Characterization of Conical Ionic Liquid Ion Sources for 2-D Electrospray Thruster Arrays on Porous Substrates

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Emission data from a new geometry of Ionic Liquid Ion Sources using porous materials are presented. Ionic liquids are molten salts at room temperature which have near zero vapour pressure. When used in electrospray thrusters, these sources provide an efficient thrust mechanism and, due to their low vapor pressure, eliminate the need for complex propellant feed systems. By emitting pure ion beams rather than mixed ion/droplet emission, small high efficiency thrusters capable of providing specific impulse levels of several thousand seconds can be realized. The latest developments of these thrusters, using conical emitters micro-fabricated from porous substrates, are presented. Porous substrates provide liquid flow over a wide range of emitted currents, accommodating steady, stable emission of ion beams. Conical type emitters, fabricated on a planar porous substrate are well suited for high density 2-D arrays as they allow for both passive propellant feed through the bulk and simplified grid alignment compared with arrays formed from multiple emitter array substrates. This paper confirms that such conical emitters can provide beam currents of 100's of nA up to several μA with beams composed of pure ions with no charged droplets detected, as has previously been observed using alternative emitter geometries.

Key Words: Micropropulsion, Electrospray, Ionic Liquids, Porous Emitters, ILIS

Nomenclature

c	: exhaust velocity (m/s)
F	: thrust (N)
I	: current (C/s)
I_{sp}	: specific impulse (s)
L	: transit distance (m)
m	: mass (kg)
$\dot{m}$	: mass flow rate (kg/s)
q	: charge (C)
t	: transit time (s)
V	: electric potential (Volts)
λ	: ratio of monomer flow to net flow

Subscripts

spec. : charged species

1. Introduction

This paper presents emission data from a new geometry of porous tungsten Ionic Liquid Ion Source (ILIS) developed at the Massachusetts Institute of Technology (MIT), Space Propulsion Laboratory (SPL). Electrospray thrusters encompass a variety of configurations, all of which extract charged species from a liquid by means of applied electrostatic forces. These include colloid thrusters, Field Emission Electric Propulsion (FEEP), and Ionic Liquid Ion Sources (ILIS). This research is concerned with the later, ILIS. Specifically conical ILIS created from porous tungsten. Ionic liquids, such as EMI-BF₄ (1-Ethyl-3Methyl-imidazolium Tetrafluoroborate) are synthetically formed molten salts composed of cations and anions in a mixture. They are characterized by extremely low vapor pressures, surface

tensions much lower than liquid metals and high electrical conductivities^{1,2)}. As in colloid thrusters, ILIS tips rely on a balance between liquid surface tension and the applied electric field, resulting in a so called *Taylor cone*²⁾, see Fig. 1. At the cone apex, emission of charged droplets, ions, or a combination of both can result depending on the liquid, the extraction fields and the flow rate. The thrust produced from a single Taylor cone is very low, typically $<1 \mu\text{N}^3)$, as a result, current research has been directed towards developing high density arrays of emitters.

Fig. 1. Schematic view of a Taylor cone formed on the tip of an emitter due to an applied electric field.

Using ionic liquids as ion sources allows for high efficiencies not easily obtained by colloid thrusters. Specifically, the overall thruster efficiencies obtainable using EMI-BF₄ ILIS were considered by Lozano⁴⁾ and are expected to lie between 85% and 90%. Particular benefits include the highly defined emission species from ionic liquids. Colloid thrusters, extracting droplets from a solvated salt, may yield droplets of varying specific charge (q/m)³⁾. ILIS emitters have

Fig. 2. Cross sectional illustration of a proposed 2-D porous Ionic Liquid Ion Source (ILIS) electrospray thruster.

been shown to primarily emit only monomer and dimer species for a range of ionic liquids when emitting both positive and negative ion species^{1,3)}. The result being a significant increase in the obtainable polydisperse efficiency⁴⁾ which is a measurement of the power lost accelerating particles with dissimilar specific charge.

Several methods of supplying liquid at the emission site exist: capillary tube emitters supply fluid to the tip through a small tube or hollow needle⁵⁾, while externally wetted emitters^{1,6)} draw liquid along the external geometry to the emission site by means of capillary forces. Porous emitters, presented here, accommodate liquid transport from a reservoir, through the bulk to the tip by means of capillarity, while allowing sufficient hydraulic impedance to sustain emission at low currents.

Implementing a porous bulk provides several enhancements over both colloid thrusters and externally wetted ILIS: (1) Vapour lock, or other clogs often found with tube type colloid emitters are no longer a concern due to the elimination of a single liquid path, (2) inconsistencies previously attributed to non uniform wetting when using externally wetted 2-D arrays are eliminated⁹⁾, and (3) the high liquid transport capabilities and micro-roughness of the porous surface allow for reduced start up voltages resulting in a wide range of stable operating currents³⁾.

1.1. ILIS sources for spacecraft propulsion

When used in a thruster configuration, the emitters would be arranged in a fashion similar to Fig. 2. As depicted in the figure, the characteristic low vapor pressure of ionic liquids, in combination with the porous bulk allow for a simple liquid supply system mounted directly behind the emitter array without the need for heavy pressure vessels, valves or other actuators commonly required with other thruster types. This capability represents a significant mass and volume savings when compared with alternative propulsion systems. The only additional components required would be the high voltage power supplies and basic control circuitry.

By using ionic liquid propellants, the ionization requirement, which inherently consumes power and can add to the physical mass in other electrostatic thrusters, can be eliminated. Furthermore, the ability to operate efficiently in both the negative and positive ion regimes allows for

electrospray thrusters to operate without the need for the external neutralizers often required with electrostatic propulsion. Hence charge neutralization can be ensured through balancing the emitted charge from two thrusters firing simultaneously at opposite polarities.

Alignment between emitters and electrostatic grids must be considered to ensure an efficient device and prevent grid degradation. For example, Gassend⁶⁾ employed an alignment mechanism for externally wetted emitters that could also be applied to porous ILIS. The results presented here focus on emission properties alone without incorporating an integrated grid structure.

1.2. Previous ILIS emission measurements

Tungsten needles, both externally wetted¹⁾ and porous^{3,7)} have been used extensively with EMI-BF₄. Electrochemical decomposition of the liquid and concomitant damage to the tungsten has been observed; however it has been shown that these effects can be prevented through alternating the extraction potential at rates on the order of 1 Hz⁸⁾. This potential alternation, which must be incorporated into functional ILIS thrusters, suppresses lifetime limitations by preventing breakdown of both the Ionic Liquid propellant and

Fig. 3. Sample flat needle arrays of varying spacing and geometry, fabricated by Legge^{3,6)}. Image source: Legge³⁾.

the emitter surfaces. Long term testing with porous emitters has not been completed. However, using externally wetted emitters, Lozano⁸⁾ did not observe any electrochemical effects after 220 hours of continuous operation.

Recently Legge^{3,7)} demonstrated that porous substrates could be used to create planar thruster arrays by etching sharp tips from thin porous substrates. Samples of the emitter geometries are shown in Fig. 3. Emitters of this form are referred to as flat emitters here. Using flat emitters, with tip curvature radii of approximately 10 μm , it was observed that beam currents from 10's of nA up to several μA per emitter

were obtainable in both negative and positive polarities. As with externally wetted emitters it was confirmed that when using EMI-BF₄ only monomer and dimer species were emitted.

Legge applied these results to create a prototype thruster using 49 flat porous emitters³⁾. The thruster demonstrated that thrusts on the order of 0.05 μ N per emitter could be obtained with emitter currents of approximately 1 μ A per emitter at roughly $\pm$ 1.5 kV total applied voltage. The corresponding average specific impulse was measured to be approximately 3000s at these conditions. Flat arrays were fabricated with linear separations as low as $\sim$ 0.5 mm, as in Fig. 3. However, the required separation between rows within a thruster is limited by, for example, the substrate thickness and support material, making the perpendicular separation much larger, on the order of millimeters. Hence, the 2-D emitter packing density of such a device is limited, further explanation is available in the reference.

1.3. Conical, porous ILIS motivation and approach

The intention of the experiments presented in this paper has been to establish the suitability of using conical type porous ILIS, similar to that shown schematically in Fig. 4. Specifically, the goals are to establish if conical emitters can produce controllable emission comparable with flat emitters with a beam composed only of pure ions. By creating planar 2-D arrays of conical emitters high packing densities and reliable grid alignment can be achieved compared with 2-D arrays produced from several flat strips of emitters^{3,7)}, as discussed in the previous section.

In order to justify compatibility between the characteristics of flat emitters, observed by Legge, to the high density 2-D conical emitter arrays proposed; this work focuses on emission from a single conical emitter. To ensure consistency with the flat emitters created by Legge, conical emitters with

Fig. 4. Schematic view of the emitter geometry created here. The emitters were fabricated using the etching process outline in Fig. 5.

tip radii less than 15 μ m were required, as in Fig. 4. For this study, coarsely separated emitters were desirable so as to monitor etch uniformity and allow for single emitter characterization. An array of 30 emitters, spaced 2.0 mm apart was fabricated using micro-fabrication techniques. This low packing density was intentionally selected in order to easily isolate the emission from a single emitter without interference from adjacent emitters. An emitter with appropriate dimensions was then isolated and ion emission characteristics from this single emitter were recorded. The data, including beam current measurements along with

measurements of the beam composition using Time of Flight (TOF) spectroscopy, are hence intended as a baseline for further development of 2-D emitter arrays. These data are then compared with the previous studies by Legge discussed in section 1.2.

2. Experimental Characterization of Porous Conical ILIS

2.1. Fabrication of conical emitters

The emitters have been fabricated from bulk tungsten samples with approximately 0.5 μ m pores (American Elements Co.). Due to the porous substrate many micro-fabrication techniques which require liquid layers to be applied to the wafer surface, for example applying photoresist, were not possible or risked contamination of the bulk. Legge⁶⁾ developed a technique for applying a polyimide mask to a porous substrate using sacrificial photoresist to temporarily clog the pores. However possible bulk contamination, which affected the etching quality, was observed particularly when attempting to create conical emitters similar to those presented here. As an alternative we have employed dry masking techniques.

The fabrication process is outlined in Fig. 5. Electrochemical etching within sodium hydroxide (NaOH) solution provided a locally isotropic wet etch technique which favored the tungsten surface, without etching the internal pores. This method has significant heritage when used to create tungsten electrospray needles^{1,6)}. DuPont Vacrel dry-film negative working photo-definable solder mask was identified as a suitable etch mask with sufficient selectivity in NaOH compared with tungsten. Due to the film thickness ($\sim$ 100 μ m) this mask may not be suitable for higher density or physically smaller emitters. The mask was patterned using transparency masks and a 200W Karl Suss MJB3 UV photomask aligner. The Vacrel masked used here consisted of 30 dots, 500 μ m in diameter, spaced 2 mm apart. Etching was performed in 1 N solution of NaOH with 5 V applied between the tungsten and a stainless steel cathode for a 4 hour period.

Fig. 5. Photomask and sketches of the tungsten substrate before and after etching through the Vacrel mask.

Examples of the fabricated emitters are shown in Fig. 6. As shown in the figure, significant variations in emitter geometries were observed. However, some emitters(a,c) shown in the figure, possessed the desired <15 μ m tip radii and were deemed suitable for obtaining sample emission profiles from a conical emitter. The emitter heights, measured using images, were between 150 and 200 μ m.

Fig. 6. High resolution images demonstrating variation between emitters fabricated on a single substrate. Tips similar to a) and c) were deemed suitable for emissions test while b) and d) were not tested.

2.2. Experimental configuration

Experiments were performed at SPL within a 20 cm diameter, 40 cm long vacuum chamber pumped by two Varian turbopumps. Vacuum levels below 5×10^{-5} Torr were maintained throughout all data presented here. A 36.8 cm long, 3.8 cm diameter extension tube was used to increase the chamber length and house the time of flight detector described below.

In order to extract species from a single conical emitter, the assembly shown schematically in Fig. 7 was used. The assembly consists of a grounded ring extractor made from 0.25 mm diameter stainless steel wire wound into a 1mm diameter loop and mounted on a 3 axis stage assembly. Using a microscope, the extractor was aligned such that the emitter tip was centered within the loop and the emitter tip was aligned axially with the base of the extractor loop with an estimated accuracy of 25 μm .

A collecting plate was placed 1.5 cm from the emitter assembly and grounded through a current amplifier (Keithley 338). The emitter was biased, through a 300 k Ω resistor, using a voltage amplifier (Matsusada AMS-5B6) controlled by a signal generator (Agilent 332200A). In order to prevent electrochemical effects, as discussed in section 1.2, the

Fig. 7. Schematic overview of the apparatus used to extract ion beams from a single conical emitter.

emitter potential was alternated at 0.5 Hz. The signal amplitude was varied by linearly increasing the signal from 0 to 100% over a 100 s period. The resultant time dependant emitter to extractor potential is shown in Fig. 8.

The assembly shown in Fig. 7 was then employed (with the collector plate removed) as a source for beam spectroscopy. Here a time of flight apparatus described previously^{1,3)} was used to evaluate the transit time of ions across a fixed 72.6 cm distance. This distance corresponds to that between an electrostatic gate and a collecting plate. With the ion source active at a fixed extraction potential, the electrostatic gate allows for short bursts of the beam to traverse the chamber toward the collector. Species of different charge to mass ratios will have different velocities and hence transit times. The recorded transit time can then be interpreted as a measurement of the species charge to mass ratio. Further details of the setup are available in the cited references.

The resistor was used to measure the emitted current by monitoring the voltage drop through the resistor using a multimeter (Fluke 21 III) floating with the emitter potential. This measurement was used, along with collected current data, to make estimates of the transmitted to emitted current ratio. As no means for measuring AC waveforms while floating at high voltage were available, a relatively small set was taken with DC signals applied for short durations (a few seconds) to minimize electrochemical contamination.

3. Characterization Results

Fig. 8. Applied extractor voltage and current collected averaged over 6 trials, each lasting 100 seconds.

3.1. Collected current

Figure 8 gives the collected current and the corresponding applied voltage as a function of time, averaged over 6 full (100 s) scans. In Fig. 9 the current magnitude is plotted against applied voltage. Here the approximate current at a given voltage has been extrapolated from Fig. 8 with indicated uncertainties corresponding to the statistical noise over each half period of voltage variation. In both positive and negative states current emission started at roughly 1.25 kV applied voltage. Two trends were visible with a transition to a greater slope at roughly ± 1.75 kV applied. The applied voltage was kept below ± 2.5 kV as high voltage breakdowns between the emitter and mounting structure were observed when manually increasing the voltage above ± 3.0 kV. By maintaining the range of potentials shown in Figs. 8 and 9 no

breakdowns were observed.

At a sample set of 8 extractor potentials, both positive and negative, the emitter current was monitored using the inline resistor as described in section 2.2. The data are presented in Fig. 10. Using these results the estimated beam current was found, on average to be 70 +/- 10 % of the emitter current. Further experimentation will be required in order to determine if the excess emitter current corresponds to current from the tip under test being collected by the extractor, or if it stems from other emission sites on the array substrate. If the former were confirmed then a more ideal extractor assembly could yield beam currents higher than those reported here.

Fig. 9. Magnitude of current collected at the indicated emitter to extractor potentials.

Fig. 10. Magnitude of currents emitted and collected at a set of applied voltages when operating for short time in a DC configuration.

3.2. Beam composition

Figure 11 and Table 1 present sample data collected at accelerating potentials of +/- 2.75 kV using the time of flight spectrometer. These data are representative of similar scans at other extractor potentials. Table 1 provides the mean transit times where step changes in collected current were observed. Given the accelerating potential and transit distance the data can be presented in terms of species mass in Fig. 11 using equation 1 if the ions are singly charged. As shown in the figure and table the results are in good agreement with known monomer, dimer and, in the negative case, trimer ion species. This agreement with known masses justifies the assumption of

singly charged ions. For example if the ions were multiply charged, lower transit times would result and the peaks would occur at lower values when plotted on the scale of Fig. 11. Hence, they would not coincide with the known mass values.

$$m_{spec.} = 2qV\left(\frac{t}{L}\right)^2 \quad (1)$$

Table 1. Tabulated time of flight measurements.

Polarity	Time (μs)	Velocity (km/s)	q/m (C/g)	Mass (a.m.u.)	Ion Candidate	Ion Mass (a.m.u.)
Positive	10.6	68.5	853.1	113.6	[EMI] ⁺	111
	17.4	41.7	316.3	306.3	[EMI-BF ₄][EMI] ⁺	309
Negative	9.5	76.4	1061.3	91.3	[BF ₄] ⁻	87
	17.1	42.4	326.9	296.4	[EMI-BF ₄][BF ₄] ⁻	285

Fig 11. Time of flight results and known species masses, expressed as a function of species mass by assuming all species are singly charged.

4. Discussion

These results have demonstrated that the conical type geometry of porous ILIS is capable of producing a range of currents with control through the applied voltage. Thus the porous substrate is capable of supplying propellant to the emission site passively without external flow systems at a rate dictated by the applied field. Furthermore, the results of section 3.2 have confirmed the emission if purely ionic.

4.1. Comparison with flat porous emitters

The data presented in Figs. 8 and 9 can be compared with that provided by Legge³⁾ for flat porous ILIS, introduced in section 1.2. Overall these preliminary results demonstrate good agreement with the emission capabilities of flat porous arrays. Similar to Fig. 9, Legge observed emission from several 10's of nA up to roughly 5 μA over the range of applied voltages used here. See Table 2 for details. Contrary to the results of this work, Legge observed relatively higher currents with negative extractor potentials compared with those at positive potentials. However, these experiments did not include a means for suppressing secondary electron emission from the collector plate. Emitted secondary electrons would alter the measured currents by effectively increasing the positive current and decreasing the negative current observed. Hence, it can be postulated that the relatively higher positive currents observed here may have been caused by this effect. As Legge³⁾ did include measures to suppress secondary

emission, this may also account for the discrepancy between studies. In order to match those trends, a correction to the data presented here by as much as 20% may be required; however this must be confirmed through further experimentation.

The change in voltage dependence around ± 1.75 kV may arise from a localization of the emission site from several points on the surface to a single Taylor cone. Although a transition from a low to high slope in the current with increasing voltage has been observed with the flat emitters, the transition was not as pronounced as that observed here. Start up voltages between ± 1 kV to ± 1.5 kV, similar to those seen in this study, were reported by Legge. However; the emitter to extractor distances and geometry were not completely consistent between studies meaning detailed comparison of start up voltages may not be suitable.

The beam composition results of Fig. 11 and Table 1 are also compatible with those observed by Legge³⁾. Specifically, in both cases no droplets were observed. Droplets are characterized by low magnitude, variable charge to mass ratios. In Fig. 11 droplets would be manifested by a slowly decreasing signal extending out to high mass values, this was not seen for any accelerating potential in either positive or negative polarities. One point of discrepancy between these data and those observed by Legge is the relative ratio of signal from monomer ions compared with heavier solvated ions. The use of an electrostatic lens in the time of flight apparatus³⁾ and the narrow portion of the beam intercepted by the collector mean that quantitative analysis of such ratios cannot be performed using this apparatus.

4.2. Estimated propulsive properties

Using the beam characterization results given in Table 1 we can confirm that in both the positive and negative cases the beam is dominated by the monomer and dimer ions (the contribution of trimer ions in the negative case is small). The range of obtainable thrusts and specific impulse can then be estimated given the current emission results of Fig. 9. Here the thrust and specific impulse are given by equations 3 and 4, respectively.

$$\dot{m}_{spec} = I * R_{spec} / q \quad (2)$$

$$F = \sum_{spec} \dot{m}_{spec} c_{spec} \quad (3)$$

$$I_{sp} = F \lambda / \left(g \sum_{spec} \dot{m}_{spec} \right) \quad (4)$$

In equation 2, R_{spec} is the ratio of the species to the net ($\sim$ monomer and dimer) species. Despite the inherent inaccuracies expected from the apparatus when measuring this ratio, discussed in section 4.1, observing Fig. 11 the monomer ratio was estimated to be 0.5 and 0.4 for the positive and negative polarities respectively. In equation 4, λ is the ratio of beam flow to emitted flow (~ 0.7 here) taking into account intercepted current. Using equations 2 through 4 and given the current from Fig. 9, predicted thrusts and specific impulses result and are presented in Table 2. Also shown are sample results of Legge^{3,7)} using flat emitters over similar voltage ranges. It should be noted that the measurements made by

Legge were not made with an ideal extractor assembly and may have suffered from current leakage at higher potentials³⁾. The relatively poor agreement with the predicted results at high voltage/thrusts was therefore not completely unexpected.

Table 2. Comparison between flat and conical porous ILIS.

Type	Polarity	Current Magnitude (μ A)	Thrust (μ N)	Specific Impulse (s)
Conical	Positive	0.3 to 5.8	0.02 to 0.56	2350 to 3250
	Negative	0.1 to 4.8	0.01 to 0.46	2400 to 3300
Flat (Legge ^{3,7)})	Positive	~ 0.01 to 4.5	0.02 to 0.12	2900 to 5500
	Negative	~ 0.01 to 7.0	0.02 to 0.05	2100 to 3800

5. Conclusion

It has been demonstrated that porous ILIS emitters of the conical type can be used to emit both positive and negative ion species with beam currents up to several μ A. The current can be controlled by means of the applied voltage and flow was supplied passively through capillarity within the porous bulk. The emission magnitudes and beam composition were comparable with previously studied flat emitters. These results support the ongoing development of densely packed 2-D porous ILIS micro-thruster arrays. Current fabrication techniques must be improved in order to achieve high packing densities and uniform emitter geometries.

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