Porous Material and Process Development for Electrospray Propulsion Applications

by

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Abstract

Ion electrospray propulsion devices rely on the transportation of ionic liquid propellant to emission regions where ions are extracted at high velocities. One such method involves the use of porous substrates to passively transport propellant towards conically shaped features of the same porous material. Historically, the methods of fabricating such small features (~150μm tapered to ~20μm over a height of ~150μm) are subtractive, in that material is selectively removed from a substrate to reveal the desired features. The limitations of these processes include but are not limited to: process repeatability, complex operation, material selection limited by the process, serial operation, and long/expensive fabrication time. With an understanding of these limitations, the goal of this research is to explore new materials and processes to identify candidates for electrospray propulsion applications. In particular, processes that allow for additive tip manufacturing, parallel processing, and uniformity in addition to materials that allow for variable and uniform porosity have been studied. As part of this research, the sol-gel and freeze casting methods for producing porous materials were characterized to better identify feasibility for electrospray propulsion. Characterization includes the feasibility of molding porous tips directly onto substrates. As a result of this research, porous substrates from different materials and varying pore sizes were fabricated via both methods. A porous emitter tip prepared by the sol-gel method was fired and shown to extract current at levels exceeding the state of the art. Finally, a new process, entitled sol freeze, was invented that utilizes the benefits of both the sol-gel and freeze casting methods.

Additionally, porous material research for the purpose of contact electrodes was investigated. In order to lengthen the electrochemical window during electrospray thruster firing, a desire for conductive porous materials with large internal surface area was discovered. Carbon xerogel electrodes with embedded wires were designed and fabricated through this research. Specifically, carbon xerogel electrodes with internal surface areas on the order of 500 m²/g were fabricated and tested.
Thesis Supervisor: Paulo C. Lozano
Title: Associate Professor of Aeronautics and Astronautics
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Chapter 1

Introduction

Spacecraft mission requirements often dictate the need for an in space propulsion system. Propulsion systems provide translational and rotational capability to spacecraft which varies markedly from mission to mission; therefore, so do in-space propulsion systems. For such propulsion systems, there are two distinct categories which these systems are grouped: chemical and electric propulsion.

The most succinct comparison of chemical to electric propulsion systems is with performance. Because of the operating physics, chemical propulsion systems offer much higher thrust than electric propulsion systems. On the contrary, electric propulsion systems offers much higher specific impulse than their chemical counterparts. Specific impulse is a performance parameter that serves to represent the ability of a propulsion system to use a unit of mass of propellant. Because of the commonality of its use, it is useful to define specific impulse mathematically as follows:

\[ I_{sp} = \frac{F}{\dot{m}g_0} \]

where \( g_0 \) is the gravitational acceleration of earth (9.81 m/s\(^2\)), \( \dot{m} \) is the propellant mass flow rate, and \( F \) is the thrust force.

In essence, specific impulse is an efficiency that is linked linearly with the velocity of particles exiting a propulsion system. A higher specific impulse implies a greater momentum exchange per particle. Certain spacecraft requirements will call for one
system over the other, based on their respective capabilities.

1.1 Spacecraft propulsion state of the art

Chemical propulsion systems rely on the stored energy in chemical bonds to produce thrust, usually through combustion. Chemical systems include cold gas, monopropellant, bi-propellant, and solid propulsion. Cold gas propulsion is the simplest type that relies on the release of high pressure gas to produce thrust. In general, cold gas systems are robust, but offer relatively low thrust and specific impulse, usually in the 50 to 100 second range. Monopropellant thrusters rely on the decomposition of hypergolic propellants via a catalyst. This decomposition heats up the propellant and breaks it apart into smaller species which are then expanded through a nozzle. Monopropellant systems offer higher thrust, up to 500 N, and relatively good specific impulse, up to 250 seconds. Bipropellant thrusters involve the combustion of a fuel with an oxidizer. Such systems offer high thrust and the highest specific impulse of all chemical systems (nuclear systems excluded), thrust up to MN with specific impulse well over 300 seconds. However, bipropellant systems are very complex, often requiring pressurization systems and plumbing. Finally, solid propulsion systems operate by the combustion of solid fuel and solid oxidizer. Solid engines can be scaled up to thrust levels adequate for launch (MN) with specific impulses approaching 300 seconds.

In general, electric propulsion (EP) systems operate on the principal of electrostatically accelerating charged particles. There exists electric propulsion systems that rely on magnetic pressures to produce thrust, but these are less common and function more as experimental research devices. Traditional electric propulsion devices are comprised of mechanisms that serve to complete two distinct processes: the production of charged particles and the the acceleration of such particles. The two most common EP systems are ion engines and Hall thrusters. Ion engines have a dedicated ionization volume which serves to ionize neutral propellant into ions which are then accelerated through grids that are biased to a highly negative electric potential rela-
tive to the plasma potential. Ion engines are very complex systems, but offer a very high specific impulse, upwards of 4000 seconds, and thrust levels up to a few newtons. Another common type of EP system is a Hall thruster which operates by trapping electrons magnetically. These electrons collide with neutrals to produce the ions that are then accelerated electrostatically by a negative electric potential. Hall thrusters have higher thrust densities (thrust per thruster area) than ion engines, but operate with a lower specific impulse, upwards of 2000 seconds.

There are many types of less common EP devices such as arcjets, pulsed plasma thrusters (PPT), magnetoplasmadynamic (MPD) thrusters, field-emission electric propulsion (FEEP), and electrospray propulsion. The focus of the research presented in this thesis is on electrospray propulsion—a new field of propulsion with great promise.

1.2 Electrospray propulsion fundamentals

Electrospray propulsion devices require three fundamental components: a conductive liquid propellant, a method to transport such liquid, and an electric field. The conductive liquid is electrostatically stressed by a strong electric field, usually created by applying a large electric potential. If stressed enough, the liquid surface begins to perturb and thus strengthen the electric field at the surface. A sufficiently strong electric field could result in the emission of droplets or ions from the liquid surface. If, in addition, there exists some mechanism to transport this liquid, a steady state condition can be achieved where useful thrust is obtained by the emission of either droplets or ions at a steady rate, and thus a micropulsion system is created. An illustration of the mechanisms involved in electrospraying is illustrated in Figure 1-1 where a porous media is served to passively transport propellant.

Ionic liquids are commonly used as electrospray propellants as they offer many significant benefits over other options as investigated by Lozano[20]. Such benefits include low surface tension, high conductivity, and negligible vapor pressure. In particular, a negligible vapor pressure drastically simplifies propellant storage as it
Figure 1-1: Illustration of the fundamental properties required to electrospray a conductive propellant. The mechanism for liquid transport is a porous substrate.

alleviates the need for hermetically sealed tanks and plumbing. As previously mentioned, typical electric propulsion devices must ionize and then accelerate ions. The process of ionization requires much power. The use of ionic liquids eliminate the need for energy required for ionization. In essence, the ionization energy is spent in the laboratory during the synthesis of the ionic liquids.

As one could imagine, the thrust achievable from each micro tip (as illustrated in Figure 1-1) is not much. As a result, in order to obtain a non-trivial thrust force, an electrospray engine is comprised of hundreds of such tips, closely packed together in a 2-D array. Figure 1-2 is a scanning electron microscope (SEM) picture of such an array of tips. This array is simply a scaled up version of the tips shown in Figure 1-1.
1.3 Two distinct regimes: droplet and ion

As propellant (ionic liquid) is electrostatically stressed enough at tip regions, mass extraction occurs in one of two ways. Either large liquid droplets are extracted, individual ions, or a mixture of both. The pure droplet and ion regime are very efficient (theoretical limit nearing 100%) whereas everything else in between is less so. In general, the droplet regime involves higher flow rates while the ion regime requires low flow rates. As a result, and as one could imagine by comparing droplets and ions, the droplet regime has a higher thrust than the ion regime, but the ion regime has a higher specific impulse. Electrospray propulsion systems operating in the droplet regime normally have specific impulses around 300 seconds at 2kV whereas ion regime electrospray propulsion devices can operate with a specific impulse upwards of 4000 seconds at 2kV.

Both modes can have a niche for in-space propulsion, but it is the ion regime mode that has more practical implications. In particular, since the ion regime mode operates with very low flow rates, passive propellant transport is quite possible. The immediate benefit is a lack of plumbing and pressurization systems, but the benefits go far beyond that. Each ion regime engine can have a dedicated pumping system (i.e

Figure 1-2: Electron microscope picture of an array of hundreds of porous nickel tips.
capillaries or porous material), and therefore, scaling is a simpler feat. Additionally, neglecting any engineering difficulties that may arise, the ion regime mode can be made denser, in that more thrust per unit area can be achieved [21]. In all, the future is more promising for the ion regime mode in electrospray propulsion, and thus the research presented in this thesis will be focused on that regime.

### 1.4 Electrospray propulsion state of the art

The development of electrospray propulsion devices is still in its infancy, but the technology is incredibly promising. The implications of the technology can most clearly be theorized with the work done by Courtney [9]. Typical electrospray propulsion system characteristics for the current state of the art are reported in Table 1.1. The low thrust levels inherent with the technology foretell a few applications: such systems could provide ultra-precise attitude control capability for small and large spacecraft, a few engines could provide in-space translational capability for nanosatellites, and several hundred engines could provide in-space translational capability for large satellites.

A photograph of an electrospray engine is given in Figure 1-3. The small volume and mass of these engines are conducive to the aggregation of tens to hundreds. Perhaps the most obvious technological benefit with electrospray propulsion technology is the adaptability to many spacecraft missions.

<table>
<thead>
<tr>
<th>Metric</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine Mass</td>
<td>0.75g</td>
</tr>
<tr>
<td>Engine Dimensions</td>
<td>10mm × 10mm × 2.5mm</td>
</tr>
<tr>
<td>Specific Impulse</td>
<td>2000s</td>
</tr>
<tr>
<td>Thrust</td>
<td>30μN</td>
</tr>
<tr>
<td>Nominal Power</td>
<td>0.6W</td>
</tr>
</tbody>
</table>
1.5 The case for electrospray propulsion

As was hinted to earlier, electrospray propulsion devices inherently require less power for a given thrust level as compared to other electric propulsion systems. Power constraints on spacecraft are stringent so mitigating power use for a given amount of thrust would be a game changer. A comparison of the predicted electrospray propulsion performance to the state of the art ion engine and some commercially available Hall thrusters is given by Figure 1-4. In the figure, it is clear that over the entire spectrum of specific impulses, electrospray propulsion has a higher thrust to power than the flagship ion engine and Hall thrusters. In particular, the benefits of electrospray propulsion over traditional electric propulsion are more evident at the low end of the specific impulse spectrum where many spacecraft missions fall.

Currently, the state of the art in electrospray propulsion engines have thrust densities on the same order as (as can be extrapolated with data from Table 1.1) ion engines, but less than Hall thrusters. Therefore, scaling such engines could replicate the same total thrust as ion engines. At the same thrust levels, electrospray engines would consume considerably less power than ion engines, see Figure 1-4. Future development could lead to thrust densities that rival Hall thrusters and thus create an
Figure 1-4: Thrust to power of various electric propulsion systems. Data for ion engine and hall thrusters is from real engines [23, 21, 7].

identical situation: electrospray engines outperforming the state of the art in electric propulsion[21].

1.6 Research focus

The focus of the research presented in this thesis is on the method of liquid transport. In particular, porous materials that can be used for ionic liquid transport have been investigated. In doing so, porous material processes were discovered to be equally important to the material itself. As shown in Figure 1-1, the porous material is used for both propellant transport and for directing the propellant to regions where the electric field is high (at the tip features); it is a critical aspect of the propulsion system. Additionally, the process in which the porous material is fabricated is also of utmost importance. A process which allows for the fabrication of micro-tips is necessary.

First, it is important to put the research into perspective by discussing past efforts in the topic of liquid transport for electrospray propulsion. In doing so, it should become clear as to why new investigations are necessary, and also allow one to define a set of desirable attributes in both the material and process. This will be discussed
in the section that follows.
Chapter 2

Substrate Technologies

Propellant transport is one major facet of an electrospray propulsion device. There are two distinct modes of transportation: the first is active transport by means of a pump or pressurization system, and the second is passive transport by means of capillary action. The focus of this research is on passive transport, as it is the most attractive means for the ion regime. Additionally, liquid transport as applied to arrays of tips is of particular interest as electrospray propulsion only begins to have in-space propulsion benefits when multiple tips are firing in parallel.

2.1 Externally-wetted silicon arrays

Much of the initial research in the development of electrospray emitter arrays involved externally wetted systems. Externally wetted electrospray devices rely on surface transport of liquid to emission regions, see Figure 2-2a. In particular, such systems were investigated extensively by researchers at MIT including Garza, Gassend, and Velasquez-Garcia [12, 14, 13, 34]. The fundamental operation of externally wetted systems is nearly identical to that illustrated by Figure 1-1. The main difference is that all of the liquid propellant transport is on the surface of the material and not through a bulk porous material.

The surface wetting characteristics of such a device were investigated in depth by Garza [12]. Specifically, Garza explored how thruster performance is affected by
the surface wetting characteristics. In particular, the effects of a black silicon coating were researched. Black silicon is the term given to the surface roughening of silicon by some method (laser etching, gold etching, plasma etching) to change the surface properties. In the case of externally wetted electrospray thrusters, a black silicon surface treatment increases the wettability of the material. Figure 2-1 is an electron microscope photograph of such a treatment.

![Figure 2-1: Electron microscope picture of black silicone treatment](image)

Both Velasquez-Garcia and Gassend designed, built, and tested electrospray thruster arrays that operated via externally wetting emitter tips with a black silicon surface treatment. Velasquez-Garcia focused on determining the affects of emitter geometry on emission characteristics, and in doing so built an externally wetted engine operating in the ion regime. The engine is comprised of an array of protruding tips of varying geometry with the ionic liquid EMI-BF4 as the propellant. A thrust on the order of $1 \mu N$ was measured indirectly from an engine comprised of a pencil array of 32 by 32 emitter tips operating at 1500 volts. The most impactful conclusions from this work was demonstrating the feasibility of clustering tips.

Gassend was able to build an electrospray array that operated in the ion regime, see Figure 2.1 for a summary of the engine characteristics. The device was comprised of 502 emitter tips with a black silicon coating and was tested with both EMI-BF4 and EMI-IM as ionic liquid propellants. Figure 2-2 has photographs of the emitter tips and coating. The thruster assembly was manufactured via microelectromechanical
Table 2.1: Externally wetted silicon array (502 emitters) characteristics[14]

<table>
<thead>
<tr>
<th>Metric</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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<td>Engine Mass</td>
<td>5g</td>
</tr>
<tr>
<td>Activation Voltage</td>
<td>500V</td>
</tr>
<tr>
<td>Specific Impulse</td>
<td><a href="mailto:3000s@1.5kV">3000s@1.5kV</a></td>
</tr>
<tr>
<td>Single Tip Current</td>
<td><a href="mailto:370nA@1.5kV">370nA@1.5kV</a></td>
</tr>
<tr>
<td>Single Tip Thrust</td>
<td><a href="mailto:26nN@1.5kV">26nN@1.5kV</a></td>
</tr>
<tr>
<td>Total Thrust</td>
<td>13μ<a href="mailto:N@1.5kV">N@1.5kV</a></td>
</tr>
<tr>
<td>Power</td>
<td><a href="mailto:0.275W@1.5kV">0.275W@1.5kV</a></td>
</tr>
</tbody>
</table>

systems (MEMs) processing. Deep Reactive Ion Etching (DRIE) and wafer bonding processes were used in the fabrication of the engine.

The work on externally wetted systems revealed significant limitations. It was found that there was often times an inconsistent operation (and therefore variation in performance) due to non-uniform wetting characteristics. Additionally, there was the occasional unwanted electron emission from the silicon surface which should be expected when using sharp metallic materials in large electric fields. Finally, as one could imagine, the problem of long term liquid transport could lead to a cause of concern. Gassend, in particular, commented on the need for a method to transport liquid to the emission regions. The reservoir of propellant at the base of the tips was enough for a few minutes of firing only.

The efforts made in the fabrication of externally wetted silicon electrospray thrusters were successful in many ways. Most importantly, the research illuminated the feasibility of emitter tip arrays operating in the ion regime. Additionally, such work revealed the inherent limitations with an externally wetted liquid transport system.

### 2.2 Electrochemical etching of porous tungsten

In an effort to address the issues of non-uniform wettability and long-term liquid transport, porous emitter tips were investigated. Work done by Legge was some of the first to experiment with the etching of a porous substrate to form emitter
Figure 2-2: Depiction of externally wetted electrospray mechanism (a), electron microscope photograph of externally wetted silicon tip array (b), electron microscope photograph of single externally wetted silicon tip (c), and electron microscope photograph of black silicone coating (d). [13]

tips [18]. Legge investigated the use of porous tungsten because of the prior success of externally wetted non-porous tungsten experiments carried out by Lozano [20]. Additionally, tungsten is widely known for its strength and chemical inertness. A picture of the porous tungsten microstructure is given in Figure 2-3.

The average particle size, and therefore pore size, for the porous tungsten can be estimated at around 0.5-2 μm with a total porosity of about 30%. The porous substrates were procured from a vendor who manufactured the material via a sintering process. Emitter tips were etched into the substrate by a process developed by Legge as illustrated in Figure 2-4. The pores of the substrates were first infiltrated with polyimide and then the substrate was masked with photoresist for the correct tip geometry. Finally, the substrate was etched in a NaOH solution to reveal the tips.
The remaining polyimide in the pores was removed in a piranha solution. A picture of the final tip arrays is given in Figure 2-5. It should be noted that these arrays are 1D arrays whereas the externally wetted silicon and all of the future arrays to be discussed are 2D arrays.

![Figure 2-4: Electrochemical etching of porous tungsten process](image)

The porous tungsten electrospray engines developed by Legge were able to produce on the order of 2µN of thrust at 1500 V, and time of flight spectroscopy showed the presence of nearly pure ion emission. The thrust per emitter tip (assuming uniform thrust per emitter) was approximately 40 nN which is quite comparable to the
performance of externally wetted silicon thrusters.

Legge observed with the operation of a porous tungsten thruster with emitters much like those shown in Figure 2-5 that producing uniform emitters was still a challenge. Since the shape of the emitter greatly affects emission characteristics, geometric non-uniformities in turn create performance non-uniformities. These non-uniformities, according to Legge, can be attributed to masking issues which was especially apparant at higher emitter densities. Additionally, material selectivity is hard to come by when working with tungsten. The chemistry required to etch tungsten (NaOH) severely limits the selection of photo definable masks [35].

The research by Legge proved the feasibility of ion emission from dense porous emitter tips, and also showed that uniformity is key. As a result, the limitations inherent with tungsten limit the material's applicability to porous electrospray propulsion devices.

2.3 Electrochemical etching of porous nickel

Work on porous substrates used as electrospray propulsion devices was continued by Courtney [9]. Based on the lessons learned from previous materials, Courtney decided to progress with a similar etching procedure as the one developed by Legge on porous nickel rather than tungsten. According to Courtney, nickel has good compatibility with electrochemical etching processes. Specifically, the process was developed by Courtney to yield surface micromachining without significant pore degradation.
Commercially available porous nickel was used that had a 45% total porosity with a pore size on the order of a few microns with some pores as large as 5 \( \mu m \), see Figure 2-6.

![Figure 2-6: Porous nickel microstructure [9]](image)

The electrochemical etching process used for producing tips in porous nickel was done in a more integrated manner when compared to Legge's work. Nickel substrates were first placed in silicon micromachined frames and then processed to be etched. Figure 2-7 illustrates the entire process. The resulting engine is comprised of nearly 500 emitter tips, see Figure 2-8, aligned with a silicon extractor grid.

The resulting porous nickel electrospray engine had a predicted thrust of approximately 40\( \mu N \) and a specific impulse around 2000 seconds. Courtney's work described here set the benchmark for an integrated electrospray engine. Electrospray engines fabricated by electrochemically etching porous nickel worked well, but there still existed limitations. Firstly, even though the etching process worked, it was cumbersome. With an eventual desire to mass produce these engines, this etching process is a bottleneck in the process. Secondly, the etching process left non-uniformities between emitter tips on a single thruster and between thrusters. As was hinted to earlier, variations in geometry result in performance variations. The process leaves more to be desired. Lastly, Courtney observed tip degradation that could not be totally explained at the time (refer to Section 2.4).
2.3.1 Material Permeability

In characterizing and designing for a porous material purposed to transport liquid, pore size and total porosity fall short. Pore size and total porosity help in giving a rough fluid flow comparison. In general, larger pores and higher total porosity will result in a greater volumetric flow rate. Henry Darcy, in 1856, was able to experimentally characterize the volumetric flow rate through a porous sand bed and resolved what is now known as Darcy’s Law, given by equation 2.1:

\[ Q = -\frac{kA\Delta P}{\mu L} \]  \hspace{1cm} (2.1)

where \( Q \) is the volumetric flow rate, \( k \) is the permeability constant of the material, \( A \) is the cross-sectional area, \( \Delta P \) is the pressure drop, \( \mu \) is the viscosity, and \( L \) is the thickness of the porous substrate. For a porous material, a good approximation for the pressure drop is the capillary pressure which is a function of surface tension, \( \gamma \), and the average pore radius, \( r \) as in equation 2.2.
When more fidelity is required and when various materials are being compared, permeability is a more useful specification than pore size or total porosity. Unfortunately, characterizing permeability becomes quite difficult and often times requires numerical modeling. One such model, a model that Courtney relied on in his work, is the Carman-Kozeny (CK) equation. The CK equation serves to predict the permeability constant of a certain material given available material properties and is given by equation 2.3:

$$k = \frac{cd^2\phi^3}{(1 - \phi)^2}$$

(2.3)

where $c$ is the packing constant (captures how the particles in a porous substrate are arranged, taken as 5 for random packing), $d$ is the median grain/pore size, and $\phi$ is the total porosity fraction.

Considering that other models predict vastly different permeability constants, the CK equation should be validated for the range of materials in use. This was accom-
plished by devising an experiment that could measure the permeability constant of the porous nickel used by Courtney. If the experimentally predicted permeability constant is roughly the same as that predicted by the CK equation, then the CK equation would be considered a reliable source in determining permeability constants of various materials in the electrospray propulsion realm.

2.3.1.1 Permeability measurement device

A permeability measurement device was designed and built in order to characterize the permeability constant of porous nickel. The experiment was designed to be simple and robust. A crosssection of the device is given in Figure 2-9.

![Diagram of permeability measurement device]

Figure 2-9: Illustration of permeability measurement device.

The operating principles of the device are quite simple. Water is backfilled into the void shown in Figure 2-9 where it is fed by gravity. The flow of water is choked by the presence of the porous material of which the permeability constant is desired. The entire mechanism is suspended above a sensitive mass balance, and as water slowly flows through the porous substrate, it eventually drips onto the mass balance.
where the water droplet mass is recorded. The result is the recording of a mass flow rate of water through the porous material.

### 2.3.1.2 Permeability validation

With some simple manipulation (combining equations 2.1 and 2.3), the relation between the permeability constant and mass flow rate through a porous material (with known substrate dimensions) is given by the following equation:

\[
k = \frac{\dot{m}u\gamma}{A\rho g z}
\]

where \(\mu\) is the viscosity of water, \(t\) is the substrate thickness, \(A\) is the cross-sectional area of the substrate, \(\rho\) is the density of water, \(g\) is gravity, and \(z\) is the initial height of water in the chamber.

The experiment has a measured repeatability within 1% over several runs. One such result is given in Figure 2-10. Once the system reaches a steady state (porous substrate fully saturated) a constant mass flow rate was recorded. As shown in Figure 2-10, the mass flow rate was measured to be approximately \(1 \times 10^{-4} g/s\). With equation 2.4 the resulting permeability constant is experimentally determined to be about \(2.5 \times 10^{-12} m^2\). Courtney expected a permeability in the range of \(0.5 - 1.5 \times 10^{-12} m^2\) as predicted by the CK equation (equation 2.3).

Clearly, the CK model does a sufficiently good job in predicting the permeabilities of porous substrates in the realm of this application. As a result, future porous material investigations will leverage the CK equation to determine a certain porous materials permeability. Courtney was only able to experimentally verify pure ion emission with externally wetted nickel, with time-of-flight spectroscopy, but no such test was carried out with porous nickel. Therefore, no conclusions can be made about material permeabilities that exclusively operate in the ion regime based on the porous nickel work. However, Legge was able to perform time-of-flight spectroscopy on porous tungsten [18]. Using the porous tungsten material characteristics, and the now proven CK model, the porous tungsten has a permeability constant of about
Figure 2-10: Mass flow rate of water through porous nickel substrate and appropriate curve fit to determine permeability constant. 3D rendering of setup on right.

$3 \times 10^{-13} m^2$, a value that is nearly an order of magnitude lower than porous nickel.

In order to ensure pure ion regime emission, it is best to stick with materials with roughly the same (if not lower) permeabilities than that of porous tungsten. Porous nickel might indeed operate in the pure ion regime, but there exists no experimental evidence to corroborate this.

### 2.4 The move towards non-conductive porous substrates

All of the previously described electrospray devices were fabricated with conductive porous materials. Courtney even went through the effort of making conductive porous emitters a driving requirement for his electrospray emitter tips [9]. The primary reason for having a conductive emitter is so that the emitters double as an electrical contact electrode (where the high voltage is applied). The move towards non-conductive porous electrospray emitters only occurred after revelations made by
Brikner and Lozano [5].

Brikner and Lozano discovered that during ion emission from conductive emitter tips (externally wetted tungsten), there exists a possibility for electrochemistry to occur at the tips. This electrochemistry consequently etches away the tip material. This phenomenon has clear detrimental effects. Once the tip begins to be etched, the geometry changes and the electric field decreases. Etching can continue until the electric field gets too low and thus suppresses any further emission. Moreover, electrochemistry can result in propellant degradation. Ultimately, conductive porous emitters have a limited lifetime when they are used as the contact electrode and no voltage alternation is used.

The proposed solution to this problem was to introduce what is known as a distal electrode, see Figure 2-11 for an illustration. The distal electrode is a conductive porous material separate from the emitter tips. This distal electrode serves to divert the locations where electrochemistry may occur away from the emitter tips. As a result, the requirement of having conductive porous emitter tips relaxes to allow for dielectrics. In fact, dielectrics are more desirable as they ensure that no electrochemistry will occur at the emission sites. Additionally, dielectrics offer properties that many conductive materials cannot: overall chemical inertness, temperature robustness, and selectivity for certain fabrication processes. Work on the fabrication of distal electrodes will also be presented in this thesis (Section 4).

2.5 Laser ablation of porous glass

The most recent work on electrospay propulsion engines is with the use of porous borosilicate glass as emitter tip material. Like past porous substrates, the material is purchased commercially. The porous substrates have particle sizes on the order of $2 - 5\mu m$ and a total porosity of about 40%. Rather than an electrochemical etching process, the emitter tips are laser milled. Much of the original work was carried out by Coffman et al. [8]. Laser milling involves removing material selectively by laser ablation. One such laser milled emitter tip is shown in Figure 2-12.
The borosilicate glass thrusters have similar performance as compared to the nickel thrusters. A typical thruster package produces about $20 \mu N$ of thrust at $1200$ V. The laser milling process works remarkably well with even better uniformity when compared to the nickel process, but there are still limitations. The fabrication process is serial, in that only one thruster can be milled at a time, and the operation times are usually quite long (have been decreased more recently). The laser milling process is simply not optimal for batch processing. This porous glass is procured commercially and is of some of the best quality one can find, but it still does not offer the ideal porosity and pore size for electrospray propulsion: a higher total porosity and smaller pore size is desired.

### 2.6 Additive vs subtractive processes

The progression of the porous emitter electrospray propulsion design has come a long way. The changes that were made were done so to improve upon the thruster performance and reliability. There is still much work to do on that front. Perhaps a
more pressing issue, is the ability to fabricate large amounts of thrusters repeatably. In order to obtain reliable performance data, a large data set of thrusters is needed. Thinking further ahead, spacecraft missions could require dozens or hundreds of electrospray engines on a single spacecraft to satisfy mission requirements. The current subtractive fabrication processes do not allow for the mass production of porous emitter arrays and therefore electrospray engines. Additive fabrication processes, on the other hand, could satisfy the need for mass production. To differentiate between the two processing types, subtractive processes include all processes such that material is removed, and an additive process is one where material is either added or built with the bulk material. An illustration of how an additive manufacturing process can increase production by an order of magnitude is given in Figure 2-13.

Prior investigations and experiences have identified the following desirable process and material characteristics for electrospray propulsion, but are not limited:

**Material:**

1. Variable porosity

2. Uniform porosity
Current substrate techniques are a bottleneck in the process!

Increase throughput by an order of magnitude

Figure 2-13: Processing comparison between additive and subtractive techniques.

3. Dielectric with robust physical characteristics

4. Wettability and chemical compatibility with ionic liquid propellants

Process:

1. Parallel processing

2. Uniformity

3. Consideration for additive emitter tip fabrication

4. Consideration for monolithic thruster integration

The additive manufacturing technique that will be explored in this thesis is molding. Developing the ability to fabricate emitter tips on a porous substrate in one step could be a game changer. Additive manufacturing processes could have benefits beyond increased production, many of which will be discussed in Chapter ??.
uniformity. The goal of the research presented in this thesis is to explore materials and processes to identify candidates for electrospray propulsion applications.
Chapter 3

Additive manufacturing processes for porous materials

3.1 Potential methods for porous emitter fabrication

Several methods exist for the fabrication of porous materials: both subtractively and additively. Courtney highlights many of these techniques in depth in his thesis [9]. His conclusions led him to an electrochemical etching process primarily because of its heritage in electrospray propulsion. As was explained in the previous section, all subtractive processes fail to satisfy the requirement of suitability for the eventual goal of a batch monolithic manufacturing process. As a result, only additive techniques were considered for this research. In particular, a chemical sol-gel process, a freeze casting process, and a newly invented sol freeze process were considered for the fabrication of porous emitters.

3.2 Sol-gel

The first process that was explored is a chemical sol-gel process. The term sol-gel is used to describe the process itself and not a particular material. It proves useful
to make this clear, as the term sol-gel is often times used interchangeably as both
a process and a material. For example, sol-gel methods are almost exclusively used
in the fabrication of aerogels; the material name is aerogel, and the process used to
create the material is a sol-gel process. In this thesis, the term sol-gel will refer to a
process used in the fabrication of porous materials.

Sol-gel processes are quite promising as there has been significant work with many
different variants over decades. Additionally, sol-gel work spans many academic fields
as the benefits of the processes extend from biology to aerospace engineering. The use
of such a process in the fabrication of porous electrospray emitters does not require
any new science, but rather a tweaking of existing science.

3.2.1 Sol-gel theory

A sol-gel process is a chemical process that involves a mixture of nanoparticles that
form a colloid, or a suspension such that the particles are so small that short range
forces overcome gravitational forces. These nanoparticles experience Brownian mo-
tion, or random walk, and do so indefinetely. Occasionally, these nanoparticles collide
with one another, but the effect is negligible. However, if there is a mechanism for
attachment between particles interesting things can begin to happen. In this case,
when particles collide and attach, they slowly grow in size with time. Eventually, this
crosslinking allows for the formation of macro structures and ultimately a gel. A gel
is comprised of a scaffold of solid material formed by the crosslinking of nanoparticles
and the remainder solution. The immediate goal is then to remove the liquid solution
in order to preserve the structure formed via the crosslinking of nanoparticles to form
a useful engineering material. An illustration of the process is given in Figure 3-1.

The mechanism during which particles collide and link together is known as gela-
tion. During gelation, the particles completely link together across the vessel that is
containing it thus forming a gel that appears as a solid. However, a gel still consists
of both solid and liquid; a gel is a two phase material. Gelation times vary markedly
amongst types of processes and materials. In general, the time of gelation refers to the
amount of time that the last link forms that connects spanning structures (creating
one structure that spans the container). Therefore, more crosslinking occurs after the gelation time.

After the onset of gelation, it is usually advantageous to allow the gel to age or cure. This aging process allows for more crosslinking to occur and thus increases the complexity of the network of particles. There are still many more chemical reactions that occur after the time for gelation, and the aging process refers to the period of time given for this. Aging increases the strength and stiffness of the particle linked network, but the network may also exhibit shrinkage during this time.

The next step is the removal of liquid from the gel after aging, a process known as drying. During this process, the body will shrink by an amount equal in volume to the liquid that evaporates from the pores. Therefore, a means to replace this liquid before it evaporates is sometimes employed such that this shrinkage is mitigated (supercritical drying). There are many influences that effect stresses during drying. Drying is a very sensitive part of the process as discovered in the research to be presented. The varying outcomes of drying are illustrated in Figure 3-1.

The final step in a sol-gel process is a sintering step. The sintering step is optional and is only used to strengthen the interconnected particles further. Sintering was not
investigated in this research.

3.2.2 Possible candidates

The sol-gel techniques under investigation as possible candidates for electrospray propulsion emitter tips were those that allowed for the production of dielectric materials with uniform porosity and pore size in the same range as previous research (i.e. porous nickel). Additionally, the more facile sol-gel processes were favored.

Variants on sol-gel processes allow for the creation of most types of porous metal oxides (i.e. silicon oxide, aluminum oxide). Such processes involve the mixing of the requisite amount of solvent, acidic metal salt, and a polymer in a solution. Once a catalyst is added, gelation will initiate. However, before gelation, the solution can be poured into molds so that the eventual gel can assume some desired shape. This specific type of process is illustrated in Figure 3-2, and the process that was heavily investigated in this research.

The purpose of the catalyst is to change the surface properties (such as removing or adding an electron) to make the like particles attach to each other. Often times, a proton scavenger is used for this purpose. Once the nanoparticles link together and form a gel everything is allowed to cure (more crosslinking occurs) under a well controlled temperature. Then, the liquid constituents are removed by either solvent drying or evaporation and what is left is known as a green body (pre sintering). Depending on the application, the green body could be the final product; an optional heat treatment, or sintering, is the final step if a stronger material is desired.

Even within this realm of metal oxide sol-gel processes, the list goes on and on. In particular though, Tokudome and others [33] showed the ability to vary pore size with a slight recipe change in a custom aluminum oxide (alumina) xerogel process. Such a process, according to the authors, was deemed more facile than traditional methods yet resolved equally promising results as other methods in the literature [28, 11, 2]. Additionally, the variations in pore size allows for a tweaking of the permeability of the material. For example, if it is seen that a certain ionic liquid propellant tends to emit charged droplets along with ions, it would be advantageous to decrease the
pore size to cease droplet emission. This process allows for that capability. For these reasons, it was the first method investigated within the body of research presented in this thesis.

### 3.2.3 Experimental process

The alumina sol-gel process outlined by Tokudome was reproduced in this research to first see if porosity can indeed be varied, and to obtain a grasp of the complexity and subtleties in the process. The constituent ingredients, and their respective proportions as given by Tokudome is reported in Table 3.1. It should be noted that the recipe outlined in Table 3.1 is exact as that prescribed by Tokudome. Any change in the recipe will be discussed in detail in 3.2.4.
Table 3.1: Alumina xerogel constituents as prescribed by Tokudome [33]

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Appearance</th>
<th>Vendor</th>
<th>Mass Fraction (Mole Fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water $(H_2O)$</td>
<td>clear liquid</td>
<td>Ricca Chemical Co.</td>
<td>25.2% (57.1%)</td>
</tr>
<tr>
<td>Ethanol (ethyl alcohol) $(C_2H_6O)$</td>
<td>clear liquid</td>
<td>Pharmco-AAPER</td>
<td>27.4% (24.4%)</td>
</tr>
<tr>
<td>Poly(ethylene oxide), PEO $(C_{2n}H_{4n+2}O_{n+1})$ with average $M_w$: 1,000,000</td>
<td>white powder</td>
<td>Sigma-Aldrich</td>
<td>0.3-0.8% (&lt; 0.1%)</td>
</tr>
<tr>
<td>Aluminum chloride hexahydrate $(AlCl_3 \cdot 6H_2O)$</td>
<td>crystalline white solid</td>
<td>Sigma-Aldrich</td>
<td>27.2% (4.6%)</td>
</tr>
<tr>
<td>Propylene oxide $(C_3H_6O)$</td>
<td>clear volatile liquid</td>
<td>Sigma-Aldrich</td>
<td>19.6% (13.8%)</td>
</tr>
</tbody>
</table>

The synthesis first calls for the mixing of the requisite amounts of deionized water and ethanol. The next step is to slowly mix in the poly(ethylene oxide) or PEO to dissolve fully. This is a particularly tricky step, as the PEO should be added in small increments. Too much addition of PEO at one time can result in clumping in the solution. After PEO addition, the solution should still appear as a clear liquid with a slight increase of viscosity over the water/ethanol mixture alone. An option step is to chill the water/ethanol solution to as close to 0°C as possible. This will help in dissolution of PEO.

The final addition to what will be referred to as the stock solution (solution containing all required constituents except the gelation catalyst) is the aluminum chloride hexahydrate. $AlCl_3 \cdot 6H_2O$ appears as a whitish/yellow crystalline solid, and can be added all at once to the already dissolved $H_2O$/ethanol/PEO solution. The $AlCl_3 \cdot 6H_2O$ should fully dissolve after vigorous mixing until the solution appears as a clear homogenous liquid. To increase this dissolution time, the beaker containing solution should be placed in an ultrasound bath. The stock solution can be stored for months in a sealed container which was evidenced through the course of this research. A picture of the stock solution is given in Figure 3-3.
To initiate gelation, propylene oxide (PO) is added carefully in the correct amount to the stock solution. After this step, the solution is mixed vigorously for one minute. This particular sol-gel recipe gels quite quickly so the action of pouring the solution into molds should be done swiftly, and the molds should be sealed from atmosphere immediately. The gelation should be done at a controlled 40 °C in an oven.

As mentioned previously, the gelation occurs within a few minutes. The solution will change from a clear liquid to a cloudy white solid. The gel will remain in this state during aging which should also be at 40 °C for at least 12 hours, but preferably 24 hours.

After aging, the solvents still left in the gel are allowed to evaporate. Solvent evaporation is done first at room temperature for about 12 hours and then back in a 40 °C oven for another 12 hours. A clear change in appearance occurs during the drying process. The gel will shrink significantly (on the order of 50%) and turn a very sharp white color. The drying process will be explained in depth in the following section as much work was invested in avoiding breakage during drying.
3.2.4 Alumina xerogel results

In attempting to replicate the work by Tokudome, many difficulties were incurred. The first of which was unexplainable at the time and was that the amount of PO prescribed was not enough to initiate gelation. After careful experimentation, it was discovered that 40% more PO by mass was required to initiate gelation. The reason for which was most likely due to the method at which PO was being measured.

PO is shipped and stored in a sealed container at all times and should only be accessed with syringes via a permcable self-sealing membrane, called a SureSeal. In the early stages of this research, syringes were not available, so the SureSeal cap was removed permanately. Unfortunately, PO is quite volatile and tends to degrade in the presence of water (or water vapor which is heavily present in humid climates). Because of its volatility, PO is carefully massed out in a separate beaker, but by the time it reaches the solution, it has lost significant mass due to evaporation. Additionally, when PO degrades with time it becomes less potent in its ability to act as a proton scavenger or catalyst. These two reasons were presumed to be the cause of the need for more PO. Fortunately, a second bottle of PO was procured and syringes were exclusively used to retrieve and transport the compound. This solved the problem of requiring more PO than neccesary.

The second difficulty involved the effectiveness of sealing the solution pre-gelation. Sealing is crucial, as many of the constituents have no problem evaporating readily. It was discovered that excess volume in a sealed container should be avoided. An excess of volume could be enough to cause solvent separation pre gelation. When small specimens are produced, additional solvent was used to create an artificial atmosphere so as to prevent evaporation of solvent in the gel. Figure 3-4 illustrates this setup.
Effective sealing also plays in important role during the aging process. If the seal fails or has a slow leak, instead of aging, the gel will instead begin to evaporate or dry out. It will enter the drying process too soon. If this occurs, it is almost guranteed that the xerogel will break apart.

Finally, the last difficulty that was overcome dealt with breakage during drying. If not dried carefully, a specimen has a good chance of breaking apart. First after aging, the gel should be flushed with ethanol to perform a solvent exchange. This ethanol solvent exchange is done by wetting the specimen, sealing the container for several hours, removing excess liquid, and repeating the process at least one more time. The purpose of a solvent exchange is to rid the gel of impurities. After this process, the gel is gently dried by opening the container to air at room temperature for 12 hours before moving to the same 40°C oven for another 12 hours. If possible, the gel should be removed from the mold after aging to get as close to isotropic drying as possible (otherwise, the surfaces in contact with the mold will exhibit a slower drying rate when compared to the surfaces in contact with air).

3.2.4.1 Microstructure

The variations in PEO concentrations are hinted to in Table 3.1. It is these variations that markedly change the microstructure of the final alumina xerogel material. The ability to change the microstructure of a material by slightly altering one ingredient
could be incredibly useful for electrospray emitter tips. After months of working out the kinks in the recipe, the fabrication of alumina xerogels was successful. The spectrum of microstructures that was created is given in Figure 3-5. The pore size decreases with decreasing PEO concentration.

![Photograph of alumina xerogel monolith (a), electron microscope photographs of microstructure given a PEO mass fraction of 0.7% (b), 0.45% (c), and 0.35% (d).]

Figure 3-5: Photograph of alumina xerogel monolith (a), electron microscope photographs of microstructure given a PEO mass fraction of 0.7% (b), 0.45% (c), and 0.35% (d).

Changing the pore size of the alumina xerogel requires a slight change in PEO concentration. As can be seen in Figure 3-5, minute variations in the concentration result in significant microstructure differences. Another nice result, is that the pore uniformity is exemplary. Figure 3-6 serves to exaggerate this uniformity by comparing the microstructure to the currently used porous borosilicate glass. In this comparison,
the first distinct conclusion that can be made is that the porosity is much more uniform than the current technology. The size of the borosilicate glass shards seem to vary from < 1 to 10\(\mu m\), and the pore sizes themselves vary tremendously. The second conclusion is that the total porosity of the alumina xerogel is significantly greater than the borosilicate by comparing the relative darkness to lightness in each photo: dark spots are pores and light spots is the material.

![Electron microscope photographs](image-url)

Figure 3-6: Electron microscope photograph displaying pore uniformity of 0.6% PEO mass fraction recipe (a) and microstructure of porous borosilicate glass used by Coffman (b) [8].

### 3.2.4.2 Electrospray firing characteristics

In order to validate the compatibility with electrospray propulsion, the alumina xerogel was first tested to see if it was compatible with ionic liquids. In particular, wettability and long-term exposure was of interest. The alumina xerogel wets with ionic liquids (both \textit{EMI-BF}_4 and \textit{EMI-IM}) very well, in that the material readily wicks up propellant and dispersion actually occurs faster than borosilicate substrates (observed qualitatively). A quick experiment was setup to see if there is any observable degradation of the alumina xerogel after a long exposure to ionic liquid. Specifically, a sample was wetted with \textit{EMI-BF}_4 and allowed to sit for at least 2 months. There was no change in material characteristics, so the material was deemed compatible with ionic liquid.
The next step in validating a material for electrospray propulsion applications is to characterize the material’s firing characteristics. This was done by obtaining a piece of the material and sharpening one single emitter tip. A pyramid shaped emitter tip was sharpened by hand, and is depicted in Figure 3-7.

![Figure 3-7: Electron microscope photograph of sharpened alumina xerogel tip with 0.6% PEO mass fraction and its corresponding microstructure at the tip.](image)

The experimental setup for electrospray firing involves mounting the sharpened alumina tip on a stainless steel ev plate. The connection between tip and plate was made via double sided conductive tape and an auxiliary wire spot welded to the ev plate on one side and wrapped around the tip on the other. This double redundancy was done so to ensure electrical connectivity and to minimize the impedance between power supply and tip. The setup is both shown and illustrated in Figure 3-8. An extractor grid was made by mounting another ev plate with a small circular hole in the center. The tip was secured to its ev plate in such a way as to align with the center hole of the extractor grid ev plate. A wire mesh grid, serving as a secondary electron suppression grid was placed a few centimeters downstream of the extractor grid. Finally, a Faraday cup was used to measure the beam current directly. High voltage was applied to the tip ev plate and the extractor grid ev plate was grounded. Data was recorded by scanning across voltages applied to the tip and measuring current collected at the Faraday cup. The resulting raw current data is reported in
Figure 3-9 with *EMI-BF*\(_4\) as the propellant.

Figure 3-8: Experimental setup for alumina xerogel electrospray firing.

Figure 3-9: Measured current-voltage data.
It is observed from Figure 3-9 that the positive and negative emission regimes are very close to being symmetric. It should be noted that the plot is of the magnitude of current (obviously measuring negative ions would result in a negative current). It appears that there is a longer tail in the positive regime, in that more current is measured at the high end of the voltage spectrum. This is due to the differences in starting voltages: the negative regime starts a little higher than the positive. In all, the shapes of the curves look very similar, and any differences in the curve slopes are most likely due to the differences in ion mass. Start-up voltages on the order of 1500 V on either side is higher than the current state of the art (<1000 V [8]). However, this is expected, as the alignment was done by hand and alignment plays a significant role in start-up voltage. Additionally, the emitter tip was not as sharp as current state of the art (larger radius of curvature); the smaller radius of curvature of the emitter tip the lower the start-up voltage, see equation 3.3. Also, the extractor grid was much further away than current thruster packages. These differences are to be accounted for in a normalization scheme to be discussed.

It should be noted, that the current offset that can be seen in Figure 3-9 before emission occurs is due to the inherent capacitance between the Faraday cup and extractor plate. A constant current offset will occur with a steady increase in applied voltage.

Perhaps the most obvious result is that the measured current is remarkably high. In fact, the measured current for a single tip was over an order of magnitude greater than that reported by Coffman [8]. This high measured current is most likely due to the incredible pore uniformity and the wettability of the alumina xerogel with ionic liquids. Also, multiple emission points could have led to this high current. For a better one-to-one comparison with the current state of the art, the data was normalized. The normalization for measured current was accomplished quite simply by dividing all of the current values by the nominal current, see equation 3.1, for the state of the art thruster package, or 200μA [8]. This normalization scheme will allow one to easily translate the number of alumina xerogel tips that are required to match the performance of the current technology. For example, an $I^*$ value of 0.1 means that 10 alumina xerogel tips are required to match the current technology.
Voltage normalization was performed by determining a new start-up voltage based on the tip geometry for glass thrusters as described by Coffman [8]. Equation 3.3 is a theoretical prediction of the start-up voltage for given geometry and experimental setup. In the equation, a perfectly conical emitter shaped was assumed. This is obviously not true with the tip depicted in Figure 3-7, but it serves as a good approximation.

\[ I^* = \frac{I}{I_{\text{nom}}} \]  
\[ V^* = \frac{V}{V_{\text{start}}} \]  
\[ V_{\text{start}} = \sqrt{\frac{\gamma r_c}{\varepsilon_0}} \ln \left( \frac{4d}{r_c} \right) \]  

where \( \gamma \) is the surface tension of propellant (does not effect normalization), \( r_c \) is the tip radius of curvature, \( d \) is the distance between tip and extractor grid, and \( \varepsilon_0 \) is the permittivity of space.

The resultant normalized current-voltage curve is given in Figure 3-10. From the figure, it can now be seen that the start-up voltage is actually very close to current technology (i.e. almost starts at unity). The normalized start-up voltage is most likely greater than current technology because of measurement errors in the extractor to tip distance as well as a slight breakdown of equation 3.3 as the tip shape is not a perfect cone. From the normalized current, it can be concluded that on the order of 10 alumina xerogels tips performing as predicted by this data would match the performance of the glass thrusters with 480 tips. Each individual alumina tip emits nearly 50 times more current than the current glass emitters.

The repeatability of alternating polarity during firing was also investigated with this alumina tip. Voltage alternation between \( \pm 2500V \) was performed with a sawtooth waveform at a frequency of 0.5 Hz. The recorded data is given in Figure 3-11. The performance uniformity over a length of 18 seconds is quite favorable. The maximum current reached is steady over the time period. The maximum currents that were observed with this rapid alternation experiment were slightly less than the currents achieved in Figure 3-9. This is most likely due to the fast alternation, in that the
voltage starting decreasing before emission got to the levels reported in Figure 3-9.

Figure 3-10: Sol-gel tip normalized current-voltage plot with $BF_4$ as the propellant.

Figure 3-11: Rapid alternation of alumina xerogel tip firing.
The last pieces of data that were extracted from the single alumina xerogel tip firing were energy distributions. The ion energy distribution was captured by means of a retarding potential analyzer (RPA). An RPA was built, see Figure 3-12, and was integrated in between the Faraday cup and extractor ev plate. The purpose of an RPA is to selectively choose to measure current for ions of different energies. This is done by slowly ramping up voltages to repeal ions of a given energy and measuring the current of those ions that are able to overcome the retarding ion filtration grid. The resulting energy spectrum for both negative and positive ions is given by Figure 3-13.

![Retarding potential analyzer schematic.](image)

**Figure 3-12:** Retarding potential analyzer schematic.
Figure 3-13: Energy scans for negative ions (left) and positive ions (right) ±2.2kV extractor voltage.

The first thing to notice from Figure 3-13 is the symmetry around the zero voltage line. Both positive and negative ions have very similar energy distributions. In comparison to Coffman's glass firing data [8], the energy spectra are similar. If anything, the alumina xerogel tip has more high energy ions than the glass. The sharper transitions that appear in the curves separate groupings of ions with same or similar energies. The ions with lower energy are most likely solvated. It appears that the positive ions energy distribution has more higher energy ions than the negative distribution as evidenced by the last sharp transition which occurs at a higher voltage for the positive species.

3.2.4.3 Molding

After the alumina xerogel material had been validated for use as an electrospray emission source, experimentation with the molding of micro-tips directly for use as emission sources was performed. Many molding experiments using many techniques were performed over the course of many months with limited success. Some of the results of which are given in Figure 3-14. The mold materials that were explored include: polydimethylsiloxane (PDMS), paraffin wax, PTFE (teflon), glass, and aluminum. The best results were achieved using PDMS molds, but this could be due to the fact the PDMS was the material that was most experimented with as a mold.

The resounding conclusion for molding alumina xerogels is that it is difficult. Fig-
Figure 3-14a is a picture of one of the few successful mold attempts where a nice alumina column with a diameter and height of about 100μm. Figures 3-14b and 3-14c show molding attempts with deformities. It appears that the first had a surface tension bubble that formed, and the second experienced breakage after drying. Figures 3-14d and 3-14e depict mold attempts for full tip arrays. Figure 3-14d is interesting as the side of the tips show a nice uniform porosity, but the tips themselves seem to be covered with the mold material (paraffin wax). Figure 3-14e is a great illustrative summary of the molding results with PDMS: few tips stayed intact after molding and demolding.

Figure 3-14: Electron microscope photograph of successfully molded tip (a), failed molded tip due to bubble formation (b), failed molded tip due to breakage (c), attempt at tip array using paraffin wax as mold material (d), and attempt at tip array using PDMS as mold material (e).
3.2.4.4 Shrinkage and other limitations

The majority of issues with molding for the alumina sol-gel process arise from shrinkage during drying. As one could easily fathom, a structure that shrinks while still in mold is likely to break apart. Also, considering that the recipe requires sealing and placement in an oven as soon as possible, attempting to fill molds, placing molds in a sealed container, and then transferring container to oven is a precarious process.

However, during the course of this research, some improvements were made in both shrinkage and breakage that can occur over the course of the sol-gel process. In particular, the addition of the following processing steps were found to mitigate shrinkage: friendly solvent exchange post gel aging, pinhole drying, and organic additives. A solvent exchange helps to rid the gel of impurities pre-drying which can be detrimental to the structural integrity of the material. Pinhole drying is a simple solution to control drying rate. Instead of exposing the entire specimen to air, a small hole can be punctured in parafilm covering the specimen in a beaker so as to slow down the drying process. Organic additives such as glycerol can bond to the gel surface and reduce the capillary pressure when liquid in pores finds its way out of the porous structure. The one caveat to the use of organic additives is that their use requires an additional removal step such as a high temperature burn-off.

The benefit of the implementation of additional drying steps to mitigate breakage and shrinkage can be seen in Figure 3-15. Capillaries with diameters of less than 50\(\mu m\) were filled with alumina xerogel and dried with and without the additional processing steps. The additional processing steps prevented the breakage of material within the capillary.
3.2.5 Sol-gel conclusions

The sol-gel process investigated in this thesis offers many characteristics that are desirable for electrospray propulsion. For one, the uniformity in pore size is phenomenal. Such uniformity in microstructure nearly guarantees a uniform permeability across a substrate. A non-uniform permeability can result in non-uniform performance across one array, but it can also lead to differences in performance from array to array. The alumina xerogel prepared by a sol-gel route would prevent these problems. Therefore, if one were able to fabricate flat tiles to be used in a laser ablation process tweaked for alumina, the sol-gel process could work wonders. However, the sol-gel process fails when it comes to molding. The inevitable shrinkage that occurs throughout the process simply prevents one from using it for molding micron sized features that require alignment on the order of microns. Even though one distinct process was researched in depth, it offered insight into the difficulty of using sol-gel as a process to mold micro-tips for electrospray propulsion.
3.3 Freeze casting

Investigations into sol-gel methods revealed that such processes were not suitable for molding features to be used for electrospray propulsion applications, the reason of which mainly stems from the shrinkage inherent in the process. As such, a literature search was carried out that shined light on other, perhaps more suitable, processes that do not exhibit shrinkage. In particular, freeze casting was researched in depth. Freeze casting is a process that relies on the state transition of solvent to hold particles in place in the formation of a porous structure. Most of the time, a sintering step is required, but organic binders might alleviate the need for high temperature sintering. The process drew particular interest as it was not as well studied for scientific or engineering applications, and therefore could offer benefits not seen with other processes. Much of the early and current research was summarized by Deville [10]. Moreover, freeze casting exhibits practically no shrinkage, with some recipes actually exhibiting expansion. The most attractive feature of freeze casting is that some studies have shown the ability to mold and replicate features on the order of microns [1, 30].

3.3.1 Freeze casting theory

The freeze casting process, also referred to as freeze gelation, is one that relies on the solidification of a solvent that is then sublimated to reveal a porous structure. Often times, freeze casting is considered a sol-gel process, but in this thesis it will be referred to uniquely. An illustration of the process is given in Figure 3-16. Typically, a solvent is mixed with a colloidal silica solution, metal oxide powder, and additives if desired to form a viscous slurry. This slurry is then poured into a mold and frozen such that the solvent solidifies.
To explain the process, water will be used as an example solvent (water is commonly used in freeze casting processes). When water freezes, it forms ice crystals and expands. As water begins to solidify, the remaining constituents are forced to exist in the volume between ice crystals (a small percentage of the original volume). Since the volume is quite small, the colloidal silica links with itself while the metal oxide powder is forced to form a structure in the remaining volume. Then, the water is forced to sublimate off by placing the entire frozen solution into a vacuum dryer. Sublimation allows for the gentle removal of solvent without disrupting the metal.
oxide/silica structure that is left. The final step is a sintering step that serves to strengthen the porous structure. Depending on requirements, sintering may not be totally necessary as the colloidal silica helps in holding the structure together. Additionally, a binder can be used as an additive to further increase the strength of the final product before sintering.

In general, freeze casting does not exhibit shrinkage. In fact, if water is used, the specimen actually expands slightly (about 8%) when water transitions from liquid to gas. After the water ice is removed by sublimation, the volume should be nearly identical to that of the mold. This inherent fact with the process was the primary motivation for in depth investigations into molding with freeze casted porous structures.

### 3.3.2 Possible candidates

Many studies have been pursued in the realm of alumina freeze casting (using alumina particles). This is most likely due to the availability and favorable characteristics of alumina as practically any powdered ceramic or glass can be implemented in a freeze casting process. As such, most of the work that will be reported in this thesis is on the freeze casting of powder alumina. Some work on the freeze casting of soda lime glass microspheres will also be presented.

In terms of alumina freeze casting, the main solvent of focus is conveniently water. These recipes are mixed at room temperature and then the slurry is brought below water's freezing point or the freezing point of the water and additives mixture. Regardless, this requires one to be able to cool specimens below around 0°C. Such processes are tractable because the slurry can be formulated at room temperature and placed in a conventional freezer to solidify. However, if cooler temperatures or faster freeze rates are required, the freezing process might become more complex. In order to sublimate water, the frozen slurry must be dried under a reduced pressure. This is traditionally done in a vacuum dryer, but can be also done in a simple desiccator as long as the pressure is below the vapor pressure of water at room temperature. As one can imagine, if the slurry is allowed to warm up to the point where solid water
liquifies again, the freeze casting process fails. The solid solvent must be sublimated. As such, the post freezing step is quite time sensitive (especially for small samples) as the frozen slurries must be brought to a reduced pressure as quickly as possible. Many water based freeze casting processes have been published [37, 30, 29, 22].

Another common freeze casting field of interest is the use of camphene \((C_{10}H_{16})\) as a solvent. Camphene is an organic compound that is solid at room temperature, but it also volatizes at room temperature. In order to work with camphene in its liquid state, the slurry must be prepared at around 55 or 60 °C, and simply allowed to come back to room temperature for solidification. Then, for sublimation, camphene can just be left out until all of the solid volatizes. This, however, is usually a non-trivial amount of time; therefore, camphene based freeze casted slurries are usually also placed in a desiccator at reduced pressures. Camphene based freeze casting processes by Koh et al. and Araki et al. [16, 1] were of particular interest for demonstrating the moldability of very porous ceramic structures.

Both solvents have their trade-offs, and the optimal recipe will depend on the application. For water based solutions, the slurry formulation step is relatively more simple than that for camphene based solutions which have to be brought up to higher temperatures during the entire process. Camphene based solutions, on the other hand, have a sublimation step that is more simple and less time sensitive than a water based solution. The work presented in this thesis is almost exclusively on water based solutions, with some preliminary investigations with camphene solutions.

### 3.3.3 Experimental processes

Experimentation on freeze casting involved many materials for both use as the porous structure and other components for the process itself. A list of all components is given in Table 3.3. Many iterations on different recipes were carried out. Initially, all experiments were with water as the base solvent, with only a chosen few on camphene experimentation. With water, freezing was first accomplished in a conventional freezer at a temperature slightly below freezing.
A literature search revealed that the freezing rate also affects the final microstructure. In general, a faster freezing rate will result in smaller ice crystals and thus smaller pores [10]. The pore sizes created with the slow freezing method (conventional freezer) were producing pore sizes too large for electrospray propulsion applications. As such, the preliminary work in freeze casting with water based slurries was followed by an exclusive use of fast freezing, and deep freezing methods, or cooling to well below 0 °C. Deep freezing is further beneficial as it aids in increasing the time between freezing and transporting the specimen to a desiccator. This new freezing method was accomplished with use of liquid nitrogen as a cooling apparatus. Figure 3-17 depicts the setup used for liquid nitrogen freezing.
Liquid nitrogen freezing using the method illustratively explained with Figure 3-17 also aids in producing flat specimens. Since the specimen is floating on liquid nitrogen, it is more or less forced to be level with respect to gravity. This is especially beneficial in producing small porous tiles for direct replacement in the current laser ablation process.

3.3.3.1 Design and fabrication of a multi-chamber desiccator

In order to increase the experimentation progress rate, a custom multi-chamber desiccator was designed and built as part of this research. The purpose of which was to be able to have several compartments available to perform freeze casting sublimation or for other generic lab purposes. The desiccator that was fabricated, see Figure 3-18, has five separate chambers that each have the ability to hold vacuum uniquely from each other. In other words, one could open one chamber and place a specimen in without disturbing other chambers already at vacuum. Additionally, the desiccator has the capability to back flow inert gases such as nitrogen or argon such that items can be stored indefinitely under an inert atmosphere at close to atmospheric pressure. The device is fully functional and has been in constant use ever since its completion.
3.3.4 Preliminary results

As was mentioned earlier, many methods were investigated. In particular, the most successful recipes were custom formulations based on recipes found in literature. Specifically, work by Statham et al. and Sofie et al. was adapted for this research[30, 29]. The details of chosen recipes is given by Table 3.3. The overall conclusion is that freeze casting processes offer incredible versatility; freeze casting allows for a large spectrum of solid loadings, additives if necessary, vastly different particles sizes and materials, and most importantly, zero shrinkage.
Table 3.3: Selected freeze casting recipes

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Recipe A</strong></td>
<td></td>
</tr>
<tr>
<td>Alumina, α-phase powder, ~325 mesh</td>
<td>30%</td>
</tr>
<tr>
<td>Deionized water</td>
<td>60%</td>
</tr>
<tr>
<td>Glycerol</td>
<td>5%</td>
</tr>
<tr>
<td>Aerosil R202</td>
<td>4%</td>
</tr>
<tr>
<td>Darvan C-N</td>
<td>1%</td>
</tr>
<tr>
<td><strong>Recipe B</strong></td>
<td></td>
</tr>
<tr>
<td>Alumina, α-phase powder, ~325 mesh</td>
<td>60%</td>
</tr>
<tr>
<td>LUDOX TM-50</td>
<td>40%</td>
</tr>
<tr>
<td><strong>Recipe C</strong></td>
<td></td>
</tr>
<tr>
<td>Alumina, Calcined A16 SG</td>
<td>70%</td>
</tr>
<tr>
<td>LUDOX TM-50</td>
<td>28%</td>
</tr>
<tr>
<td>Glycerol</td>
<td>2%</td>
</tr>
</tbody>
</table>

It should be noted that Recipe A compared to the other two has more additives. This is because, a literature review revealed that additives are useful in tweaking final product results. Glycerol, for example, is used as a cryoprotectant as it not only lowers the freezing point of water if used in a solution, but also binds to water molecules and hinders the complete crystallization of ice [27]. Also, the result is for more amorphous, smaller ice crystals and thus smaller pores. Aerosil R202 is used as a binder which serves to add structural rigidity to the green body before sintering, or to the final product if sintering is not required. Darvan C-N is a dispersant which helps in preventing the slurry from settling. As one could imagine, a slurry would eventually separate, as heavier particles sink due to gravity. This mechanism is time dependent, and therefore a dispersant buys one more working time between slurry creation and freezing. Finally, it should be mentioned that a 325 mesh size alumina powder has a grain size no larger than about 40μm. Therefore, such a powder could
have a large dispersion of particle sizes.

For Recipe B, the additives that were included in A were excluded. This is because the additives have a distinct effect, one that is well characterized in literature. Therefore, it seemed more beneficial to take additives out of the experimentation while recipes were being explored. Recipe B is a two component recipe that now includes the colloidal silica solution. Colloidal silica is simply a solution comprised of deionized water and nanopowder silica. The size of the silica particles is so small such that the gravitational forces on the particles are overcome by the short range forces. The colloidal silica solution links together to form a structure as the solution is frozen, thus forcing the alumina particles into a small volume. A freeze casting recipe with a large mass fraction of colloidal silica will result in a more robust final product, but will also decrease the total porosity. Once again, herein lies another tradeoff.

Recipe C is a result of a culmination of knowledge of what works and what does not. In particular, it was found that glycerol plays an important role in pore uniformity. Therefore, a small percentage of glycerol was included in this recipe. The most important difference between Recipe C and the others is with the particular alumina grain size. A much smaller grain size is used: A16 SG has a mean pore size of about 0.37\(\mu\)m. This pore size was used as it was intended to produce pores on the order of 1\(\mu\)m, a value that is much closer to the heritage materials for electrospray propulsion. Additionally, the overall solid loading is the highest for this recipe.

3.3.4.1 Microstructure and molding

Initial investigations in freeze casting as a proof of concept process involved slow freezing rates with water/alumina based slurries. Such a process involved mixing in the requisite amount of powdered alumina, water, and other additives. In particular, Recipe A, in Table 3.3 was one such recipe that was experimented with using the slow freezing method, results of which are given in Figure 3-19. It should be noted that none of the results that will be presented involve a sintering step as the capability was not accessible.
Figure 3-19: Electron microscope picture of freeze casted alumina microstructure, at a slow freeze rate. Single molded tip with dendrite shaped pores (a) and tip array with overall random dendrite directions (b).

The first of these results was attempted with a PDMS mold consisting of an array of cylinder shaped structures. As can be seen in Figure 3-19, this initial molding attempt was actually quite successful. The molding process as simple as preparing the Recipe A slurry, pouring the slurry on top of the PDMS mold, and placing the mold in a conventional freezer. The results reveal many things. First, and perhaps most importantly, there was no observed shrinkage. The resultant structures have a diameter of about 250μm, the same as the mold itself. Also, it is clear that molding was very much a success, in that most of the features were replicated with little breakage through the process. The observed pore size for these samples was much larger than what is desired for electrospray propulsion. The shape of the pores themselves reveal that the pores are in fact the void left from where ice crystals used to exist. The pores are classically dendrite shaped which should be expected with a slow freezing process. Also, in general, the dendrite growth direction dictates the direction of freezing. Considering that the freezing was carried out in a traditional freezer, it is impossible to know the direction of cool air currents, and in fact, it appears as if the cool currents were in random directions. The main takeaway from this first freeze casting attempt is that smaller pores are desired, but the process is inherently
appealing for electrospray applications.

Further experimentation relied on the fact that smaller pores sizes are required. Recipe B was used to explore the benefits of a fast freezing method. Experiments were carried out that involved the fast freezing, following a procedure outline by Figure 3-17. The results of which are reported in Figure 3-20. In the figure, (a) displays the result of fast freezing Recipe B. It is clear that the pores are now more randomly dispersed with no dendrite shaped pores. This is a desirable feature. However, there are still pores with sizes on the order of tens of microns. Also, there is apparently a large fraction of alumina particles with large size (approaching 40\( \mu m \)) producing a non-desirable result.

Figure 3-20: Electron microscope pictures of freeze casted alumina microstructure via Recipe B (a), Recipe C (b) and simple soda-lime microsphere method (c).
As such, Recipe C was employed, and the result is shown in Figure 3-20b. In the figure, it is clear that the pores are now much smaller and more uniform. The cause and effect of a change in constituents now becomes more clear. This final alumina recipe (Recipe C) is the recipe that was employed for future alumina molding results. It should be noted that the total porosity of this formulation, (shown in Figure 3-20b) can be increased with a smaller solids loading. However, a smaller solids loading will result in a weaker green body. As such, a sintering step might be required for structural rigidity. Another option that can be used to increase substrate strength is to introduce a binder additive to the recipe.

The final microstructure revealed in Figure 3-20c is quite a simple recipe involving the freeze casting of soda-lime glass microspheres and water. The recipe was explored, in part because of work by Xie et al. whose work involved the sintering of soda-lime glass microsphere porous structures [36]. Considering that a scheme to sinter such glass beads was well defined, a freeze casting process was developed to leverage this knowledge. The process involved saturating glass beads with enough deionized water such that a very dense slurry was produced, and then frozen. The act of freezing, and expansion, forces the beads together such that after sublimation, the beads remain together. Granted, the attractive force is quite weak, but after a sintering step, the porous structure becomes robust.

After a preliminary consensus on a desirable freeze casting alumina recipe was found, research into molding with a freeze casting process was pursued. The first molding attempt served to compare the ability in filling capillaries to that with the alumina sol-gel process, the results are presented in Figure 3-21. The alumina freeze casting process was able to fill sub 50μm diameter capillaries with a near 100% repeatability. Unlike the sol-gel method, which required additional processing steps to prevent intense shrinkage and breakage during drying, the freeze casting method was quite easy to carry out and resulted in no breakage.

Experiments in molding monolithic porous materials via a freeze casting process were also carried out, see Figure 3-22a. The purpose of which was to see if substrates could be produced to yield a product with better uniformity than the borosilicate
glass used by Coffman. Such substrates could immediately be implemented into a laser ablation process to produce emitter tips. The fabrication of nicely uniform (on the macro and micro scale) substrates was possible with the use of molds comprised of many materials. Specifically, break-away molds were used. A break-away mold is one that has no desire to adhere to the specimen and even breaks apart and releases from the specimen after the freezing procedure. Parafilm served as a break away mold material; once Parafilm freezes, it becomes extraordinarily brittle and breaks apart from the substrate.

Figure 3-21: Electron microscope photograph of capillaries filled with porous alumina via a freeze casting method.

Additionally, molding attempts involving emitter tips were explored. One such result is presented in Figure 3-22b. The mold material consisted of layers of Parafilm, where a thin metal rod was sharpened and pressed to imprint a conical geometry. An alumina slurry was then dropped onto the mold and freeze casted. The process allowed for the direct replication of the mold.

Further experimentation was carried out with soda-lime glass beads. As described before, a simple soda-lime glass microsphere and water slurry was formulated and freeze casted. One experiment involved freeze casting this material onto a ridge that was produced by cover slips. A electron microscope picture of the ridge is given in Figure 3-23a. One noticeable feature is the very sharp interface between the ridge
protrusion and the rest of the porous material.

Figure 3-22: Photograph of a molded porous alumina tile (a) and a molded porous alumina tip array (b) via freeze casting processes.

Figure 3-23: Electron microscope photograph of molded soda-lime freeze casted ridge (a) and molded tip array via a camphene/soda-lime freeze casting recipe (b).

Subsequent work in experimenting with soda lime beads was carried out with a camphene based freeze casting solution. The preparation of such a solution involved heating up camphene to its melting tempearture and mixing in the requisite amount
of glass beads to make a dense slurry. Then, while still hot, the slurry was poured into a mold where it immediately hardened. A photograph of a tip array molded via this freeze casting method is given by Figure 3-23.

3.3.5 Freeze casting conclusions

Freeze casting processes have been shown to provide results in alignment with what is desired for electrospray propulsion applications. Specifically, freeze casting allows for the molding of features with sizes on the order of microns, and without shrinkage. Additionally, there exists vastly different methods and materials to go about producing a porous material via a freeze casting process. The one downside of the process, at least compared to an alumina sol-gel process, is that the pore uniformity leaves more to be desired. Through this research, it was found that pore sizes in the range required for electrospraying are achievable even though the uniformity is not ideal.

3.4 Sol freeze

The final process that will be discussed in this thesis is a process entitled sol freeze. The sol freeze process is a new and novel process which combines both the sol-gel and freeze casting processes. By leveraging the benefits of both technologies, the sol freeze process involves using the uniform porosity created by the sol-gel process and the ease of molding inherent with the freeze casting process to produce moldable, porous substrates.

3.4.1 Experimental process

The sol freeze process first starts with the same alumina xerogel (see Section 3.2) with a desired porosity prescribed by the process. This xerogel monolith is then ground into small particles, ideally less than (50\(\mu m\)). These particles are then used in a traditional freeze cast process by replacing the nanopowder alumina with the ground up xerogel alumina. The benefit of this combined process is to ensure that
even the larger particles found in a freeze casted substrate have the same porosity as the xerogel. This should theoretically increase pore uniformity with the added benefit of the ease of molding associated with freeze casting (primarily because there is no shrinkage). Figure 3-24 depicts an illustrative process diagram for the new sol freeze process.

Figure 3-24: Illustration of the sol freeze process and how both the sol-gel and freeze casting processes play a role.

In the process figure, the sol-gel process is highlighted in blue, the additional steps that comprise in total what is called a sol freeze process in white, and the freeze casting process is highlighted in green.
3.4.2 Microstructure

The preliminary formulation that was carried out as a proof of concept started with taking an already fabricated alumina xerogel monolith with a 0.6% PEO content by mass and grinding down the material to as small of a size as possible. In general, there should be some way of verifying the actual particle size, and there exists methods to do this, but they were not employed in this research. It should be noted that grinding down a monolithic material will almost surely result in a dispersion of particle sizes. Generally, filtering can be used to narrow the spectrum of sizes, but this is not necessary with the sol freeze process. In fact, it is preferred. With the sol freeze process, particles of different sizes can orient themselves accordingly to fill available free volume densely, and since every particles has the correct microstructure, the result will be a uniformly porous, rigid material. Figure 3-25 shows a picture of a sol freeze microstructure.

![Porous substrate microstructure created via sol freeze process.](image)

The uniformity is clear in the figure. In essence, the process serves to reassemble an alumina xerogel into the correct geometry by using a freeze casting process as the vehicle to both mold features and hold particles together.
3.4.3 Sol freeze conclusions

After extensive investigations into processes that could potentially be used for the fabrication of porous substrates and porous emitter tips for electrospray propulsion, knowledge from the experiments carried out have allowed for the invention of a new and novel sol freeze process. Such a process has yet to be extensively explored, but it should allow for the molding of micron size features with uniform porosity, and eventually lead to a monolithic thruster integration.

3.5 Monolithic thruster integration

All of the investigations into processes and materials to be used for electrospray propulsion are for the far reaching goal of a monolithic thruster integration. As detailed early on in Chapter 2, the current state of the art electrospray propulsion engines are serially fabricated. First, a flat porous substrate is purchased, and if not perfect, which occurs often, additional processing must be used to polish the substrate into the correct shape or geometry. Silicon frames and extractor grids are fabricated by microelectromechanical systems (MEMs) processing. The substrates are then epoxied by hand into the frames. Substrate and frames are then placed in a laser ablation system that mills emitter tips into the porous substrate and is referenced to the frame. Finally, grids are placed on the frame, aligned with the newly formed emitter tips, and epoxied in place. Such a process involves many steps with potential for misalignment through the process.

A monolithic thruster integration, on the contrary, would involve replacing many of the earlier steps with one casting process. Such a process is illustrated in Figure 3-26. Frames and grids would still MEMs fabricated, but the frames are now placed into a reusable mold that seats the frame above a bed of a negative of a tip array. Once the frame is in place, a precise amount of slurry is injected into the backside port such that it fills all of the emitter tip features and the crevices around the frame. The slurry can either be a traditional freeze casting recipe or a sol freeze recipe, and after either is carried through its entire process, the frame can be demolded from the
mold. The result should hopefully be a fully aligned porous substrate with emitter tip array already attached to the frame. All that is left is to add the frame in the same manner as before. A monolithic thruster integration can theoretically simultaneously increase the processing time and improve the emitter to extractor grid alignment.

Figure 3-26: Depiction of monolithic thruster integration concept.
Chapter 4

Carbon aerogel electrode

4.1 Motivation

As discussed in Section 2.4, the motivation for moving towards non-conductive porous emitter tips is coupled to the investigation of porous distal electrodes. With the implementation of a distal electrode, degradation of the emitter tips due to electrochemistry is no longer a cause for concern. However, electrochemistry can still occur at the distal electrode and create detrimental effects such as propellant contamination and electrode degradation. Therefore, the goal is to identify the mechanisms behind the electrochemistry that is occurring.

The presence of electrochemistry is due to the creation of an electrical double-layer in the propellant on the surface of the distal electrode. The ionic liquid propellant consists of cations and anions. One could imagine a situation where an electrode submerged in this conductive liquid is biased to a positive potential and forces a flow of current as illustrated in Figure 4-1. The cations become attracted to the electrode surface and anions follow them to form a layer of separated charge. This electrical double layer produces an electric field that continues to increase in time; if this electric field becomes larger than the electrochemical window (the voltage range at which the liquid is stable) of the ionic liquid, the liquid will break down.

In order to avoid the break down of propellant, one must stay within the electrochemical window. The electrical double-layer can be released by polarity alternation,
as discovered by Lozano [19]. Lozano found that voltage alternation on the order of 1 Hz is enough to obtain steady emission, but in order to ensure that no electrochemistry occurs, faster alternation is desired. Unfortunately, high frequency, high voltage alternation is no easy feat, especially in a small form factor power processing unit. Fortunately, there is a method of increasing the time needed for alternation.

The contact electrode with a double-layer formation is ultimately a supercapacitor, in that it operates by the same principle. Supercapacitors can store extreme amounts of charge in a small form factor because the mechanism behind charge storage is the build-up of an electrical double-layer. The alternation time can be resolved by looking at the charge build up on a traditional capacitor as represented in equation 4.1.

\[ q = cV \rightarrow I = c \frac{\Delta V}{\Delta t} \]

\[ \text{with} \Delta V \approx V_w \Rightarrow \Delta t = \frac{cV_w}{I} \quad (4.1) \]

where \( V_w \) is the electrochemical window voltage, and \( c \) is the electrode capacitance. The capacitance of a particular electrode can be resolved by the material’s specific capacitance, \( c' \), as:

\[ c = c' A \quad (4.2) \]

where \( A \) is the contact area. Therefore, by combining equations 4.1 and 4.2 it can be seen that the alternation time increases with the electrode contact area. This realization establishes the requirement of a porous electrode with high internal surface area. A porous metal like the porous tungsten and nickel discussed earlier might seem like the obvious choice for the porous distal electrode, but there are better options.

Carbon aerogels offer incredible internal surface area, high porosity, shape customization, and the ability to embed electrical contact wires (see Section 4.4). Surface areas on the order of 400 \( m^2/g \) of material are easily achieved (and with some manipulation, an order of magnitude higher surface areas are obtainable). With such high surface areas, a carbon aerogel used as an electrode in electrospray propulsion
applications can increase the required alternation time over a non-porous electrode by over 9000 times.

Figure 4-1: Illustration of double-layer formation on contact electrode.

4.2 Carbon aerogel theory

The fabrication of carbon aerogels usually consists of a two step process: the chemical formation of an organic aerogel via a sol-gel process and then the carbonization of such aerogel in a high temperature furnace. Xerogels can also be used and offer very similar characteristics with the exception of minor shrinkage that occurs during drying. Of course, for practical purposes, xerogels are much easier to fabricate due to a simplicity of air drying. The work on carbon aerogels to follow will actually involve the creation of xerogels, but will be referred to as aerogels.

Organic aerogels, the foundation on which carbon aerogels are built on, include any aerogel whose framework is mostly made up of organic polymers (as opposed to silica and metal oxides as described in the previous chapter). Therefore, the term organic aerogel is quite vague and can refer to one of several types of which some are: resorcinol formaldehyde, phenol formaldehyde, melamine formaldehyde, and phenol furfuryl alcohol [24, 25, 32]. In particular, significant early work on resorcinol formaldehyde
aerogels by Pekala and others demonstrated the use of such materials for electrochemical application [26]. Moreover, the ability to tailor the porosity of a RF organic aerogel was demonstrated by Horikawa [15]. The ability to alter porosity and pore size is appealing for an application that might have changing requirements. Therefore, with consideration of heritage with like applications and recipe adaptability, the resorcinol formaldehyde (RF) recipe was pursued for electrospray propulsion distal electrodes.

To form an organic aerogel, a sol gel process is implemented with a solution of small molecules that have the ability to link together to form a scaffold structure. For RF aerogel specifically, resorcinol and formaldehyde have the ability to polymerize, or link together. Unfortunately, this process can take a significant amount of time on its own so a catalyst is used to speed up the process. For the RF aerogels formed for the research presented in this thesis, acetic acid is used as the catalyst because of its significant heritage [4, 3]. Additionally, a cure at higher than room temperature can also speed up the gellation process.

In the formation of a carbon aerogel by high temperature pyrolysis of an organic aerogel, the polymer that comprises the aerogel becomes dehydrated and leaves behind carbon. Therefore, carbon replaces polymer with the same intricate microstructure as the organic precursor.

### 4.3 Experimental processes

A carbon aerogel is fabricated by combining appropriate amounts of water, formaldehyde, resorcinol, and acetic acid. In the correct proportions, the solution will gel and harden to a dark red colored porous polymer (organic aerogel). Prior to gelation and hardening, the solution can be poured into the desired molds where it will mimic the shape of the mold with little shrinkage. The recipe that was used was adapted from the work of Brandt and Baumman [4, 3] and is presented in Table 4.1.

The formulation proceeds as follows:

1. The resorcinol is added to the deionized water and mixed until fully dissolved.
Table 4.1: Resorcinol formaldehyde organic aerogel recipe

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized Water</td>
<td>32.9%</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>26.9%</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>39.2%</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>1%</td>
</tr>
</tbody>
</table>

2. The formaldehyde is added and mixed thoroughly for one minute.

3. Acetic acid is added carefully and mixed for one minute. The gelation is sensitive to the amount of acetic acid.

4. The solution is now complete and can be poured into molds.

The formulation of RF solution and the subsequent transferring of solution to a desired mold takes on the order of one hour. Generally, an oversized mold is desired to account for slight shrinkage that occurs during the process. Once the desired mold has been created, it can be reused. In general, a mold can be fabricated out of any material that is non-reactive to the respective ingredients in the solution. Also, the molds should be made as smooth as possible to mitigate issues with de-molding. In this research, molds made from polypropylene, polyurethane, PTFE, and silicone have been used successfully.

4.3.1 Curing and Drying

The curing process is both the longest and one of the more sensitive steps of the process. In all, the curing step takes about one week. After the solution has been poured into molds, the molds must be placed in an airtight container during curing. Snap-ware brand containers, which are readily available, serve this purpose well. The container is then placed at room temperature conditions and allowed to rest for 48 hours. It is important not to disturb the container during this initial curing step. The container is then placed in a furnace where the temperature is slowly increased. The description of the curing process is detailed as follows:
Curing Steps

1. Cure sealed container with solution at room temperature for 48 hours. Care must be taken to not disturb the specimen.
   - The solution should turn from a clear liquid to an opaque white liquid. It will slowly get more viscous until it appears a solid. The opaque white gel will begin to turn a light orange color.

2. Place in oven, and cure at 35 – 40°C for 24 hours.
   - The gel will begin turning a darker orange/red color.

3. Increase oven temperature to 60°C and allow curing for 24 hours.
   - The gel continues to get darker orange/red.

4. Increase oven temperature to 85°C and allow curing for at least 72 hours, but no more than 1 weeks time.
   - The gel continues to get darker orange/red.

With the completion of the curing process, the next step is to dry the organic gel. There are many drying options depending on the desired product. To produce a traditional organic aerogel, the main drying method is with a supercritical dryer. With such a process, more care must be taken as the gel must not be allowed to dry out before it reaches the supercritical fluid (usually CO₂). Additionally, supercritical dryers (both homegrown and those that are commercially available) usually have a small operation volume. The production of organic aerogels via a supercritical drying process can be cumbersome and time consuming. However, such a process will produce organic aerogels that mimic the mold (i.e. negligible shrinkage).

Another, more facile, drying method is a controlled air drying process which is as simple as allowing the unwanted products left in the gel to evaporate. The final product is an organic xerogel. The main caveat is that xerogels exhibit shrinkage. However, considering the inevitable shrinkage that is incurred with the carbonization
process, the organic xerogel route is the most suited to the application primarily because of process simplicity. The appropriate drying procedure that was developed through this research is presented below.

**Drying Steps**

1. Remove container with organic gel from oven and cool for two hours at room temperature.

2. Saturate entire specimen with acetone.
   - Container must be opened to fill with acetone. Enough acetone should be used to fill a few cm above specimen. The container should be resealed as specimen soaks for 12 hours.

3. Repeat acetone saturation by removing old acetone and replacing with new (solvent exchange).
   - The goal is to replace some of the harder to evaporate species with acetone (readily evaporates).

4. Allow specimen to rest until all of the acetone has evaporated.

5. Dry specimen at room temperature for 24 hrs.

6. Place open container back in oven at about 60°C for 24 hours.

7. Increase oven to 85°C and cure for at least 24 hours.

8. Electrode curing process is complete.

The steps in the curing and drying process were developed to minimize shrinkage and warping. Faster curing, drying, and solvent exchange times can be experimented with, but they could result in less than ideal final products.
4.3.2 Carbonization

The resulting red porous polymer that is produced if the above steps are followed is non-conductive. A carbonization step is required to turn the polymer into a porous and conductive carbon material. The specimens are carbonized by placing them in a tube furnace at high temperature. The tube furnace should have a steady flow of inert gas (such as nitrogen or argon) at ~500 sccm and should be slowly ramped up and down in temperature. Figure 4-2 below illustrates the ramping procedure.

![Carbonization ramping procedure](image)

Figure 4-2: Carbonization ramping procedure.

If more surface area is desired, an additional step can be added which involves flowing carbon dioxide over the specimen as it is heated. Such a procedure can increase internal surface area by an order of magnitude. This has yet to be experimented with, but extensive research by Baumann has shown that carbon aerogels with internal surface area more than 3000 $m^2/g$ are possible.

4.3.3 Geometric shaping and cleaning

The final step in the fabrication of the carbon aerogel distal electrodes involve the shaping of the electrode. As was mentioned, the molding process allowed for a slightly oversized electrode which is to be polished to the desired geometry. Polishing is done carefully with high grit sandpaper. Polishing should be completed in a fume hood.
as the carbon dust can be hazardous. The center hole in the electrode (if desired) is produced by slowly hand drilling with the correct drill bit size. The last processing step is an intensive cleaning procedure which must be followed to ensure that no stray carbon dust interferes with electrospray mechanisms within a fully integrated thruster. The cleaning procedure described below has been proven to work without any cause for concern. However, if even higher cleaning standards are desired, the best way to clean out micro and nano sized pores is with a supercritical drying process.

**Cleaning Steps**

1. Submerge electrodes in a glass beaker filled with acetone.

2. Place beaker in an ultrasound bath for 1 hour.

3. Remove electrode, dispose of acetone, and clean beaker.

4. Repeat step 1, 2, 3.

5. Place electrode on a clean surface and bake in an oven or on a hot plate at 100 °C for at least 30 min.

### 4.3.4 Automated furnace for carbonization

As illustrated in Figure 4-2, the carbonization procedure is not trivial. The control of temperature, gas type, and gas flow are required. A fully automated furnace system was built for this purpose with a design based on the one developed and described by Steiner [31]. A picture of the system built for this purpose is given in Figure 4-3.

The apparatus is entirely integrated with software and a graphical user interface that allows the user to select appropriate gases, temperature ramping procedures, and gas flow rate. Once coupled with a high temperature furnace (Lindberg Blue M Mini-Mite Tube Furnace) the system is complete and carbonization can be carried out. The system as built through this research is capable of handling argon/nitrogen, carbon dioxide, and hydrogen with three separate mass flow controllers. The inert atmosphere as described is created with either argon or nitrogen gas flow. If an even
larger internal surface area (for carbon aerogels) is desired, carbon dioxide should be used as prescribed by Baumman [3]. Hydrogen gas can be used for carbon nanotube growth.

4.4 Embedded wire

Carbon aerogels alone offer much as a distal electrode in electrospray propulsion applications. However, they could prove even more useful with an embedded wire so that the electrical contact can be built in. Such an attribute ensure a good electrical connection from electronic board to ionic liquid propellant. Additionally, the porous carbon electrode can be physically fixed in the thruster tank assembly via its embedded wire which helps in preventing epoxy from wicking into the its pores. The method of embedding a wire is illustrated by Figure 4-4.

The usual RF sol gel process as described before is employed. Now though, a wire is mounted in such a way to allow for the gel to cure around certain sections of
the wire and thus embed the wire in those locations. When embedding a wire, it is important to understand the material compatibility between metal and chemical that go into the RF aerogel. In this research, three distinct wire materials were investigated: stainless steel, nickle-chromium (nichrome), and pure platinum. All wire types worked as expected, in that the aerogel was able to cure around distinct wire shapes. However, it was observed that after the high temperature carbonization step, the stainless steel wire darkened and got more brittle. The nichrome wire seemed more tolerant to the high temperatures, but also became more brittle. Finally, the platinum was entirely not effected by either the gelation or carbonization steps. If extremely ductile wire is desired, platinum is the best option.

Generally, the design process for an embedded wire carbon electrode begins with the conceptualization of the final product and working backwards. The design begins with something similar to Figure 4-5 which is the desired shape of the electrode in reference to the protruding wire (the electrode is effectively 2D and is simply extruded
1 to 2mm in the third dimension). The desired electrode shape is resolved with knowledge of the tank dimensions. Then, a mold is manufactured that is an oversized version of the electrode to account for shrinkage. Shrinkage will be characterized in the section that follows.

Shrinkage throughout the process cannot be avoided, and as such, maintaining geometric references is difficult. The best way to handle this is by making geometries simple. For instance, in Figure 4-5, the embedded wire is centered along the short face of the electrode. The depth of the wire is hard to control, but it can be designed to allow for variations in placement as long as hard requirements are satisfied (i.e. hole placement with respect to wire).

![Figure 4-5: Illustration of desired carbon aerogel electrode shape.](image)

Once one electrode of a certain variation has been shaped and tested for fit in the thruster assembly, it can be used as a master to size the remaining identical electrodes. The process of electrode formation is as much an art as it is a science.

### 4.5 Results

#### 4.5.1 Resorcinol formaldehyde aerogel preliminary results

The development of a process to produce RF aerogels (technically xerogels), was developed over the course of several months where it was optimized to prevent shrinkage
and to increase repeatability. The details of the processes final form are described in the previous section. The process should yield a porous dark red polymer-like aerogel with appearance and microstructure presented in Figure 4-6.

![Resorcinol formaldehyde aerogel appearance and electron microscope photograph of microstructure.](image)

**Figure 4-6**: Resorcinol formaldehyde aerogel appearance (left) and electron microscope photograph of microstructure (right).

### 4.5.2 Carbon aerogel preliminary results

After carbonization, the RF aerogel experiences some shrinkage and turns a black carbon color. The first carbon electron design was a proof of concept for embedding a stainless steel wire into RF aerogel. Figure 4-7 show a picture of this first iteration carbon aerogel electrode. It is clear from the figure where the wires are embedded into the electrode.

The carbon aerogels used as electrodes produced through this research have a predicted internal surface area greater than $400m^2/g$, a measured material density (without embedded wire) of about $0.5g/cm^3$, and a measured total porosity of 60%. There are many mechanisms for measuring the internal surface area and porosity of a material directly such as a porosimeter. Unfortunately, no such devices were used to measure internal surface area directly in this research. The internal surface area was

97
inferred though results in literature. The total porosity was determined by wetting the electrodes with water and determining mass before and after. If desired, more precise methods should be used in the future.

4.5.3 Batch fabrication process results

After the proof of concept was deemed successful, a batch fabrication process was developed. Such a process involved the manufacture of a mold that is capable of producing 40 RF aerogels with built in wires. The main, base mold was milled from a solid piece of polypropylene as depicted in Figure 4-8. A corresponding top piece was also milled from a solid block of polyurethane with slots that serve to correctly position the wires. Figure 4-8 also contains a picture of the top piece with 40 platinum wires positioned to be suspended in the bottom piece mold.

The platinum wires, as depicted in Figure 4-8, are short length wires with circular loops on the end to be embedded into the mold. A cross section illustration of the assembled mold with wire location is given by Figure 4-9.
Figure 4-8: Photographs of end-milled 40 electrode polypropylene mold (left) and underside of mold top piece with 40 platinum wires mounted (right).

Figure 4-9: Illustration of two-part embedded wire mold for batch fabrication of carbon aerogel electrodes.

Each wire is formed into the correct shape by hand. In the future, a custom forming tool should be manufactured to speed up the process. Such a tool will also
introduce more control in the process.

After the RF aerogel is fully cured (refer to section 4.3.1) the 40 monoliths should have shrunk to the point where they can be easily pulled out of the molds by the wire. This process was followed twice with a yield of 95% from the first batch and 100% from the second. A picture of one such batch is given by Figure 4-10.

Figure 4-10: Photograph of 40 demolded resorcinol-formaldehyde monoliths with embedded platinum wires.

The next step in the process is carbonization; depending on the furnace equipment being used, several RF aerogels can be carbonized at one time. With the setup built through this research (subsection 4.3.4), up to 10 electrodes can be carbonized at once.

4.5.4 Shrinkage Characterization

There are two distinct steps in the electrode fabrication process which involve shrinkage. Shrinkage is first incurred when the aerogels are dried. Shrinkage occurs again during the carbonization process. Knowledge on this shrinkage proves useful in order to optimize mold designs in the future. Table 4.2 reports on the shrinkage in two dimensions (see Figure 4-11) of identical electrodes by following the same drying and carbonization procedure. The shrinkage is in fact different along the two dimensions. The amount of exposed surface to atmosphere plays a role in this difference. Intu-
Table 4.2: Carbon aerogel electrode shrinkage characterization

<table>
<thead>
<tr>
<th></th>
<th>Shrinkage in dimension A after drying</th>
<th>Shrinkage in dimension B after drying</th>
<th>Shrinkage in dimension A after pyrolysis</th>
<th>Shrinkage in dimension B after pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode 1</td>
<td>8.2%</td>
<td>1.4%</td>
<td>27.6%</td>
<td>21.7%</td>
</tr>
<tr>
<td>Electrode 2</td>
<td>8.8%</td>
<td>1.8%</td>
<td>27.8%</td>
<td>21.8%</td>
</tr>
<tr>
<td>Electrode 3</td>
<td>8.4%</td>
<td>1.8%</td>
<td>27.8%</td>
<td>22%</td>
</tr>
<tr>
<td>Electrode 4</td>
<td>9.0%</td>
<td>1.6%</td>
<td>27.8%</td>
<td>22.2%</td>
</tr>
<tr>
<td>Average</td>
<td>8.6%</td>
<td>1.7%</td>
<td>27.8%</td>
<td>21.9%</td>
</tr>
<tr>
<td>Std. Deviation</td>
<td>.37%</td>
<td>.20%</td>
<td>.10%</td>
<td>.22%</td>
</tr>
</tbody>
</table>

It makes sense that dimension A shrinks more than dimension B as the two faces that define dimension A comprise a much larger area than the two that define B. Exposed surface area plays an integral role in shrinkage.

The shrinkage steps can be visualized with help from Figure 4-11 where it is clear that the electrode gets smaller at each step in the process. In particular, in Figure 4-11 it is clear that the electrodes exhibit shrinkage after carbonization.

![Figure 4-11: Photograph of the processing steps after electrode demolding and reference dimensions.](image)

The most arduous (in terms of human interaction) task is the post processing of
the electrodes after carbonization which includes polishing and drilling. Therefore, the closer the electrode is to its final dimensions after carbonization the less time is spent on human involvement. Additionally, there may be applications in the future that leverage the ability to mimic complex shapes by molding. As such, the amount of volume lost during shrinkage is invaluable knowledge.

4.5.5 Integration with propellant tank

The final step in the electrode fabrication process is the integration of the electrodes inside the thruster tanks. The thruster tanks are comprised of a series of stacked porous materials that allow propellant transport to the tips, see Figure 4-12 for an illustration.

![Illustration of components that comprise thruster tank.](image)

Figure 4-12: Illustration of components that comprise thruster tank.

However, the ionic liquid propellant has a preferential desire to wet the electrode over the porous emitter tips material because the electrodes have a smaller, more uniform pore size. As a result, once liquid wicks the electrode, it will not exit during normal operation. As such, the thruster tank is engineered to accommodate this lost propellant mass (albeit not much). Also, electrical contact is only guaranteed if there is a liquid propellant contact from electrode to emitter tips. At some point during
firing, this liquid connection will fail (once most propellant is exhausted) and the thruster will cease to fire. Therefore, the electrode placement was chosen such that it is closest to the emitter tips as possible. Figure 4-13 is a photograph of a single electrode inside a dual thruster tank without any other components. The purpose of the dual thruster tank is to operate one thruster at positive polarity and the other at negative such that the ion plume has no net charge.

Figure 4-13: Photograph of polished carbon aerogel distal electrode inside thruster tank.
Chapter 5

Conclusions and future work

5.1 Conclusions

Electrospray propulsion is a relatively new field of electric propulsion that offers incredible capability for future spacecraft mission types. Electrospray propulsion devices offer nearly the same thrust density as traditional ion engines while consuming less power. Their small form factor, high specific impulse, and simplicity are conducive for use as an attitude control device on various satellite platforms. Moreover, translational capability can also be achieved, and spacecraft thrust requirements can be meet for a large spectrum of satellite missions by scaling electrospray devices. All of these markets are already within reach with experimentally predicted performance. However, current manufacturing techniques are limiting the ability to produce nearly identical, reliable engines. In order to meet requirements for scalability, or the ability to form arrays of engines to increase capability, electrospray engine manufacturing must be a batch process with repeatable, uniform results.

The topics of research reported in this thesis are, in general, materials engineering solutions purposed for electrospray propulsion fabrication improvements. The means of fabricating electrospray emitter tips have only ever been via subtractive processes. Such processes, including electrochemical etching and laser milling, are inherently not suited for batch processing. As a result, new porous material fabrication techniques are required in order to bolster the already appealing technology of
electrospray propulsion.

5.1.1 Electrospray additive manufacturing

The breadth of research reported in this thesis is on three distinct processes: sol-gel, freeze casting, and sol freeze. The sol-gel process is a chemical process that allows for the ability of tailoring pore size and material quite readily. The process is able to produce porous materials with extremely uniform porosity. A porous alumina xerogel process was refined, and it was found that the material works quite well as an electrospray emission source. In fact, the preliminary results point to a material that outperforms the current state of the art by an order of magnitude. The one caveat of the material, a deal breaker of sorts, is that the sol-gel process incurs inherent shrinkage throughout the process. Such shrinkage makes molding features a difficult task.

The freeze casting process was explored and it was revealed that the process is even more versatile than the sol-gel process in producing porous materials. A freeze casting process can be used to produce porous materials with extremely varying pore sizes from practically any material. In this research, alumina powder was explored extensively in various freeze casting processes. In doing so, the ability to create porous materials with pore sizes in the correct range for electrospray propulsion was demonstrated. The main benefit of freeze casting processes is that there is no shrinkage penalty. Furthermore, the ability to mold micron sized features via a freeze casting process was also demonstrated.

The final studied process, the sol freeze process, is a newly invented process that leverages the most beneficial attributes of both the sol-gel process and freeze casting process. The sol freeze process was demonstrated to be able to produce, non shrinking porous materials with uniform porosity.
5.1.2 Carbon aerogel electrode

In addition to the work on porous material and process development for electrospray emitters, investigations into porous electrodes for electrospray propulsion were also carried out. In particular, through this research, high internal surface area carbon aerogel electrodes with embedded electrical contact wire were developed. In doing so, a process was also developed that begins with the production of molded organic aerogels which are then carbonized by means of a high temperature furnace. As part of this research, a controller was built with the ability to meter gas type, gas flow rate, and furnace temperature.

5.2 Future work

The nature of research presented in this thesis requires an extensive amount of trial and error, and perhaps most importantly, time. There is much more work that needs to be carried out to identify a distinct process to be used for the future of electrospray propulsion, one in which porous emitters are fabricated additively.

5.2.1 Monolithic integration

The monolithic thruster integration requires an identification of a well proven process that is able to produce uniformly porous materials that can be molded. So far, the most likely candidate is the sol freeze process which has both the benefits of moldability and uniform porosity. However, much more work is required to identify molding subtleties. In particular, the limited work on molding and demolding covered in the body of work presented in this thesis has pointed to certain difficulties. In particular, certain mold materials are more conducive to filling features that are microns in size. Hence, material compatibility is crucial in reaching the end goal.
5.2.2 Ultra-high surface area electrodes

The research presented on carbon aerogels in this thesis is more or less an open and closed book. The process has been well defined, and is able to produce a working final product via a batch fabrication process. The one avenue for improvement is a further increase in the carbon aerogel's internal surface area. If desired, one can increase the internal surface area via an additional high temperature carbon dioxide exposure. In fact, the capability has already been established as part of this research. The desire for increased internal surface area might arise for electrospray applications that require an even smaller form factor. For such an application, smaller electrodes would be required, and a certain total internal surface area must be maintained in order to satisfy frequency alternation requirements.
Bibliography


