advantages of this process aptly named "µVARTM," (2) understand the correlation between process variables and membrane quality for process improvement and accurate scalability, and (3) show its probable necessity in improving PEM fuel cells.

1.3 Thesis Organization

This thesis begins with a literature review on the current state-of-the-art. This topic focused on analyzing the processes of electrospinning, nanofiber consolidation, and PEM fuel cell operation. Following this, Chapter 2 focuses more on the scientific basis for conducting this research and preliminary results from the past publications to be co-authored with Jacob, specifically identifying the processes and methods of electrospinning and nanofiber consolidation. This area will provide the results and analysis of Jacob's work, identifying electrospinning and polymer-polymer composite

generation. The chapters that follow provide the procedure, processing parameters, and results for electrospun nanofiber production and composite membrane production. Finally, in Chapter 7, the thesis culminates with the final findings and results of testing, with the final conclusions of this work.

Appendix A provides an in depth look into producing polyvinylidene fluoride– carbon nanotube (PVDF-CNT) electrospun nano-composites. This provides the processing parameters for producing electrospun PVDF nanofibers infused with CNTs. This can be utilized as a possible path forward to further reinforce the produced membranes.

Chapter 2

CURRENT STATE-OF-THE-ART

2.1 Introduction

Current understanding of PEM fuel cell membranes is rather limited. Today, these fuel cells don't last very long, mainly due to one critical flaw. Inside every PEM fuel cell is a proton exchange membrane which allows for hydrogen proton transport, causing a proton gradient on either side of the membrane. To cross the boundary and complete the chemical reaction, the electrons are repelled and have to go around this membrane, in which they pass through a circuit that harnesses the electric power produced, which is essentially how these fuel cells work. The current issue is that most of these fuel cells don't last very long because this membrane has a low fatigue life. When subjected to the harsh expansion and contraction due to hygrothermal stresses within the fuel cell environment, the membranes rupture. Ultimately, the main problem is the fatigue life of the material used for these fuel cell membranes.

However, suggestions by scholars today have led to the possibility of being able to reinforce membranes in a variety of different ways, the most promising of these methods being the creation of electrospun nanofiber reinforcements [2]. This suggests that the process of electrospinning can be used to create reinforcements to be used in polymer-polymer composites. If applied to this area of study, this method can provide a solution to the PEM fuel cell membrane lifespan dilemma.

2.2 Electrospinning

Electrospinning is a well-known technique of manipulating polymers and has been around for over a century. However, it wasn't seen as a very useful technique until proper imaging technology was created later in history, effectively showing that the polymer solution fluid was *spinning*, rather than just spraying. Finally in 1995, researchers discovered that the spinning of the polymer solution fluid was actually creating nanofibers [3]. This discovery resulted in a vast expansion of research in the topic of electrospinning and is now a very popular nanofiber processing technique.

Currently, electrospinning is being used and assessed for the creation of hierarchical structured composite materials. It is a process in which a polymer dissolved into solution is subjected to a high strength electric field potential, creating a transport effect wherein the fluid particles flow from anode to cathode. The fluid particles begin by flowing in a straight line from the point of injection. However, at some point along the path of electron transport, the particles reach an instability condition. This instability condition, brought about when the viscous, gravitational, and electrical forces approach similar magnitudes, causes the fluid particles to whip around violently in a circular pattern. Whipping causes the particles to elongate into longer and longer fibers while simultaneously narrowing their diameters. This successfully produces fibers with very high aspect ratios and nano-scale diameters, which are collected on the cathode.

The resulting nanofiber morphology is mostly dependent on processing conditions, such as polymer solution preparation, evaporation rate, solution injection rate, and electric field strength. However, environmental conditions, such as relative humidity and air temperature, play a decisive role in morphology control as well. The balancing of these processing and environmental conditions is absolutely paramount

for the continuous production of accurate micro-scale morphology and surface morphology nanofibers.

The process of electrospinning allows for the control of the polymer nanoscale, or crystal structure as some polymers have multiple formations, and also allows for the inclusion of reinforcing materials, such as carbon nanotubes. Drawing of submicron fibers along with the inclusion of nanoscale reinforcement can drastically increase the stiffness and strength of the nanofibers. Strength is maximized when their morphology is produced accurately according to the aforementioned processing and environmental conditions.

2.3 Polymer-Polymer Composites

Polymer-polymer composites are another growing field today. According to composites theory, any given polymer that has a specific advantage, like high ionic conductivity, and disadvantage, like low mechanical strength, can be combined with another polymer to form a composite that now possesses the advantages of both. After the combination, if formulated accurately, the polymer-polymer composite would display high ionic conductivity coupled with high mechanical strength, effectively eliminating its disadvantages.

This field of study is now very common, as it is seen as the next step forward. For example, certain polymer-polymer composites can actually possess higher strength than common metal alloys. And though, these high grade polymer-polymer composites aren't used as often as they should, due to their high cost margins, there is still a continuously growing market for them. This market will only continue to grow as efficient and scalable manufacturing processes for these composites are developed.

A number of different processes for creating such polymer-polymer composites have been developed and range from bonding polymers together using adhesives to the *in situ* formation of polymer structures to reinforce weaker polymers. When considering the latter, a very common process for achieving this is through a micro-infusion. This micro-infusion would take the nanoscale polymer structure and re-infuse it with a liquid polymer solution of a higher strength. If this were applied to the before mentioned process of electrospinning, the nanoscale polymer structure would be the nonwoven nanofiber mats. So, according to composites theory, the nanofiber mat would essentially reinforce the polymer used for the reinfusion, creating a polymer-polymer composite possessing an increased mechanical strength due to the nanofibers. This application is the main area of focus for this research.

2.4 PEM Fuel Cells

Proton exchange membrane (PEM) fuel cells are being developed for many applications, with primary applications in transportation as previously mentioned. Key characteristics of these fuel cells are their low temperature to pressure ratios, low weight, and a special "polymer electrolyte membrane." These fuel cells harness their energy, as do all fuel cells, by means of chemical reaction. PEM fuel cells take the chemical energy freed during the chemical reaction of hydrogen and oxygen and convert it into usable electricity.

This chemical reaction works just like electron transport and begins with the introduction of a stream of hydrogen to the anode of the fuel cell assembly. Once at the anode, the hydrogen is split catalytically into protons and electrons. The protons that are formed are attracted to the polymer membrane and pass through it to the cathode. The electrons, since they repel the polymer membrane, are forced to travel

along an external electric circuit to reach the cathode. This passing through the external electric circuit produces the electrical power output of the fuel cell. In the meantime, oxygen is being supplied to the cathode, where the hydrogen protons and electrons are beginning to deposit. The oxygen then begins to react with the hydrogen protons, having just permeated through the membrane, and electrons, having just passed through the external circuit, to form water molecules, of which is the only byproduct of the system reaction [4].

This is how a fuel cell operates, and certain requirements of the system must be met in order for the successful production of electricity. First, in order for the fuel cell to avoid essentially short-circuiting, the polymer membrane must conduct with the hydrogen protons but not the electrons. The membrane also cannot allow the different gases to pass to either side of the cell. Lastly, the membrane must be strong enough to withstand the deteriorating environment at the cathode and the intense oxidative environment at the anode [5].

However, even with these requirements, PEM fuel cells still struggle to produce. First, a large source of electrical loss in these fuel cells is due to the resistance of the membrane to proton flow. This can be minimized, though, by making the membranes as thin as possible, yet without impeding the material's proton conductivity. Mostly, however, the main issue that occurs is that most common membranes are made of Nafion. Nafion performs exactly to the standards that make such fuel cells work as mentioned above, especially in terms of proton conductivity. However, Nafion is not a reliable enough structural material. Most of these fuel cells thus have rather short life cycles because the Nafion membranes don't have high enough mechanical strength to withstand the harsh environment within the fuel cell.

With this knowledge in mind, the ultimate goal of this project will then be to increase the mechanical strength of Nafion membranes by creating electrospun reinforcements to be consolidated in Nafion solution. The hypothesis is that the incorporation of an electrospun fiber mat will increase the Young's modulus of the composite membrane without seriously detracting away from Nafion's high proton conductivity. If this hypothesis is true, and the produced reinforcement membranes meet all the above criteria for a functional PEM fuel cell, it is theoretically correct that it should result in an increased life span for the fuel cell.

Chapter 3

SCIENTIFIC BASIS AND PRELIMINARY RESULTS

The following summarizes previous research conducted in the field of electrospinning for electro-active polymer composites conducted with Ph.D. student Cedric Jacob.

3.1 Introduction

From the previous research, electrospinning was used as a way of manipulating the polymer polyvinylidene fluoride (PVDF) to create electro-active composites. The ultimate goal of the research was to gauge how effective the inclusion of nano-scale reinforcements would be on piezoelectric properties of a ferroelectric polymer with the intent of creating sensors at the nanoscale level. For this work, PVDF was the material chosen and was used as a model for other such ferroelectric polymers because of its widespread use and ease of processing.

PVDF is a common fluoropolymer that is shown to have crystallinity in between 50% and 60%, with the capability of forming in four different phases. Of these phases, three of them are piezoelectric. This means that when these three phases are subjected to mechanical stress, an electric charge accumulates within the material, hence its relevance for creating electro-active composites. Furthermore, PVDF happens to exhibit a higher piezoelectricity than most other associated polymers, such as nylons and polyurea. Specifically, PVDF's mechanical flexibility and high thermal stability make it an appealing polymer for actuating and sensing purposes, as opposed to other current piezoelectric ceramics.

These qualities are why PVDF was chosen as the model for ferroelectric polymers in the study. But, as stated before, PVDF has four different crystal structures, of which only three are piezoelectric. Therefore, for the purposes of the research conducted, it was essential to achieve the phase of PVDF that exhibits the highest piezoelectricity, which, if achieved, would create the best electroactive composite. Additionally, with the proposed correct phase of PVDF acquired, it was shown that the inclusion of CNTs could significantly improve this piezoelectric property even further.

These two main reasons are why the electrospinning technique was chosen. As stated in the previous chapter, electrospinning allows for the customization of polymers at the nano-scale level and also for the inclusion of filler materials, like CNTs. Therefore, the first priority of the study was to use electrospinning to harness the phase of PVDF shown to exhibit the highest piezoelectricity, which is named the β -phase. In order to procure this phase of PVDF, research was directed towards figuring out the necessary processing and environmental conditions to apply to the electrospinning process to achieve not only this β -phase, but also to acquire the best morphology nanofibers.

3.2 PVDF Electrospinning

The following figures display the processing and environmental conditions necessary in achieving PVDF nanofiber mats of β -phase crystallinity and of accurate morphology. For this study, all processing was done using the common name PVDF powder of Kynar 761 in high molecular weight. To dissolve into solution, dimethyl

formamide (DMF) was purchased from Sigma Aldrich at 99.9% purity. All solutions prepared for electrospinning were dissolved using a hot plate with a magnetic stirrer at 100°C in a tightly sealed glass bottle for about 24 hours. These solutions were then either used directly for electrospinning or for solution casting to prepare carbon nanotube stock.

Electrospun nanofiber mats were then produced in an environmentally controlled polycarbonate chamber, which can be seen in Figure 3.1. The process first begins with the loading of a given solution into a syringe and then is pumped into the control chamber by means of a syringe pump injecting the solution through a sealed bulkhead at a chosen flowrate. An electric field potential is then applied between a stainless steel injection needle and an aluminum collection plate at specified voltages. An electrically grounded ring is placed in between these two points and surrounds the entire process to ensure electric field stability. The high voltage is applied by two high voltage power units, which are controlled manually. Temperature and relative humidity is also monitored by a humidity sensor placed at the top of the enclosure. The air supply is always regulated to 80 psi and desiccated before flowing through a custom built diffuser at the base of the enclosure, which ensures an even and reliable airflow through the enclosure. This desiccated air is conditioned to be under 3% relative humidity and at a room temperature of 25°C.



(a)





⁽b)

Figure 3.1 (a) A diagram of the entire electrospinning setup with appropriate labelling. (b) Photographs of the electrospinning setup used for this research developed by Jacob (2015).

For full comprehension of morphological control, the phrase "accurate morphology" is meant to emphasize a low formation of "beading," as it is called when there is slightly too much solvent left over after electron transport causing the nanofibers to slightly re-dissolve or completely re-dissolve, depending on the electrospinning parameters. For example, a solution of PVDF-DMF of 15 wt% is shown to have a high bead formation. However, a solution of 10% PVDF-DMF is shown to almost completely re-dissolve the nanofibers entirely. It's also worth noting that this same morphological issue can occur when there is a high solution flow rate into the system. SEM imaging examples of this phenomenon are displayed as follows and correlate the electrospinning parameters to morphology control.

3.2.1 Experimental

The following parameters created the most accurate morphology nanofibers for each specific solution concentration. Each solution concentration was of PVDF dissolved in 99.9% pure DMF. Note the correlation between solution flowrate and solution concentration. This is due to the viscosity of the polymer solutions. The lower viscosity solutions passed through the injection needle more easily than the higher solution concentrations, creating a need for a higher solution flowrate to increase the pressure through the injection needle so as not to clog the needle and keep a steady continuous electrospun sample. Table 3.1Processing conditions used for C. Jacob's research. They are the derived
parameters for electrospinning at the different weight concentrations of
PVDF needed for the study. Note the correlation between solution weight
concentration and the solution flow rate into the system.

Solution Concentration	Voltage (kV)	Solution Flowrate	Relative Humidity	Temperature (°C)
(WL%)		(mi/min)		
10%	+13/-13	0.08	<3%	18
13%	+13/-13	0.07	<3%	18
15%	+13/-13	0.05	<3%	18
18%	+13/-13	0.05	<3%	18
20%	+13/-13	0.04	<3%	18

The correlation between process and environmental variables, however, is more prevalent in the nanofiber imaging. After the samples of each concentration were created, they were visually inspected using scanning electron microscopy (SEM) to analyze nanofiber size and to ensure nanofiber morphology. In Figure 3.2 (a), it shows that higher concentration solutions produce great morphology nanofibers with little to no bead formation. As the solution concentration decreases to about 15wt%, shown in Figure 3.2 (b), the nanofiber morphology begins to deteriorate as the nanofibers are redissolved into solution due to a low concentration of residual solvent left over. Lastly in Figure 3.2 (c), it shows the lowest end of the solution concentration spectrum at about 10 wt%. The ratio of solvent to solute in these concentrations is so high that there's too much residual solvent left over after electrospinning, causing almost the entire sample to re-dissolve. However, small areas of the electrospun sample remain intact, as shown in Figure 3.2 (d), which shows the smallest diameter nanofibers produced during the study, at under 20 nm.



(a)



(b)







⁽d)

Figure 3.2 The SEM imaging shows the nanofiber morphology for different solution concentrations of PVDF in DMF. (a) 20 wt%; (b) 15 wt%.; and, (c) 10 wt%. (d) A close up of the nanofibers that weren't re-dissolved after electrospinning and were produced from 10 wt% solution. They were the smallest nanofibers produced during the study, at under 20 nm in diameter.

3.3 PVDF Consolidated Polymer-Polymer Composites

Following these two different electrospinning processes, the next priority was to consolidate the produced PVDF and PVDF-CNT nanofiber mats. However, the corona discharge effect will not allow for electricity to pass through the nanofiber samples. This is because air is a poor dielectric, and in between each nanofiber are miniscule pockets of air. Thus, when an electric current is applied to the nanofiber mat, the current will pass through the air pockets first before it passes through the actual sample. This won't make a very useful electro-active composite. Therefore, a method had to be invented so as to consolidate the nanofiber mats while simultaneously eliminating the porosity of the sample.

Consolidation can typically be done through the process of a micro-infusion; however, this process doesn't rid the nanofiber mats of its porosity. Furthermore, it generally leaves the final sample in a crippled, unusable shape because of residual stresses of the processing method, causing the sample to collapse on itself. With this knowledge, an iterative design process led to the invention of a vacuum based microinfusion process, called μ VARTM process. This process allows infusion of PVDF in solution to occupy the interstitial space left behind by the air pockets within the nanofibers. Also, the hydrostatic pressure from the vacuum keeps the sample flat while it dries, instead of allowing it to collapse on itself, effectively solving the consolidation dilemma.

For this method, the PVDF must be applied in solution in order for the vacuum to capture the air bubbles from the samples. This solution, used for the infusion, is then mostly evaporated through a slow diffusion process and via a high permeability layer surrounding the tooling. What is left is a polymer-polymer composite with an electrospun fiber reinforcement and a PVDF matrix [6]. In the end, PVDF's pure,

transparent form is acquired with greatly increased mechanical properties due to the electrospun fiber reinforcement within it. In the case of the PVDF-CNT nanofiber mats, the mechanical properties were even further increased.

3.3.1 Experimental

The PVDF solution used for infusion, always of 20 wt%, in the μ VARTM process was dissolved using a hot plate with a magnetic stirrer at 100°C in a tightly sealed glass bottle and left to dissolve for up to 24 hours. After this allotted time frame, the solution is ready to be used for the micro-infusion process.

Following from Figure 3.3, the electrospun nanofiber mat is placed on top of a flat machined plate of aluminum, with the 20% wt PVDF solution carefully dispensed on top of it. The solution is then rapidly absorbed into the interstitial space of the nanofibers. This creates a composite preform, with the nanofiber mat acting as its scaffold. After this, a flat circular machined plate of aluminum is placed on top of the composite film. Highly porous distribution fabric is then placed over the top of the entire apparatus to ensure that the air around the sample is removed. This also creates an evaporation path for the solvent of the applied infusion PVDF solution. With a vacuum line placed directly onto this porous fabric, the whole layup is then sealed under vacuum.



Figure 3.3 The composite formulation method is shown with appropriate labelling of components. These include aluminum tooling and caul plate to produce tooling-quality finish on the film, highly porous fabric connected to a vacuum line to alleviate the air and solvents, and a vacuum bag to ensure a proper seal. The layup is left under vacuum for 48 hours and, afterwards, left in ambient pressure for 24 hours to ensure complete solvent evaporation and flat film geometry.

The vacuum pressure is applied to the micro-infusing composite layup for up to 48 hours to ensure full evaporation of the infusion solvent. After this time interval, the vacuum is released. However, the circular aluminum caul plate remains over the composite sample for another 24 hours to keep it from collapsing onto itself and to ensure evaporation of any remaining solvent.

This entire process can also be performed over a hot plate to heat the casting composite. This is done by placing the entire aluminum layup over a hot plate set to

60°C for the entire duration of the process. The resulting composite films, both room temperature and heated, are then visually inspected to ensure accurate composite formation.

3.3.2 Testing

To analyze the layers of the composite films produced, freeze fracture microscopy was performed. Before microscopy, the composite film samples are placed under liquid nitrogen for a long enough time to ensure temperature equilibrium is reached. This allows for the samples to fracture in a brittle manner, ultimately creating a clean fracture surface revealing the layers within the composite. Afterwards, the samples were covered with a 6:4 ratio of gold and palladium for one minute. Scanning electron microscopy (SEM) was then used to view the fracture surface of the composite samples. The SEM imaging was taken with an accelerating voltage of 3kV in secondary electrons secondary ions (SESI) detection.

To predict the mechanical properties of the composite as well, tensile tests were performed to derive approximate mechanical property values. The mechanical testing specimens were prepared by cutting to width using a fixed-width razor paired blade and cut to one inch long respectively. To ensure accurate load testing of such thin films, the samples were end-tabbed with fiberglass tape. However, some error may still be present due to some compliance in the tape, but is assumed to be negligible. The testing was then performed using an Instron with mechanical grips and a strain rate of 1 mm/min.

3.3.3 Results

The following figures illustrate the final results of the μ VARTM process and confirm its viability. First, imaging analysis of the surface of the composite film samples, found in Figure 3.4 (b), reveals surface voids that most likely resulted from air and evaporated solvent trapped during the infusion process. Further examination, in Figure 3.4 (b), shows the electrospun structure to still be intact in the form of a very dense fibrous structure under the cast PVDF matrix.

Next, the freeze fracture imaging analysis was taken following the procedure outlined above in Section 3.4.2. Figure 3.4 (a) shows the fracture surface for a PVDF-PVDF polymer composite micro-infused at room temperature. The fracture surface reveals a layered structure within the composite with visible broken off nanofibers. The effect of processing on stiffness and strength was then examined for each micro-infusion consolidation. The results revealed that the micro-infusions produced a stronger and stiffer composite than standard PVDF. With this new data, accurate conclusions can be made about the process of μ VARTM. Firstly, the process was a success and accurately produces mechanically reinforced composite films containing intact electrospun reinforcements. The results show that the processing technique for the micro-infusion produces a much higher strength membrane. With this important process discovery in hand, it will be sought to be applied toward the PEM fuel cell membrane dilemma in the following chapters used various electrospun reinforcements and Nafion infusion solutions.



(a)



(b)

Figure 3.4 SEM micrographs showing (a) a freeze fracture surface of the μVARTM film, demonstrating the internal structure maintains the electrospun morphology while (b) shows the surface morphology showing a high degree of consolidation.

Chapter 4

ELECTROSPUN REINFORCEMENT PRODUCTION

The hypothesis of the research found in this thesis is that by mechanically reinforcing Nafion membranes through the µVARTM process, it will increase the tensile strength and elastic modulus of the membranes. The end goal, thus, is to confirm or deny that the µVARTM process works such that it accurately consolidates electrospun nanofiber mats and creates polymer-polymer composite films with increased mechanical strength, which will hopefully prolong the lifespan of PEM fuel cells. Since this is the goal of this work, the materials used for the electrospinning phase of experimentation were chosen as proof-of-concept, with more emphasis being places on the infusion solvent material. Therefore, it should be noted that the final results will be based on whether or not the µVARTM process succeeded in creating electrospun reinforced films that are mechanically stronger than pure Nafion membranes. Furthermore, should the μ VARTM process succeed in mechanically reinforcing Nafion films but, however, not prolong the lifespan of the fuel cell, this will show that material selection and further analysis of the chemical stability necessary for PEM fuel cells should be regarded with higher importance in future work.

4.1 Materials

The materials chosen for electrospinning were polyvinylidene fluoride (PVDF) and polystyrene (PS). The PVDF used for electrospinning is the same Kynar 726

powder form PVDF previously mentioned in Chapter 3.2. The PS was purchased from Sigma Aldrich in pellet form and has a molecular weight of 260,000. These materials were chosen for three important reasons. First, these materials are both very common and easily processed. Particularly, they can be electrospun with ease after solving for their appropriate processing and environmental conditions. Secondly, these materials exhibit high mechanical strength, specifically tensile strength. Tensile strength is of great importance here since the nanofibers produced through electrospinning are strongest in the axial direction. And according to the electrospinning method previously described, it produces nonwoven nanofiber mats and are, hence, isotropic.

Thus, after the μ VARTM consolidation process, the reinforced membranes should present increased tensile strength in all directions, with this strength increase dependent on how strong the chosen reinforcement material is when subjected to tensile stress. Finally, the most important reason for choosing PS and PVDF was for their chemical resistance. PS and PVDF have high chemical resistance, making them good candidates for the μ VARTM consolidation process. These materials should remain un-deformed in their electrospun formation even when subjected to the solution solvent used for the micro-infusion, since they're not compatible with the same solvents as Nafion.

Following from the previous research conducted by Jacob (2015) and from Tamer *et. al.* (2008), it was confirmed that the same solvent could be used for both electrospinning polymers, PS and PVDF. Therefore, dimethyl formamide (DMF) was purchased from Sigma Aldrich of 99.9% purity and was used as the solvent for both PS and PVDF during the electrospinning process.

4.2 Solution Preparation

For PVDF and PS alike, the solution preparation was identical to the process Jacob (2015) used in his work, previously mentioned in Chapter 3.2 of this thesis. All solutions prepared for electrospinning were dissolved in DMF using a magnetic stirrer in a tightly sealed glass bottle for about 24 hours. However, PVDF was dissolved using a hot plate digitally set to 100°C, whereas PS was dissolved at room temperature. These solutions were then used directly for electrospinning.

4.3 Electrospinning Parameters

For the electrospinning process parameters that follow, the same apparatus described in Section 3.2 that was used by Jacob (2015), was used again for this research (see Section 3.2).

In Table 4.1, the electrospinning parameters for processing both PS and PVDF solutions to form *reasonable* morphology nanofibers are shown. Here, "reasonable morphology" is used show that some beading formation in the nanofiber production is acceptable, since the main objective is simply just to form nanofibers of each material. Since bead formation is a sign of inaccurate morphological control, it is worth noting that for future research in this topic, morphological control will be emphasized more should the mechanical testing of the composite yield only slightly higher strength. However, again, for the purposes of this thesis, some beading formation is acceptable since electrospinning is not the main area of focus.

Table 4.1The processing conditions used for electrospinning Polyvinylidene
Fluoride and Polystyrene. Note the difference in solution concentration
due to the difference in molecular weight of each polymer.

Material	Solution	Voltage (kV)	Solution Flowrate (ml/min)	Relative Humidity	Temperature (°C)	Time (min)
PVDF	20%	+13/-13	0.04	<3%	18	10
PS	25%	+15/-15	0.04	<3%	18	7

Notice the similarity in processing conditions for each material. The main difference between each one was their solution concentration. And although these solution strengths were different by only 5 wt%, their viscosities were very similar, which is an accurate way of predicting whether a solution will electrospin or not. This ended up being the case because of their differences in molecular weight, which plays the defining role in solution concentration and viscosity.

As for the duration of electrospinning for each sample, time was minimized so as to produce small enough nanofiber mats so that the composite membranes eventually produced will be as thin as possible. Recall from Section 2.4 that proton permeation in PEM fuel cells is maximized when the membrane thickness is minimized. Therefore, each material was electrospun for approximately 7 and 10 minutes for PVDF and PS respectively. This is because after 7 and 10 minutes, the electrospun sample is thick enough to be subjected to further experimentation. Here, these nanofiber mats average between 10-25 μ m. For any time less than 7 and 10 minutes, the electrospun nanofiber mats produced were too thin and fragile to be used at all. The difference in correlation between time interval and thickness is due to the size of the nanofibers produced, which is shown in the next section.

4.4 Nanofiber Results and Imaging

In Figure 4.1 below, the imaging results for both material nanofiber mats are shown. First, Figure 4.1 (a) and (c), show the imaging analysis for the samples viewed under a confocal laser microscope at a maximum magnification of 150x. The other two images, Figure 4.1 (b) and (d), show the same imaging analysis for the same samples, however, under scanning electron microscopy (SEM).

Figure 4.1 (a) and (b) are of the electrospun PVDF samples, while Figure 4.1 (c) and (d) are of the electrospun PS samples. Notice their difference in size and diameter. Through further adjustment of PS electrospinning parameters, the same size and diameter fibers for both PS and PVDF could be achieved [7]. However, this is not the focus of the research, so the processing conditions were left unchanged. For the purposes of this research, both electrospun samples will work just fine, as size differences are seen as of negligible importance. It will be noted, nonetheless, since this could provide an inaccurate comparison between the two end result composites.



(a)



(b)



(c)



Figure 4.1 Electrospinning samples viewed under a laser microscope at 150x magnification for (a) PVDF and (c) PS. Also, (b) and (d) are the samples viewed under SEM imaging for PVDF and PS respectively. Notice the differences in morphology such as overall fiber size and bead formation. This could be a source of error at the end of research due to their morphological differences, in which case, future research will hold morphology of much higher regard.

4.5 Electrospinning Remarks

As stated previously, viscosity of a polymer solution is an accurate way of predicting whether the supposed solution will electrospin or not. This is because low viscosity solutions have a much higher concentration of solvent. This solvent is meant to evaporate quickly when subjected to the electrospinning process. However, if too much solvent is present, the solutions will not electrospin. It will either partially electrospin and then re-dissolve because of left over residual solvent, or it will simply "electrospray," which is the term used when the solution simply sprays across the environmentally sealed chamber. Therefore, solutions of higher viscosity tend to electrospin properly, since the solvent concentration within the solution is much lower, allowing it to evaporate throughout the process of electrospinning.

However, as previously shown above, the solutions of PS and PVDF used for electrospinning differ by about 5 wt%. Yet, they both displayed very similar viscosities. This is because of their differences in molecular weight. PS has a lower molecular weight, which means that it will take a higher wt% of PS in solution to equal the same viscosity as 20 wt% PVDF in solution.

Chapter 5

NANOFIBER CONSOLIDATION & MEMBRANE PRODUCTION

Now that the PS and PVDF reinforcement nano-webs have been created in bulk, they can be subjected to the consolidation process for creating reinforced Nafion membranes. The following information delves into this derivation of reinforced films.

5.1 Materials

For the consolidation of the previously electrospun reinforcements, Nafion perfluorinated resin solution, with 5wt% lower aliphatic alcohol and water, was purchased from Sigma Aldrich. Nafion is, of course, used here because it is the most commonly used material for the production of the PEM fuel cell membranes. It has excellent chemical and thermal stability, lacks in mechanical durability, and has excellent proton conductivity to harness the transportation of ions within an operating fuel cell. Nafion was derived by incorporating certain polymer chains on a Teflon backbone structure to make the overall polymer highly stable [8]. For these reasons, the following research will be directed towards increasing its lacking mechanical durability while limiting changes to its advantageous qualities, like proton conductivity.

As for the solvent needed to dissolve the Nafion into solution, methanol of 99% purity and dimethyl acetamide (DMAc) of 99.8% purity were both purchased from Sigma Aldrich as well. These solvents were chosen for two separate reasons. The DMAc was chosen first because it has been shown to maximize the properties of

Nafion when casted [9]. However, the reinforcement polymers (PS and PVDF) are not chemically resistant enough to withstand being subjected to DMAc, since they are not compatible without experiencing serious degradation. Therefore, methanol was chosen as an appropriate substitute, since it is chemically compatible with both PVDF and PS and will only minimally degrade the reinforcement polymer nanofibers.

5.2 Solvent Degradation Rate (Reinforcement Degradation)

Since DMAc is not compatible with PS and PVDF, the electrospun reinforcements will likely degrade quickly and dissolve during the consolidation process. However, DMAc can be quickly and easily evaporated at elevated temperatures [9]. It follows then that if the heated μ VARTM technique previously described was applied to this scenario, maybe the DMAc will evaporate quickly enough to not completely destroy the reinforcements while at the same time present the necessary properties of Nafion.

To evaluate this, a series of degradation tests were then performed on the reinforcement polymers, PVDF and PS. About 3 grams of each polymer was placed in a sealed glass jar and then subjected to 8 grams each of DMAc over a hot plate. A stop watch was then carefully monitored to record the time it took each polymer to fully dissolve in the DMAc. To provide comparison, the reinforcement polymers were also tested against methanol and dimethyl formamide (DMF), since DMF was used in the previous studies of Jacob (2015) for the consolidation of PVDF reinforcements. Table 5.1 displays the results from these polymer degradation tests.

Table 5.1The testing method and parameters for analyzing the degradation rate for
PVDF and PS respectively when subjected to DMAc, DMF, and
methanol for a set time interval.

Reinforcement	Material	Solvent	Solvent	Heat (°C)	Degradation
Material	Weight (g)		Weight (g)		Time (mins)
PVDF	3.0	DMAc	8.0	60	< 20
PVDF	3.0	methanol	8.0	60	> 60
PVDF	3.0	DMF	8.0	60	< 20
PS	3.0	DMAc	8.0	60	< 20
PS	3.0	methanol	8.0	60	> 60
PS	3.0	DMF	8.0	60	< 30

The above testing method was mainly performed due to budgeting for the project as a whole. Nafion is an expensive material to purchase, so ordering an abundance of the material was not an option. This test sought to save as much Nafion as possible for the solvent solution that would present the most likely success. The results of the test clearly show that DMAc and DMF will easily dissolve the reinforcements regardless of heating the samples, like in the heated µVARTM process, to allow for optimal evaporation. However, to fully confirm this result, a small amount of Nafion was set aside to make one solution with DMAc and another with DMF, both at 20 wt% concentration, to test a few samples using the µVARTM technique as well as an improved version of the consolidation process, described below.

The solutions were mixed in a tightly sealed glass jar using a magnetic stirrer at 60°C. However, when both solutions reached fully homogenous form, they were shown to have very low viscosity, which isn't beneficial for the micro-infusion process. With a lower viscosity, there will be a higher amount of solvent subjected to the micro-infusion process. Because of this, the solvent will not be evaporated through the permeability fabric and out the vacuum in the μ VARTM layup quickly enough to allow minimal degradation to the reinforcements. This effectively eliminated these

solvents' involvement in μ VARTM testing. Figure 5.1, below, shows the results of the preliminary testing described. As shown, the polymer reinforcements almost completely dissolve and yield low continuity membrane surfaces with large holes.

However, an improved μ VARTM consolidation setup can be created to allow optimal evaporation of the solvents, which would provide the reinforcements with minimal exposure to deformation. By eliminating the "VARTM" portion of the layup and placing the tooling surface and caul plate in a vacuum oven, the consolidation method can still be performed under vacuum and exposure to heat. The main advantage of this layup is that by eliminating the vacuum bag of the μ VARTM setup, it allows for full exposure of the consolidation sample to heated vacuum. This full exposure will result in optimal evaporation of the solvents and will hopefully result in minimally deformed nanofiber reinforcements, if the evaporation time of the solvents can be minimized. However, with the evaporation time of the solvents minimized, it will undoubtedly, according to material science, result in membranes of higher brittleness than those created over a longer evaporation period because the process will create a micro-porous surface morphology. This, however, is seen as possibly negligible until further investigated.

Figure 5.2 shows the improved layup for optimal solvent evaporation and is described further in the next chapter.



(c)

- (d)
- Figure 5.1 The preliminary test results for the μVARTM technique using (a) PS and (b) PVDF consolidated using DMAc as the solution solvent, and (c) PS and (d) PVDF consolidated using DMF as the solution solvent. Both solution types were of 20wt% concentration Nafion. As can be seen from the images, the reinforcements are completely dissolved, leaving discontinuous surfaces of Nafion combined with dissolved PS and PVDF.



Figure 5.2 The improved composite processing layup, μ VO method, for creation of reinforced Nafion films (a) and (b). The new layup effectively removed all but the aluminum tooling surface and caul plate. The whole layup is placed in a sealed vacuum oven for either neat consolidation (non-heated) or heated consolidation of nanofiber mats at 60°C.

However, in the end, the samples were still clearly visible and showed complete deformation of the reinforcement nanofiber webs in a very similar fashion to the μ VARTM technique. These preliminary tests showed that the original consensus of the reinforcement degradation tests proved that, again, regardless of optimal solvent evaporation, both DMAc and DMF solvent consolidations result in complete reinforcement degradation. Thus, Methanol became the solvent of choice to be used, since PS and PVDF are mostly chemically resistant to this solvent material.

5.3 Solution Preparation

The solutions used for micro-infusion were then 10 wt% to 30 wt% Nafion solution dissolved in a Methanol/Water mixture at a 4:1 ratio. To make these solutions, first, the Nafion solution, purchased from Sigma Aldrich, was casted down into pellets over a hotplate set to 60°C. This was done because the Nafion purchased was in a solution of water and various unknown alcohols. Casting the Nafion, thus, allowed for control of solvent choice in experimentation.

Once complete evaporation of the solvent was confirmed, the pellets were redissolved in the 4:1 Methanol and deionized water mixture at various concentrations in a tightly sealed glass jar using a magnetic stirrer over a hot plate set to 60°C. The solution was then let to mix for 24 hours until fully homogenous. Afterwards, the solution was immediately used for micro-infusion in the μ VARTM process and improved process.

5.4 Nonwoven Nanofiber Mat Consolidation

The experimentation that follows is a continuation of the work conducted with Jacob (2015) discussed in Chapter 3.3.

First, recall the previous diagrams of the μ VARTM tooling setup as well as the improved consolidation layup just introduced, now to be referred to as μ VO layup. The μ VARTM setup of Jacob was optimized, to create the μ VO layup, so as to increase evaporation of the infusion solvent to accommodate the previously disqualified infusion solvents. Even though this method didn't work for the previous solvents, it simultaneously allowed for saving of time and an increase in overall scalability of membrane production. Thus, the following consolidation testing will look into creating membranes using the 4:1 methanol and water solvent ratio applying both consolidation methods as comparison.

As stated previously, the μ VO layup is an optimization of the μ VARTM technique and effectively eliminates everything except the tooling surface and the aluminum caul plate from the μ VARTM infusion setup. Instead, a vacuum oven will be used in the place of a vacuum tube and covering vacuum bag. The process is as follows and is illustrated above in Figure 5.2. This method applies to both PS and PVDF electrospun reinforcements.

Once the infusion solution of Nafion has been mixed to a fully homogenous solution and the electrospun reinforcements have been made, the μ VARTM and the μ VO methods can be applied. For control of testing, both methods were subjected to heating, since Nafion behaves like a thermoplastic and will present higher strength due to crystallinity alignment when the process is heated. An example of this occurrence was shown in the previous results of C. Jacob, showing that heated PVDF μ VARTM tests resulted in the highest strength increase. However, a heated consolidation presents the evaporation time and brittleness dilemma previously alluded to for the

 μ VO layup. Therefore, it is hypothesized that the μ VO layup will produce much more brittle samples than that of the μ VARTM layup test.

5.4.1 µVO Method

The process is as follows for the μ VO consolidation testing. First, the vacuum oven was set to 60°C for micro-infusion. Next, the electrospun sample was prepared for infusion by placing the reinforcement on the tooling surface, glass or aluminum. Once accurately placed, the Nafion infusion solution was applied over the top of the reinforcement. Only enough solution was applied to completely cover the surface of the reinforcement. Then, the aluminum caul plate was placed over the reinforcement and infusion solution. The aluminum caul plate is necessary so that the evaporated solvent and the excess air within the reinforcement are forced outward by the caul plate and the intense vacuum pressure. When the oven has reached its temperature set point, the entire layup was placed in the oven and vacuum applied. The sample was allowed to infuse for about 15-20 minutes to ensure full evaporation of the solvent within the Nafion infusion solution. The infusion for the duration is under vacuum to alleviate bubble formation due to solvent evaporation.

After 15-20 minutes, the vacuum was released and the layup removed from the oven. The membrane produced is completely consolidated at this point. However, the dried Nafion was bonded to the tooling surface and the aluminum caul plate. To get the membrane off without causing damage to it, the composite was covered with deionized water. The water will cause the Nafion to expand and will de-bond from the tooling surfaces. The layup was left under water for about 5-10 minutes and then slowly and carefully the composite membrane was peeled off of the tooling and caul plate surfaces. The process is shown in Figure 5.3.



(a)



(b)

Figure 5.3 Photos (a) and (b) show the μ VO technique in action within the vacuum oven. These tests were run with various caul plates and tooling surfaces of either glass, aluminum, or teflon. The images above show a glass tooling surface with an aluminum caul plate. Each test trial was set to 60-65°C and let to cast for a duration of 15-25 minutes for total evaporation.



(a)



⁽b)

Figure 5.4 (a) Image taken using a confocal laser microscope of a 20 wt% Nafion infused PS reinforcement. (b) An image of the same except with a PVDF reinforcement. As seen from both (a) and (b), the reinforcements remain completely intact. However, the surface structure of the composite seems not be present, it is assumed that the Nafion concentration was not high enough to completely diffuse through and cover the entire reinforcement.

5.4.2 µVARTM Method

For the purposes of this research, this testing method was applied in the exact way performed with Jacob (2015) previously described in Section 3.3. Obviously, the only difference here is the Nafion infusion solution and the materials for the reinforcement nanofiber mats. The advantage of this setup is that the consolidation is not directly subjected to vacuum, minimizing the sample's exposure. Thus, this effectively causes the infusion solvent to evaporate much more slowly, since it infuses over the course of about 24 hours. This is advantageous because it will give Nafion enough time for its crystal structure to align and allow the infusion solvent to evaporate slowly enough to create a less brittle composite with a continuous surface structure. Figure 5.5 shows an image of the μ VARTM process.



(a)

Figure 5.5 Image of the μ VARTM technique in progress. Here, the pyramid type structure on top of the aluminum tool surface is made of Teflon to help keep Nafion from bonding to the tool surface.



⁽b)

Figure 5.6 (a) Image of final membrane showing layers of diffusion and the brittle structure formed when the caul plate was removed. (b) Confocal laser microscope image of the composite structure at 150x magnification showing consolidation with no change in nanofiber structure. Images of (b) and (c) are very similar for different reinforcement material types, with PS being the reinforcement represented here.

5.5 Results

Table 5.2 shows the processing parameters used for both the μ VO and μ VARTM methods described above. Both methods are compared against each other to analyze overall effectiveness of the respective processes. However, at the same time, the Nafion infusion solution concentrations are varied from 10wt% to 30wt% to understand the correlation between each layup's process conditions and membrane quality.

Table 5.2The processing parameters for both the μ VO and μ VARTM
consolidation techniques.

Infusion Method	Infusion Solution Concentration (wt%)	Heat (°C)	Infusion Time (hrs)
μVΟ	10% 20% 30%	60	< 0.33 < 0.25 < 0.17
μVARTM	10% 20% 30%	60	24

The above values are presented as a statistical average out of 5 trials for each method and infusion solution concentration. Unfortunately though, for all trials and both methods, the consolidations failed. The most notable reason for these failures is due to the Nafion infusion solution.

After each attempt at both μ VO and μ VARTM consolidations, the final composite formulated nicely. However, attempts to de-bond the composite from the tooling surfaces resulted in total failure of the membranes. At first, this was seen as a result of using too low of a concentration of the Nafion infusion solution. At 10 wt% Nafion, it appeared that there wasn't a high enough Nafion content in solution to completely cover the reinforcement will at the same time diffusing into the nanofiber gaps and layers. Therefore, additional trials with higher Nafion concentrations were attempted, at 20 wt% and 30 wt% respectively. And though the increase in Nafion concentration actually helped in complete immersion of the reinforcements, the brittle nature of the end composite remained the same.

It was later discovered that the main issue with the composite membrane brittleness dilemma was not the infusion solution concentration, but the infusion solution solvent, Methanol in particular. The reason why DMAc is seen as the most beneficial solvent for Nafion membrane production is because it is a high-body solvent, and results in a much stronger membrane. However, methanol, though compatible with the reinforcement materials, is not high-body enough to present the same results. This is because methanol's boiling temperature is much lower than that of DMAc and DMF. Therefore, the use of methanol as the infusion solution solvent presents a limit on how high the infusion temperature set point can be. This set point must be lower than methanol's boiling point but however, must be its upper limit so that the Nafion's crystal structure can align as best as possible, which is why the tests were run at about 60-65°C. However, this isn't a high enough temperature to allow Nafion's crystal structure to arrange, hence why the final composite is so brittle after total evaporation of the solvent. Therefore, the methanol was the main reason why the consolidation methods produced very brittle membranes that broke apart upon disassembling of the consolidation setups.

However, this brittleness effect brought about by methanol can be partially mitigated by subjecting the final composite membranes to an elevated temperature of about 120°C after total evaporation of solvent while still under the consolidation setup.

Since Nafion's melting temperature is slightly higher than this set point, it will allow Nafion's crystal structure to align more accurately before thermal degradation occurs. However, this will only slightly mitigate the brittle nature of the final composite, as all samples subjected to this, though appeared stronger in nature, still broke apart during disassembly.

5.6 µVO & µVARTM Remarks

Unfortunately, since neither μ VO nor μ VARTM techniques resulted in usable samples for accurate analysis of results, mechanical testing could not be applied, as it would present inaccurate findings. However, qualitative analysis of both methods shows that one may be particularly better than the other.

For μ VO testing, the differences in Nafion concentration resulted in interesting effects. When the lowest concentration Nafion solution, 10 wt%, was applied to the setup under vacuum, the solvent evaporated quickly underneath the caul plate. However, when higher concentration Nafion solutions were applied in the same configuration, there was minimal diffusion of the Nafion through the reinforcement layers. This is because of the viscosity of the higher concentration solutions, i.e. 30wt%. This could be seen during testing because, while in the vacuum oven, the Nafion solution solvent struggled to evaporate under the caul plate. Typically, the caul plate would force the evaporating solvent and any air bubbles to exit out around its edges. However, with such high concentration solution, the evaporated solvent and gasses could not exit out and, thus, became trapped under the caul plate to elevate as the vacuum caused increased expansion of the gas bubbles and resulted in an expanded, highly porous composite membrane. For this reason, it shows that lower

concentration Nafion infusion solutions result in a much higher diffusion of Nafion in the final composite. However, this contradicts what was previously stated, that consolidation trials using the higher concentration Nafion infusion solutions typically result in composite membranes with fully immersed reinforcements within Nafion.

So, in any solution concentration used for the μ VO technique, there will always be associated disadvantages. For lower concentration infusion solutions, it allows for full diffusion of the solution throughout the reinforcement, but not enough Nafion to fully immerse the reinforcement. For higher concentration solutions, it allows for the reinforcement to be fully immersed in Nafion, but the solution doesn't diffuse all the way through the reinforcement and leaves it porous.

Hence, only the µVARTM technique will work to consolidate the reinforcements, especially with high concentration infusion solutions because it has the major advantage of allowing the solvent to evaporate much slower. This lets the Nafion solution fully diffuse throughout the reinforcement layers before it casts, while providing a continuous, flat membrane surface for which the reinforcement is fully "sandwiched" within.

Thus, the advantages of the μ VARTM technique are clear. And though the μ VO technique would increase scalability and production of membranes, it presents membranes with a serious lack of quality when compared to membranes produced using the μ VARTM technique.

Chapter 6

CONCLUSIONS

6.1 Summary

Following from the previous work of Jacob (2015), the μ VARTM technique was sought be more thoroughly understood, improved, and applied to improve the overall lifespan of PEM fuel cells, as is the goal of this thesis. Though not all goals were achieved, understanding and improvement of the μ VARTM process were thoroughly analyzed.

For this work, nanofiber reinforcements of PS and PVDF were created using the electrospinning technique. Following this, the μ VARTM process was applied, infusing the nanofiber reinforcements with Nafion, the material most commonly used for PEMFC membranes. Although the μ VARTM process, applied towards improving the mechanical strength of such membranes, did not succeed, the reasons for why it did not succeed are known, and, now, a suitable path forward can be followed to finish the study.

6.2 Conclusions

The consolidation of electrospun PVDF and PS failed to produce mechanically reinforced Nafion membranes for a variety of reasons. However, the most notable reason for failure was the choice of solvent versus the choice of reinforcement material. Methanol, though compatible with PS and PVDF reinforcements, produces very brittle Nafion membranes. These membranes were created successfully, however,

were so fragile, that upon carefully disassembling the consolidation equipment, broke apart. On the other hand, DMAc, which is not compatible with PS or PVDF, produces Nafion membranes of much higher strength but completely destroys the reinforcement. Hence, if reinforcement materials of greater chemical stability were chosen, specifically compatible with DMAc, then it should produce reinforced Nafion membranes very well.

However, since this was not the case, Methanol was used as the principle solvent for the study, since it is compatible with both PS and PVDF reinforcement materials. And though, this resulted with no usable membranes being produced, understanding of the consolidation process was still able to be achieved. Through consolidating the reinforcements using different Nafion infusion concentration solutions and by comparing the μ VARTM technique to the μ VO technique, it provided an understanding of nanofiber consolidation and was concluded that the μ VARTM technique had inherent advantages that the μ VO technique simply cannot achieve.

Though the μ VO technique allows for improvements in consolidation time and scalability of membranes, it produces inferior membranes due to surface morphology discontinuities and high porosity. However, the μ VARTM technique produces membranes of continuous surface morphology, completely immersing the reinforcement in Nafion. This is due to the vacuum bag that covers the consolidation setup. This allows for indirect contact of the infusion with the vacuum, allowing the infusion solution solvent to evaporate as slowly as possible through the vacuum. This is highly advantageous because then higher concentration infusion solutions can be used to consolidate the reinforcements. The slow evaporation allows the high

concentration solutions to slowly diffuse into the reinforcement nanofiber layers and completely immerses the reinforcement in Nafion, creating a highly consolidated composite membrane. If this same high concentration infusion solution was applied to the μ VO technique, the solvent would evaporate so quickly that the Nafion would barely diffuse through the reinforcement layers and create discontinuities within the membrane. This is why the μ VARTM technique is so useful and advantageous. The μ VO technique provided an interesting alternative and possible improvement, but after analysis, proved substandard.

And, the reason why the µVARTM technique works so well only with high concentration infusion solutions is because it allows enough Nafion to fully consolidate the reinforcement, ultimately "sandwiching" the reinforcement in Nafion. If a lower concentration solution were to be used in the same process, i.e. 10wt% solution, then there wouldn't be enough Nafion in solution to achieve this same result. Instead, the small amount of Nafion left over after the solvent evaporates will simply be small particles within the layers of the un-consolidated reinforcement. This is why different solution concentration infusions were tested, and thus, the correlations between processing conditions and final membrane quality are now known.

6.3 Future Work/Path Forward

Since the largest source of failure in producing membranes of increased mechanical strength was due to the choice of solvent versus the choice of reinforcement material, in future work, the solvent of choice will be controlled as DMAc. This work showed that high-body solvents produced stronger Nafion, while lower-body solvents, like Methanol, produced weaker and more brittle Nafion. Thus, DMAc will be held as constant in the future work. Instead, the materials for the

electrospun reinforcements will be of much higher importance. Materials will need to be chosen so as to represent high enough chemical stability to be compatible with DMAc, yet still have the ease of processing for producing nanofiber reinforcements using the electrospinning technique. Specifically, Teflon will be researched as a possible reinforcement, since it has very high chemical stability. However, Teflon and other chemically inert polymers have certain characteristics that make them more difficult to process. So, improvements in the electrospinning setup will need to be made so as to be able to process such chemically stable polymers.

Since this dilemma was the heart of the issue for this thesis, there should be minimal issues in producing usable Nafion reinforced membranes. Thus, with the membranes produced, testing and quantitative analysis of the membranes can be performed to see how the reinforced membranes fare against the standard Nafion membranes used today. For these tests, there will be *ex* and *in situ* testing of the membranes. *Ex situ* testing will predict the membranes' mechanical durability. These include tensile tests, which will be performed to calculate the membranes' elastic moduli. Also, hydration tests using acidic water will be performed to predict the lifespan of the membrane when subjected to the harsh environment of the fuel cell. Lastly, ionic conductivity tests will predict any differences in proton conductivity of the membrane due to the reinforcements.

In situ testing will then be performed to see how the membranes react within an actual fuel cell. This testing procedure will predict the electrochemical properties of the membranes including polarization and electrochemical crossover.

Another interesting option for future work would be comparing reinforced Nafion membranes with CNT reinforced Nafion membranes. Jacob's previous work

(2015) also showed that the addition of CNTs within the electrospun nanofiber mats greatly increased the mechanical strength of the membranes produced. Therefore, if this same process were to be applied with CNTs, specifically non-conductive CNTs, then the Nafion membrane could exhibit yet even greater strength. For specifics on how to formulate CNT reinforced nanofibers of PVDF, see Appendix A.

REFERENCES

- 1. Jacob, C. A. "Sub percolation threshold carbon nanotube based polyvinylidene fluoride polymer-polymer composites", Ph.D. Dissertation, *Department of Mechanical Engineering*, University of Delaware (2015).
- 2. Surya Subianto, Monica Pica, Mario Casciola, Paula Cojocaru, Luca Merlo, Graham Hards, Deborah J. Jones. "Physical and chemical modification routes leading to improved mechanical properties of perfluorosulfonic acid membranes for PEM fuel cells. *Journal of Power Sources*. Volume 233. 1 July 2013. Pages 216-230.
- Doshi, Jayesh, and D.H. Reneker. "Electrospinning process and applications of electrospun fibers." *Journal of Electrostatics 35*. Volumes 2 & 3. 1995. Pages 151-160
- 4. Frano Barbir. "Introduction, In PEM Fuel Cells." *Academic Press*. Burlington. 2005. Pages 1-16.
- 5. Garland, Benjamin, and Kopasz. "Material issues in polymer electrolyte membrane fuel cells." *Material Matters*. (2008). Issue 85.
- Yamashita, Yoshihiro, Akira Tanaka, and Frank Ko. "Characteristics Of Elastomeric Nanofiber Membranes Produced By Electrospinning." *Www.mat.usp.ac.jp*. Department of Materials Science, The University of Shiga Prefecture; Department of Materials Science and Engineering, Drexel University. Web. 1 Sept. 2014.
- Tamer Uyar, Flemming Besenbacher. "Electrospinning of uniform polystyrene fibers: The effect of solvent conductivity." *Polymer*. Volume 49. Issue 24. 10 November 2008. Pages 5336-5343
- 8. Mauritz and Moore. "State of Understanding of Nafion." *Department of Polymer Science*, University of Southern Mississippi. Pdf. (2004). Pages 4535-4585.
- 9. Sacca, Carbone, Pedicini, Portale, and Passalacqua. "Development of nation recast membranes for polymer electrolyte fuel cells." *Institute for Advanced Energy Technologies*, Italy.

- 10. Huang, Z. "A review on polymer nanofibers by electrospinning and their applications in nanocomposites." *Composites Science and Technology* 63, no. 15 (November 2003). Pages 2223-2253.
- 11. Eda, Goki, and S. Shivkumar. "Bead-to-fiber transition in electrospun polystyrene." *Journal of Applied Polymer Science* 106, no. 1 (2007). Pages 475-487.
- Naotaka Kimura, Takeaki Sakumoto, Yuki Mori, Kai Wei, Byoung-Suhk Kim, Kyung-Hun Song, Ick-Soo Kim. "Fabrication and characterization of reinforced electrospun poly(vinylidene fluoride-co-hexafluoropropylene) nanofiber membranes." *Composites Science and Technology*. Volume 92. 24 February 2014. Pages 120-125.
- Teo, Wee-Eong, and Seeram Ramakrishna. "Electrospun nanofibers as a platform for multifunctional, hierarchically organized nanocomposite." *Composites Science and Technology* 69. Volume 11-12. Semptember, 2009. Pages 1804-1817.

Appendix A

PVDF-CNT ELECTROSPUN NANOCOMPOSITES

The addition of carbon nanotubes (CNTs) has been shown to greatly improve the mechanical strength of nanofibers produced during electrospinning. From the previous collaborative efforts with Dr. C. Jaob, the following shows how to create such PVDF-CNT nanocomposites.

It's true that by the inclusion of CNTs within nanofiber mats drastically increase load carrying ability. However, CNTs can't just be put into solution with PVDF. They need to be accurately dispersed throughout in solution. So, for this research, to accurately ensure the dispersal of these CNTs into solution, the twin screw extrusion method was chosen. For this method, stock material of the specified nanotube loading were prepared by mixing CNTs into the same tightly sealed glass bottles and stirred until roughly homogenous. In order to ensure reduce agglomeration, the stock material was then casted and pelletized for use in the twin screw extruder. The pellets were then fed into a micro-scale twin screw extruder at 300°C for 15 minutes and extruded to yield highly dispersed non-agglomerated pellets. These pellets were then re-dissolved into the appropriate solution concentrations for the electrospinning process.

The following parameters represent the necessary conditions for accurately electrospinning this PVDF-CNT composite solution.

Table A.1 For the electrospinning of PVDF with a concentration of dispersed CNTs, only 15 wt% and 20 wt% PVDF solutions were used, since these weight concentrations yielded the best nanofibers of pure PVDF. With these solution concentrations, the CNT weight concentrations varied between 0.1% and 0.25%.

Solution	CNT Concentration	Voltage (kV)	Solution Flow Rate (ml/min)	Relative Humidity	Temperature (°C)
15%	0.1%	+13/-13	0.06	<3%	18
20%	0.1%	+13/-13	0.05	<3%	18
20%	0.25%	+13/-13	0.04	<3%	18

As can be seen from Table A.1, the parameters for electrospinning the PVDF-CNT composite solution remained almost the same as the parameters for electrospinning PVDF alone. And since these parameters for electrospinning didn't change, it can be inferred that the nanofiber mats produced will display the same accuracy morphology. Figure A.1 proves this inference and shows that electrospun morphology remains identical regardless of CNT inclusion.



Figure A.1 Electrospun morphology is nearly identical with or without carbon nanotubes with fibers approximately 200nm, though some larger fibers and beads also exist.