Performance of Heavy Ionic Liquids with Porous Metal Electrospray Emitters

Robert S. Legge Jr.* and Paulo Lozano†

A porous metal electrospray emitter has been tested with four different ionic liquids including those comprised with heavy ions. Time of flight experiments were conducted to characterize the emitted species for each liquid and the amount of emitted current as a function of applied voltage. The results indicate that for each ionic liquid, high quality pure ions were emitted containing no observable charged droplets. Additionally, the emitters produced currents that are much higher than those reported for externally wetted needle emitters, with currents greater than 800 nA for EMI-BF₄, and greater than 200 nA for heavy ionic liquids. Propulsive figures of merit including thrust and specific impulse are given and analysis shows that while the heavy ionic liquids produce more thrust per unit current than EMI-BF₄, the reduction in emitted current causes actually performance to be lower than that of EMI-BF₄. Preliminary time-of-flight data is also given for a mixture of two ionic liquids.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>f</td>
<td>Current Fraction</td>
</tr>
<tr>
<td>Iₜot</td>
<td>Total Emitted Current</td>
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<tr>
<td>I_sp</td>
<td>Specific Impulse</td>
</tr>
<tr>
<td>L</td>
<td>Flight Distance</td>
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<tr>
<td>ṁ</td>
<td>Mass Flow Rate</td>
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<tr>
<td>n</td>
<td>Degree of Solvation</td>
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<tr>
<td>r_eff</td>
<td>Effective Radius of Curvature</td>
</tr>
<tr>
<td>Δt</td>
<td>Time of Flight</td>
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<tr>
<td>v</td>
<td>Species Velocity</td>
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<tr>
<td>V_a</td>
<td>Extraction Voltage</td>
</tr>
<tr>
<td>V_s</td>
<td>Emitter Starting Voltage</td>
</tr>
<tr>
<td>T</td>
<td>Thrust</td>
</tr>
<tr>
<td>η</td>
<td>Efficiency</td>
</tr>
<tr>
<td>λ</td>
<td>Thrust Ratio</td>
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<tr>
<td>Φ_B</td>
<td>Beam Potential</td>
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I. Introduction

Porous metal electrospray emitters are ionic liquid ion sources (ILIS’s) where the propellant is supplied to the emitter tip by passive capillary forces as needed by the electrospray emission process. Similar to externally wetted needle ILIS’s, porous metal emitters operate in the pure ionic regime at room temperature, albeit at much larger current levels due to the increase in fluid transport provided by the emitter porosity. The use of porous and externally fed emitters in vacuum is possible with ionic liquids. These liquids are molten salts at room temperature and exhibit extremely low vapor pressures. These compounds are formed by positive and negative ions which both can be directly extracted and accelerated to produce thrust when

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used in bipolar operation. Two thrusters operating with different emission polarities can also be used simultaneously to achieve overall beam neutrality and prevent the buildup of charge on the spacecraft.

Since the typical thrust of a single ILIS is on the order of 10-100 nN, there is a need to find ways to increase this thrust to make the technology feasible for a variety of space applications. One way to increase the thrust of a device is to miniaturize the individual emitters and cluster them together to create vast emitter arrays. Previous studies have shown that the amount of current emitted stays roughly constant with the miniaturization and clustering of porous metal emitters, provided that the localized tip geometry stays constant. This means that many small emitters can be clustered together to significantly increase the total amount of current produced by a device. Another way to increase the thrust given by a single electrospray emitter is to operate with ionic liquids comprised of considerably heavier ions. Previous studies using these heavier ionic liquids show that the pure ion emission regime is difficult to achieve with capillary sources, often requiring substantially elevated temperatures. Externally wetted needle emitters with heavy ionic liquids have shown that they produce high quality ions beams with narrow energy distributions at room temperature, although they tend to have small emission currents. It is proposed that porous metal emitters will produce high quality ions with substantially larger currents since they have been shown to increase the amount of current emitted over externally wetted ILIS’s.

In this paper we present an analysis of the porous tungsten emitter performance of four ionic liquids with different physical properties including ion and cation masses, conductivity and surface tension. These porous emitters allow more current per emitter than traditional externally wetted needles by allowing flow through the volume. It is proposed that high quality ion beams will be observed for heavier ionic liquids, with higher emitted currents than externally wetted devices. Time-of-flight experiments are carried out to determine the composition of the ionic beams while current measurements characterize the emitted current density as a function of the applied extraction potential. The performance of these emitters is summarized in terms of characteristics of interest to propulsion including thrust, specific impulse and a rough estimate of emitter efficiency.

II. Emitter Fabrication

The porous metal electrospray emitter was fabricated using electrochemical etching with a polyimide film masking layer. Mask fabrication was carried out at the MIT Microsystems Technology Laboratories while emitter etching was conducted at the MIT Space Propulsion Laboratory. Figure 1 shows the main steps in the process which can be used to create single emitters as well as arrays of multiple emitters. First, porous tungsten samples of 0.5 μm pore size (American Elements, Los Angeles, CA) are cut into 1.5 by 3 cm pieces using a Disco Abrasive System Model DAD-2H/6T diesaw. The samples were then filled with Shipley 1827 positive photoresist using a surface puddle technique. Then, they are spincasted to create a thin and uniform surface layer and baked to drive off remaining solvents.

Following the photoresist application, the samples were exposed on both sides with UV light in an Karl...
Suss MJB3 photomask aligner and then developed in Microposit MF-319 (Rohm-Haas). This left the surface of the porous tungsten samples clean while the porosity was blocked (Step 1). Next, a 2 \( \mu m \) layer of PI-2556 polyimide (HD Microsystems) is applied to the front side using the puddle and spincast technique, and is prebaked to drive off solvents (Step 2). Polyimide was chosen as the masking material for its resistance to Sodium Hydroxide and ability to be precisely patterned using photolithography techniques.

After the initial polyimide curing, a 5 \( \mu m \) layer of Shipley 1827 positive photoresist is applied on top of the polyimide, again, using the puddle and spincast technique (Step 2). The top layer of photoresist is then patterned by UV light exposure through a transparency mask containing the intended emitter geometry (Step 3). The sample is developed in Microposit MF-319 developer to remove the exposed photoresist areas and to etch the underlying polyimide, thereby transferring the pattern from the photoresist to the polyimide (Step 4). Acetone is then used to remove the photoresist from the samples.

Following the photoresist removal, the polyimide is cured in an oven to harden it against the electrochemical etch chemistry. The samples are then electrochemically etched in 1N Sodium Hydroxide, using stainless steel as a cathode, until the excess tungsten is removed and the emitter geometry is formed (Step 5). The polyimide masking layer is then removed in a piranha bath consisting of a 4:1 \( H_2SO_4 \) and \( H_2O_2 \) mixture and the emitters are complete (Step 6). Figure 2 shows the emitter used to conduct the time of flight measurements. The emitter has a length of 2140 \( \mu m \), a base width of 1196 \( \mu m \), an emitter thickness of 600 \( \mu m \) and tip radius of curvature of 8.25 \( \mu m \) and 9.77 \( \mu m \) in the two principal directions, giving an effective tip radius of curvature of 4.47 \( \mu m \), calculated by Equation 1.

\[
rc_{,eff} = \frac{rc_1rc_2}{rc_1 + rc_2}
\]  

(1)

The predicted starting voltage \( V_s \) is then a function of the emitter tip geometry and ionic liquid properties as given in Equation 2. This starting voltage for EMI-BF\(_4\) is 430.6 V, while it is 343.4 V for EMI-Beti.

\[
V_s = \sqrt{\frac{\gamma (rc_1 + rc_2)^3}{2\varepsilon_0 rc_1rc_2}}
\]  

(2)

Figure 2. Micro-fabricated porous Tungsten electrospray emitter with 0.5 \( \mu m \) porosity

III. Experimental Setup

The extractor used in this experiment consisted of a stainless steel plate with a 1.5 mm circular aperture. The emitter was aligned such that the emitter tip was aligned with the entrance plane of the extractor aperture using a clamping assembly mounted on a movable xy stage. A Matsusada AMS-5B6 bipolar high voltage power supply is connected to the emitter and provides the extraction voltage difference \( V_a \) between the emitter and the grounded extractor.

The single gate time of flight setup has been described in detail elsewhere. A diagram of the time-of-flight assembly is shown in Figure 3. Briefly, the emitter assembly is aligned to the entrance of a three electrode Einzel lens, which provides beam focusing and collimation with a focusing voltage \( V_f \) similar to the extraction voltage. Following the Einzel lens, an electrostatic gate comprised of interleaved wires is attached to an amplifier driven by a BNC-555 pulse generator. When the gate is turned on, the amplifier biases the grids to \( \pm 900V \), and the beam is deflected so that no current reaches the collector, located...
a distance of 750-765 mm away. The collector plate is a 38 mm diameter metallic plate connected to an Agilent Oscilloscope after having the signal amplified by a MAX477 high speed amplifier. Secondary electron emission is suppressed by a grid biased to -50V just prior to the collector plate.

Figure 3. Time-of-flight experimental setup

Materials: The porous metal emitter is to be characterized with four ionic liquids of differing physical properties including: ion mass, conductivity and surface tension. Their properties are given in Table 1. The ionic liquids to be tested in order of increasing ion mass are: EMI-BF$_4$ (1-ethyl-3-methylimidazolium tetrafluoroborate), EMI-IM (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonylimide), EMI-Beti (1-ethyl-3-methylimidazolium bis(pentafluoroethyl) sulfonylimide), and C$_5$MI-(C$_2$F$_5$)$_3$PF$_3$ (1-methyl-3-pentylimidazolium tris(pentafluoroethyl) trifluorophosphate). For the rest of the paper, C$_5$MI-(C$_2$F$_5$)$_3$PF$_3$ will be referred to as MPI.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Anion Mass [amu]</th>
<th>Cation Mass [amu]</th>
<th>Surface Tension [dyn cm$^{-1}$]</th>
<th>Density [kg m$^{-3}$]</th>
<th>Conductivity [$\mu$S m$^{-1}$]</th>
<th>Viscosity [cP]</th>
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<tr>
<td>EMI-BF$_4$</td>
<td>111.2</td>
<td>86.8</td>
<td>45.2</td>
<td>1240</td>
<td>1.4</td>
<td>38</td>
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<tr>
<td>EMI-IM</td>
<td>111.2</td>
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<td>1517</td>
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<tr>
<td>EMI-Beti</td>
<td>111.2</td>
<td>380.15</td>
<td>28.75</td>
<td>1600</td>
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<td>MPI$^4$</td>
<td>153.24</td>
<td>445.01</td>
<td>30.33</td>
<td>1590</td>
<td>0.16-0.229</td>
<td>140</td>
</tr>
</tbody>
</table>

Table 1. Properties of the ionic liquids tested.

IV. Theory

The time of flight experiments measure the time that it takes each emitted species to travel from the electrostatic gate to the collector plate. The charge to mass ratio can then be calculated from this experimental time of flight $\Delta t$, the known gate to collector distance $L$ and the beam potential $\phi_B$ through an energy balance:

$$\left( \frac{q}{m} \right) = \frac{(L/\Delta t)^2}{2\phi_B}$$  \hspace{2cm} (3)

It has been previously seen that $V_a$ approximates the beam potential to within 99%$^8$ and therefore is used to estimate $\Phi_B$ in the absence of direct beam energy measurements. Assuming that the beam is comprised of only singly charged particles, the mass corresponding to each observed species is then:

$$m = \frac{2eV_a}{(L/\Delta t)^2}$$  \hspace{2cm} (4)
Propulsive parameters including the mass flow rate, specific impulse, thrust and polydispersive efficiency \((\eta_p)\) can be estimated following the identification of the beam species. The polydispersive efficiency is a measure of how having emitted species with dissimilar specific charge contributes to the overall inefficiencies of the system and is a good measure of overall efficiency.\(^{12}\) The mass flow rate for each species is estimated as the total amount of current emitted by each species divided by the corresponding charge to mass ratio:

\[
\dot{m}_i = \frac{f_i I_{tot}}{q\cdot m_i}
\]  

(5)

Where \(f_i\) is the \(i^{th}\) species current fraction and \(I_{tot}\) is the total emitted current. The thrust is then given as:

\[
T = \sum_i \dot{m}_i \left( \frac{L}{\Delta t} \right)_i
\]  

(6)

The specific impulse and the polydispersive efficiency\(^{12}\) estimation considering only the monomer and dimer contributions is:

\[
I_{SP} = \frac{T}{\dot{m} g}
\]  

(7)

\[
\eta_p = \frac{\left[ 1 - (1 - \sqrt{\xi}) f_0 \right]^2}{1 - (1 - \xi) f_0}
\]  

(8)

Where \(\xi\) is the specific charge ratio of the monomer to dimer and \(f_0\) is the monomer current fraction. For the simplified case in which we only consider the contributions from the monomer and dimer, these are given as:

\[
\xi = \frac{(q/m)_2}{(q/m)_1} \quad f_{n=0} = \frac{I_0}{I_0 + I_1}
\]  

(9)

Where \(I_0\) is the total monomer current and \(I_1\) is the total dimer current.

V. Experimental Results

The 8 subplots displayed in Figure 4 show the time of flight spectra obtained for the four ionic liquids tested in each polarity. The plots on the left show the collected current as a function of species mass, where the mass was found from the flight time \(\Delta t\) using Equation 4. The vertical lines show the masses corresponding to the expected emitted species and include the monomer, the dimer as well as the trimer for some liquids. The plots on the right show the collected current as a function of time showing that there were no observed droplets for any of the ionic liquids. Table 2 gives more detailed data collected during the TOF experiment including: the time of flight, the species velocity, the corresponding ion mass, the ion energy, and the species contribution to the total collected current. The ion energy is composed mostly of the kinetic energy calculated from the species velocity obtained by the time of flight experiment. The energy is given by the following equation:

\[
E = \frac{1}{2} m \left( \frac{L}{\Delta t} \right)^2
\]  

(10)

Figure 4A shows the results obtained for EMI-BF\(_4\). In the positive mode \((V_a = 2590 \text{ V})\), there is roughly a 68% current contribution from the monomer \(([\text{EMI}]^+)\), a 29% contribution from the dimer \(([\text{EMI-BF}_4][\text{EMI}]^+)\) and less than 2.5% of indistinguishable heavier ions. In the negative mode \((V_a = -2710 \text{ V})\), the monomer \(([\text{BF}_4]^-)\) contributes around 53% of the current, the dimer \(([\text{EMI-BF}_4][\text{BF}_4]^-)\) contributes 43% and the trimer \(([\text{EMI-BF}_4][\text{BF}_4]^-)\) contributes 5%. The TOF results for EMI-IM are shown in Figure 4B. In the positive mode \((V_a = 2490 \text{ V})\), there are almost equal contributions of the monomer \(([\text{EMI}]^+)\) and dimer \(([\text{EMI-BF}_4][\text{EMI}]^+)\), and roughly 0.5% heavier ion current. In the negative mode \((V_a = -2410 \text{ V})\), we see a 64% monomer current \(([\text{IM}]^-)\) and a 33% dimer current \(([\text{EMI-IM}][\text{IM}]^-)\), with less than 3% of heavier ions.

EMI-Beti results are shown in Figure 4C. In the positive mode \((V_a = 2490 \text{ V})\), there are almost equal contributions of the monomer \(([\text{EMI}]^+)\) and dimer \(([\text{EMI-Beti}][\text{EMI}]^+)\). The trimer \(([\text{EMI-Beti}][\text{EMI}]^+)\) and
Figure 4. Time of flight results for the ionic liquids EMI-BF$_4$ (subplot A), EMI-IM (subplot B), EMI-Beti (subplot C), and MPI(subplot D). On the left, the normalized current is plotted as a function of species mass as given by Equation 4. Note that the x-axis is not equal for the different ionic liquids due to the increasing ion masses. On the right, the normalized current is plotted vs time showing that all liquids are being emitted in the pure ionic regime with no droplets.
Table 2. Time of flight results for the four ionic liquids tested showing some measured quantities including: the time of flight, the species velocity, the corresponding ion mass, the calculated ion energy, and the species contribution to the total collected current. The energy to $V_a$ ratio is a measure of how well the TOF spectrum corresponds to the expected species, and all values fall within experimental error.
tetramer ([EMI-Beti]₄[EMI]⁺) account for less than 6% of the total collected current, but display large masses of 1094 and 1595 amu respectively. In the negative mode (Vₐ = -2910 V), we see a 56% monomer current ([Beti]⁻), a 33% dimer current ([EMI-Beti][Beti]⁻) and a 6% trimer current ([EMI-Beti]₂[Beti]⁻), with less than 5% of heavier ions. Figure 4D shows the TOF results for the ionic liquid MPI. In the positive mode (Vₐ = 2910 V), there is a 66% current contribution from the monomer ([C₅MI]⁺), a 31% contribution from the dimer ([MPI][C₅MI]⁺), and less than 3% contributions from the trimer ([MPI]₂[C₅MI]⁺) and heavier ions. In the negative mode (Vₐ = -2590 V), the monomer ([C₂F₅₃PF₃]⁻) comprises 58% of the total current, the dimer ([MPI]₂([C₂F₅₃PF₃]⁻) is 31% while the trimer and heavier ions contribute around 10%. As with the other three ionic liquids tested, there were no observed droplet emission.

The current emitted as a function of applied voltage was also measured and is shown in Figure 5. We see that as the average mass of the ionic liquid increases, the amount of current emitted decreases. It is important to note that the current emitted by the porous emitter far surpasses that shown to be emitted from externally wetted needle emitters.

![Figure 5. Emitted Current vs. Applied Voltage](image)

VI. Significance to Propulsion

As was given in Equation 6, the thrust produced by an emitter is equal to the total mass flow rate times the effective ion exhaust velocity. By combining Equation 6 and Equation 5, we obtain:

\[
T = \frac{I_t}{(q/m)} \sqrt{\frac{2}{m} V_a} = I_t \sqrt{\frac{2V_a m}{q}}
\]  

(11)

If we use the thrust produced by EMI-BF₄ as a reference, and take the ratio of the thrust of some heavy ionic liquid \(T_H\) to that of EMI-BF₄ \(T_{BF_4}\) given the same acceleration voltage, then we arrive at the following relationship:

\[
\frac{T_H}{T_{BF_4}} = \frac{I_H}{I_{BF_4}} \sqrt{\frac{m_H}{\bar{m}_{BF_4}}}
\]  

(12)

Therefore, for a heavy liquid to produce more thrust for a given emitter than EMI-BF₄, then the following inequality must be met where \(\lambda\) is the critical ratio of currents required to match the thrust obtained by EMI-BF₄.

\[
\lambda = \frac{I_H}{I_{BF_4}} > \sqrt{\frac{m_{BF_4}}{\bar{m}_H}}
\]  

(13)

The time of flight experiments allow us to calculate the average ion mass being emitted during bipolar operation (both polarities are averaged together), the average charge to mass ratio and the square root of
the ion mass ratio. These are shown in Table 3. Taking the measured current magnitudes for each liquid at $V_a = \pm 2200$ V, we can calculate the average current for bipolar operation, the actual ratio $\lambda$, the thrust and the specific impulse. We see that the porous metal emitters do not emit enough current to make the heavier ionic liquids produce more thrust than EMI-BF$_4$ given the same applied voltage. They do operate with lower specific impulses which could be beneficial to some in space applications. Further studies are needed to see if the heavier ionic liquids will emit comparable currents to EMI-BF$_4$ with higher applied voltages.

$$\text{Liquid} \quad \bar{m} \quad \frac{\bar{q}}{\bar{m}} \quad \sqrt{\bar{m}_{BF_4}/\bar{m}_{H}} \quad \bar{I}^* \quad \lambda \quad \bar{T}^* \quad I_{SP}^* \quad \eta_p$$

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\bar{m}$</th>
<th>$\frac{\bar{q}}{\bar{m}}$</th>
<th>$\sqrt{\bar{m}<em>{BF_4}/\bar{m}</em>{H}}$</th>
<th>$\bar{I}^*$</th>
<th>$\lambda$</th>
<th>$\bar{T}^*$</th>
<th>$I_{SP}^*$</th>
<th>$\eta_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMI-BF$_4$</td>
<td>184.38</td>
<td>523.29</td>
<td>1.00</td>
<td>695.88</td>
<td>1.00</td>
<td>0.064</td>
<td>4891</td>
<td>0.929</td>
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<td>EMI-IM</td>
<td>362.83</td>
<td>265.92</td>
<td>0.71</td>
<td>236.85</td>
<td>0.34</td>
<td>0.030</td>
<td>3487</td>
<td>0.917</td>
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<tr>
<td>EMI-Beti</td>
<td>544.18</td>
<td>177.30</td>
<td>0.58</td>
<td>214.33</td>
<td>0.31</td>
<td>0.034</td>
<td>2847</td>
<td>0.910</td>
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<tr>
<td>MPI</td>
<td>581.80</td>
<td>165.84</td>
<td>0.56</td>
<td>102.13</td>
<td>0.15</td>
<td>0.017</td>
<td>2754</td>
<td>0.907</td>
</tr>
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</table>

* at 2200 V

Table 3. Comparison of Propulsive Performance at an applied voltage of 2200V

Another possibility is that ionic liquids can be mixed together to enhance performance and balance between the high current operation with light ionic liquids and the desirable large ions contained in heavy ionic liquids. Preliminary analysis indicates that emitters will emit both ionic liquids. Figure 6 shows the time of flight response for a mixture of EMI-IM and EMI-Beti and clearly shows the monomer, dimer and trimer of both ionic liquids.

![Figure 6. TOF spectra for the positive polarity showing a mixture of EMI-IM and EMI-Beti ions](image)

VII. Conclusions

Our results show that electrospray emitters fabricated from porous tungsten emit in the pure ionic regime for a wide variety of ionic liquids, including liquids comprised of heavy ions. We have seen that the emitted beams primarily consist of monomer and dimer contributions with small contributions of heavier ions and the currents produced by porous metal emitters are significantly larger than those observed with externally wetted emitters. Additionally, the amount of emitted current falls as the average ion mass within the liquid increases. The reason behind this trend is related to both the liquid viscosity and conductivity, and identifying the precise role of each will be the target of future research.
Acknowledgments

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References


