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Technical Notes

Fragmentation in Time-of-Flight Spectrometry-Based Calculations of Ionic Electrospray Thruster Performance

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Nomenclature

c_k = speed of species k, m/s
f = fraction of solvated ions that fragment
$\bar{I}$ = normalized collected current
I_b = total thruster beam current, A
I_{sp} = specific impulse, s
K_k = kinetic energy of species k, J
L = time-of-flight distance
$\dot{m}$ = calculated mass flow rate, kg/s
m_k = mass of species k, kg
q = ion electric charge, C
T = calculated thrust, N
t = flight time
V_0 = applied (maximum) potential, V
V_1 = electric potential at point of breakup, V
Z^* = metric Z corrected for fragmentation
α_n = current fraction due to ion solvation n
Γ = particle emission rate, particles/s
η = propulsive efficiency

I. Introduction

TIME-OF-FLIGHT (TOF) spectrometry measurements have been frequently applied to calculate the performance of electrospray propulsion systems [1–4], where the emitted beam may comprise a wide range of species mass-to-charge ratios. Electrospray sources targeting purely ionic emissions, without large droplets, are currently in active development due to the associated high specific impulse and power efficiencies [2,4–6]. Tending to emit ions from room-temperature ionic liquids (ILs), such sources are often referred to as ionic liquid ion sources (ILIS). In this Note, we show that, in some instances, TOF-based calculations that do not correctly account for fragmentation of accelerating solvated ions may underestimate ILIS thrust and mass flow rate by 10% or more.

Figure 1 provides a normalized, schematic overview of a typical ILIS TOF measurement made with a Faraday cup type detector. The emitted beam has been interrupted using a high-speed electrostatic gate at time $t = 0$. The current collected at some distance L from the gate is then recorded versus time, providing a distribution of collected current versus particle speed. Alternatively, an inverted trace can be acquired by recording the current immediately after releasing the beam [5] (which can be easily transformed to the form shown).

In this Note, collected current $\bar{I}$ refers to the coulombs per second incident on a Faraday cup type detector, normalized by that rate at $t < 0$; hence, collected neutrals are not recorded, and the instrument current is equal to that collected. Such detectors have been prevalent in electrospray thruster characterization, for example the arrangements applied in [1,3,4,7]. The instrument output would differ for particle impact detectors, such as a channel electron multiplier or microchannel plate, which can respond to neutrals. Such detectors are frequently used in TOF mass spectrometery [8] and have been applied to characterize electrospray propulsion sources [9]; however, the corresponding output is not considered here.

For an IL with constituent species A^+ and B^-, emissions comprise ions of the form $[AB]_nA^+$ and $[AB]_nB^-$ in the positive and negative polarities, respectively, where n is the degree of solvation. Consistent with typical ILIS [2,4,7,10–12], Fig. 1 assumes a beam primarily composed of $n = 0$ and $n = 1$ ions along with a small but not insignificant proportion of $n = 2$ ions. Assuming these particles accelerate through the same electrostatic potential V_0, known constituent ion masses permit discrete drops to be readily attributed to unfragmented, monoenergetic ions at calculated flight times t_0, t_1, and t_2,

Sloped transitions between discrete collected current drops indicate a population of ions with distributed flight speeds. Such a distribution could manifest due the spread of trajectories over angle, such as when using a large detector [13], or to a largely negligible [10] extent due to a distribution of energy loss mechanisms associated with ion extraction. In this Note, we consider a third mechanism, potentially prevalent even when sampling a narrow beam angle: solvated ion fragmentation within regions of nonzero electric field.

Referring to Fig. 2, ion fragmentation yields both a separated ion along with a neutral particle. If this occurs during electrostatic acceleration, the fragmented ion and neutral pair will exit the thruster at differing speeds. Ions that subsequently breakup in field free regions travel at the same speed of the original parent yet with reduced kinetic energy. In the context of TOF measurements from a Faraday cup type detector, these ions are not discernable from their parents due to the unchanged speed. Because such events do not modify the propulsive performance, the benignity of TOF to such transitions is welcome. Conversely, ions stemming from fragmentation events while accelerating do influence propulsive performance, and their distributed speeds do permit identification by TOF measurements. However, whereas the mass to charge ratio of unfragmented species can be attributed to flight time by assuming a known energy, the energy of fragmented ions and their associated neutrals must be determined from their flight time, with the constituent masses inferred based on the assumed parent ion.

Ion fragmentation in the context of ILIS has been previously examined using retarding potential analyzers (RPAs) [4,10–14]. Those studies have identified both discrete populations corresponding to breakup in field free regions and distributed populations. The latter, comprising at times tens of percent of the beam, largely correspond to fragmentation in nonzero fields. However, unlike TOF measurements, RPA measurements inherently include sensitive nonzero field regions within the instrument preventing assured allocation as to the degree to which fragmentation has occurred within the source itself, clouding the influence on performance.

Without adjustment for fragmentation, and therefore assuming monoenergetic particles, the thrust T and mass flow rate $\dot{m}$ are calculated from TOF measurements using Eqs. (1) and (2), respectively [1]. Here, the beam current I_b is the total electrical current emitted from the thruster, and $\bar{I}$ is the fraction of that current collected at flight time t:

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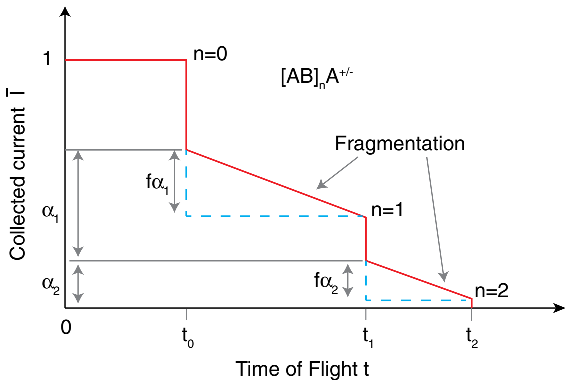


Fig. 1 A prototypical TOF trace from a purely ionic electrospray source using a Faraday cup type detector. Sloped regions between discrete drops can largely be attributed to ion fragmentation during acceleration.

$$T = -\frac{2V_0 I_b}{L}\int_0^\infty t\frac{\mathrm{d}\bar{I}}{\mathrm{d}t}\mathrm{d}t \tag{1}$$

$$\dot{m} = -\frac{2V_0 I_b}{L^2}\int_0^\infty t^2\frac{\mathrm{d}\bar{I}}{\mathrm{d}t}\mathrm{d}t \tag{2}$$

The specific impulse and propulsive efficiency are then obtained by Eqs. (3) and (4). In this context, where other loss mechanisms [4] are ignored, the propulsive efficiency refers to the effective power loss associated with the simultaneous acceleration of particles of distributed mass and is often referred to as a polydispersive efficiency [15]:

$$I_{\mathrm{sp}} = \frac{T}{g\dot{m}} \tag{3}$$

$$\eta_{\mathrm{prop.}} = \frac{T^2}{2\dot{m}V_0 I_b} \tag{4}$$

II. Elemental Adjustments to Thrust and Mass Flow Rate

In calculating thrust by Eq. (1), the ion flight time has been attributed to speed and mass to charge ratio by the relations $c_i = L/t$ and $m/q = 2V_0(t/L)^2$, respectively, such that elemental thrust contribution is

$$\delta T = -\frac{2V_0 I_b t}{L}\frac{\mathrm{d}\bar{I}}{\mathrm{d}t}\mathrm{d}t = \frac{2qV_0 I_b t}{L}\delta\Gamma \tag{5}$$

where

$$\delta\Gamma = -\frac{I_b}{q}\frac{\mathrm{d}\bar{I}}{\mathrm{d}t}\mathrm{d}t$$

is the elemental emission rate of charged particles with flight time between t and $t + \mathrm{d}t$.

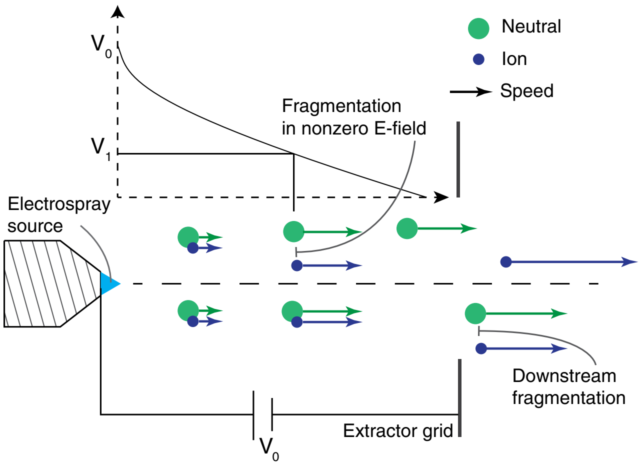


Fig. 2 Solvated ions that fragment within the electrostatic acceleration field of a thruster yield a neutral that is not accounted for in unaltered TOF calculations.

To arrive at fragmentation correction factors applicable to TOF-based calculations, we consider the simple scenario depicted in Fig. 2, where species accelerate from the emission source through a single extractor grid electrode. However, the relations described later are unchanged, or could easily be modified, when intermediate electrodes are included to accelerate particles downstream as in [6,16].

If an element of current at flight time t can be attributed to fragmented ions, $\delta\Gamma$ indicates the emission rate of both fragmented ions and corresponding neutrals. Packets of solvated ions of mass m_s fragmented into an ion of known mass m_i and a neutral of mass m_N then contribute a total thrust element given by

$$\delta T^* = (c_i m_i + c_N m_N)\delta\Gamma \tag{6}$$

Here, $c_i = \sqrt{2K_i/m_i}$ and $c_N = \sqrt{2K_N/m_N}$ are the ion and neutral speeds with kinetic energies K_i and K_N, respectively. The ratio $\delta T^*/\delta T$ can then be considered as a correction factor, valid within regions of flight time where collected charged particles are known to be due to fragmented ions:

$$\frac{\delta T^*}{\delta T} = \frac{K_i}{qV_0} + \left(\frac{m_N}{m_i}\frac{K_N K_i}{q^2 V_0^2}\right)^{1/2} \tag{7}$$

Both particle energies are less than qV_0, and given the known ion mass and calculated speed ($c_i = L/t$), it is straightforward to show that

$$\frac{K_i}{qV_0} = \frac{t_i^2}{t^2} \tag{8}$$

where t_i is the calculated flight time assuming complete acceleration of m_i through the potential qV_0. The neutral energy is then, by energy conservation,

$$\frac{K_N}{qV_0} = 1 - \frac{K_i}{qV_0} = 1 - \frac{t_i^2}{t^2} \tag{9}$$

Following the same reasoning, the mass flow rate when $\delta\Gamma$ is known to be due to fragmented ions will be simply $\delta\dot{m}^* = m_s\delta\Gamma$, whereas the standard elemental contribution to mass flow calculated by Eq. (2) is

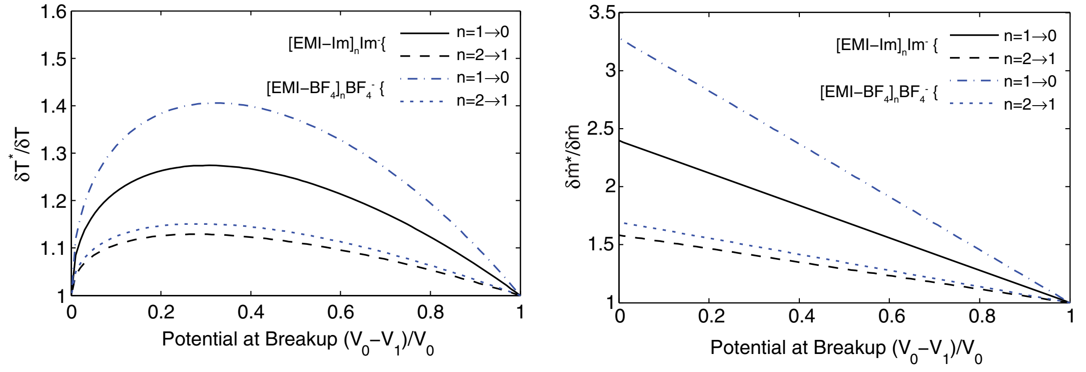
$$\delta\dot{m} = -\frac{2V_0 I_b t^2}{L}\frac{\mathrm{d}\bar{I}}{\mathrm{d}t}\mathrm{d}t$$

Dividing these elements, Eq. (10) then follows:

$$\frac{\delta\dot{m}^*}{\delta\dot{m}} = \frac{m_s}{m_i}\frac{K_i}{qV_0} \tag{10}$$

To consider the degree to which TOF thrust measurements underestimate thrust and mass flow, it is useful to express the correction factors [Eqs. (7) and (10)] as functions of the electric potential at the point of breakup (V_1 in Fig. 2). The ion kinetic energy is related to this potential by Eq. (11) [10]:

$$\frac{K_i}{qV_0} = \frac{m_i}{m_s}\left(1 - \frac{V_1}{V_0}\right) + \frac{V_1}{V_0} \tag{11}$$



a) Thrust **b) Mass flow rate**

Fig. 3 Elemental adjustments to TOF performance calculation integrands for negative ions undergoing $n = 1 \rightarrow 0$ and $n = 2 \rightarrow 1$ transitions from the EMI-Im and EMI-BF$_4$ ILs.

ILIS have been demonstrated using numerous ILs; see for example [2], where four ILs were sprayed. However, emissions of EMI-BF$_4$ ($m_{\mathrm{EMI}} = 111.2\ Da, m_{\mathrm{BF}_4} = 86.8 Da$) and EMI-Im ($m_{\mathrm{Im}} = 280.2 Da$) have been particularly prevalent in recent studies (e.g., [2,5,7,17]), including investigations of ion fragmentation [10,13]; hence, it is topical to consider these liquids.

In Fig. 3, the thrust and mass flow rate correction factors by Eqs. (7) and (10) for, as an example, EMI-Im and EMI-BF$_4$ negative ions have been plotted against the electric potential gained before breakup ($V_0 - V_1$). Here, the ion kinetic energy was determined using Eq. (11) and the corresponding neutral kinetic energy was then calculated with Eq. (9). The figures include the prominent $n = 2 \rightarrow 1$ and $n = 1 \rightarrow 1$ transitions. Energy analyses in the literature [10] have not indicated a propensity for transitions such as $n = 2 \rightarrow 0$; however, if found to be significant, the large ratio of parent solvated ion to fragmented ion mass would correspond to large adjustment factors. Figure 3a demonstrates that, although standard TOF calculation integrands do attribute thrust to fragmented ions, the true thrust output may be larger by some 10% or more. The correction to mass flow, in Fig. 3b, is clearly significant, reaching maxima equal to the parent ion to fragmented ion mass ratio when fragmentation occurs immediately after emission ($V_1 = V_0$). In such a scenario, the neutral particle would not contribute to thrust, yet it represents a significant mass flux contribution.

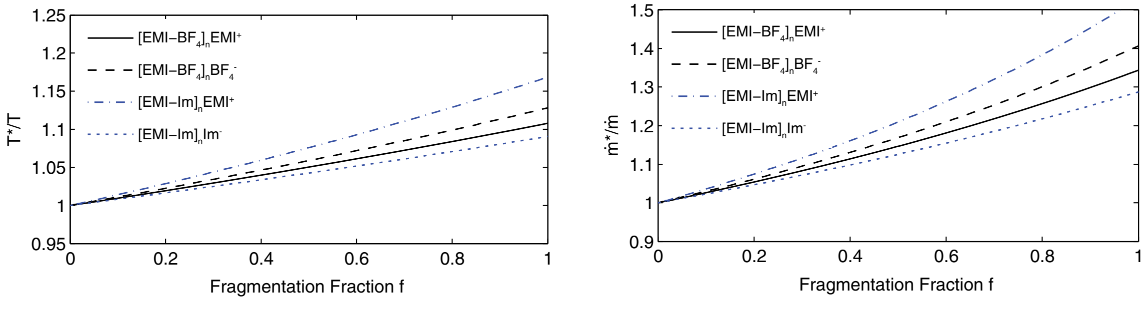
III. Application to Performance Calculations

The prototypical TOF trace in Fig. 1 permits normalized quantification of the aggregate effects of fragmentation as applied to typical ILIS emissions. In the figure, solvated ion contributions to the total current are indicated by α_1 and α_2, corresponding to $n = 1$ and $n = 2$, respectively, with $1 - (\alpha_1 + \alpha_2)$ then being the fraction of $n = 0$ ions. As a simple model, we consider a uniform (over current) distribution of fragmented ions and a single parameter f describing the fraction of solvated ions that fragment, leading to a linear slope between nominal solvated ion flight times.

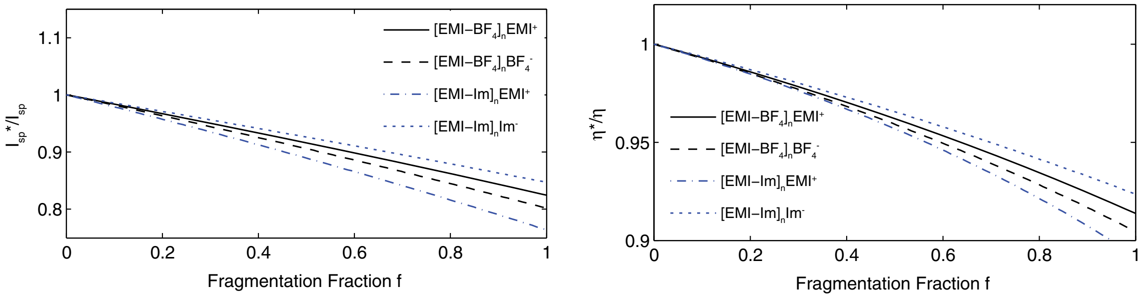
Consistent with measurements of energy spectra [10], we assume that $n = 2 \rightarrow 0$ transitions are negligible. Charged particles detected between expected flight times t_n and t_{n+1} are therefore taken to represent ions of solvation n, which are fragments of an original $n + 1$ solvated ion. That is, we take $t_i = t_n$ in Eq. (8) to determine the ion kinetic energy for each region $t_n < t < t_{n+1}$.

Equations (12) and (13) are modified calculations for the thrust T^* and mass flow rate $\dot{m}^*$, respectively, where Eqs. (7) and (10) are applied as piecewise modifiers to the integrands in the standard relations [Eqs. (1) and (2)]. These expressions can be applied to more accurately account for fragmentation:

$$T^* = -\frac{2V_0 I_b}{L} \int_0^\infty \frac{\delta T^*}{\delta T}\, t \frac{\mathrm{d}\bar{I}}{\mathrm{d}t} \mathrm{d}t \tag{12}$$



a) Thrust **b) Mass flow rate**



c) Specific impulse **d) Propulsive efficiency**

Fig. 4 Corrections to propulsive parameters calculated when accounting for fragmentation assuming the prototypical TOF characteristic depicted in Fig. 1, with $\alpha_1 = 50\%$, $\alpha_2 = 5\%$, and identical fragmentation fractions for both $n = 1$ and $n = 2$.

$$\dot{m}^* = -\frac{2V_0 I_b}{L^2}\int_0^\infty \frac{\delta\dot{m}^*}{\delta\dot{m}}\, t^2 \frac{\mathrm{d}\bar{I}}{\mathrm{d}t}\,\mathrm{d}t \tag{13}$$

Figure 3 demonstrates the influence of these corrections for the ILs EMI-Im and EMI-BF$_4$ with $\alpha_1 = 50\%$ and $\alpha_2 = 5\%$, levels similar to reported measurements (e.g., [2,4,10]). In the figures, the calculated metrics have been scaled by those obtained using the unmodified expressions (1) and (2). Corresponding fractional changes to specific impulse and propulsive efficiency by Eqs. (3) and (4), respectively, are also indicated. The specific influence of fragmentation on performance must be considered on a case by case basis; however, the figures offer some insight into the potential influence. Changes to the calculated thrust (Fig. 4a) are limited to a few percent even as up to 50% of the solvated ions fragment; however, the total mass flow in such instances may exceed 10% of that calculated without correction. As indicated in Figs. 4c and 4d, this effect would measurably reduce the specific impulse and efficiency of the device. Although small, efficiency reductions of a few percent may be comparable to the energy deficit losses [4] and could be significant, considering the potential for very high ILIS thruster efficiencies in excess of 90% [15].

In a recent study, we observed fragmentation effects when using a TOF system without an electrostatic lens and with a narrow beam acceptance angle [4]. There, 30% or more of solvated ions may have been fragmented, and application of the described procedure resulted in ~3 and ~5% increases in thrust and mass flow rate, respectively. We anticipate that larger modifications may be required after installing a downstream acceleration grid [6], which will increase the residence time of solvated ions within regions of nonzero electric field and could thereby increase the fraction of fragmented ions.

Comparisons with other studies are often convoluted due to the frequent application of focusing Einzel lenses (see for example [2,10,14]). Because such lenses focus a relatively narrow energy range [10], ions that fragment before the lens would not, and typically do not, appear in the TOF traces reported. However, in [18,19], no Einzel lens was applied and, similar to our findings, ~30% or more of the solvated species may have fragmented based on nonzero TOF trace slopes between the t_0 and t_1 flight times for several ILs, including EMI-BF$_4$.

In [10], Lozano reported as much as 20% of an EMI-Im ILIS beam could be attributed to fragmented $n = 2 \rightarrow 1$ transitions when using a detuned Einzel lens, whereas only a few percent of $n = 2$ solvated ions were evident at the optimal lens setting. That result demonstrates a possible loss of calculation accuracy when using an energy-discerning lens to focus ions. In Fig. 1, the dashed line would be the expected output if fragmented species were emitted yet not detected. Performance calculations made from these TOF traces may overemphasize the contribution due to low mass $n = 0$ ions and therefore underestimate thrust and mass flow rate. For EMI-BF$_4$ positive ion emission with $\alpha_1 = 50\%$, $\alpha_2 = 5\%$, and $f = 30\%$, the mass flow rate calculated by the method outlined here would be 8% higher than that without fragmentation adjustment, which is in turn a further 7.5% higher than the result when all fragmented species are removed from the signal. Hence, even with a low degree of fragmentation, performance calculations should ensure that all particles have been recorded and that they are properly accounted for.

IV. Conclusions

A method has been presented for accounting for ion fragmentation that occurs within the nonzero field of an ionic electrospray thruster. Given the complexities associated with direct thrust measurements, indirect means (and time-of-flight (TOF) in particular) remain a primary method for researchers to evaluate performance. It has been shown, through examples and reflections on results reported in the literature, that such performance calculations should consider fragmentation to increase the accuracy of reported results. The described method applies to measurements made with Faraday cup type detectors and requires an assumption as to the specific fragmentation events that occur, yet it is otherwise easily applied through modifiers to the integrands used to calculate thrust and mass flow rate from TOF traces. Energy-resolved TOF measurements could segregate contributions and provide improved fidelity but may be convoluted by further fragmentation within the filtering instruments and add system complexity when compared with this analytical approach.

Acknowledgments

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References

[1] Gamero-Castao, M., and Hruby, V., "Electrospray as a Source of Nanoparticles for Efficient Colloid Thrusters," *Journal of Propulsion and Power*, Vol. 17, No. 5, 2001, pp. 977–987.
doi:10.2514/2.5858

[2] Legge, R. S., and Lozano, P. C., "Electrospray Propulsion Based on Emitters Microfabricated in Porous Metals," *Journal of Propulsion and Power*, Vol. 27, No. 2, 2011, pp. 485–495.
doi:10.2514/1.50037

[3] Alonso-Matilla, R., Fernández-García, J., Congdon, H., and de la Mora, J. F., "Search for Liquids Electrospraying the Smallest Possible Nanodrops in Vacuo," *Journal of Applied Physics*, Vol. 116, No. 22, 2014, Paper 224504.
doi:10.1063/1.4901635

[4] Courtney, D. G., Dandavino, S., and Shea, H., "Comparing Direct and Indirect Thrust Measurements from Passively Fed and Highly Ionic Electrospray Thrusters," *Journal of Propulsion and Power* (submitted for publication).

[5] Coffman, C., Perna, L., Li, H., and Lozano, P. C., "On the Manufacturing and Emission Characteristics of a Novel Borosilicate Electrospray Source," *49th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit*, AIAA Paper 2013-4035, 2013.

[6] Dandavino, S., Ataman, C., Ryan, C. N., Chakraborty, S., Courtney, D. G., Stark, J. P. W., and Shea, H., "Microfabricated Electrospray Emitter Arrays with Integrated Extractor and Accelerator Electrodes for the Propulsion of Small Spacecraft," *Journal of Micromechanics and Microengineering*, Vol. 24, No. 7, 2014, Paper 075011.
doi:10.1088/0960-1317/24/7/075011

[7] Lozano, P., and Martnez-Sánchez, M., "Ionic Liquid Ion Sources: Characterization of Externally Wetted Emitters," *Journal of Colloid and Interface Sciences*, Vol. 282, No. 2, 2005, pp. 415–421.
doi:10.1016/j.jcis.2004.08.132

[8] Guilhaus, M., "Special Feature: Tutorial. Principles and Instrumentation in Time-of-Flight Mass Spectrometry, Physical and Instrumental Concepts," *Journal of Mass Spectrometry*, Vol. 30, No. 11, 1995, pp. 1519–1532.
doi:10.1002/jms.1190301102

[9] Terhune, K. J., King, L. B., Hause, M. L., Prince, B. D., Jain, N., and Hawkett, B. S., "Species Measurements in the Beam of an Ionic Liquid Ferrofluid Electrospray Source," *50th AIAA/ASME/SAE/ASEE Joint Propulsion Conference*, AIAA Paper 2014-3694, 2014.

[10] Lozano, P., "Energy Properties of an EMI-Im Ionic Liquid Ion Source," *Journal of Physics D: Applied Physics*, Vol. 39, No. 1, 2006, pp. 126–134.
doi:10.1088/0022-3727/39/1/020

[11] Romero-Sanz, I., Bocanegra, R., Gamero-Castao, M., de la Mora, J. F., and Lozano, P., "Source of Heavy Molecular Ions Based on Taylor Cones of Ionic Liquids Operating in the Pure Ion Evaporation Regime," *Journal of Applied Physics*, Vol. 94, No. 5, 2003, pp. 3599–3605.
doi:10.1063/1.1598281

[12] Krpoun, R., Smith, K. L., Stark, J. P. W., and Shea, H., "Tailoring the Hydraulic Impedance of Out-of-Plane Micromachined Electrospray Sources with Integrated Electrodes," *Applied Physics Letters*, Vol. 94, No. 16, 2009, Paper 163502.
doi:10.1063/1.3117191

[13] Fedkiw, T. P., "Characterization of an Iodine-Based Ionic Liquid Ion Source and Studies on Ion Fragmentation," M.S. Thesis, Massachusetts Inst. of Technology, Cambridge, MA, 2010.

[14] Fedkiw, T. P., and Lozano, P. C., "Development and Characterization of an Iodine Field Emission Ion Source for Focused Ion Beam Applications," *Journal of Vacuum Science and Technology B*, Vol. 27, No. 6, 2009, pp. 2648–2653.
doi:10.1116/1.3253604

[15] Lozano, P., and Martnez-Sánchez, M., "Efficiency Estimation of EMI-BF4 Ionic Liquid Electrospray Thrusters," *41st AIAA/ASME/SAE/ASEE*

Joint Propulsion Conference & Exhibit, AIAA Paper 2005-4388, July 2005.

[16] Lenguito, G., and Gomez, A., "Development of a Multiplexed Electrospray Micro-Thruster with Post-Acceleration and Beam Containment," *Journal of Applied Physics*, Vol. 114, No. 15, 2013, Paper 154901.
doi:10.1063/1.4822029

[17] Dandavino, S., "Microfabricated Electrospray Thrusters for a Modular Spacecraft Propulsion System," Ph.D. Thesis, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland, 2014.

[18] Castro, S., Larriba, C., Sumer, S., Saito, G., Yoshida, Y., Lozano, P., and de la Mora, J. F., "Effect of Liquid Properties on Electsprays from Externally Wetted Ionic Liquid Ion Sources," *Journal of Applied Physics*, Vol. 102, No. 9, 2007, Paper 094310.
doi:10.1063/1.2802547

[19] Garoz, D., Bueno, C., Larriba, C., Castro, S., Romero-Sanz, I., de la Mora, J., Yoshida, Y., and Saito, G., "Taylor Cones of Ionic Liquids from Capillary Tubes as Sources of Pure Ions: The Role of Surface Tension and Electrical Conductivity," *Journal of Applied Physics*, Vol. 102, No. 6, 2007, Paper 064913.
doi:10.1063/1.2783769

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