Emission Capabilities of Nafion-Based Emitting Geometries

by

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Abstract

The propulsion field is home to numerous technological advancements, ranging from the mechanisms of their operation to the propellants used. All of these have enabled numerous space missions, either for technological demonstrations, or for other commercial, and even government use. Fortunately, with the dawning age of miniaturized electronics, these engines can be downsized to lower the system mass requirements, while ensuring the execution of mission specifications. Electrospray propulsion, therefore, is one of the propulsion areas in which this is possible.

Numerous technological advancements have been realized in the field of electrospray propulsion, ranging from the use of exotic plasma propellants, otherwise referred to as ionic liquids (IL, ILs), to the exploitation of various materials to fabricate surfaces for ion emission. All of these have reported attractive results ranging from competitive emission currents that range between nano- and micro-Amperes for single and array emitters, respectively, to characteristic velocity outputs on the order of kilometers per second.

Although the thrust levels are small, usually of the order of micro-newtons, the specific impulse values go as high as 3000 seconds. Unfortunately, with the available materials used in fabricating emitter geometry, with either porous to non-porous bulk properties, the emission characteristics are normally compromised either by off-axis emissions or high hydraulic impedance due to low to no IL transportation to emission sites. As such, it warrants the necessity to opt for materials that ensure smooth geometries for predictable and axially symmetric emissions, thereby fostering increased thrust densities.

Fortunately, ionomers, a group of polymers capable of transmitting electricity, pose as attractive options for this situation. Nafion\textsuperscript{TM}, a fluorocarbon main-chain and sulfonic end groups composition, is the material used in the research presented in this work. Due to its extensive use in fuel cells, Nafion\textsuperscript{TM} presents as a viable choice since numerous research has been performed to understand the material’s morphological and physical behavior in situ. This resource was beneficial, especially in the research presented in this composition.

From the work done in the past using this material, it was clearly proven that ion emission, initiated via an electrified meniscus, was possible. Unfortunately, due to some unreliable manufacturing results, including bubble-filled tip structure, it was theorized that the emission results were, to some capacity, compromised. The presence of these air pockets inside the
tip bulk, including broken apexes, interfered with emission characteristics, either by limiting effecting liquid transport through the bulk, or by necessitating high start-off voltages for ion emissions.

Therefore, the main contribution of the research presented herein is to develop a manufacturing process that eliminates bubble structures in the tip bulk, and testing said geometries under high enough electrostatic forces for ion emissions to occur. Thus, this research presents the new manufacturing process, and communicated some results obtained for fabricated single and array geometries.

Fortunately, it was proven that for tip geometries impregnated with IL, the absorbed solution is available for transportation to the emission site. It was also shown that the Nafion$^{TM}$ geometries always mimicked the structural properties of the parent counterparts.

For emission results, it was shown that for single emitters, the emission characteristics were competitive, with emission currents that were higher than those obtained from other single emitters reported elsewhere.

Thesis Supervisor: Paulo Lozano
Title: Miguel Alemán-Velasco Professor of Aeronautics and Astronautics
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"The journey of a thousand miles begins with a single step," people say. Well, I say that is sometimes begins with a step, a fall, a stand, and various permutations of the latter set. The activities so afforded in this work were not always smooth sailing, but I am especially proud to have made it this far. Therefore, the MIT mentality has always resonated with me; that is to never stop trying even when things do not seem to show immediate results. One common saying usually coined everywhere, that would supplement this idea, goes a little something like, "the creation of the bulb did not suffice from the first but rather after the nine hundred and ninety ninth try."

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# Contents

1 Introduction ........................................... 17  
  1.1 General Introduction to Space Propulsion .................... 17  
  1.2 Electric Propulsion ..................................... 20  
  1.3 Advancements in Electrospray Propulsion ................... 28  
    1.3.1 Emitter Material Advancements .......................... 28  
    1.3.2 Motivations for Present Research ...................... 30  

2 Polymers in Electrospray Propulsion .......................... 33  
  2.1 A General Introduction to Electroactive Polymers ............... 34  
  2.2 Nafion$^{TM}$, an Emitter Material Alternative ................ 36  
  2.3 Past work with Nafion$^{TM}$ for Electrospray Propulsion .......... 40  
  2.4 Research Contributions .................................... 41  

3 Nafion$^{TM}$ Tip Fabrication ................................ 43  
  3.1 Synthesis Methods for Emitter Substrates .................... 43  
  3.2 Manufacturing Capabilities at MIT for Soft Materials .......... 45  
  3.3 Nafion$^{TM}$ Structure Development .......................... 46  
    3.3.1 Items of Interest for Tip Manufacturing ................. 46  
    3.3.2 Nafion$^{TM}$ Film Extraction and Solution Development .... 50  
    3.3.3 Tungsten Needle Development ............................. 53  
    3.3.4 Making of Polydimethylsiloxane (PDMS) Molds ............ 53  
    3.3.5 Manufacturing Resorcinol-Formaldehyde Xerogel Substrates .... 55  
    3.3.6 Nafion$^{TM}$ Structure Manufacturing ..................... 58
3.4 Manufacturing Results and Discussion ................................................. 67

4 Emission Examination ........................................................................... 77

4.1 Theory of Ion Emission Testing ................................................................. 77

4.2 Testing Capabilities Available at SPL ....................................................... 78

4.3 Results and Discussion ........................................................................... 79

5 Conclusion ................................................................................................. 87

A Catalogue of some single emitters developed using the new manufacturing method ................................................................. 91
List of Figures

1-1 Generalized plot depicting the relationship between the mass of power unit and $I_{sp}$. .............................................................. 22
1-2 General electrothermal propulsion operation. A given propellant is passed over a electrical heating configuration and passed through an expanding nozzle. 22
1-3 One dimensional depiction of electromagnetic acceleration for propulsion devices that utilize this mechanism. Electric and magnetic fields interact to generate a force vector that is perpendicular to them, i.e., ideally parallel to the flow. ........................................................... 23
1-4 Generalized 1D demonstration of the acceleration of charged particles with the use of an electric field. ....................................................... 24
1-5 Ion Electrospray Propulsion System (iEPS) as developed at the Space Propulsion Laboratory (SPL) at the Massachusetts Institute of Technology (MIT) [31] ................................................................. 26
1-6 Illustration of ion emission due to an electrified meniscus subjected to electric fields that exceed a threshold value. ................................. 26
1-7 Emitter bulk structure consisting of three available classifications of emitters for electrospray propulsion. ................................................. 27
1-8 Porous material-derived emitters as obtained from literature. (a) represents an emitter, made of porous Nickel [41]. (b) shows a needle-like structure made from porous tungsten [39]. (c) is an array of emitter manufactured from porous glass [31]. (d) is an image of pyrolized xerogel as vied from a digital microscope, and scanning electron microscope (SEM). The SEM shows the close up view of the structure of the apex region [40]. .......................... 29
1-9 Manufacturing results of silicon-based tip geometries as obtained from [16].

1-10 Tips structured made from porous Nickel with apexes consisting of irregular profiles. Etch time increased from (a) to (d) [37].

1-11 Illustration depicting emitter substrate profiles with predicted emission behavior. Smooth tips discharge ions in a predictable manner, where as tips with rough profiles have more unpredictable emissions.

2-1 Illustration of a crystalline and amorphous arrangement of polymer chains as obtained from [44].

2-2 Schematic of the chemical structure of Nafion$^\text{TM}$ with acidic (first depiction) and neutralized states (last two depictions) using protic ionic liquids [48].

2-3 Chemical structure of Nafion$^\text{TM}$ showing the fluorohydrocarbon chain and sulfonate acid group as obtained from various literature. Structure 2-3a was obtained from [55], while Figure 2-3b was extracted from [56]. The depiction from Figure 2-3c was interpolated from [57], and Figure 2-3d was from [49]. All these structures were used to depict the chemical structure of Nafion$^\text{TM}$, although they all have some stoichimetric variation either in the covalent bond placement of the main branching chain, or the repeat unit representation of the main chain.

2-4 Figure showing the behavior of Nafion$^\text{TM}$ ion groups behave in the presence of water. This depiction was derived from Gierke et. al’s micelle model [49], [55], [59].

2-5 Manufacturing results of tips from varied Tungsten masters as obtained from the work done by Andrew Adams. These and more of the results can be found in [66].

3-1 Figures 3-1a and 3-1b shows tip structures, with the former being the 3D drawn using SolidWorks, while the latter is the printed results of said features using the nanoscale printing tool. In Figure 3-1b, the image was taken from the top only since this was the only view available at the time with the imaging tool used.
3-2 Figure shows the micro-scale image of these pore-like cavities etched through a silicon wafer.

3-3 Image shows a set of valves, which are squares containing a conglomerate of holes, as fabricated using facilities available at MIT.nano [72].

3-4 Process used in fitting teflon paper into a beaker. 3-4a through 3-4c includes details of properly placing the teflon paper into the beaker. The final result should include a beaker that is completely covered with teflon paper.

3-5 Nafion™ film delamination from a teflon paper. This process includes gently spreading the teflon paper (3-5a and 3-5b), and gently separating the film from the paper (3-5c). This film was manufactured using the process described above.

3-6 An example image of a processed tungsten rod using the process outlined above, with increasing magnification from left to right. These images were taken with a scanning electron microscope (SEM).

3-7 These two parts represent the patterns of interest in this research endeavor. Figure 3-7a shows the single emitter patterns machined on teflon plastic. The raised squares will provide square pockets in which substrates can be fitted into. Figure 3-7b contains a white square, made of borosilicate glass, that was exposed to a laser in order to develop numerous needle-like structures resulting in an array.

3-8 Assembled parts to be filled with PDMS. 3-8a is Teflon plastic fitted with four tungsten tips. The tips are inserted and fixed at some desired height, preferably on the order of about 1500 μm at most as measured from the surface of the raised square to the apex of the needle. On the other hand, 3-8b is an borosilicate array tapped into a container. This circular container was lined with transparent paper to simplify the de-molding process.

3-9 PDMS negative molds of parent array from Figure 3-7b. Figure 3-9a is a regular image of the array negative after de-molding while Figure 3-9b is a series of digital microscopic images of the pattern captured by the polymer.

3-10 PDMS negative mold of parent tungsten tips arranged in a manner as displayed in Figure 3-8.
3-11 Sample carbon substrates manufactured using the process described above. These specific samples were sanded into shape and cleaned.

3-12 Illustration of a singularity forming at the region where the tip pattern occurs on the PDMS parent mold.

3-13 Nafion\textsuperscript{TM} material layering as defined and utilized in this section.

3-15 Data plot of the set pressure and measured chamber pressure for the desiccator used in this process. The black arrows show saddles at moments when the valve was left partially opened. These points show that the chamber managed to maintain a set pressure consistently until the state of the valves was changed.

3-14 Sequence of events for desiccating the first layer of Nafion\textsuperscript{TM} material.

3-16 Desiccator setup with the valve connected to the vacuum pump opened all the way. The bubbling effect within the solution inside the pockets of the mold stabilized during the desiccation process.

3-17 Mechanism used to assemble the tips before placing them in the oven.

3-18 Scheme used to measuring tips manufactured with the described process above. \( R_c \) is the radius of curvature of the tip, \( a \), and \( b \) represent the corn base and cylinder base length of the tip, respectively. Finally, \( c \) and \( d \) are the height measurements for the cylinder and corn, respectively.

3-19 Conditions of the solution inside the Array PDMS mold withing vacuum condition in the duration of about 10 – 20 minutes.

3-20 Measuring technique used on manufactured Nafion\textsuperscript{TM} arrays.

3-21 Images showing three different views of the same disk made of pure Nafion\textsuperscript{TM} at two different states. The top three images show the disk before loading with EMI-BF\textsubscript{4}, while the bottom three show the disk after the sample was baked at 80\textdegree C for about 88 hours.

3-22 Measuring metrics for the pure Nafion\textsuperscript{TM} disk in Figure 3-21.

3-23 Measured PH level of IL solution in which the pure Nafion\textsuperscript{TM} disk was submerged, before and after baking at 80\textdegree C.

3-24 SEM image of a pure Nafion\textsuperscript{TM} single tip coated with about 9nm of Ti. This thin coating enabled retrieval of clear images from the polymer structure.
3-25 SEM images of a pure Nafion\textsuperscript{TM} tip loaded with IL. This tip was baked in EMI-BF\textsubscript{4} for about 3 days at 80\degree C. As the magnification increases, the IL beads increase in size.

3-26 Images showing tips from a Nafion\textsuperscript{TM}-based array and a parent array made from borosilicate glass.

4-1 Stage onto which single emitters were mounted for testing.

4-2 Images of Toasty staged onto the setup in Figure 4-1. An extractor was also added to complete the setup.

4-3 Square wave emission current response from Toast as tested in a vacuum chamber, where the applied voltage was about 1000 volts.

4-4 Emission current from Robin response an applied voltage of about 1750 volts in a square wave with a frequency of 0.067 Hz.

4-5 Image of Robin before and after testing.

4-6 Test results of SquarePan during the first few minutes of test firing at a firing voltage of about $\pm$1900 volts.

4-7 Test results of SquarePan after about 50 minutes of test firing at a firing voltage of about $\pm$2300 volts.

4-8 SquarePan tip before and after testing. The external meniscus around the base of the tip before testing is not present after testing.
# List of Tables

1.1 Example of available space propulsion systems as documented in [11] .......................... 19

3.1 Tools used in making Nafion\textsuperscript{TM} solution .......................................................... 48

3.2 Tool list used to develop tungsten tips .......................................................... 49

3.3 Equipment used in making polymer negative molds .................................................. 49

3.4 Equipment list used in making carbon electrodes .................................................. 49

3.5 Apparatus used on making Nafion\textsuperscript{TM} tips and arrays ........................................... 50

3.6 Needle-like structure made from pure Nafion\textsuperscript{TM} solution, and feature dimensions. This tip was name Robin, and will be referred to as such for the entirety of this paper. .......................................................... 67

3.7 Array of Nafion\textsuperscript{TM} tips assembled onto a carbon substrate. The dimensions were measured using a digital microscope. .......................................................... 68

3.8 Summarized data of the mass and dimension change experience by pure Nafion\textsuperscript{TM} disk in Figure 3-21 after being loaded with EMI-BF\textsubscript{4}. .......................................................... 70

3.9 Some radius of curvature measurements of a few tip structures before and after baking them in IL at elevated temperatures. .......................................................... 70

A.1 Needle-like structure made from pure Nafion\textsuperscript{TM} solution soaked in IL 80\degree C for about 4 days, and feature dimensions. This tip was named Robin, and will be referred to as such for the entirety of this paper. .......................................................... 92

A.2 Needle-like structure made from pure Nafion\textsuperscript{TM} solution, and feature dimensions. This tip was name Toasty, and will be referred to as such for the entirety of this paper. .......................................................... 92
A.3 Needle-like structure made from pure Nafion™ solution soaked in IL 80°C for about 3 days, and feature dimensions. This tip was name Toasty, and will be referred to as such for the entirety of this paper.

A.4 Needle-like structure made from 10% IL by weight of Nafion™ IL-polymer solution mixture, and feature dimensions. This tip was name SquarePan, and will be referred to as such for the entirety of this paper.

A.5 Needle-like structure made from 10% IL by weight of Nafion™ IL-polymer solution mixture, soaked in IL 80°C for about 3 days, and feature dimensions. This tip was name SquarePan, and will be referred to as such for the entirety of this paper.

A.6 Needle-like structure made from 20% IL by weight of Nafion™ IL-polymer solution mixture, and feature dimensions. This tip was name SunnySide, and will be referred to as such for the entirety of this paper.

A.7 Needle-like structure made from 20% IL by weight of Nafion™ IL-polymer solution mixture, soaked in IL 80°C for about 3 days, and feature dimensions. This tip was name SunnySide, and will be referred to as such for the entirety of this paper.
Chapter 1

Introduction

Over the years, the propulsion industry has grown, inviting various innovations ranging from novel operation capabilities [1]–[3], to propellant selections [4]–[7]. All of these advancements have paved the way for improved aviation performance and even fostered complex space exploration ventures [1]. In this chapter, we will briefly trace the general aspects present in the propulsion industry as it pertains to the space propulsion field, which would allow us to dive deeper into the ideas that foster the research reported herein.

1.1 General Introduction to Space Propulsion

Propulsion in the Aerospace field makes use of Newton’s laws to explain the intricacies of flying vehicles. These laws allow for the understanding of these flying objects using their extrinsic and intrinsic properties [8]. The ideas derived from these three principles have allowed for detailed characterization of different forms of propulsion which include aircraft engines, solid rockets, chemical propulsion systems, nuclear, and electrical propulsion devices.

In the field of space propulsion, Newton’s mechanics still take center stage. From Newton’s third law, the action force generated by an available propulsion devices produces a reaction force where the flying object exhibits motion. This phenomenon must be preserved in order to maintain motion that can ultimately get the vehicle into space. It encouraged the need for propulsion units that include propellant storage capabilities that supported longer missions ventures, thus, enabling executions of different actions such as orbital and altitude
correction, and reaction wheel de-saturation, among others [1]. As a result, the entire accelerating body will exhibit mass changes over time, described in Newton’s second law, as exhibited in Equation 1.1.

\[ F = \dot{m}c \]  

(1.1)

Therefore, Equation 1.1 helps describe the magnitude of the force vector generated from the propulsion devices within the vehicle of choice. The variable \( \dot{m} \) is used to denote the amount of mass per unit time discharged by the propulsion device, while \( c \), usually described as the characteristic velocity, is normally associated with how efficient a propulsion system makes use of its propellant [9]. Although there is a more specific relation used to express this fuel efficiency, known as the specific impulse, as provided in Equation 1.2, the direct proportionality allows for a cross relation between these two parameters [10], [11]. Here, \( g_0 \) describes Earth’s gravitational acceleration. It is important to note that available propulsion devices exhibit different \( I_{sp} \)’s. Some examples of propulsion systems used in space propulsion are provided in Table 1.1

\[ I_{sp} = \frac{c}{g_0} \]  

(1.2)

In an ideal case, a higher value of \( c \), or in this case \( I_{sp} \), characterizes a system that uses its propellant efficiently, and is usually the most desirable, as described below. This feature ensures a small mass fraction, summarized in Equation 1.3 [10]. The mass fraction is a ratio between the mass of the propellant to the total mass of the space craft.

\[ \text{Mass fraction} = \frac{m_p}{m_0} \]  

(1.3)

From Newton’s first law, describing the realities of momentum available within an object in motion, Equation 1.4 surfaces, well known as the rocket or the Tsiolkovski equation [9]. For starters, this equation is only valid when either the force generated is much larger than the force due to gravity available in the region in which the vehicle is flying, if a large force is generated over a very short period of time, or if the exhaust velocity of the vehicle is time invariant [10]. Additionally, two quantities present in Equation 1.4, i.e., \( c \) and the mass
fraction, suggest an inverse proportionality. Therefore, a large enough characteristic velocity, will endorse a low mass fraction.

\[
\frac{m_p}{m_0} = e^{-\frac{\Delta V}{c}} \tag{1.4}
\]

One quantity of interest, especially in mission requirement definitions, is the total amount of velocity change required to achieve one or all needed activities such as orbit change, altitude control, and so on. This parameter, denoted as \(\Delta V\), is present in the Rocket Equation. As defined in Equation 1.4, this variable is directly related to the mass fraction. Therefore, for high \(\Delta V\)’s, the associated mass fraction will increase, despite high values of \(c\).

Not all propulsion systems are characterized with high specific impulse. As summarized in Table 1.1, chemical propulsion systems are good examples. High specific impulse thrusters in this specific category call for exotic chemicals that require elaborate storage and handling metrics. For instance, atomic hydrogen must be stored at temperatures close to absolute zero in order to provide specific impulses of about 2000s [11]. These storage temperatures will require storage devices that have thick walls or elaborate cooling systems, all of which add
weight to the overall spacecraft. Similarly, nuclear propulsion calls for similar requirements, despite the significantly high $c$ values reported [11], [12].

Solid propellants have also found their place in the space propulsion fields. The most well-known examples include solid rocket boosters used in the space shuttle missions performed in the past by the National Aeronautics and Space Administration (NASA). Unfortunately, even with advancements in incorporating lighter chemical materials and even more energetic materials, such as Glycidyl azide polymer [13], the advancements realized in this category are not sufficient to place these devices in the same performing capacity as some chemical, nuclear, or electrical propulsion devices [13]. Fortunately, these propulsion devices provide substantial support in mission that require force generated over a short period of time (impulsive maneuvers). This describes a quantity well known as the total impulse, characterized in Equation 1.5 [10]. In this equation, the force parameter is integrated over the period in which it was acting on the vehicle.

$$I = \int Fdt \quad (1.5)$$

On the other hand, electric propulsion has been present in the propulsion conversation for many years. As summarized in Table 1.1, this classification of thrusters has been documented to deliver high $I_{sp}$’s. Although not as high as that delivered by some Nuclear propulsion devices [11], the exhaust velocity delivered by propulsion system manage to support various space missions, such as interplanetary, or deep space missions [10], [14]. Fortunately, advancements in electric propulsion are still taking place, ranging from power generation capabilities, to system integration prospect. The possibilities available present attractive areas of research, some of which are explored at MIT.

### 1.2 Electric Propulsion

Electric propulsion makes use of an electric field to accelerate particles for the purpose of generating thrust [10]. As the definition so implies, electric propulsion requires some external power in order to provide the energy needed for thrust generation. Unfortunately, this arrangement depends on the performance of the system, as discussed below [10]. For
starters, the relation provided in Equation 1.6, where \( m_{\text{power}} \) is the mass of the power unit, \( P \) is the power of the unit used, and \( \alpha \) is the specific mass per unit power, provides a limit on the mass of the power supply needed by the system.

\[
m_{\text{power}} = \alpha P \tag{1.6}
\]

In addition, the system’s efficiency must be taken into account. This thrust efficiency level is measured using the Equation 1.7. The expression \( \frac{1}{2} \dot{m}c^2 \) describes the usable power available to the entire system; jet power. Despite the fact that this ratio does not always equal unity, the numbers reported in various works suggest that this ratio range from around 30\% to above 80\% [15]–[17].

\[
\eta = \frac{\dot{m}c^2}{2P} \tag{1.7}
\]

When Equation 1.6 and 1.7 are combined, a clear relation between the power unit mass and the characteristic velocity, and consequently the specific impulse as from Equation 1.2, exists. The description of this relation, as made available in [10], shows a direct relation between \( m_{\text{power}} \) and \( I_{sp} \). This suggests that the power unit must be designed relative to the performance level of the propulsion system. Therefore, for a system using a small amount of propellant over a set time step, so that a description that alludes to an inverse proportionality between the change in mass and the specific impulse is satisfied [10], an optimum specific impulse exists, where the power unit weight is minimize, and specific impulse maximized, as provided in Figure 1-1.

Although constraints as a result of power are present in the design of these systems, their popularity among research and industrial institutions have not wavered. In fact, various missions have been performed using these devices. A few examples include: NanoSpace CubeSat propulsion device known to have flown in the TW-1 CubeSat from China, a micro Cathode Arc Thruster (\( \mu \)CAT) successfully demonstrated by the Naval Academy, among others [1].

Fortunately, three categories, so far, have been developed to further classify the family of thrusters making use of electricity to generate propulsive forces. These include eletrothermal,
Electrothermal-based thrusters are those that use electricity to warm up propellant gases to higher temperatures, which are later expelled through an contracting-expanding nozzle (see Figure 1-2) [1], [10]. Unfortunately, due to the mechanism of operation of these thrusters, frozen flow limitations, a situation where gas reactions and flow velocity lag during operation, lower thrust efficiencies. Despite this limitation, these thrusters has been able to provide high performance capabilities either via propellant management or power use [1]. $I_{sp}$ values documented in literature range from low (about 60 seconds [1]) to high (about 1500 seconds from [18]) numerals, all of which depend on the requirements put forth for a specified mission. Some example of thrusters that fall into this category include arcjets like those used by NASA in the 1960’s [19], and resistojets [20].
Figure 1-3: One dimensional depiction of electromagnetic acceleration for propulsion devices that utilize this mechanism. Electric and magnetic fields interact to generate a force vector that is perpendicular to them, i.e., ideally parallel to the flow.

On the other hand, electromagnetic propulsion includes a family of thrusters that incorporates magnetic fields to accelerate ionized propellant particles. Ideally, for a given gas flow characterized with some initial velocity, $u$, and current density ($\vec{j} = q(\vec{E} + (u \times \vec{B}))$ that is acting perpendicular to the flow, the interaction between the flow and magnetic field will result in a thrust vector parallel to the flow (see Figure 1-3). Here, $\vec{E}$ is the electric field, while $\vec{B}$ is the magnetic field. In reality, various non-uniformities exist in the flow and magnetic fields. As such, when field interactions occur, the thrust vector does not mimic the clean predictions provided in Figure 1-3. This and other issues related to the gas flow itself like frozen flow, viscous losses, among others, contribute to system inefficiencies. Fortunately, resolutions comprising of magnetic field correctors and nozzle cooling configurations, are available for realization, although, depend entirely on the needs of a given mission.

Fortunately, electromagnetic accelerations has aided in systems with characteristically high specific impulses, going as high as $3000 - 6000$ seconds [10], [21]. An example of electromagnetic thrusters include Hall thrusters, which take advantage of the hall effect. It is the phenomenon when charged particles, also characterised with lamar rotations in the presence of a magnetic field, manifest an $\vec{E} \times \vec{B}$ drift that occurs in the direction perpendicular to the electric and magnetic fields, and exhibit collision frequencies that ultimately favor current generation [10], [22].

Finally, electrostatic propulsion units include a family of thrusters that make use of an electric field to accelerate ions liberated from an ion source (see the animation in Figure
1-4). In some of these thrusters, the liberated charged particles are of one species, thus, the design of the thruster ends up including a neutralizer placed close to the acceleration grid; In this case, the neutralizer, devices used to generate oppositely charged particles to those accelerated from the ion source, would occur on the right end of the acceleration grid in Figure 1-4 [10], thereby neutralizing the beam and maintaining neutrality of the propulsion system.

In an ideal case, the accelerated particles migrate across the acceleration region, traveling in a uniform velocity and monotonic direction. In reality, various conditions are non-uniform across the chamber, such as particle velocity, ionization emissions from ion sources, among others, which cause flow behaviours that promote losses. For consistent and continuous ion generation by ion engines, the source should do so at the desired potential and sustain emissions at current density levels corresponding to space charge current limiting values. In addition, they should generate ions at desired energy levels, with charged particles population exceeding neutrals generated simultaneously over long periods of time [10]. Otherwise, interactions between neutrals may result in low ion velocity while increased neutral speeds contaminate ion sources and permeate into the surrounding system, causing unforeseen system damage. Despite these limiting factors, ion engines have been reported to exhibit high

Figure 1-4: Generalized 1D demonstration of the acceleration of charged particles with the use of an electric field.
Ion particles can be extracted and accelerated similarly from a molten salt or Ionic Liquid (IL) solution. Since the solution consists of a mixture of both positive and negative ions, forming a metastable solution, emission of both positive and negative ion species is possible, especially when the electric field polarity is switched between positive and negative modes. Therefore, the need of a neutralizer is eliminated, and the system architecture simplified to constitute something very similar to the depiction provided in Figure 1-4. However, the delivery of these ions for emission and acceleration differs such that needle-like structures or capillaries\(^2\) are used instead for effective formation of taylor-cone structures and acceleration of dislodged ion particles [24].

Therefore, in the presence of an electric field, a liquid meniscus becomes electrified and reshapes itself into what is referred to as a Taylor-cone (see Figure 1-6. Once a critical electric field is reached, the electrodynamic forces exceed surface tension forces, causing the surface to rupture into a micro-jet consisting of liquid droplets, ion particle or both. However, for high specific impulse\(^3\), emissions must consist only of ion particles (Pure Ionic Regime (PIR)) [28]. Either way, the particles emitted form a spray, hence, the term electrospray, and, therefore, electrospray propulsion devices\(^4\) [24], [29]–[31], although this ion spray phenomenon has also seen applications in mass spectrometry micromolecules [32].

Since the mechanisms of these propulsion systems involves electrostatic forces, the extrinsic properties, such as the characteristic velocity and mass flow rate, will also depend on the potential used to accelerate the charged species from the IL meniscus, and emission current, respectively. Thus, \(c\) will vary proportionally with the square root of the potential, \(V\), as provided in Equation 1.8, while \(\dot{m}\) will depend on the emission current, \(I\), as made available in Equation 1.9 [10]. In these equations, \(q_i\) represents the charge of the ion emitted, and \(m_i\) is the mass of the charged species.

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\(^1\)Viewed to be the most developed propulsion systems, ion engines have taken part in space missions, like the Dawn mission, where the system operated for several hours at \(I_{sp}\) values ranging from 2000 – 3000 seconds [23]

\(^2\)Various mechanisms exist in the delivery of ILs to regions where the charged particles can be displaced and accelerated. This idea will be explored in more detailed later on in this chapter.

\(^3\)Electrospray propulsion devices are characterized with \(I_{sp}\)’s ranging between 60 – 2000 seconds [25]–[27]

\(^4\)Figure 1-5 shows an iEPS as developed at MIT.
Figure 1-5: ion Electrospray Propulsion System (iEPS) as developed at the Space Propulsion Laboratory (SPL) at the Massachusetts Institute of Technology (MIT) [31]

Figure 1-6: Illustration of ion emission due to an electrified meniscus subjected to electric fields that exceed a threshold value.
Various emitter surfaces can be leveraged in the development of electrospray thrusters. More specifically, these emitters can either be capillary or needle like structures that allow transportation of liquid from a reservoir. As displayed in Figure 1-7, electrospray emitters can be classified into at least three categories [28]. The first is the solid structure, on which IL is coated for delivery to the apex region for emission. The external wetting phenomenon allows the system to be used with any form of conductive liquid, be it molten salts or doped solutions, especially if their surfaces are treated to promote liquid migration to the emission sites. Alternatively, the emitter structures can be perforated, allowing for liquid to permeated through the structure’s bulk, for delivery onto the emission site. These porous configuration is suitable for operation with conductive liquids with low vapor pressure, a characteristic available in molten salts or ILs. On the other hand, a through orifice or capillary from which liquid can be transported to the emission site presents another feature available for liquid delivery to emission sites, similar to the third illustration in Figure 1-7. These capillaries
are well suited for use with doped organic salts [33].

1.3 Advancements in Electrospray Propulsion

The above discussion has revealed the complexities present in the propulsion field. So far, it is clear that there exist several propulsion systems, all of which have been used in space missions in the past. Despite this availability, the focus of the research reported in this document is electrospray propulsion. Fortunately, this field has experienced various technological advancements, all in the name of exploring different research questions, improving performance, and making this technology available to a wider range of interest groups. These advancements include, but are not limited to, exploring different material in the development of emitter geometries for ion emissions, increased IL inventory as propellants with species that affect the thrust densities of these systems [34], and novel spacecraft staging concepts that extend the life cycle of CubeSats powered by these ion generating thrusters. All of these and more research questions are being explored at SPL here at MIT, but of interest, specifically in this research, is the materials fields as it pertains to electrospray propulsion.

1.3.1 Emitter Material Advancements

Several materials have been used to develop emitter geometries for electrospray applications. Some prevailing reasons to exploring all the materials reported in literature today include improving liquid delivery to emission sites, to exploring the possibilities of their use in the field for possible extension into space missions. Thus, these materials either fall to the porous or non porous material categories.

Plenty of research on externally wetted emitter geometries for electrospray application is available. The materials used in this area include tungsten, nickel, stainless steel, and silicon, all of which were used to fabricate needle-like geometries for ion emission applications [16], [34]–[38]. The materials used, at least in the available research, all demanded a specialized electronically etch procedure, making use of contrasting chemicals. Loaded with IL, these structures were subjected to high electric fields and their emission characteristics examined in detailed. From the literature, emission currents from these tips ranged from 40nA to
Figure 1-8: Porous material-derived emitters as obtained from literature. (a) represents an emitter, made of porous Nickel [41]. (b) shows a needle-like structure made from porous tungsten [39]. (c) is an array of emitter manufactured from porous glass [31]. (d) is an image of pyrolized xerogel as viewed from a digital microscope, and scanning electron microscope (SEM). The SEM shows the close up view of the structure of the apex region [40].

150nA for single emitters. For those that managed to include time of flight (TOF) mass spectrometry, results showed that the resultant emission beam mostly contained monomers and dimers (suggesting almost, if not fully, pure ionic regime (PIR) operation).

On the other hand, porous materials have also been used in the development of tip structures as surfaces for ion extraction. Some of these materials include porous nickel, porous tungsten, porous glass, and porous carbon substrates [28], [31], [37]–[40]. Due to their porous nature, these structures, as depicted in Figure 1-8, can be passively loaded with IL which managed to penetrate the pores to the apex region. As a result, at high electric fields, emission characteristics included current values of the order of \( \mu \)m for arrays. These emission currents corresponded to thrust values of approximately 10\( \mu \)N or higher.

With the emission results provided from the research of both porous on non-porous materials, the field of electrospray propulsion in this respect has enormous potential. More and more fabrication techniques are becoming available as more materials are used in this field of study, allowing for more research questions to be explored. Unfortunately, even with emission results that convey competitive current amounts, some limitations still persist within the research areas explored in these literature examples. These and other issues realised in the area of materials for electrospray propulsion warrant the underlying motivation of the work reported in this research. These issues are covered in more detail in Section 1.3.2.
1.3.2 Motivations for Present Research

With the work made available by various researchers in materials for electrospray propulsion, it is clear that emission of ions is possible provided they have constant supply of ILs, a needle-like structure with a smooth profile, and electric fields high enough to displace ions from the IL used. The materials reported in Section 1.3.1 meet all these requirements. However, as reported in the respective literature, the overall experiment, from manufacturing to testing of these emitters, was met with some limitations, all of which depend on the manufacturing process, and material properties.

For non-porous materials, the electrochemical etch technique, with most recipes including a surface roughening treatment that is known to promote liquid adhesion and migration to the apex upon meniscus electrification, sometimes yielded unreliable results. This is because liquid transportation was not always achieved and sometimes imposed more processing steps to be performed, and if not addressed, disrupting emission behavior. For arrays manufactured from silicon, for instance, the resultant collections usually came out with varied positions, a situation that is problematic as this leads to emissions that interact with other emission sites, thereby contributing to edge effects, while off-axis emissions lower thrust outputs. (See

(a) Family of needle-like structures with their apex pointing in varied directions. (b) Left over mask material on top tip structures after etching.

Figure 1-9: Manufacturing results of silicon-based tip geometries as obtained from [16].
Figure 1-10: Tips structured made from porous Nickel with apexes consisting of irregular profiles. Etch time increased from (a) to (d) [37]

Figure 1-9a with a depiction of tip alignment disparities). Additionally, the tips obtained from batch processing, especially when the step calls for the use of a mask to develop and preserve the sharp quality of a given tip, was accompanied with incomplete etching results, with features resembling an hour glass (see Figure 1-9b). With these types of results, one has to incorporate significant trial and error changes, which may include over etching attempts to the point where emission results are affected [16].

For porous materials, the techniques used in the manufacturing process of these structures led to the development of irregular features that interfered with emission characteristics. Apart from possible tip misalignment, a feature also available in externally wetted silicon arrays [16], the tip profile can be greatly compromised either by the manufacturing process or by the material properties. The manufacturing process sometimes yields structures with irregular apex profiles (see Figure 1-10) [37], [39], paving the way to over etching in order to promote better tip structures. However, if these abnormalities are not resolved, the jagged topographies could potentially introduce secondary emission sites, affecting overall results. On the other hand, the material’s granularity also influences tip surface properties. In an ideal situation, the topography of a given tip should be smooth and continuous, terminating into a region of small radius of curvature at the apex region where uniform emission can be initiated and maintained over the course of testing. Unfortunately, due to the granularity of
the material, the tip terrain ends up having a roughness quality that introduces secondary emission sites, or favor off-axis emissions that are detrimental to maintaining high thrust efficiencies (see Figure 1-11).

In order to address these issues, materials with low granularity (i.e. with physical and chemical properties that promote formation of smooth tip shapes), and simple manufacturing processes (i.e. amount of chemical processing is minimized) should be considered. So far, metals and non-metal solid materials have taken center stage in this conversation. Alternatively, polymers, also defined as viscoelastic materials, could present possible choices for use in fabricating these tip geometries. Fortunately, in this research, electroactive polymers are an attractive choice, as they are conductive (the presence of ionomer groups promote conductivity), and malleable materials. Therefore, the research reported here will constitute the manufacturing and testing of emitters made of an electroactive polymer known as Nafion™. More information regarding this material is available in Chapter 2.
Chapter 2

Polymers in Electrospray Propulsion

Polymers, hydrocarbon-based materials with degree of polymerization larger than 10, are present in most of the products and items used today. With applications in the medical field and the cosmetics industry, among others, these materials has found appreciation in our everyday life [42]. It was only a matter of time before they found their way into the space propulsion field.

There exist many different families of polymers, with classification metrics dependent on methods of polymerization, main chain attributes, and even chemical compositions. Of interest in this research, is a group of polymers, referred to as electroactive polymers, with a chemical composition that also incorporates ionic intermolecular forces [43]. These types of materials are sometimes referred to as ionomers, and their associated conductivity have allowed their use in electronics as well [44]. An example of such a material is Nafion\textsuperscript{TM}, made up of a fluorocarbon main chain, and an acid end group where these ion groups reside. This material does possess attractive properties, especially in the space propulsion field, particularly in the development of emitter structures for extraction of ions due to electrostatic stresses, as discussed later in this chapter.

Therefore, an understanding of electroactive polymers will be developed in this chapter. This will ultimately lead us to understanding the properties available in these materials, particularly Nafion\textsuperscript{TM}, providing insight into why this polymer was chosen for this research endeavor. Afterwards, a summary of any and available work already done in this subject will be provided, which will lead into the core contributions of this research for electrospray
2.1 A General Introduction to Electroactive Polymers

Electroactive polymers are materials that conduct electricity. Given that these materials are characterized with extensive chains consisting of mainly covalently bonded elements, these polymers afford sites in which electrical conduction is favored. For polymer electrolytes, polymers with salts dissolved in their bulk, conduction is mainly via ion migration, from one site to another, usually involving multiple chains with active exchange sites. As noted by Scrosati, this form of conduction is especially limiting since the motion of the chains is reduced, thus, lowering the material’s conductivity [44].

On the other hand, electrically conductive polymers, also conductive polymers, which are materials with groups where a redox reaction usually occurs or active exchange sites are embedded into the chain’s chemistry, providing locations in which guest particles, possibly from an electrolyte, can plant themselves to, rely on the conduction band to transmit electric current [44].

Apart from electrical conductivity characteristics, ionomers possess other bulk features that make them interesting indeed. As a general feature among polymers, the chains can exist in random coils, distributed in a dis-ordered manner in the material’s medium. This phase is referred to as the amorphous phase, a location known for ion transport for polymer electrolytes [44]. However, the chains can order themselves in a regular prescription, folding on each other to form layers. This behavior constitutes a crystalline phase. For polymers, usually, both of these phases occur together (see Figure 2-1), since the measured crystallinity for these materials has been found not to exceed seventy percent [44]. Consequently, various generalized model’s have been developed to describe these phases in detail, especially as it pertains to the location of the ion groups (for polymer electrolytes, or conductive polymers). They range from the homogeneous model, with the ion groups distributed in the amorphous phase with no specific order, and cluster phase, where the ion groups existing in finite sized clusters in the amorphous phase [43]. Still, more specialized models have been conceived for specific materials, all in the attempt to understand the ion groups present within these
In order to understand these chemical structures in terms of the arrangements present within the materials volume, various measuring techniques exist, and have been used to further validate models founded for various materials including the homogeneous and cluster models mentioned above. These measuring techniques include small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS), Small angle neutron scattering (SANS), differential scanning calorimetry (DSC) among many others [43], [44]. These techniques, which includes diffraction and thermal measurements, aim to reveal structural properties of the material, especially in regards to reflection angles and intensities, and bragg spacing. At different sample conditions, be it temperature or moisture or compositions alterations, these data will change accordingly, thereby revealing environmental influences on the polymer’s bulk physical and chemical properties.

The information from these measurements allow for classifications, and even understanding the material’s properties in an intrinsic level. Thus, there are various materials that fall into any of these categories, either from their mode of electrical conduction, or via their structural compatibility with general or specialized models. From instance, as Marx et. al so notes in their literature, studies performed on a sodium ionized ethylene-methacrylic acid
copolymer showed x-ray peak corresponding to a finite bragg spacing of about 80Å, which were not present in the unionized copolymer, making this material a more likely candidate of the cluster model [43]. Alternatively, poly(ethylene oxide) - based electrolytes exist as examples of polymer electrolytes [45].

Nafion$^{TM}$, with is a fluorocarbon main chain and sulfonate acid end groups, is an example of an ionomer. It is more likely a polymer electrolyte given that the mode of conduction has been reported to include proton mobility when the membranes are loaded with water, and ion migrations when loaded with ILs [46]–[48]. In addition, the sulfonate groups act as sites for guest materials to embed themselves to, as depicted in Figure 2-2. However, this allocation is not a definitive result. With the culminated polymer properties; long fluorocarbon chains, and acid end chains, this material seems very versatile in the field of electrospray propulsion, especially in manufacturing emitter geometries. Fortunately, given the available examination tools, this material has been studied in detail. This information is made available in the following section.

2.2 Nafion$^{TM}$, an Emitter Material Alternative

Nafion$^{TM}$ is a polymer ionomer developed by the E.I. du Pont de Numeours establishment, obtained from the polymerization reaction between perfluorinated vinyl ether and tetrafluoroethylene [49]. (see Figure 2-3 for the chemical structure of Nafion$^{TM}$). This ionomer is an extensively studied material, especially since it is an excellent candidate for
use in fuel cells [49]–[54]. Given that these cells require precise temperature and hydration environments for optimum operation, various studies have been completed into understating the material’s behavior in situ, all of which are relevant in the research provided here. Unfortunately, literature on this subject also incorporate different Nafion™’s chemical structures (See Figure 2-3). Fortunately, the commonality persist in the arrangement of the ion group, and the presence fluorocarbon chains.

Figure 2-3: Chemical structure of Nafion™ showing the fluorohydrocarbon chain and sulfonate acid group as obtained from various literature. Structure 2-3a was obtained from [55], while Figure 2-3b was extracted from [56]. The depiction from Figure 2-3c was interpolated from [57], and Figure 2-3d was from [49]. All these structures were used to depict the chemical structure of Nafion™, although they all have some stoichiometric variation either in the covalent bond placement of the main branching chain, or the repeat unit representation of the main chain.

Numerous studies into how water affects Nafion™ reveal some very interesting and consistent results. Considering a set of Nafion™ films loaded with increasing water content, studies show that the membrane with high water content will exhibit high ion clustering as end chains preferably assemble near water beads (see Figure 2-4) [55]. This is particularly present in Nafion™ with lower equivalent weight (EW), where EW is a ratio of the number of water molecules to the number of sulfonate groups [49], [58], [59]. As such, this arrangement of end chains suggest a phase separated mixture, especially since the main chains are hydrophobic, preferably arranging themselves away from water aggregates [49], [57]. Upon extreme hydration, however, water molecules get trapped in between the pockets formed by
chain cross-linking (increased swelling) [53]. This causes water to behave as a plasticizer, lowering the elasticity of carbon chains [47]. Fortunately, most studies revealed that higher degrees of hydration corresponded to higher measured conductivity [60]. High hydration result in higher levels of proton solvation and mobility [52]. On the other hand, conductivity is still present in membranes with relatively low moisture content. However, this is brought about by the vibration of end chains [52]. Unfortunately, Nafion$^{TM}$ is not considered as an ohmic material since the measured conductivity of films with varied thickness and the same EW produces different conductivity values [61].

Apart from understanding Nafion$^{TM}$ material behavior under water environments, researchers have also considered ILs environments, and how they influence this material’s properties. Morphologically, the results from Bennet et. al. [55] and Bennett et. al. [62] seem to contradict each other. From the results reported by Gierke et. al. [59], increasing cation size decreases ion clustering as observed in a water environment. This occurrence was attributed to the change in water absorption and light scattering, especially since the heavier cations are less hydrophilic, and increase the materials electron density [59]. Bennett et. al. [62] reported observations that conformed to this generalized model when Nafion$^{TM}$ was impregnated with 1-ethyl-methylimidazolium trifluoromethanesulfonate (EMI-Tf) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-Im). Therefore, from the SAXS data, ion clustering increased with decreased cation size [62]. On the other hand,
Bennet et. al [55] reported SAXS data behavior where the cation size did not seem to directly influence the cluster peaks. In fact, the present argument is rested on the idea that ILs do not necessarily swell the clusters alone, as registered by Gierke et. al.’s micelle model. The possible incorporation of the ionic liquid into the material’s backbone chain and the cluster domains seems to facilitate the low amplitude peak measured for EMI-Im compared to that for EMI-Tf [55]. Regardless of this result, the conductivity of Nafion$^{TM}$ increases with increased IL uptake, with the highest conductivity recorded for Nafion$^{TM}$ composites developed at higher temperatures [62]. For studies performed Schmidt et al. [58] on Nafion$^{TM}$ with several ILs, results revealed that the polymer material was able to absorb, on average, more material, and displayed high conductivity levels from the BF$_4$ IL than from any other solution used in the study. This is a favorable result, especially in relation to the present research.

Temperature is also a crucial parameter when comprehending Nafion$^{TM}$’s properties. In recent studies, acidified Nafion$^{TM}$ was observed to decompose in three stages when heated continuously with increasing heating temperatures of the rate of 20°C min$^{-1}$ [63]. Additionally, testing temperature also affect the morphological architecture of Nafion$^{TM}$ membranes. For the former case, WAXS experimentation performed by Gierke at. al. [59] displayed reduced measured intensity as the temperature was increased, which was associated with the material’s reduced crystallinity with increase in temperature. Therefore, cumulatively, melting of Nafion$^{TM}$ takes place over a wide range of temperature.

Membrane preparation temperature also affect material response to testing environment. For tests performed by Hinatsu et. al. [64], membranes pretreated at elevated temperatures absorbed less water. For Nafion$^{TM}$ films that were annealed before testing, testing attempts showed increased hydrophobicity, especially for samples annealed at temperatures above the materials glass transition temperature, $T_g$ [60]. Their measured contact angles, however, decreased after some time to stable more wetting conditions, although the angles were still above 90° [60]. At $T_g$, the morphology of the material transitions from the glass-like nanostructure, where the chains are mostly fixed, to increased chain mobility. This morphological restructuring possibly promoted main chain segments to advance to the surface of the membrane. In addition, with decreased wettability, these membranes exhibited reduced
proton conductivity, with percentage decrease going as high as 90% relative to non-annealed polymer membranes [60]. On the other hand, for Nafion\textsuperscript{TM} films consisting of material layers, possibly due to the preparation process, annealing at temperatures above \( T_g \) caused a reduction in the layer spacing [65].

In summary, temperature, and hydration with water or ILs interact with Nafion\textsuperscript{TM} to cause changes in its morphological, physical, and chemical properties. Increases water or IL content in polymer’s bulk mostly involves increased ion clustering, swelling, proton conductivity, and decreased elasticity. On the other hand, increased annealing temperature, on average, increases hydrophobicity while increased testing temperature leads to reduced crystallinity but increased water uptake. These results inform present research, especially as in pertains to material fabrication, and testing ventures to be discussed in Chapters 3 and 4.

2.3 Past work with Nafion\textsuperscript{TM} for Electrospray Propulsion

Here at the MIT SPL group, research in the aforementioned area of study was performed before, by Andrew Adams [66]. Motivated by the same concerns raised in the literature reported in Chapters 1 and 2, Adams developed a simple manufacturing procedure for these Nafion\textsuperscript{TM}-based emitters. The method involved a simple solution cast method from prepared Nafion\textsuperscript{TM} solutions, as described in the unpublished manuscripts developed by Dr. Zhou [67]. As a result, Figure 2-5 represent the fabrication results from his attempts. The apex of these tips displayed radius of curvature ranging from 12–15\( \mu \text{m} \) [66].

Since the manufactured tip geometries can be approximated as an assembly of a cone and cylinder shape, the formulations available in [68], in addition to the approximations expressed in the theoretical analysis of an emitter tip using the prolate coordinate system (see reference [66] for more details on this discussion), was employed in estimating the structures’ hydraulic impedance, a measure of the flow resistance withing a given structure. For existing electrospray tips, the most favorable hydraulic impedance for pure ionic emissions was found to be at least \( 1.5 \times 10^{17} \frac{kg}{m^3 s} \) [69], [70]. Fortunately, the calculated hydraulic impedance was ideal, with flow resistances ranging between \( 5.9 \times 10^{17} - 2.0 \times 10^{18} \frac{kg}{m^3 s} \) [66].
Most of the manufactured tips were prepped and tested in vacuum conditions using the facilities available at SPL. The reported results show that ion emissions are possible for these Nafion\textsuperscript{TM}-based emitters. It also confirms that the transportation of the IL to the emission site is possible, especially with the evidence of the IL depleted meniscus, i.e. liquid pinned around the base of the tip geometry (see more detailed discussion in [66] Section 5.3.1). In addition, the emission currents were competitive for single emitters, at least relative to other emitters as reported in Chapter 1. These numbers ranged between 20 – 1000nA [66].

2.4 Research Contributions

Despite the promising results so reported by Andrew Adams in his thesis, there were some concerns, all of which further fed the motivations presented in the research here. As
described in his work, Andrew Adams reported structural defects in the tips that he managed to manufacture. The most persistent deformity reported was the presence of internal bubbles or air pockets within the volume of the tip\(^1\). These structures have been theorized to interfere with the flow of IL through the tip\(^66\). Other defects including broken apexes, among others, greatly limited the testing venture so undertaken in the work reported\(^{66}\).

Therefore, the work reported herein will endeavor to address the issues encountered from previous work:

1. The first course of action would be to develop a reliable manufacturing procedure that will favor repeatable extraction of smooth and homogeneous tips. This will ensure that the polymer chemical and physical attributes are leveraged for these ion emission surfaces (see Chapter 3).

2. Next, depending on the direction of this manufacturing endeavor, an appropriate stage onto which these geometries can be mounted for testing, would be developed.

3. Using a scanning electron microscope, and a digital microscope, numerous images will be taken, paying close attention to the tip dimensions, and bulk appearance, for conditions before and after impregnating the material with the prescribed ionic liquid (see Chapter 3).

4. For structures successfully synthesized and mounted for testing, emission tests that include short term and long-term testing will be performed in order to provide incite into the emission behavior due to the new Nafion\(^{TM}\) tips. If more time becomes available other emission characteristics such as time of flight mass spectrometry, reterding potential analysis, and beam divergence behavior will be obtained for these geometries. However, the focus of this research is to ensure the first two data fields are acquired (see Chapter 4).

5. From this data, and referencing emission features from alternative material-based emitters, a comprehensive analysis will be developed.

\(^1\)Figure 2-5 shows an example tip where the base of the structure has a large air pocket
Chapter 3

Nafion$^{TM}$ Tip Fabrication

The discussion presented in Chapter 2 has revealed some very interesting polymer properties. So far, temperature and hydration conditions affect the nano-structural and morphological properties of Nafion$^{TM}$. Therefore, these conditions must be taken into consideration, especially when preparing ion emitter tips. It will guarantee product repeatability.

Fortunately, there exist various manufacturing techniques for developing substrates for use in electrospray applications. All of these depend on the starting and end products, in addition to the availability of processing equipment. In this chapter, a brief discussion will transpire for these manufacturing techniques, followed by the availability afforded here at MIT. This will, thus, lead into the discussion of the current method used for Nafion$^{TM}$ tip manufacturing, ending with preliminary results obtained from said process.

3.1 Synthesis Methods for Emitter Substrates

The following list includes some manufacturing techniques available for emitter substrates:

1. **Solution-Cast method.** This is, arguably, the simplest form of manufacturing method on the list. A homogeneous mixture, usually consisting of a solute and a solvent, is divided into small volumes, and the solute evaporated, either at room or elevated temperatures, leaving residual particulates, or film behind. This method is particularly favorable for polymer solution mixtures.
2. **Sol-gel process.** This process involves the preparation of a solution via mixing of a number of desirable chemicals. The resulting colloidal mixture is left dormant for a while to allow the chemicals to interact chemically, creating a gel constituent [40], [69]. Afterwards, the gel can then be cured to form preferred structures. This process is particularly common in the manufacturing of Xerogel substrates [40].

3. **Electrochemical etching.** This method makes use of a chemical to etch the structure of interest into a desirable profile. For electrospray propulsion purposes, this method has been used in fabricating emitters using Tungsten [36], and silicon wafers [16].

4. **3D printing.** 3D printing is a growing field, with technology advancements that favor precision and even nano-fabrication. There exist various types of printing mechanism, ranging from laser printing, to extrusion based printing. For some laser based 3D printing, the energy from the laser is used to initiate a polymerization reaction within a specialized resin, thereby creating a 3D structure. This type of reaction is referred to as two photon polymerization (2PP) [71]. Alternatively, cold laser ablation is a technique in which a high frequency laser rapidly disintegrates (ablates) material particles from a selected substrate [70], either drawing the feature of interest or removing excess material to leave behind the desired features [70]. The latter form of fabrication is extensively used on fabricating arrays used in most SPL experimentation, while the former is of interest for polymer-based manufacturing.

Items 2, 3 and 4 consists of processes currently used in developing tips for electrospray applications. Although these methods yield promising results, as reported in their respective literature, they incorporated complex recipes that currently seem unnecessary in handling Nafion\textsuperscript{TM} material. Therefore, as a starting approach, especially since this method was used in previous Nafion\textsuperscript{TM} tip research, the solution cast method was used in the synthesis of Nafion\textsuperscript{TM} tips. The details are reported in Section 3.3.

44
3.2 Manufacturing Capabilities at MIT for Soft Materials

MIT is fortunate to house a facility that fosters the exploration of nanoscale devices [72]. The tools available promote development of nanoscale structures usually used in microfluidics, microcomputing, and so on. With the tools available, fabricating small structures is possible at this institute, especially in the development of structures used in electrospray devices.

Apart from chemical and laser aided etch recipes available in this facility, MIT.nano is home to a 3D nanoscribe device, whose operation relies on the principle of two photon polymerization. Since the needle-like structures for ion emissions are small, with micro-scale radius of curvature, it was relevant to explore the capabilities of this tool as it pertains to the electrospray field. Although limited manufacturing research has been done here, some preliminary printing ventures were rendered, revealing important scaling metrics needed for the development of desired structural dimensions. For instance, due to some scaling errors incorporated into the drawing in Figure 3-1a, the image translated to the software used by the printing tool excluded some features as depicted in Figure 3-1b\(^1\). Fortunately, as confirmed on the tool, the dimensions extracted, at least for printed features, were of the order of nanoscale, implying that the tool has very high resolution capabilities. All in all, this manufacturing enterprise is paving the way for the author to use the available equipment in the future.

Another activity in which the author partook related to electrospray device development was in the manufacturing of micro-channels for electroactivated flow of IL from a reservoir to the emitter substrate bulk, and ultimately to ion emission sites. Some pictorial depictions are provided in Figure 3-2 and 3-1b.

\(^1\)The structures fabricated here are three-dimensional, like the drawing afforded in Figure 3-1a. The imaging tool, however, was not capable of providing a 3D view of the print.
3.3 Nafion\textsuperscript{TM} Structure Development

Fortunately, since the solution-cast method makes use of a simple and straightforward process, and does not require use of complex equipment, it was chosen in fabricating Nafion\textsuperscript{TM}-based ionic liquid ion sources. Therefore, all Nafion\textsuperscript{TM} structures were developed outside the nano facilities with tools provided below.

In this section, various processes will be explored in the making Nafion\textsuperscript{TM}-based structured for this research experience. Therefore, a list of tools will be provided, followed by specific processes used on fabricating all the material used in this research. This includes, Nafion\textsuperscript{TM} solutions, parent tungsten tips, carbon substrates, and Nafion tips\textsuperscript{2}.

3.3.1 Items of Interest for Tip Manufacturing

Table 3.1 includes a list of items used in manufacturing the Nafion\textsuperscript{TM} solution needed in this experiment. This list includes chemicals and equipment used.

\textsuperscript{2}The reader should note that the processes of interest in this research include the Nafion\textsuperscript{TM} solution, PDMS mold and Nafion\textsuperscript{TM} structure fabrication methods. Other methods availed in this literature provide inside into how other items, also used in this research, were made, but is not the focus of the research presented here. They should, however, provide enough information for any and all interested parties.
Figure 3-2: Figure shows the micro-scale image of these pore-like cavities etched through a silicon wafer
Figure 3-3: Image shows a set of valves, which are squares containing a conglomerate of holes, as fabricated using facilities available at MIT.nano [72].

Table 3.1: Tools used in making Nafion\textsuperscript{TM} solution

<table>
<thead>
<tr>
<th>List of items for use in making Nafion\textsuperscript{TM} Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion\textsuperscript{TM} Solution purchased from [73]</td>
</tr>
<tr>
<td>1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF\textsubscript{4}) from [74]</td>
</tr>
<tr>
<td>1-methyl-2-pyrrolidinone (NMP) from [74]</td>
</tr>
<tr>
<td>Temperature controlled oven</td>
</tr>
<tr>
<td>Thermometer</td>
</tr>
<tr>
<td>Pipette</td>
</tr>
<tr>
<td>Teflon paper</td>
</tr>
<tr>
<td>Beaker</td>
</tr>
</tbody>
</table>

This experiment also makes use of needle-like structures, to be referred to as tungsten tips. To generate these structures, Table 3.2 list of tools were used.
Table 3.2: Tool list used to develop tungsten tips

<table>
<thead>
<tr>
<th>List of items for use in making tungsten tips</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC power supply</td>
</tr>
<tr>
<td>DC power supply</td>
</tr>
<tr>
<td>1M Sodium Hydroxide (NaOH)</td>
</tr>
<tr>
<td>2-5cm long Tungsten rods with a diameter of 500μm [66]</td>
</tr>
</tbody>
</table>

This experiment makes use of molds that contain patterns of interest, in this case, needle-like structures. Making these molds requires the use of the list of items available in Table 3.3.

Table 3.3: Equipment used in making polymer negative molds

<table>
<thead>
<tr>
<th>List of items for use in making polymer negative molds</th>
</tr>
</thead>
<tbody>
<tr>
<td>A machined/assembled part with patterns of interest</td>
</tr>
<tr>
<td>Clear Sylgard 194 Silicone elastomer kit [73]</td>
</tr>
<tr>
<td>Plenty of Fab-wipes</td>
</tr>
<tr>
<td>Disposable stirrer</td>
</tr>
<tr>
<td>Prepped tungsten tips/arrays</td>
</tr>
<tr>
<td>Weighing scale</td>
</tr>
<tr>
<td>A beaker / disposable container</td>
</tr>
<tr>
<td>A desiccator</td>
</tr>
</tbody>
</table>

All these tips, as manufactured in this research experience, were bonded to pyrolyzed carbon electrodes. Table 3.4 provides a list of tools needed to make these substrates:

Table 3.4: Equipment list used in making carbon electrodes

<table>
<thead>
<tr>
<th>List of items for use in making pyrolyzed carbon electrodes [40] [75]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Machined/Assembled part with patterns of interest</td>
</tr>
<tr>
<td>Parafilm</td>
</tr>
<tr>
<td>Argon gas fed tube furnace</td>
</tr>
<tr>
<td>Acetic acid</td>
</tr>
<tr>
<td>Resorcinol and 35%</td>
</tr>
<tr>
<td>Formaldehyde solutions</td>
</tr>
<tr>
<td>Ultrasonic bath</td>
</tr>
<tr>
<td>De-ionized water</td>
</tr>
<tr>
<td>Beaker</td>
</tr>
<tr>
<td>Temperature controlled oven</td>
</tr>
</tbody>
</table>
Finally, in making Nafion\textsuperscript{TM} tips and arrays from negative molds, one needs the items available in Table 3.5.

Table 3.5: Apparatus used on making Nafion\textsuperscript{TM} tips and arrays

<table>
<thead>
<tr>
<th>List of items used on making Nafion\textsuperscript{TM} structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion\textsuperscript{TM} solutions</td>
</tr>
<tr>
<td>Polydimethylsiloxane negative molds</td>
</tr>
<tr>
<td>A desiccator</td>
</tr>
<tr>
<td>EMIBF\textsubscript{4} solution</td>
</tr>
<tr>
<td>Square carbon electrodes</td>
</tr>
</tbody>
</table>

3.3.2 Nafion\textsuperscript{TM} Film Extraction and Solution Development

For starters, fresh Nafion\textsuperscript{TM} solution was manufactured for purposes of this research endeavor. The process implemented by Adam in his masters thesis here [66], was clearly referenced in the beginning. It called for systematically applying layers of the purchased Nafion\textsuperscript{TM} solution, as documented above, onto Teflon paper, and baking the assembly at 80\textdegree{}C to evaporate the solvent. This was repeated 3 – 5 times to generate a film of Nafion\textsuperscript{TM} on the Teflon paper.

Although this process was used initially in this project, it was deemed to be unfeasible given the facility restrictions established due to the pandemic. In addition, given that layers of this solution were applied to the paper, it was difficult to handle the solution without spilling what was applied. Finally, the Nafion\textsuperscript{TM} films obtained gave back small vials of Nafion\textsuperscript{TM} solution that did not support the extensive trial venture employed in this manufacturing process. As such, it was necessary to implement a new and possibly easier process that was simple to perform, with less hand-on work.

Given the discussed properties of Nafion\textsuperscript{TM}, as reported in Chapter 2, such as temperature sensitivity [46], [59], and hydration memory [52], [59], [64], it was imperative to monitor the temperature environment in which to initiate evaporation, or solution development. Thus, during the development of the Nafion\textsuperscript{TM} films, temperatures were maintained between 40\textdegree{}C and 60\textdegree{}C, depending on how fast one wants the parent solvent to evaporate. In addition, the
Figure 3-4: Process used in fitting teflon paper into a beaker. 3-4a through 3-4c includes details of properly placing the teflon paper into the beaker. The final result should include a beaker that is completely covered with teflon paper.

waiting period between film making and solution development was kept as short as possible. The tools used to prepare the films, as documented above, allowed for easy material handling. Thus, teflon paper was fitted into a beaker such that a pocket was preserved inside the entire system (see Figure 3-4). After this was done, a plastic pipette was used to siphon the purchased Nafion\textsuperscript{TM} solution from its original bottle into the teflon-lined beaker. One pipette full was enough for the first layer, although, this method allowed for more solution to be added to the beaker. The beaker was then placed into the oven and the temperature was set to 40\textdegree C, and left for 2 – 3 days. This process was repeated 2 – 3 times, or more, depending on the constrains of the experiment.

Once the membrane making process was complete, the films were carefully removed from the teflon paper. Figure 3-5 shows a film that was obtained using the described process above. The film(s) obtained were then broken into small pieces before moving forward with the process.

The small Nafion\textsuperscript{TM} films were transferred onto a pre-weighted plate. This would determine how much of the solvent to use in the solution making process, since the solute-solvent combination used in this experiment was 1 : 10.

The solvent used in this experiment was 1-methyl-2-pyrrolidinone (NMP) since prior work showed both material compatibility and favored reproducible results in terms of solution manufacturing and, consequently, emitter structure development. This solvent was
measured, maintaining a 1 : 10 solute-solvent ratio, and placed in a beaker. A magnetic stirrer was placed inside the beaker, followed by Nafion\textsuperscript{TM} films. Keep in mind, the order in which the latter items were added into the beaker did not matter. Once everything was assembled, the beaker was placed on a heater capable of performing magnetic stirring. The temperature was maintained at around 80\degree C. A thermometer was used to monitor the temperature at the desired value. It is worth noting that this part of the procedure was extracted from Adams thesis [66].

Once all the Nafion\textsuperscript{TM} films were dissolved in the beaker, the heater was turned off. This allowed the solution and the beaker to cool down to room temperature. This solution, thus, constituted "Pure" Nafion\textsuperscript{TM} solution, and was stored in a compatible bottle.

Other Nafion\textsuperscript{TM} solution composites can be obtained after the above process is complete. One needs to take a portion (the entire solution created from the above process is still acceptable) and weigh its contents. This weight will determine what percentage of desired solution to add to make a composite solution. For this research, Nafion\textsuperscript{TM}-ionic liquid composite solutions were created using 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF\textsubscript{4}). For instance, to create a Nafion\textsuperscript{TM}-EMIBF\textsubscript{4} solution composite, where the IL is 10\% by weight of the pure Nafion\textsuperscript{TM} solution, one simply measures 10\% by weight of the Nafion\textsuperscript{TM} solution for the EMIBF\textsubscript{4}, and gently adds it into the beaker with the magnetic stirrer. The solution is mixed at room temperature for about 5 minutes, as documented in [66]. For this research activity, five different Nafion\textsuperscript{TM}-ionic liquid solution composites were created where
the EMIBF₄ solution was 10%, 20%, 30%, 40%, and 50% by weight of the pure Nafion⁷⁴⁷ solution used. Given that a 50% by weight EMIBF₄-Nafion⁷⁴⁷ solution gave desirable wetting results on resultant tips that were manufactured [66], fifty-percent EMIBF₄ Nafion⁷⁴⁷ solution was deemed as the desired stopping point in this mixing process.

3.3.3 Tungsten Needle Development

In this section parent tip geometries, made from tungsten rods, were extensively used in developing molds for making tips. This specific rod was used since this material and the manufacturing process was readily available and well known in SPL, respectively. In addition, this process has been well documented in [66], and used repeatedly, producing consistent results. Therefore, as outlined in [66], the tools listed in Table 3.2 were crucial in removing any oxide layer present on the rod, resulting in a smooth exterior⁴, and obtaining sharp apexes⁴. In the final step, the sharp needle-like end of the tungsten tip was dipped into the alkaline solution with the AC power set at 5V to slightly increase the radius of curvature of the needle [66]. This exercise led to the development of tip geometries like the one available in Figure 3-6.

3.3.4 Making of Polydimethylsiloxane (PDMS) Molds

See list of tools in Table 3.3. In this research endeavor, the teflon-based part, intended for single emitters, available in Figure 3-7a, and the tip array in Figure 3-7b, were used to develop the PDMS tip negatives. Since the substrate used to make up the array in Figure 3-7b was porous, the material was coated with a thin layer of teflon to prevent the PDMS material from penetrating and clogging the substrate’s pores. Doing so made the de-molding process much easier to execute.

The procedure available in [76], was a good reference in mixing the elastomer base and cure agents. Other mixing processes exist, however, this recipe was adopted since it gave

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⁴This was done by exposing the rod to the alkaline solution while connected to an AC power supply, set at 5V, for a few minutes

⁵This was achieved by partially dipping the smoothed tip into the NaOH solution and allowing 20V of DC power in the circuit and the solution to decompose the exposed region of the rod into a sharp pointy end
Figure 3-6: An example image of a processed tungsten rod using the process outlined above, with increasing magnification from left to right. These images were taken with a scanning electron microscope (SEM).

Figure 3-7: These two parts represent the patterns of interest in this research endeavor. Figure 3-7a shows the single emitter patterns machined on teflon plastic. The raised squares will provide square pockets in which substrates can be fitted into. Figure 3-7b contains a white square, made of borosilicate glass, that was exposed to a laser in order to develop numerous needle-like structures resulting in an array.
repeatable results after performing many mixing attempts. Other mixing procedures, such as the one available with the elastomer kit could be used to make these types of molds.

Thus, in this process, the first step was to determine the volume required to fill the pocket of the machined part of interest. Once the volume was determined, and since the density of PDMS is about 965 kg/m$^3$, a resource that is available in the internet and the data-sheet that comes with the elastomer kit, one can apply the inverse relationship between density and volume to obtain the required mass of PDMS material. Obtaining this quantity is crucial as this allows one to estimate a 7 : 1 base-cure ratio mixture as directed in the procedure provided in [76].

With the right mixing ratios determined using the above procedure, the elastomer was mixed thoroughly for about 10 minutes to ensure the components making up the PDMS were homogeneously distributed within its bulk. This mixture was then placed under low vacuum to evacuate any and all air bubbles that accumulated during the mixing process. The mixture was left inside vacuum for about 30 minutes, or until the medium appeared clear with no apparent bubbles trapped within its volume. At the same time, the tungsten tips were assembled inside the teflon plastic and glass parts as depicted in Figure 3-8 and prepped for the final step.

The PDMS liquid was, afterward, gently poured into the mold in a way to minimize the creation of new air bubbles. The final result was then left in a fume hood at room temperature for about 24 hours to cure. In [76], the process calls for the use of an oven at about 100°C. This step is still acceptable and will provide desirable results of the PDMS mold.

Finally, once the PDMS mold was cured, the mold was gently removed from the teflon plastic (See Figure 3-9 and 3-10). The negative pattern lifted off by the PDMS, thus, aided in making the ion emitting geometries using Nafion$^{TM}$, to be described later on in this chapter.

### 3.3.5 Manufacturing Resorcinol-Formaldehyde Xerogel Substrates

From literature, Xerogels have been described to be pore-filled substrates with electrical conductivity properties [40], [75]. Their low thermal conductivity and high surface area make them suitable materials to attach the Nafion$^{TM}$ tips onto them. Fortunately, the
Figure 3-8: Assembled parts to be filled with PDMS. 3-8a is Teflon plastic fitted with four tungsten tips. The tips are inserted and fixed at some desired height, preferably on the order of about $1500\mu m$ at most as measured from the surface of the raised square to the apex of the needle. On the other hand, 3-8b is a borosilicate array tapped into a container. This circular container was lined with transparent paper to simplify the de-molding process.

compatibility test that was performed in [66] between Nafion$^{TM}$ and Xerogel confirm that the materials are compatible, thus, allowing for the one to progress with the following steps.

The development of these devices involves a sol-gel process where the Resorcinol and Formaldehyde and are introduced to an acidic environment to initiate a poly-condensation reaction [40]. At SPL, however, there exist several recipes that have provided some reliable results, some of which have been explored in [40], [75]. However, what is important is the general series of steps that are consistent in all of them.

The measured quantities of Resorcinol and de-ionized water were mixed thoroughly in a sonic bath. Formaldehyde was then added in the later and the solution mixed until everything appeared uniform. Afterwards, the acid was added into the mixture. The resulting solution was further mixed together and transferred into molds.

The development process includes gelation, curing or otherwise described as the aging process, drying, and thermal activation [40], [75]. In the gelation process, the mixture was left at room temperature for almost an entire day to allow chemical reactions to occur,
Figure 3-9: PDMS negative molds of parent array from Figure 3-7b. Figure 3-9a is a regular image of the array negative after de-molding while Figure 3-9b is a series of digital microscopic images of the pattern captured by the polymer.

Figure 3-10: PDMS negative mold of parent tungsten tips arranged in a manner as displayed in Figure 3-8.
forming a gel, while in the curing or aging process, the mixture was placed in an oven and left to bake at three different temperatures, sequentially, from the lowest to the highest, each over a set period of time. Fortunately, for the substrates used in this experiment, the samples were baked at 40$^\circ$C, 60$^\circ$C, and 80$^\circ$C. At the drying step, the samples were left at room temperature for 24 hours, after which they were placed in an argon gas-fed tube furnace where thermal activation, otherwise known as pyrolysis, occurred.

An example of these substrates are provided in Figure 3-11. Additional details to this process are available in references [40] and [75].

3.3.6 Nafion$^{TM}$ Structure Manufacturing

Tip manufacturing using Nafion$^{TM}$ material has been attempted before. The work by Adam [66] presented some real breakthrough in this subject. His work outlined a simple procedure in preparing and making these polymer devices. It called for a straightforward approach where only one Nafion$^{TM}$ material layering was used to compose the entire body of a single Nafion$^{TM}$ tip [66]. However, the results obtained were accompanied with numerous structural problems that included bubbles within the tip structure, de-molding issues, and
bonding difficulty between the carbon substrate and the Nafion\textsuperscript{TM} material, among others reported here [66].

When one layer of Nafion\textsuperscript{TM} material was used, after desiccating the material [66], a singular crater-like feature occurred at the region where the tip pattern was situated in the PDMS mold (see the illustration in Figure 3-12). This behavior was amplified when the material dried considering that the Nafion\textsuperscript{TM} chains package more tightly as the solvent evaporates. Other issues included small bubble-like features around the apex of the tip (see Reference [66] in Subsection 3.3.1). Since only one layer was used during this process, no time was available to evacuate these bubbles effectively, which sometimes require high vacuum environments to promote high pressures inside these bubbles so as to encourage self detachment from the region around the apex of these tips, without excessively evaporating the solvent. Additionally, one layer did not provide enough material to both form the structure of interest and successfully bond with the carbon substrates [66]. As such, in this research endeavor, a new process was developed to address all these issues.

To start, a Nafion\textsuperscript{TM} ‘layer’ will be defined here as the amount of Nafion\textsuperscript{TM} solution placed into a PDMS pocket mold before placing the entire assembly into a vacuum environment. This is the amount of solution added to the PDMS molds manufactured in Subsection 3.3.4 to fill their respective pockets up to the brim, as depicted in Figure 3-13. Thus, the first layer of Nafion\textsuperscript{TM} will be the amount of solution added to fill an empty PDMS pocket mold before the first set of desiccation is performed. While a second layer will be the amount of Nafion\textsuperscript{TM} solution added to the pocket molds with most of the first solution evaporated during desiccation, and so on. Fortunately, no curing is performed between these layering actions. This is the terminology that will be used from this point forward.
New Process for Making Nafion\textsuperscript{TM}-Based Single Emitters

The process implemented here is a slow but reliable procedure that aids in addressing most of the issues encountered in [66]. It requires the use of items available in Table 3.5. Additionally, pure Nafion\textsuperscript{TM} solution, including 10\% and 20\% EMI-BF\textsubscript{4}-Nafion\textsuperscript{TM} solution were use in making the tips presented in this document. Work is still being done to realize a reliable technique for solutions with higher IL concentrations.

To begin, the first layer of Nafion\textsuperscript{TM} material was transferred into the PDMS parent mold for single emitters. The assembly was then placed into a desiccator as depicted in Figure 3-14. The system was isolated from the lab environment before the pump was turned on.

Two possible ways exist for making sure the pressure inside the chamber is at an ideal state to ensure any trapped air inside the deposited solution is evacuated while maintaining an appropriately slow NMP evaporation rate. It prevents the Nafion\textsuperscript{TM} material from drying before all the trapped air evacuates. The first way is more of a visual pathway. Once the vacuum pump is turned on, the valve separating the pump and the desiccator chamber is opened slowly such that one can visually see the o-ring between the chamber and the glass...
cover (See Figure 3-14a) flatten due to the suction effect created by the vacuum. At the same time, since this is the first layer, the frequency of bubble formation and evacuation should be low enough to preserve the amount of liquid available in the PDMS mold (See Figure 3-14c and 3-14d).

The second way involves the use of an Arduino set up that incorporates an electrically controlled valve and pressure transducer, where the pressure is controlled automatically. In this experiment, both of these pathways were attempted. It was observed, however, that the available desiccator was capable of maintaining a set pressure at any level, depending on how far the valve was turned (see Figure 3-15). For example, if the valve was opened all the way, and the pressure inside the chamber at this state was about 1000 Pa, the chamber would maintain this value, provided the pump was left on. After performing this task numerous times, it was clear that the first pathway was a much easier action to execute and was used for the entirety of this research endeavor. Fortunately, for either of these pathways, the PDMS molds was left in the chamber for about 20 minutes for the first layer of Nafion™ material.

Figure 3-15: Data plot of the set pressure and measured chamber pressure for the desiccator used in this process. The black arrows show saddles at moments when the valve was left partially opened. These points show that the chamber managed to maintain a set pressure consistently until the state of the valves was changed.
(a) Valve is opened to create a vacuum inside the chamber.

(b) Solution in vacuum for about a minute.

(c) Pump on for about two minutes. Bubbling begins at center of squares.

(d) Pump on for about four minutes. Bubbling persists.

(e) Vacuum pump on for about ten minutes.

(f) Vacuum pump on for about sixteen minutes. Bubbling diminishing over time.

Figure 3-14: Sequence of events for desiccating the first layer of Nafion™ material.
Figure 3-16: Desiccator setup with the valve connected to the vacuum pump opened all the way. The bubbling effect within the solution inside the pockets of the mold stabilized during the desiccation process.

Afterwards, the valve connecting the vacuum pump and the desiccator chamber was closed, and the pump turned off, paving the way for the user to increase the pressure inside the chamber. This was done by rapidly re-introducing air into the chamber without creating a strong gush of air that might dislodge the Nafion™ material from the mold pocket. The purpose of this step was to cause air turbulence with random low and high pressure regions that might aid in displacing micro-bubbles still embedded within the bulk of the Nafion™ material. Alternatively, these bubbles could migrate and merge to create larger bubbles that evacuate at lower vacuum. Fortunately, for more advanced systems, one can increase the chamber pressure using nitrogen gas.

Once this was accomplished, the entire system was reassembled and the chamber pressure lowered to the amount similar to the first attempt. This step was accompanied by decreased bubble formation frequency, especially around the region where the tip feature was situated. After about 10 minutes or so, the chamber was isolated once more, followed by an pressure increase, similar to what was done after the first desiccation step. This gassing and de-gassing exercise described above was repeated 2-3 times, or until minimal to no bubble formation, especially around the tip region, occurred. As a sanity check, if this process was successfully completed, exposing the mold to lower pressures would not initiate extreme, if any, bubble formation (See Figure 3-16).
Finally, the mold was desiccated for 10-20 minutes, at around the same chamber pressure as the first desiccation step, and isolated for a few days until about half of the solution in the pockets escaped via solvent evaporation. This was repeated three more times to result in 4 layers of Nafion\textsuperscript{TM} material desiccated into a mixture that was much more viscous (thick goo) than the actual Nafion\textsuperscript{TM} solution used.

With the Nafion\textsuperscript{TM} material ready for curing, IL-loaded carbon electrodes were mounted onto the molds in a process shown in Figure 3-17. Material spillage around the edges of the pocket was experienced, especially since 4 layers of Nafion material was used. The polymer material trapped between the PDMS and substrate, however, was sufficient to constitute a tip geometry and provide adequate adhesion to the electrode. For good measure, a glass slide and small weight were added on the assembly to provide added pressure in order to ensure complete polymer-electrode bonding. The PDMS assembly was left inside the oven at 40\textdegree C for about 2 days, or until the structure was completely cured.

The tips were then de-molded (see Figure 3-17), preserving the integrity of the tip region, and measured using the scheme provided in Figure 3-18. The image in Table 3.6 shows an example Nafion\textsuperscript{TM} tip obtained from this process.

**New Process for Making Nafion\textsuperscript{TM}-Base Arrays**

With the mold(s), similar to the once provided in Figure 3-9a, the procedure began at the same point as that used for single emitters. It started by placing the first layer of Nafion\textsuperscript{TM}
material into the PDMS mold, and evacuating any trapped air using a desiccator.

The next part of this process slightly diverged from the one assigned for single emitters. The Nafion\textsuperscript{TM} material was desiccated only once, without repeated gassing-degassing practices. In fact, as shown in Figure 3-19, the bubbling effect started off vigorous and diminished over time. This was observed to occur over a span of about 15 minutes. Afterwards, the pump was turned off, and the chamber pressure increased, after which one final pump-down was performed. The set up was left in the evacuated chamber until about half of the solution was evaporated.

Fortunately, for arrays, given their small aspect ratios relative to the single tip in Table 3.6, the desiccation process was not as involved as that for single emitters. However, if the air bubbles are difficult to eliminate with this simple step, the single emitter procedure can be used, and was proven to give effective results.

After the first layer, about 3 more layers were added in the same manner as described for single emitters, after about half of the Nafion\textsuperscript{TM} material had evaporated. The baking and de-molding process, however, were similar to that for single emitters (see Figure 3-17. The measuring metrics available in Figure 3-20, was used to catalogue the fabricated arrays. Table 3.7 shows an example of a successfully manufactured array using pure Nafion\textsuperscript{TM} solution.
Figure 3-19: Conditions of the solution inside the Array PDMS mold within vacuum condition in the duration of about 10 – 20 minutes.
Table 3.6: Needle-like structure made from pure Nafion\textsuperscript{TM} solution, and feature dimensions. This tip was name \textbf{Robin}, and will be referred to as such for the entirety of this paper.

<table>
<thead>
<tr>
<th>Nafion\textsuperscript{TM} Tip before loading with IL</th>
<th>Tip Region</th>
<th>Tip measurement [\mu m]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R_c )</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>352</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>321</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>647</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>711</td>
</tr>
</tbody>
</table>

Figure 3-20: Measuring technique used on manufactured Nafion\textsuperscript{TM} arrays.

3.4 Manufacturing Results and Discussion

In this section, the key topics of interest discussed will allow for the exploration of Nafion\textsuperscript{TM}’s behavior as measured in a finite number of conditions. Therefore, it will involve the measurement of tip geometries before and after IL loading, observing their swelling behavior to IL at elevated temperatures, simple IL ph tracking before and after introducing the ion-filled solution to fabricated polymer electrolyte structures, and finally mapping the topology of the needle-like features obtained from tip masters.

Since EMI-BF\textsubscript{4} solution is extensively used at SPL in testing electrospray devices, it
Table 3.7: Array of Nafion\textsuperscript{TM} tips assembled onto a carbon substrate. The dimensions were measured using a digital microscope.

<table>
<thead>
<tr>
<th>Nafion\textsuperscript{TM} Array</th>
<th>Array Region</th>
<th>Array measurement $[\mu m]$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$R_c$ 25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$a$ 230</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$s$ 447</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$h$ 280</td>
</tr>
</tbody>
</table>

Figure 3-21: Images showing three different views of the same disk made of pure Nafion\textsuperscript{TM} at two different states. The top three images show the disk before loading with EMI-BF\textsubscript{4}, while the bottom three show the disk after the sample was baked at 80°C for about 88 hours.
became extremely relevant to observe how much IL Nafion$^TM$ is capable of absorbing after being exposed to it. It involved the use of a Nafion$^TM$ structure, manufactured using the procedure provided above for single emitters, in form of a regular geometry. Figure 3-21, simplified into an approximate structure as defined in Figure 3-22, was used in this experiment. This structure was exposed to IL at 80°C for about 3 days, such that its weight and dimensions were recorded (See Table 3.8). Swelling of at least 1% was observed to occur, a behavior theorized to occur due to the interaction of the anion and cation with the polymer chain [48], [58]. This was accompanied with about 10% by weight of IL absorbed into the bulk of the structure, as obtained from weight measurements of the polymer. The discrepancy between the calculated and measured data, however, may be attributed to the approximation made on the Nafion$^TM$ structure as presented in Figure 3-22. The approximation availed in the calculations overestimated the Nafion$^TM$ disk, which was evidently translated to the estimated amount of absorbed IL.

Fortunately, when considering a set of Nafion$^TM$ tips soaked in IL at the same conditions and time frame, the swelling behavior observed on the tips’ radius of curvature was minimal. Apart from random names assigned to the tips, Figure 3.9 summarizes the measured radius of curvature before and after IL loading for structures with varied percentage of IL before baking occurred at 80°C for a few days. This data shows that the swelling behavior observed for this parameter is minimal, and goes as low as zero percent for higher IL-Nafion$^TM$ tip composites. Therefore, despite evidence of swelling in the bulk of Nafion$^TM$ structures, the radius of curvature is mostly preserved, an attractive outcome especially since the radius of curvature is desired to occur around a small range of values.

This absorption behavior informs what might happen to the tip geometries developed here in. Most of the tips prepped for testing were submerged in IL and baked at the same temperature for about the same time duration. As such, it is reasonable to conclude that for tips made from pure Nafion$^TM$ solution, the amount of IL absorbed after three days is about 10% by weight, with an approximate 3.33% by weight of IL per day. In addition, a 1% dimension increase is tolerable for tips used in this endeavor especially since small radius

---

5This temperature was used because hydration capabilities were reported to be high for BF$_4$ cation-based ionic liquids absorbed at around this temperature as reported in [58]
Table 3.8: Summarized data of the mass and dimension change experience by pure Nafion\textsuperscript{TM} disk in Figure 3-21 after being loaded with EMI-BF\textsubscript{4}.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Measure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of disk without IL [g]</td>
<td>0.0064</td>
</tr>
<tr>
<td>Mass of disk with IL [g]</td>
<td>0.0071</td>
</tr>
<tr>
<td>Measured % by weight of IL absorbed</td>
<td>10.98</td>
</tr>
<tr>
<td>Calculated % by weight of absorbed IL</td>
<td>37.52</td>
</tr>
</tbody>
</table>

Figure 3-22: Measuring metrics for the pure Nafion\textsuperscript{TM} disk in Figure 3-21.

Table 3.9: Some radius of curvature measurements of a few tip structures before and after baking them in IL at elevated temperatures.

<table>
<thead>
<tr>
<th>Nafion tip</th>
<th>Before baking in IL R\textsubscript{c} [$\mu$m]</th>
<th>After baking in IL R\textsubscript{c} [$\mu$m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Robin (Made from pure Nafion\textsuperscript{TM} solution)</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Toasty (Made from pure Nafion\textsuperscript{TM} solution)</td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td>SquarePan (Made from 10% by weight IL-Nafion\textsuperscript{TM} solution)</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>SunnySide (Made from 20% by weight IL-Nafion\textsuperscript{TM} solution)</td>
<td>13</td>
<td>13</td>
</tr>
</tbody>
</table>

of curvature are desired for these systems.

During swelling experimentation, the IL ph was documented before and after the Nafion material was introduced into the solution (see Figure 3-23). In the event of ionomer swelling as a result of exposure to some electrolyte, it is expected that the $H^+$ ions, available in the
Figure 3-23: Measured PH level of IL solution in which the pure Nafion\textsuperscript{TM} disk was submerged, before and after baking at 80\textdegree{}C.

Acid end groups in the case of Nafion\textsuperscript{TM}, will be displaced and replaced by the electrolyte cations [48]. Therefore, in some capacity, these positive hydrogen ions will infiltrate the electrolyte solution, and consequently change the solution ph. Figure 3-23 shows the measured ph of the IL solution before and after introducing the polymer electrolyte. Keeping in mind the neutral ph of the parent unadulterated IL solution, and air conditions, it is clear that some cation exchange activity took place since the new ph, displayed by the black arrow, reads close to 6, a point lower than the estimated 7 read from the baseline IL and air readings. In conjunction to the swelling observation, therefore, this ph reading further confirms that Nafion\textsuperscript{TM} was able to not only absorb, but interact with the IL.

In order to confirm that the tip structural profiles are consistently smooth, an SEM was used. For high resolution images, pure Nafion\textsuperscript{TM} tips were coated with about 9\textit{nm} of titanium using a sputter coating machine. When this structure was viewed under the microscope, it was clear that the topology of these tips were desirably smooth, terminating at a singular point characterized with a small radius of curvature (see Figure 3-24). Therefore, given the ionomers long fluorocarbon chains, this image in Figure 3-24 confirms the long chains were successfully packaged into a structure mimicking the profile of a parent tungsten...
(a) SEM of a pure Nafion$^{TM}$ single tip.  

(b) SEM of parent tungsten tip.

Figure 3-24: SEM image of a pure Nafion$^{TM}$ single tip coated with about 9nm of Ti. This thin coating enabled retrieval of clear images from the polymer structure.

tip.

When IL loaded pure Nafion$^{TM}$ tips were examined under the SEM, something interesting emerged. Figure 3-25 shows a series of images of one Nafion$^{TM}$ single emitter at different magnification. As the magnification increased, small liquid beads emerge and grew proportionality, until when they all merged and "flooded" the apex region of the tip. One explanation for this behavior may be attributed to the presence of pressure generated on the sample by the particle produced by the specimen. Given that an SEM works by emitting primary electrons (PE) and generating secondary electrons (SE) from the specimen which it then detects [77], it was, therefore, theorized that the fast moving PE bombarded the IL loaded ionomer creating an external pressure around the tip, which then 'squeezed' the apex causing the liquid to slowly emerge from the bulk to the surface. As the magnification increase, this pressure increases causing more liquid to percolate through and increase the volume of the already forming liquid beads. Ultimately, the liquid droplets overgrow and merge to eventually floor the apex (This behavior is clearly evident in Figure 3-25).

Alternatively, the energy that these PE have may be transmitted onto the samples. Since Nafion$^{TM}$ has been document to have a thermal expansion lower than that of EMI-BF$_4$ [53], [78], the IL will undergo rapid expansion, more so than the polymer, thereby exiting out of the ionomer to occupy more volume. On the other hand, these two ideas may be occurring
simultaneously, working together to bring the IL to the polymer surface. Fortunately, in
addition to the swelling and ph information, this 'leaking' behavior further endorses the idea
that the liquid so absorbed my the ionomer at elevated temperatures is not only absorbed
into the bulk, but also available for allocation to the emission site provided high electrostatic
pressures are introduced to both extract IL from the bulk, and eventually initialize ion
discharge form the apex.

Apart from single emitters, manufactured arrays were examined and compared to their
parent geometries. Figure 3-26 shows two images, one made from Nafion\textsuperscript{TM}, while the other
from borosilicate glass. The parent geometry seems to contain some ill-defined tip geometries
(broken apexes). This defect was, unfortunately, transferred to the Nafion\textsuperscript{TM} array, a result
that communicates two interesting things about this exercise. One, the polymer material is
capable of extracting any and all features from the parent geometry. Two, the topological
properties of Nafion\textsuperscript{TM}-based structures depend entirely on the features available on the
parent structure. Therefore, if the parent geometry is defective, so will the polymer structure.

It raises a very important concern about this exercise, which affects the motivation of
this work. From the motivations (see Chapter 1), it was stated that polymer materials could assist in improving tip profiles to accommodate axially-symmetric emissions, at a predictable location. This was theorized to increase thrust efficiency, and ultimately, engine performance. However, given that the manufacturing process makes use of preexisting features known to have these structural problems, then the motivation seems to be negated. Fortunately, since these ionomers can be molded into any patterns of interest, the only query would be to ensure the parent structure are regularly defined. Alternatively, one could consider other manufacturing ventures that would possibly eliminate the need for compromised tips. Manufacturing avenues such as the 2PP 3D printing [71], is of interest in this conversation, and is currently an area being examined as we speak. The idea here is to develop either flexible and smooth geometries, like those available in Figure 3-1, that could be copied onto a PDMS mold and used to develop structures. Alternatively, the 2PP 3d manufacturing method could be used to fabricate negative PDMS patterns, thereby eliminating the need for parent geometries all together. Either way, this pathway would provide more control on defining tip geometries, hence, possibly solving the problem exposed in this exercise.

One persisting issue observed with the tips manufactured using the process provided above includes persistent micro- and nano-bubbles defects. The process provided above was tailored to mostly eradicate small air bubbles. Unfortunately, some results had these features
still present, like the tip in Table A.1. Even with extended degassing and gassing exercises performed on the single emitters during the manufacturing process, these tiny bubbles did not successfully detach from the PDMS surface or polymer solution. The pressure inside the bubble was lower than the force provided by the air-liquid-PDMS surface tension. Inducing a lower pressure in order to overcome this force may dislodge the bubble, but will also induce rapid NMP evaporation, preventing effective fabrication of tip structures. Thus, in this experiment, a compromise was made in favor of reduced solvent evaporation over the micro-bubble, especially since this defect occurred on very few single tips (only about 2 out of about 20 manufactured tips).
Chapter 4

Emission Examination

Emission examinations of some of the fabricated tips will be performed in this section, relying heavily on the physics and analytical provisions from various documentations provided in [40], [41], [66], [70], [79], [80]. Therefore, more details will be provided on the general physics explored in this section, including the equipment used, and results obtained. It will, ultimately, provide some direction and understanding of the preliminary observed behavior, information that will be discussed in more detail towards the end of this chapter.

4.1 Theory of Ion Emission Testing

As implied in the previous chapters, electrospray mechanics, usually involving the extraction and acceleration of charged particles, involves a set of species with varied translational velocities, and charge to mass ratio. In order to understand the emission characteristics of any given emitter geometry, these parameters must be considered in more detail. At SPL, however, various techniques, both experimental and analytical, have been developed to foster increased understanding of these geometries in this capacity.

Experimentally, two very extensively used techniques take precedent. Time of flight (TOF) spectrometer, for one, is a measuring technique that measures the time taken by these species to travel from the electrified meniscus to the detector. Given that in most known ILs, these ion species travel at varied speed, they will, therefore, be detected differentially by this detector. For un-fragmented species, the particles arrive at the detector
at about the same time, such that lighter particles will arrive first, ultimately describing a monoenergetic beam [66], [80]. For fragmented species, however, they will incorporate measurements where particulates arriving at the detector together include species of more than one identity [80]. As such, TOF will no longer be sufficient in understanding the ion composition of the emissions.

Therefore, retarding potential analysis (RPA) becomes useful in further understanding the beam characteristics. This experimentation technique is able to map the energy distribution of the beam. This is normally done when a stopping potential is applied to the beam, thereby 'stopping' the particles in their motion and recording the potential at which this occurs for particles detected by the instruments. For monoenergetic beams, the stopping potential usually equals that used to accelerate the beam [80]. On the other hand, for a beam with fragmented ion particles, the stopping potential depends, to some measure, on the ratio of the mass of broken up particles to the mass of the parent ion from which the fragments originated [80]. As such, the energy of this particles is reduces, which ultimately impacts the thrust generated by the emitter.

In the work reported in this document, these two interesting measuring techniques were not explored in detail, due to time constrains and tool availability. However, the equipment listed in Section 4.2, used in these measuring methods were of interest especially in understanding the emission behavior of some of the single emitters. Therefore, of interest here is how the emission profile of these single tips appear due to an applied potential, mostly in the form of a square wave form, to be reported in more detail in Section 4.3.

4.2 Testing Capabilities Available at SPL

Fortunately, SPL has tools necessary to perform both TOF and RPA emission testing. The list of tools are available in the following references [66], [79], [80]. The vacuum chambers, where samples are exposed to pressures below $1 \times 10^{-5}$ torr, are configured to contain equipment necessary for both tests mentioned above and, therefore, were suitable setups to perform emission tests on the samples manufactured here. Unfortunately, the measurements of interest include basic current-voltage responses, and possible long-time emission behavior.
Figure 4-1: Stage onto which single emitters were mounted for testing.

Fortunately, the stage in Figure 4-1, was used to stage the manufactured emitters for testing. For single tips, the apex was systematically aligned with an 800$\mu$m radius aperture on an extractor as shown in Figure 4-2.

4.3 Results and Discussion

Figure 4-3 shows a current response plot from Toasty, after a voltage of $\pm$1000 volts was applied to the sample. As shown on the Figure, the blue plot corresponds to the magnitude

Figure 4-2: Images of Toasty staged onto the setup in Figure 4-1. An extractor was also added to complete the setup.
of the voltage applied on the sample over a set time, while the orange plot corresponds to the current emitted by the tip structure. The black plot represents the current intercepted by the extractor. This plot reveals some very interesting results as discussed below.

Due to an applied voltage of about 1000 volts, the needle-like structure emitted ions at a current magnitude of as high as $1.3\mu$A in the positive mode and $0.9\mu$A in the negative mode, in the beginning. The current magnitudes seem to eventually settle around $130\text{nA}$ and $-180\text{nA}$ in the positive and negative modes, respectively. From this response, it is clear that the overall current response decays over time. In addition, the emissions display a spike of current at the instance the polarity changes, but ultimately settles into what seems like a steady current response. And finally, the overall current response is asymmetric, with the positive mode consisting mostly of higher current magnitudes.

A more likely explanation to this general transient behavior would be tied to the competing transport mechanisms available in and around the tip. The tip preparation process, before testing, includes steps that expose the structures to excess IL. Therefore, to some
capacity, the tip geometries have very high IL concentration, especially in the external regions, before testing begins. When high electrostatic fields are introduced, the induced ion extraction from the electrified meniscus creates an ion deficit that is immediately replenished by the surrounding liquid, more so from the external region of the tips, since the impedance to the flow from this reservoir is much less than that from the tip's bulk. Over time, the external IL is depleted, causing the meniscus at the apex to draw ions from the bulk of the tip, an area with a much higher resistance to flow, especially due to the chemistry of the polymer (physical cross-links, chain branches, long chains, coiled chains, among others.). This behavior, in turn, reduces the emission current, as observed in Figure 4-3. Over time, a concentration gradient is induced, initiating a flow of ion from the entire bulk, and even from the substrate attached to the Nafion\textsuperscript{TM} tip. These competing transport mechanisms, therefore, contribute to the initially high current during the start of the emissions as displayed in Figure 4-3, which then decays rapidly over time.

For Toasty, this transport issue happens very fast, causing a significant current decrease in a matter of seconds, suggesting that the external IL reservoir is depleted proportionally.

Other faculties which include contaminants from the parent solvent used in manufacturing Nafion\textsuperscript{TM} solutions could have some amount of influence in the emission characteristics. Additionally, electrochemical reactions may be occurring within the bulk of the structures, especially between the Nafion\textsuperscript{TM}-carbon substrate interface, influencing the flow dynamics through the bulk of the tip in such a way that the hydraulic impedance is increased. Either way, more testing is needed here in order to shed some light into these attitudes hypothesised here.

The current asymmetry, on the other hand, clearly displayed during the beginning of the current response is an interesting result. It may be attributed to the interaction between the end chains of the polymer and some of the particles available in the IL. As proven in the previous chapter, the H\textsuperscript{+} ions get displaced and replaced by the cations present in the IL. Therefore, the particles involved in this interaction will also experience intermolecular forces that will require a little more energy to break. As such, in order to attain the same emission current in the negative mode, one would need a higher potential.

Fortunately, when Robin was tested under similar conditions to Toasty (see Figure 4-
Figure 4-4: Emission current from Robin response an applied voltage of about 1750 volts in a square wave with a frequency of 0.067 Hz.

4), similar current behavior over time was observed. The overall current response decayed over time, and the positive mode displayed overall more current response compared to the negative mode emitted current. This particular tip has an even smaller radius of curvature (See the Appendix section for more detail), in addition to a micro-bubble situated around the apex region. This "air pocket" eventually popped inside the chamber, increasing the radius of curvature to about 16\(\mu\)m, with the apex taking an almost rugged appearance (see Figure 4-5). All of these issues would have worked together to lower the magnitude of the emitted current obtained from Robin compared to Toasty.

Now, let's consider SquarePan Nafion\(^TM\) tip (See Table A.4), originally made from a Nafion\(^TM\) solution with about 10% IL by weight present in its contents before curing and soaking it in IL for about 3 day at 80\(^\circ\)C. This tip was tested under similar conditions as the first two Pure Nafion\(^TM\) tips above. Figure 4-6 shows the emission results from a square wave input voltage, over a couple of minutes. The current emitted by the tip at 1900 volts is about \(\pm 50\)nA. From first glance, the asymmetry, although subtle, persists in this emission data as well, proving once more that the interaction between the IL cations and the
sulfonic acid group present in the polymer end chains influences the emission characteristics. Unfortunately, due to the current magnitude, the resolution of the data is not sufficient to provide clear information about the transient behavior, if any, as observed on the pure Nafion\textsuperscript{TM} structures. What is interesting, however, is the somewhat sinusoidal behavior of the current response (also present in Figure 4-7). It is unclear as to what would cause this general emission instability. More testing is needed in order to shed additional light into the emission current behavior here.

Figure 4-7 shows more emitted current response from the SquarePan tip, after about 50 minutes of test firing. The applied voltage was increased to provide more data resolution to the response. The emitted current at this potential was about ±400nA, with clear current asymmetry between the positive and negative modes. Additionally, although a very subtle behavior, the current seems to display some general transient current response, such that the emitted current magnitude during the start of the emissions at this new voltage decrease over time.

The transient behavior is a very interesting behavior indeed, especially since it was also present in the initially pure Nafion\textsuperscript{TM} tips measured above. The present hypothesis mentioned above seems to be the likely explanation here as well. The absence of the external meniscus present in Figure 4-8, seems to endorse this idea further. Therefore, during the initial testing ventures, the IL from the external reservoir was depleted more rapidly than
Figure 4-6: Test results of SquarePan during the first few minutes of test firing at a firing voltage of about ±1900 volts.

that from the tip’s bulk, resulting in a decreasing current output over time. The decreased rate of current transient relationship reveals that the tip is now mostly accessing IL from its bulk, although the external reservoir is still being accessed. Despite these transient responses, the current measured from these exercises show values higher than those reported for single emitters fabricated from other materials and tested with EMI-BF$_4$ [36].

However, the amount of IL in the ionomer structures before soaking them in the former does not seem to have any influence in the emission data presented here. This and other testing alluded to in the begin of this chapter are still being explored here at MIT. This will, ultimately, shed some light into the throughput$^1$ characteristics of these structures, including their beam properties.

$^1$Throughput summarizes the behavior of the current measured from the emitter during ion extraction as a response to varying the applied voltage magnitude in a predictable fashion.
Figure 4-7: Test results of **SquarePan** after about 50 minutes of test firing at a firing voltage of about ±2300 volts.

Figure 4-8: **SquarePan** tip before and after testing. The external meniscus around the base of the tip before testing is not present after testing.
Chapter 5

Conclusion

Despite the many forms of propulsion devices available today, electrospray propulsion is more attractive here due to the recorded high specific impulse and small scale size. Even with the several available technological advancements ranging from increased IL inventory, to expanded choices in materials for developing emitter geometries, there are available limitations that warrant further exploration and examination. In this document, we propose an alternative material, Nafion\(^{TM}\), which is a polymer electrolyte that has seem applications in the fuel cell fields, to realize better defined tip structures. This is because the materials currently used to manufacture single or array emitters incorporate abnormal features, ranging from rough profiles that affect beam properties to extensively smooth exteriors that limit external IL transportation to the apex, all of which have been discussed in more detail in the chapters above. All these deformities seem to have an effect on the emission characteristics, lowering thrust efficiencies.

Nafion\(^{TM}\), a polymer characterized with end chain acid groups, is capable of conducting electricity. In addition, its long chain allow them to be packaged into small spaces, thus, seems as the most attractive choice in solving these issues. In addition, the available literature providing its behavior in various environments, provide useful information that informed the research performed here.

From the literature examined in this thesis document, Nafion\(^{TM}\) behaves very interestingly in various temperature and hydration environments:
1. Nafion$^{TM}$ is characterized to have a glass transition temperature of about 110°C [63]. Below this temperature, the chains of the polymer do not experience any significant motion, so that the material behaves more like a glass. Above this temperature, however, the chains have higher kinetic energy and are capable of moving around more freely. In addition, it is above this temperature where the morphology of the material begins to change, accompanied with reduced crystallinity [59], leading to chain decomposition, or onset of melting at even higher temperatures [63]. This response to temperature changes have been observed in various SAXS and WAXS examinations.

2. Under varied hydrated conditions, Nafion$^{TM}$ has been observed to display higher proton conductivity behavior in the case of water, attributed to increased ion clustering around electrolyte liquid beads [49], [59]. Unfortunately, this is accompanied with reduced material elasticity [54]. Fortunately, when exposed to electrolytes with varied cation size, Nafion$^{TM}$ has been observed to develop increased ion clusters with increased IL content [59]. Fortunately, other research has shown that this ionomer is capable of absorbing more BF$_4$ ions when compared to others used in that experiment [58].

From these properties, it was clear on how to handle the material during this experiment; (1) ensure the material is exposed to temperatures below its glass transition, and (2) ensure material is hydrated by the choice of electrolyte entirely as the equipment available can allow.

Research on Nafion$^{TM}$-based emitters has been done before, with data confirming that these structures can emit ions [66]. Unfortunately, the manufacturing results obtained for these structures in the mentioned literature included deformities that were theorized to interfere with emission characteristics. Therefore, this work aimed to provide a new manufacturing method that addressed these limitations, including basic current-voltage emission results showing evidence of ion emission.

The manufacturing method employed in this research endeavor included a simple solution cast method. It aided in obtaining interesting results for both single and array tips. For single tips, it was shown that the structures obtained mimicked the patterns and profiles afforded on the parent features. When loaded with IL, the bulk of the materials experience
swelling, however, the radius of curvature did not experience significant change, and was, for higher IL-Nafion$^{TM}$ composites, preserved. More importantly, the ionomer interacted with the IL (EMI-BF$_4$) used in this experiment by exhibiting ion change between the IL cation and the H$^+$ ion formally present in the acid group. Finally, the polymer material was capable of availing the absorbed IL to the emission sites.

When the polymer-based tip structures were exposed to high electric fields, ions were successfully extracted and accelerated, yielding emission currents above the range of those obtained for needle-like structures manufactured from alternative materials. Other behaviors like emission current asymmetry from the positive and negative applied potentials, and the current decay over time, are also interesting behaviors, all of which have been theorized to depend on the inter-molecular process realized between the Nafion$^{TM}$ end groups and IL cations, and IL transport mechanisms available on the tip structure, respectively.

Moving forward, more testing will be performed to understand the beam composition produced from the meniscus developed on these polymer structures. This includes an examination of the TOF of the emitted spices and the beam energy distribution through RPA studies. This experimentation would, also be extended to Nafion$^{TM}$ arrays.

In the manufacturing section, more IL-Nafion$^{TM}$ composite structures will be developed for both single and array emitters. This will be done on both available and new PDMS negative molds, where the latter are derived from new tip geometries. This exercise will, ultimately, provide more samples for testing, and provide more data for a detailed analysis and characterization of these structures for electrospray propulsion.

Another subject of interest includes the exploration of alternative parent or even polymer structure manufacturing. This may include 3D manufacturing avenues, as described in Chapter 3. These methods would allow for increased control in tip geometrical parameters, especially the radius of curvature. All of these and more present a field of challenging questions that will, eventually, be addressed.
Appendix A

Catalogue of some single emitters developed using the new manufacturing method

In this section, a list of single tips, before and after IL loading, is provided. The bulk dimensions are approximate values. However, these bulk dimensions, except that for the radius of curvature, $R_c$, did not provide enough information regarding the swelling behavior of the polymer after loading with IL. For more information about this subject, however, please reference Chapter 3.

On another note, at least one of the tips reported here was prepped for testing, with emission results available in Chapter 4. All other tips are still being examined under similar potentials.
Table A.1: Needle-like structure made from pure Nafion$^TM$ solution soaked in IL 80$^\circ$C for about 4 days, and feature dimensions. This tip was named Robin, and will be referred to as such for the entirety of this paper.

<table>
<thead>
<tr>
<th>Nafion$^TM$ Tip after loading with IL</th>
<th>Tip Region</th>
<th>Tip measurement $[\mu m]$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_c$</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>383</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>337</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>643</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>705</td>
</tr>
</tbody>
</table>

Table A.2: Needle-like structure made from pure Nafion$^TM$ solution, and feature dimensions. This tip was named Toasty, and will be referred to as such for the entirety of this paper.

<table>
<thead>
<tr>
<th>Nafion$^TM$ Tip before loading with IL</th>
<th>Tip Region</th>
<th>Tip measurement $[\mu m]$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_c$</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>379</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>322</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>327</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>500</td>
</tr>
</tbody>
</table>
Table A.3: Needle-like structure made from pure Nafion\textsuperscript{TM} solution soaked in IL 80\textdegree{}C for about 3 days, and feature dimensions. This tip was name \textit{Toasty}, and will be referred to as such for the entirety of this paper.

<table>
<thead>
<tr>
<th>Tip after loading with IL</th>
<th>Tip Region</th>
<th>Tip measurement [\mu m]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>R\textsubscript{c}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d</td>
</tr>
</tbody>
</table>

Table A.4: Needle-like structure made from 10\%IL by weight of Nafion\textsuperscript{TM} IL-polymer solution mixture, and feature dimensions. This tip was name \textit{SquarePan}, and will be referred to as such for the entirety of this paper.

<table>
<thead>
<tr>
<th>Tip before loading with IL</th>
<th>Tip Region</th>
<th>Tip measurement [\mu m]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>R\textsubscript{c}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d</td>
</tr>
</tbody>
</table>
Table A.5: Needle-like structure made from 10%IL by weight of Nafion™ IL-polymer solution mixture, soaked in IL 80°C for about 3 days, and feature dimensions. This tip was name SquarePan, and will be referred to as such for the entirety of this paper.

<table>
<thead>
<tr>
<th>Nafion™ Tip after loading with IL</th>
<th>Tip Region</th>
<th>Tip measurement [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R_c</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>322</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>701</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>239</td>
</tr>
</tbody>
</table>

Table A.6: Needle-like structure made from 20%IL by weight of Nafion™ IL-polymer solution mixture, and feature dimensions. This tip was name SunnySide, and will be referred to as such for the entirety of this paper.

<table>
<thead>
<tr>
<th>Nafion™ Tip before loading with IL</th>
<th>Tip Region</th>
<th>Tip measurement [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R_c</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>389</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>321</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>387</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>459</td>
</tr>
</tbody>
</table>
Table A.7: Needle-like structure made from 20%IL by weight of Nafion™ IL-polymer solution mixture, soaked in IL 80°C for about 3 days, and feature dimensions. This tip was named SunnySide, and will be referred to as such for the entirety of this paper.

<table>
<thead>
<tr>
<th>Nafion™ Tip after loading with IL</th>
<th>Tip Region</th>
<th>Tip measurement [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R&lt;sub&gt;c&lt;/sub&gt;</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>401</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>337</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>384</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>475</td>
</tr>
</tbody>
</table>
Bibliography


98


[53] C Feng and PF He. “Moisture and thermal expansion properties and mechanism of interaction between ions of a Nafion-based membrane electrode assembly”. In: RSC advances 7.55 (2017), pp. 34556–34566.


