Propellant Transport in Electroactive Polymer-Electrospray Thrusters

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Abstract: Porous emitters compromise the resolution achievable on emitter geometries developed for electrospray propulsion. Due to the large granule size characteristic of porous substrate materials, the roughened tip topology creates surfaces for unpredictable emission behavior ranging from off-axis to multiple-site emissions, decreasing thruster efficiency and operation time, specifically for thrusters designed for one uniaxial plume per tip. Bonded to porous carbon substrates, electroactive polymers were used to develop ultra-smooth tips to solve this problem. However, this approach introduced a polymer-electrode interface, which seems likely to play a role in the polymer’s ability to transport liquid during electrospray activity. More specifically, long-duration testing performed on a soaked polymer emitter revealed bulk transport behavior limited by increased flow impedance, resulting in emission currents that started at $5\mu A$ but later decreased to about $30nA$. This work reports and interprets emission behavior observed from one such emitter assembly.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>EP</td>
<td>Electrospray Propulsion</td>
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<tr>
<td>IL</td>
<td>Ionic Liquid(s)</td>
</tr>
<tr>
<td>$EMI - BF_4$</td>
<td>$1$-ethyl-$3$-methylimidazolium tetrafluoroborate</td>
</tr>
<tr>
<td>$Q$</td>
<td>Volumetric flow rate [$cm^3$ per second]</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume [$cm^3$]</td>
</tr>
<tr>
<td>$I$</td>
<td>Current [nano-Amperes]</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density [$g$ per $cm^3$]</td>
</tr>
<tr>
<td>$q_m$</td>
<td>Charge-to-mass ratio</td>
</tr>
<tr>
<td>T-subscript</td>
<td>Denotes &quot;Total&quot;</td>
</tr>
<tr>
<td>m-subscript</td>
<td>Denotes &quot;monomer&quot;</td>
</tr>
<tr>
<td>d-subscript</td>
<td>Denotes &quot;Dimer&quot;</td>
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I. Introduction

A. Motivation

Electrospray propulsion (EP) is a form of electric propulsion that uses electrostatic forces to accelerate charged species from an ion-filled liquid, like ionic liquids or molten salts, to generate thrust. Unlike most chemical and solid propulsion units, systems that rapidly express large amounts of exhaust material for large maneuvers, electrospray vehicles generate small mass flows at large specific impulses, providing microscale thrusts suitable for macro maneuvers in space. Additionally, since these systems rely on capillary...
forces to transport propellant during operation, their overall size is small, and assembly is simple enough for CubeSat applications.

Emitter geometries are central to the assembly of these systems since they provide surfaces for ion plumes to pin during the extraction and acceleration of species. Three main configurations exist for these emitters: capillary emitters, externally wetted tips, and porous substrate-based emitters. Capillary-based and externally wetted (solid) emitters have been used extensively in past investigations, with beams mainly composed of both droplets and ions (mixed regime). The geometries configured into these two liquid transport modes can be further optimized thanks to improving nano-fabrication techniques, tailoring the system towards an emission regime with decreased droplets in the beam. However, the feature resolution, cost of production, and complexity of fabrication processes are still limiting factors, such that features are hard to replicate across arrays, let alone across devices, preventing access to predictable performance characteristics.

Conversely, porous emitter configurations have gained popularity in developing EP systems. With tip geometries defined on these substrates in most cases using subtractive fabrication techniques like laser ablation, ILs can travel through the emitter bulk at high electrostatic fields, eliminating the need for capillary features or surface treatments like those performed on externally wetted emitters. Thrusters assembled with these substrates, like those developed at MIT, have displayed high-performance characteristics with even higher thruster efficiencies than capillary and solid emitters. It all depends on the bulk porosity, which, for materials used in this application, have characteristically small pore radii shown to support high enough flow impedance for pure-ionic emission operation.

However, the granular nature of porous emitters compromises the emitter geometry, limiting access to even higher system performance. The tip resolution heavily depends on these substrates’ granular size since the curvature tip radius is usually on micro-scale order, as depicted in Figure 1. Therefore, with ‘roughened’ geometries, the surface creates sites for unpredictable emission characteristics that range from multiple site emissions to off-axis emissions. Since most electrospray thrusters are designed to support one uniaxially aligned spray of particles, anything outside this assumed operation, which is more likely for roughened emitters, reduces the overall system thruster efficiency and shortens their operation due to increased beam-extractor interactions.

Figure 1: Illustration of the beam behavior obtained during emission from a coarse surface.

Solutions to this problem can take many forms. An interesting example is using porous substrates with even smaller pore sizes so that the bulk’s granularity is theoretically small enough to develop smooth tips. However, substrates with structural pore features do not seem to be the most ideal options in this application as liquid transport in these materials can be restricted, especially for materials with pore radii of the order of the characteristic size where non-slip conditions take effect. Additionally, pushing the limit of these structural pores leads to dense substrates that are heavier and not attractive for systems where small size and mass are central to their bottom line. Therefore, materials without structural pores, like polymers, are better alternatives for this application.

B. Background on Electroactive Polymers

Polymers are viscoelastic materials composed of long carbon chains. Electroactive polymers, in particular, have their end chains modified by an acid group, allowing them to conduct electricity through the migration of counter-ions, usually available when exposed to a compatible electrolyte. NafionTM is one such material. Its flexible polymer chains, nano-scale polymer molecule size, and bulk stability at room temperature make it compatible with fuel cell applications.
Therefore, with targeted research launched in the study of Nafion\textsuperscript{TM}, several observed behaviors make this material suitable for developing emitter substrates for space applications\cite{21,22}. Nafion\textsuperscript{TM} forms ion clusters when water or select IL, some of which are used in electrospray thrusters, are absorbed into its bulk\cite{22,23}. It means that the liquid of interest can be introduced into the bulk in preparation for transport when differential pressure is introduced across opposing mediums by, say, high electrostatic forces. Additionally, even though the material does not have structural pores, its ability to swell when it absorbs liquid shows that it can allow liquid to travel in its bulk\cite{22}. Finally, its chain flexibility allows easy molding into smooth features, like those intended for emitter geometries, because these molecules can take any shape of interest when simple fabrication methods like the solution cast method are used\cite{13}.

At MIT, the development and testing of emitters made of electroactive polymers is underway, with preliminary results reported in\cite{25,26}. From these investigations, it was shown that the fabrication of polymer emitters using the solution cast method, a simple approach utilized in Nafion\textsuperscript{TM} based investigations referenced in this work, was possible and resulted in smooth geometries as intended, pushing us one step closer into realizing predictable emissions from these devices. Additionally, results reported in the referenced work showed that these structures can operate under electrospray environments. On the other hand, little is known about how the emitters transport propellant during operation. Therefore, this work is meant to extend previous investigations and provide some insight into propellant transport through the emitter bulk. This will be achieved by performing long-duration testing of prepared emitters and observing emission behaviors as a function of time and temperature at a fixed firing potential.

II. Methodology

Nafion\textsuperscript{TM} was used to fabricate single emitters using the procedure highlighted in\cite{23,24}. The polymer material was bonded to a porous carbon electrode made from a sol-gel reaction between resorcinol and formaldehyde in an acidified environment\cite{25}. The electrodes provided a distal contact surface for high-voltage application\cite{25}. Additionally, since the latter have about half their volume open, the emitter assembly will sample the propellant available in an external reservoir during operation, readily replenishing the liquid meniscus consumed at the tip’s apex\cite{27}. Afterward, these dry tips were soaked in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF\textsubscript{4}) at 80°C to swell them before testing.

![Figure 2: Tip configuration during testing. $A_e$ is the emitted current as measured from the emitter while $A_b$ is the emitted current collected by a rectangular stainless steel plate as measured from the beam. $A_i$ is the current intercepted by the extractor. $AR$ is the particle acceleration region after extraction, while $FFR$ is the field-free region. $V_0$ is the firing potential applied directly to the emitter.](image-url)
A. Testing Configuration

The emitters were assembled as shown in Figure 2, where the plume emission profile, as collected from a rectangular stainless steel plate, can be measured and analyzed in depth.

Due to the preparation method employed for these emitters, different transport mechanisms can arise during testing. As shown in Figure 3a, liquid coating on the external surface, which occurs after soaking the emitters in the propellant, would result in a reduced impedance to flow. It could ultimately feed the meniscus at the apex of the emitter faster than fluid from the bulk, potentially supporting an emission mode that results in a lower specific charge, possibly into the droplet-mixed regime at best. Furthermore, since there is no direct way to supply liquid to the surface while in operation, the emitter tip would soon starve once the surface liquid is consumed. Since the objective here is to demonstrate the bulk transport of IL to ion emitters, the surface will be de-wetted completely, thereby supporting the configuration in Figure 3b. In addition, long-duration emission tests will be performed to demonstrate that the liquid can be transported exclusively through the bulk, such that thruster designs based on the flow from an upstream reservoir could be implemented.

![Figure 3: Summary of propellant transport mechanisms in an electrospray emitter.](image)

B. Analysis

The emitters developed for this investigation, which includes initially dry Nafion\textsuperscript{TM} emitters that were afterward soaked in EMI $-$ BF$_4$ solution for at least seven days, at $T = 80^\circ$C, were assembled into the configuration provided in Figure 2 where the firing potential, $V_0$, was fixed at $\pm 2500$V in a 30sec period square wave. In this experiment, the beam current $A_b$ measured from a rectangular plate was particularly interesting since this measurement can be converted into volume via Equations 1 and 2. In these equations, $Q$ is the volumetric flow rate equivalent to the ratio of the emission current, $I$ integrated over the entire test duration and normalized relative to the product of the propellant density $\rho$, and effective charge-to-mass ratio $q_m$. As a note, in these calculations, the beam mass spectrum was assumed to be of a monomer-dimer composition in the positive and negative mode, all of which are considered to approximate a 50-50 contribution, as measured in other experiments reported in\textsuperscript{1}. This is a conservative assumption, indicating that the resultant volume calculated represents the lowest amount of propellant that the emitter could have consumed over the test duration.

$$Q_T = \frac{I}{\rho \frac{m}{I}} = Q_m + Q_d = \frac{I}{\rho \frac{m}{I}} + \frac{I}{\rho \frac{d}{I}}$$

$$V = \int_a^b Q_T dt = \frac{1}{\rho \frac{m}{I}} \int_a^b I dt$$

The emitters examined in this work were subjected to a continuous long-test duration of at least 90 hours. However, as provided in Figure 4 for every polarity change, the current response was accompanied by random spikes, which ultimately obscured the overall current trend over the test duration. As a result, the first and last few data points were excluded during averaging so that the bulk of the mid-region of the current response, composed mostly of stabilized emission, was averaged for each square wave for easy data presentation and analysis.
Figure 4: Sample emission current $A_b$ for a soaked emitter where (left) shows the presence of random current spikes and (right) shows the averaging criteria applied during data processing, which excludes the spikes.

III. Results

A single emitter, initially dry with an apex radius of curvature of 12$\mu$m but afterward soaked in $EMI-\text{BF}_4$, was considered in this examination stage. Two key components were examined rigorously during this experiment: 1) the emitter structure before and after testing and 2) the emission profile during the test duration. Below are the results observed for this emitter configuration.

Figure 5: Tip geometries examined at different stages of the test. (a) through (d) are the emitter before testing, seconds after testing, three days after testing, and seven days after, respectively. Figures (b) through (d) were overlapped on top of that in (a) to create (e) through (g), respectively.

Figure 5 reports images of the tip as examined in this test. It is composed of the emitter images after soaking in liquid but before testing (Figure 5a) and seconds after 90 hours of continuous electrospray activity (Figure 5b) with Figure 5e showing it overlapped on top of its appearance prior testing for a visual comparison. The emitter was afterward stored in a nitrogen-fed dry box and examined three days (Figure 5c) and seven days (Figure 5d) after testing. Thus, Figures 5f and 5g are these tips, respectively, overlapped over the tip geometry before testing for visual comparison. These visual inspections show that the emitter shrunk due to the prolonged testing. It then reverts to its initial geometrical specification when left unperturbed in a dry environment.

The $A_b$ obtained from the emitter in Figure 5 is provided in Figure 6, where the emission profile and temperature applied on the emitter are set as a function of time. During the first 2 hours of emission, the
emitter was heated to about 100° C. It resulted in a corresponding increase in current to an order of 5 μA. After decreasing the firing temperature to about 70° C, with the latter maintained as the emitter temperature throughout the emission activity as summarized in Table 1, the current from the emitter decreased significantly with a value of about 30 nA, which is about a 6-thousandths of the value observed at $T \approx 100° C$.

### Table 1: Region A average temperature and emission current.

<table>
<thead>
<tr>
<th>$T[°C]$</th>
<th>$I[nA]$</th>
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<tbody>
<tr>
<td>69.2683 ± 0.8437</td>
<td>PM: 32.7341 ± 14.2019</td>
</tr>
<tr>
<td></td>
<td>NM: 32.9412 ± 14.7894</td>
</tr>
</tbody>
</table>

Plotting $A_b$ provided in Figure 6 against temperature results in Figure 7a. In this plot, the region where temperature changes were applied is brought into focus, showing how the emitted current from this tip changes as a function of temperature. Additionally, the temperature changes rapidly, of the order of a few minutes, which is a much smaller time scale than in Region A of the emission profile.

Figure 7a shows significant current hysteresis, with the initial heating attempt showing much higher current magnitudes than that obtained in the final cooling step. Increasing the temperature in the "Initial Heating" step further increases the emitted current, indicating that a) the ionic liquid was transported in the tip bulk more rapidly due to its decreased viscosity and b) the emitter is rapidly consuming the propellant available in the bulk since its surface tension is also inversely affected by temperature. Lowering the temperature during the mid-step (cooling) stage is followed by a much lower emitted current, further sustained in Region A of the emission profile. This decrease in current is an interesting observation and, together with the geometrical changes observed in Figure 5, gives additional insight into the propellant transport mechanics available in this emitter. This insight will be discussed further in the following paragraphs.

In examining the history of the volume consumed, assuming a conservative beam composition of a 50-50 monomer-dimer specification, we obtained Figure 7b. In this figure, the volume history of this soaked Nafion$^{TM}$ emitter is observed to increase over time. Despite its approximation being lower than the tip’s geometric volume provided by the black dashed line, the following ideas assert that the initial intention of this investigation, i.e., demonstrate and sustain bulk liquid transport at high firing potentials, was met: 1) the emitter was configured to comply with the transport mode illustrated in Figure 3b so that no visible liquid was present in its external surface before testing, and 2) the testing time was long enough to suggest that the emitter was sampling liquid primarily from the bulk.

Additionally, from Figure 7b, the emitter almost instantaneously consumes propellant volume that approximates half of its geometric volume two hours into the testing phase. This rapid use of the bulk
volume could explain the structural changes observed on the tip in Figure 5. The emitter consumed the propellant faster than the bulk could replenish, creating a flow-limited emission profile. The flow limitation results from increased flow impedance, a parameter also proportional to the differential bulk pressure. And since this tip assembly is made of an elastic material\textsuperscript{18,21}, the tip shrunk to compensate.

IV. Discussion

Porous substrates have been used to develop emitter geometries used in electrospray propulsion. Their ability to support liquid bulk transport enables the development of simple assemblies with interesting emission characteristics, as observed by other investigators. However, since these tip geometries are dimensionally small, usually of the microscale order, their resolution heavily depends on the granular size of the porous material. As a result, for porous-based emitters, the topology of the emitter is compromised, supporting unpredictable emission characteristics that ultimately lower the system’s thruster efficiency and operation time. Therefore, there is a need to explore other emitter substrate materials that not only support liquid transport through the bulk but also provide increased tip resolution, pushing the performance of these engines towards higher propulsive efficiencies. This work proposes the use of electroactive polymers to achieve this goal.

Since much information on the material’s behavior is readily available, Nafion\textsuperscript{TM}, an electroactive polymer, was chosen to develop smooth emitter tips. As an ongoing investigation at MIT, exploring the electrospray behavior of these new-generation ionic liquid ion sources is essential in providing performance that can inform other interested parties.

From previous examinations, smooth geometries were successfully developed, and initial preliminary testing showed evidence of electrospray activity at high firing potentials. However, little was known about the emitter’s liquid transport capabilities, especially since limited information was available concerning long-duration tests. Therefore, the work presented here is intended to add to previous findings. Evidence of sustained operations at high firing potentials and testing temperatures was confirmed by performing long-duration testing, bringing insight into a soaked single polymer emitter’s internal liquid transport mechanics.

Emission currents were flow-limited for a dry Nafion\textsuperscript{TM} emitter soaked in ionic liquid. The observation from examining the structural changes of the emitter geometry before and after testing, the emission current as a function of time and temperature, and measurements that were successfully replicated from separate test attempts informed this finding. Rapid consumption of propellant, observed at high testing temperatures, forced the geometry to starve itself, so much so that upon decreasing the firing temperature and maintaining a constant voltage, it failed to sufficiently replenish the emitting meniscus as fast as the particles were extracted. It was seen more clearly in the temperature-current plot, where the profile obtained displayed data hysteresis, such that lowering back to room temperature was met with much lower emission currents than when the testing began.

We propose an interesting hypothesis in an attempt to explain this observation. This hypothesis draws attention to the fabrication sequence employed in the emitter used in this investigation. For clarity, the polymer substrates were bonded to porous carbon substrates, with the entire geometry dried to ensure the
development of solid tips. Thus, a new interface is created, the polymer-electrode interface. Upon soaking in IL, the emitter geometry manages to swell. However, since the substrate is bonded to a solid structure, swelling happens more significantly in one direction, in the outward plane perpendicular to the porous carbon surface bonded to the polymer. This means that despite some overall volume increase in the polymer geometry, swelling is felt less at the polymer-electrode interface due to decreased freedom of motion. As a result, it is hypothesized that since less swelling occurred at this interface, most of the impedance to bulk flow was situated here, limiting the liquid transport during testing.

To fully understand the contribution this interface has to the propellant transport ability of the polymer emitter, we intend, in ongoing and future experiments, to fabricate different emitters where the sequence of steps applied is changed to alter the morphology of this interface. We propose to develop pre-saturated emitter geometries. These tips are initially fabricated with some ionic liquid already in their bulk. Doing so ensures that upon bonding the polymer to a porous electrode, the polymer-electrode interface attains a "pre-swollen" state, so to speak, allowing for improved transport. The results from this venture will be compared to emission data from soaked emitters, thus providing additional insight into the transport capabilities of polymer emitters for EP applications.

V. Conclusion

This work proposes using electroactive polymers to develop emitter geometries for EP applications. Emission behaviors over long-test durations were obtained, which provided helpful information about the emitter’s capability to transport propellant through its bulk in supporting high-voltage electrospray activity. A hypothesis was proposed to explain the observed flow-limited emission behavior, which will be addressed in more depth in future work.

Acknowledgments

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References


