Investigation of Electrospray Plume Composition during Voltage Transients

IEPC-2019-794

Elaine M. Petro,[*] Mina Cezairli,[†] Madeleine Schroeder,[‡] and Paulo C. Lozano[§]
Massachusetts Institute of Technology, Cambridge, MA, 02138, USA

A technique has been developed to probe the mass spectrum of an ion plume at discrete times in a repeated firing profile. While traditional time of flight (TOF) measurements require a steadily firing ion beam, this transient TOF approach enables the analysis of a beam with emission characteristics that change over time. This technique is developed in order to investigate changes in the mass spectrum of an electrospray ion beam as it is repeatedly cycled between positive and negative currents. Measurements are made of the current emitted from ionic liquid ion source (ILIS) emitter arrays at various time delays from start-up in the positive emission mode. The time-varying mass spectra are compared with the spectra recorded for the same source during steady firing. Initial results indicate that the beam composition in the first 10 ms of operation differs from the steady-state composition.

Nomenclature

L_{TOF} = time of flight test section (field-free) length
m = mass
q = charge
t_{delay} = time of from emission onset
τ = gate pulse width
V_0 = emitter voltage

[*]Post Doctoral Associate, Aeronautics and Astronautics, and epetro@mit.edu.
[†]Visiting Undergraduate Research Assistant, Department Name, and mina.cezairli@yale.edu
[‡]Undergraduate Research Assistant, Department Name, and msch1@mit.edu
[§]M. Aleman-Velasco Professor, Aeronautics and Astronautics, and plozano@mit.edu.

I. Motivation

Electrospray thrusters are capable of providing very fine thrust and attitude control for spacecraft. While electrospray ion sources fire very stably under a fixed set of conditions, start-up transients are observed at the onset of ion emission. Though these transients are short-lived, the current released can be several times that of the steady-state value.[1] Such start-up transients have long been observed in externally wetted liquid metal and ionic liquid ion sources,[2],[3] Many factors influence the dynamic response of the liquid meniscus to a rapid voltage change including properties of the liquid itself, such as viscosity and conductivity, in addition to the geometry of the emitter. Beyond start-up, transients occur in response to the periodic polarity reversal required to prevent electrochemical degradation of the ionic liquid.[4] In thruster operation, the voltage polarity is alternated approximately every 30 seconds for this reason.[5] Thus understanding these transients is necessary to fully characterize the thrust profile and operation of the device.

It is possible that the spikes in current during this phase may coincide with the release of charged droplets which, due to their large mass, reduce the effective Isp of the thruster. Erratic droplet emission may also result in impingement on and degradation to sensitive surfaces, such as the extraction grid.[5] Even in the absence of current transients voltage polarity alternation may cause unsteady droplet emission or beam composition changes that negatively impact the long term performance of the thruster. Capturing the characteristics of the plume during this transient period will help elucidate the critical underlying physical processes. If off-optimal emission is observed at start-up, resolution of plume composition will be useful in evaluating alternative firing profiles.

II. Methodology

The composition of charged particles in electrospray thruster beams can be analyzed using a time of flight (TOF) mass spectrometer. Typically the time of flight measurement is taken during steady-state emission and averaged over tens of seconds of firing.[6] However, in order to detect the beam composition during the transient period, which occurs on the millisecond timescale, a new measurement approach is required. In this work, we report an approach to capturing temporal variations in ion beam composition. A description of the testing apparatus which consists of vacuum facility fitted with the time of flight instrument is given below. Modifications which have been made to a traditional apparatus to enable these measurements will be described. The approach is validated by comparing time-resolved measurements to steady-state results.

A. Apparatus

The time of flight instrument is installed in a 40 x 80 cm cylindrical vacuum chamber which includes a cylindrical extender flange mounted along the central axis to create a long test section for good mass resolution as depicted in Fig. 1. The electrospray ion source is mounted at the front of the chamber approximately 16 cm in front of the entrance gate to the spectrometer. For the transition time-of-flight measurements performed in this study, the background pressure in the test section has to be reduced in order to improve CEM sensitivity and decrease signal noise. The apparatus has been modified to include differential pumping with the addition of a turbomolecular pump in the test section. The two turbomolecular pumps (685 and 45 L/s respectively) are operated in parallel and backed by a dry mechanical pump. The pressure is monitored both in the main chamber and near the detector and remains below 1e-6 torr in the main chamber and 1e-7 torr in the test section for all tests.

The time of flight spectrometer was developed in house to characterize ion beams from electrospray thrusters. A detailed view of the components is shown in Fig. 2. An electrostatic deflection gate is located approximately 16 cm downstream of the ion source and is shielded by a grounded aperture plate on the source facing side. The electrostatic gate consists of a pair of rectangular electrodes spaced 1.3 cm apart. The gate electrodes are pulsed at +/-950 V using two DEI PVM-2410 pulse amplifiers to periodically interrupt the flow of ions to the detector. When the gate is opened, ions will travel to the detector through the field-free region (102.5 cm in length) defined by a grounded cylindrical tube. The ions will traverse this distance in an amount of time that depends on their charge-to-mass ratio. Assuming the ion has been accelerated to the source potential,V_0, the flight time depends on the charge-to-mass ratio as:

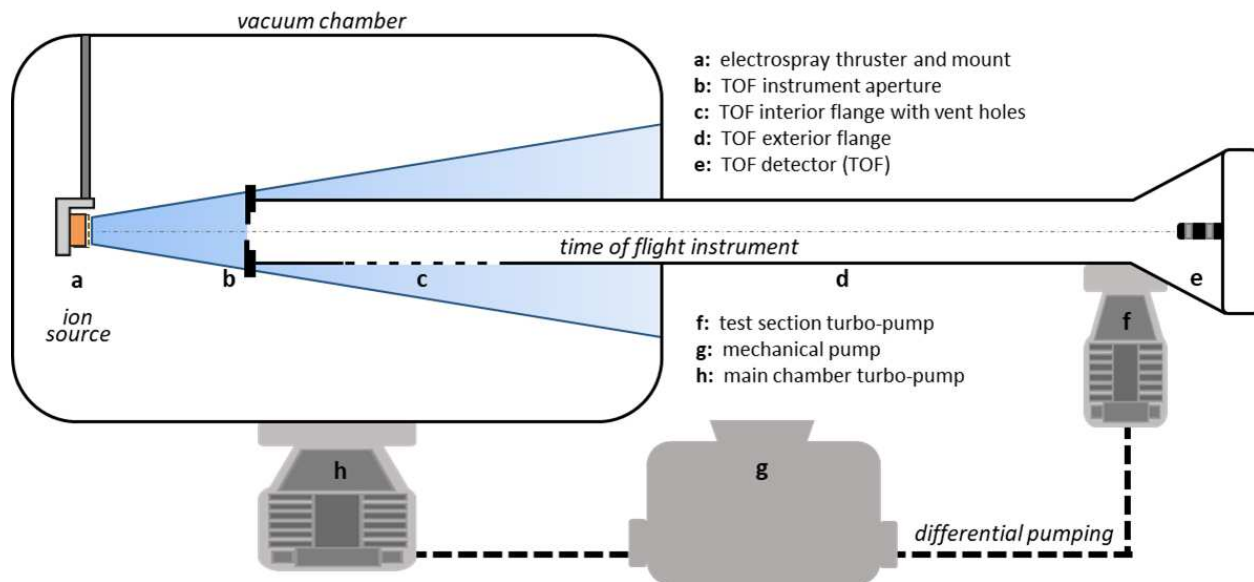$$t_{TOF} = \frac{L_{TOF}}{\sqrt{2\left(\frac{q}{m}\right)V_0}} \tag{1}$$

Figure 1. Diagram of the test apparatus consisting of a time of flight spectrometer installed in a cylindrical vacuum chamber.
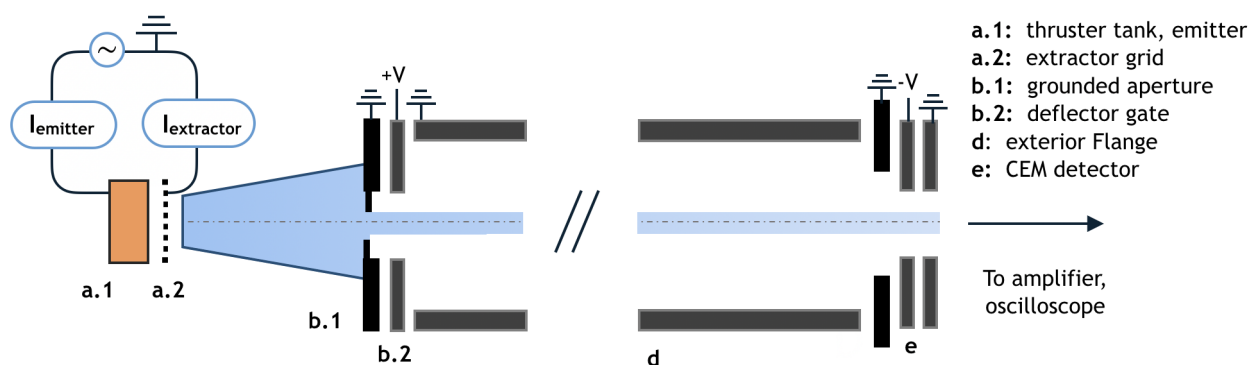

Figure 2. Diagram of the time of flight spectrometer developed for electrospray source characterization. In this case, the current is detected and amplified by a Channeltron Electron Multiplier (CEM) configured to measure positive ion beams.

The time dependent current is collected and amplified by a Channeltron Electron Multiplier (CEM) by a factor of 10^5 to 10^8. The CEM output is then further amplified by a fast op-amp circuit (rise time ≤ 30 ns) by a factor of 50 and recorded by a digital oscilloscope (Keysight DOSX3024A). In steady-state operation, the electrostatic gate is pulsed at 100 Hz using an Agilent (33220A) signal generator. A TOF signal is recorded at each pulse and averaged ≥ 2064 times on board the oscilloscope and thus represents ≥ 20.6 seconds of steady emission. The raw signal is a trace of current versus time where each increment or decrement in current represents the portion of the beam with a particular charge-to-mass ratio traversing the TOF distance (Fig. 3(a)). The derivative of the current trace can be taken to give a spectral representation (Fig. 3(b)).

B. Transient Approach

To capture the mass spectrum at a particular time, the operation of the ion source and the electrostatic gate must be modified and coordinated. A mass spectrum equivalent to that of Fig. 3(b) can be generated with a singular finite-width gate pulse. The gate is pulsed at the exact time that the beam is to be sampled by opening the gate some finite time, t_{delay}, after the source voltage is switched on. The pulse time delay and pulse width, τ, are modulated using a Berkeley Nucleonics (Model 555) Pulse Generator.
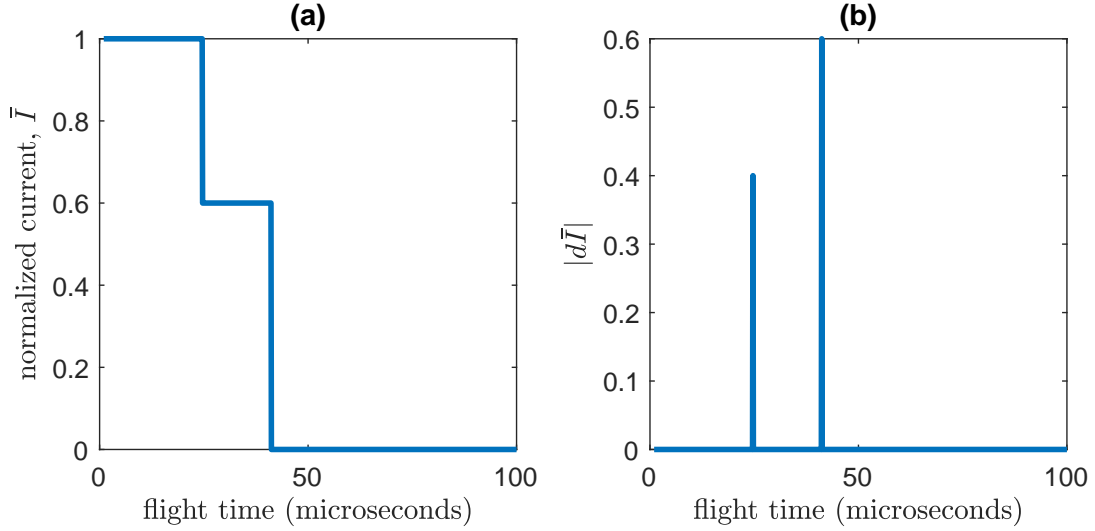
Figure 3. Theoretical TOF results for a monoenergetic 1 kV EMI-BF$_4$ ion beam with 40% monomers and 60% dimers.

If the pulse width is shorter than the temporal resolution of the current trace, the mass spectrum is displayed directly. Ions will traverse the field-free region and will appear as a current spike at the time that matches their charge-to-mass ratios given above by Eq. 1. Note that in the present configuration, the time resolution is constrained by the oscilloscope and for the present measurements has a minimum value of 0.5 μs. A time difference of 0.5 μs is equivalent to a mass resolution of $\sim$5 amu at 1000 V or an energy resolution of $\sim$40 V (4%) for EMI$^+$ ions. When the gate pulse is smaller than one horizontal time step, there is no observable stream of ions of equal charge-to-mass ratios, instead each ion type appears at its unique time step. Alternatively, longer pulse widths may also be used but they will result in a horizontal spreading of the signal which must be addressed through more sophisticated post-processing. The effect of the pulse width on the transient signal, following normalization, is shown in Fig. 4.
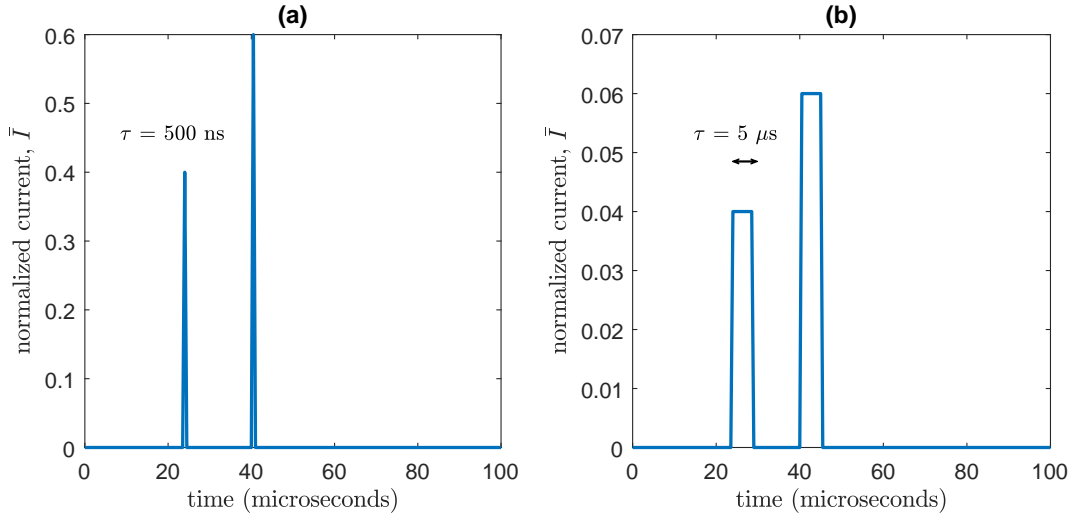

Figure 4. Theoretical, normalized $\left(\int_0^{t_f} \bar{I}(t)dt = 1\right)$ transient TOF results for a monoenergetic 1 kV EMI-BF$_4$ ion beam with 40% monomers and 60% dimers with (a) 500 ns and (b) 5 μs gate pulse widths sampled at 2 MHz.

Even with differential pumping, the noise present in a single measurement inhibits adequate resolution. Thus this process is repeated many times by firing the source in a repeating pattern (e.g. square wave) and activating the gate at the same time with respect to start-up during each period. A diagram illustrating

the sampling configuration is given in Fig. 5. For all tests, the source is fired using a Matsusada Model AP-3B1-L2 high voltage amplifier. The response of the HV amplifier and of the source to the applied voltage (V_{emit} and I_{emit}) are explored in Section IV.
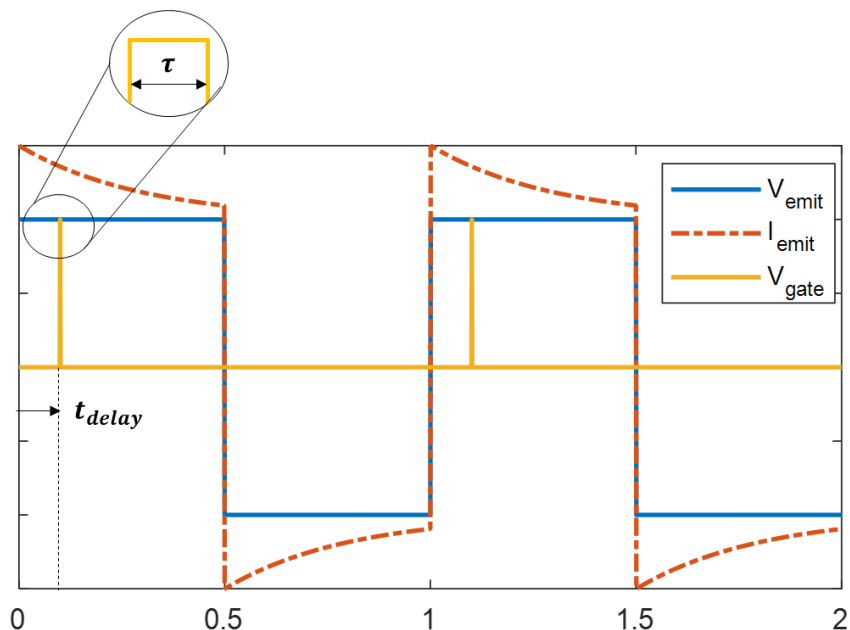

Figure 5. Diagram showing coordination between source firing and gate pulsing for two firing cycles.

Experiments were performed with electrospray thruster arrays made in-house and fabricated from a porous glass. The arrays were wetted with ionic liquids such as EMI-CF3BF3 and EMI-BF4.

III.   Technique Validation

In order to validate the transition time-of-flight (TOF) method, data acquired from steady firing of the thruster can be compared to traditional TOF measurements. This comparison is done in two ways. Initially, the thruster is fired at a constant voltage and only the gate pulsing is changed. First, the gate is pulsed with a 100 Hz square wave (traditional method). Then, with the source operation unchanged, the gate is changed to a 100 ns wide pulse repeated at a rate of 100 Hz. Note that this pulse width is a factor of 5 smaller than the time resolution of the data collection. In both cases, the signal is averaged over 2064 repeated gate pulses on-board the oscilloscope. For this test, a borosilicate emitter array wetted with EMI-CF3BF3 was fired at 1150 V, emitting between 60 and 70 μA of current. The data collected under the traditional technique is normalized, differentiated, and compared to the transition TOF data in Fig. 6. Fig. 6(a) shows differentiated traditional TOF data alongside the transient data and Fig. 6(b) highlights the difference in magnitudes at each point.

It can be seen that the general shape of the curves agree, including distinguishable monomer, dimer, and trimer peaks (at ~ 24, 44, and 57 μs, respectively). Smaller, secondary peaks, likely representing populations of fragmented ions of similar energies, can be seen accompanying each primary ion peak in both datasets. The exact ion fractions predicted by each method vary slightly. For example, the particles can be approximately binned according to their flight times and summed over the current fraction in each bin as shown in Fig. 7. Note that the transition TOF data significantly overpredicts the fraction of high mass (flight time longer than a trimer) particles as compared to the traditional approach. Further investigation is required to assess the accuracy of the high mass tail of the distribution for these measurements.

Next, instead of firing the thruster at a constant voltage, the thruster is fired using a square wave voltage signal of varying time periods. The gate pulse can then be placed anywhere within the firing profile (as shown in Fig. 5) and averaged over many firing cycles. A minimum voltage alternation frequency of 0.03 Hz has been recommended for preventing electrochemical degradation in the propellant reservoir.[5] However
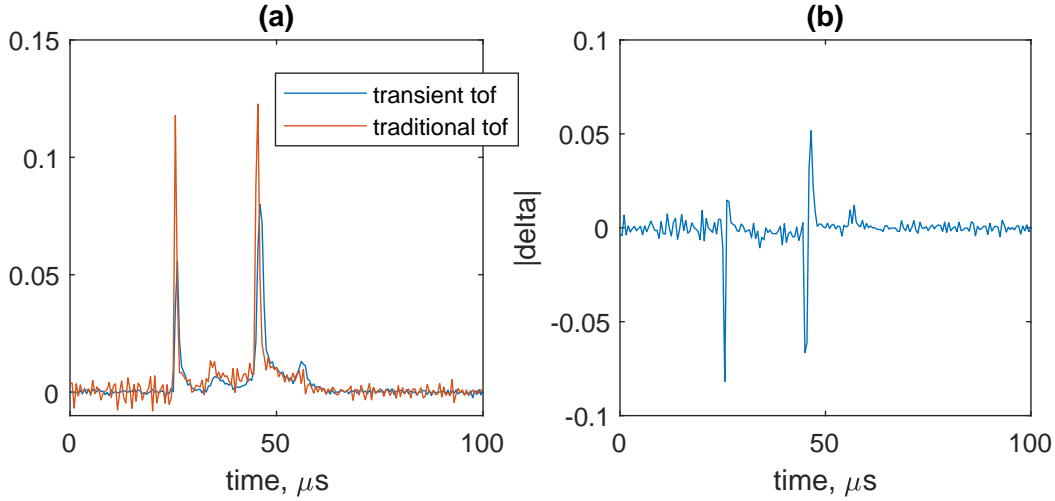
Figure 6. Comparison of traditional and transient TOF data for a thruster firing at constant voltage.

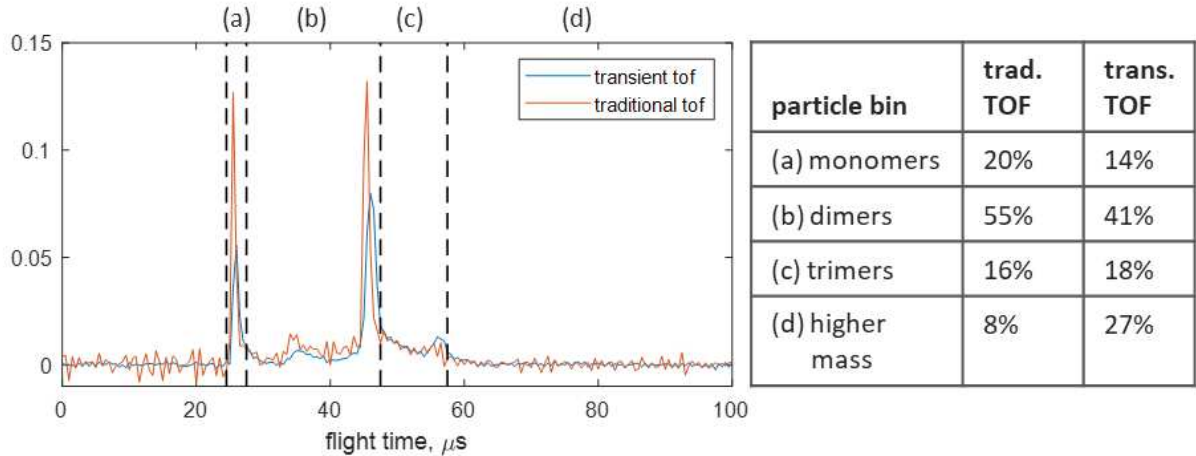| particle bin	trad. TOF	trans. TOF
(a) monomers	20%	14%
(b) dimers	55%	41%
(c) trimers	16%	18%
(d) higher mass	8%	27%

Figure 7. Comparison of binned particle fractions when summed over distribution functions.

larger frequencies may be used provided that the period remains much longer than the dynamic response time of the ionic liquid. The response time is dependent on the fluid properties and emitter geometry and is discussed Section IV.

Results of initial tests of the transient TOF method in coordination with alternating the voltage applied to the ion source are shown in below in Fig. 8. For these tests, a borosilicate emitter array is wetted with EMI-CF3BF3 and emits ∼30 μA during the positive voltage cycle of a 1 Hz +/- 750 V square wave. The transient data is captured halfway through the positive cycle (t_{delay}=250 ms) and t_{delay}=100 ms from the beginning of the cycle, again with a 100 ns pulsewidth. The TOF spectrum for the periodic firing is compared with both transient and traditional TOF spectra for steady firing. All datasets are normalized such that ($\int_0^{t_f} \bar{I}(t)dt = 1$).

In Fig. 8(a) all four spectra are overlaid and Fig. 8(b) shows each curve offset in comparison to the traditional TOF result for the same source. While the traditional TOF result is the average of 2064 gate pulses, the transient results contain only ≤100 averages. Good agreement between the various transient results is observed. These data provide proof of concept for the approach. Further investigation will be required to resolve differences in the spectra. Potential areas for refinement could include: (1) averaging over more cycles, (2) sampling beams at higher currents, and (3) evaluation of different post-processing and normalization approaches. More precise data is obtained and presented in the context of thruster characterization in Section IV.
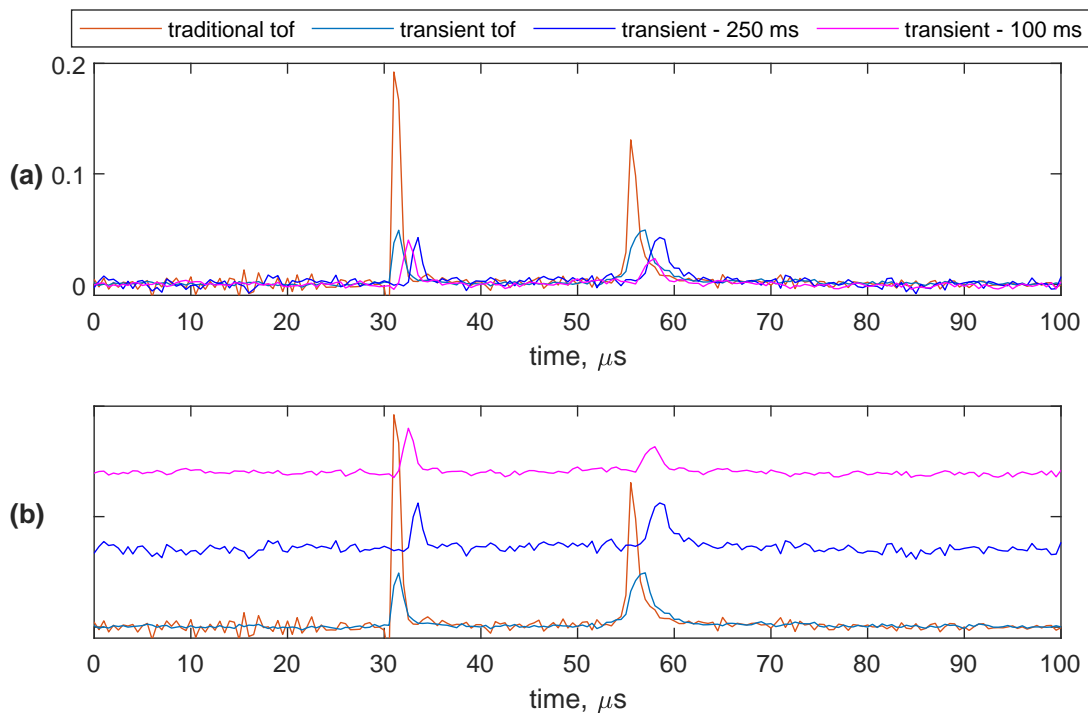
Figure 8. Comparison of TOF spectra recorded with both traditional and transient techniques and for different delay times (100, 250 ms) from startup.

IV. Transient Investigation

The transient TOF approach has been shown to capture the dominant particles in the ion beam. Use of this technique allows for investigation of possible changes in composition throughout the firing period. First, the emission of the source throughout the firing period is characterized, including the response immediately following start-up. Then the transient TOF method is used to sample the mass spectrum at several different points in the emission.

A. Current Profile

When alternating the polarity of an electrospray source, transient features are often observed.[1,7] These features can include large current spikes immediately following voltage alternation or steadily increasing or decreasing current throughout the cycle. To illustrate and assess these effects, the emission of an electrospray emitter array wetted with EMI-CF3BF3 was characterized under various firing profiles. Fig. 9 shows the current versus time profile for a 0.02 Hz square wave at 3 different voltage levels. Note that as the voltage increases the slope of the emitted current versus time grows. Additionally, the resolution of these data (100 ms) is insufficient to reliably detect startup transients although one is observed in the 1000 V data.

As the emitted current measurements were low resolution, another method was used to investigate the emission at start-up. The response time of the CEM and its external amplifier is below 30 ns with sub-microsecond resolution provided by the oscilloscope.[8] Fig. 10 shows the evolution of the ion current immediately following the voltage change at 3 different timescales. In this case, a 750 V square voltage wave is applied to an emitter array wetted with EMI-CF3BF3. Emission is detected at the CEM $\sim$100 μs after startup. As noted earlier, flight times for monomers and dimers are $\sim$20-50 μs from the source to the detector. Thus it is likely that either these light ions make up a small fraction of the initial beam or there is a start-up delay on the order $\gtrsim$50 μs before detectable emission occurs. It takes $\sim$500 μs for the initial current to reach its maximum value and then $\sim$10 ms to settle to a constant value. While this is an example startup profile for one operating point and configuration, changing any variable such as the applied voltage, the liquid, or the propellant reservoir may produce a different result. Note that the first and last curves were recorded during the same test and the 500 μs curve was recorded separately yet the same startup features
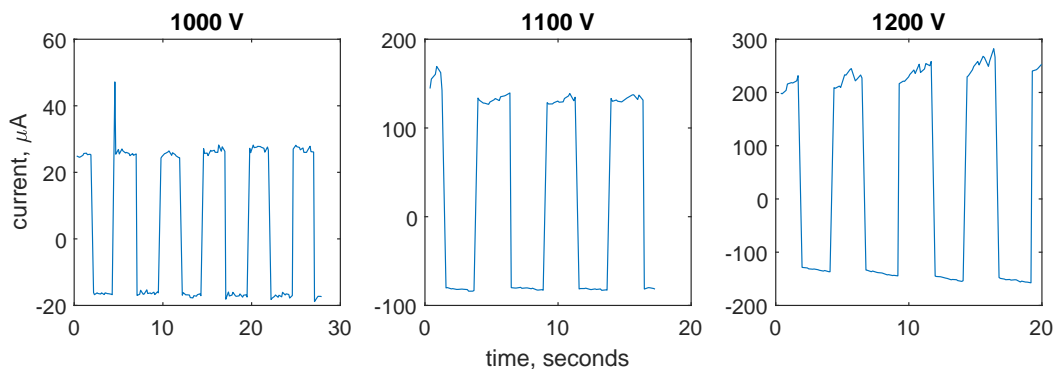
Figure 9. Current emitted from electrospray array operated in alternating polarities.
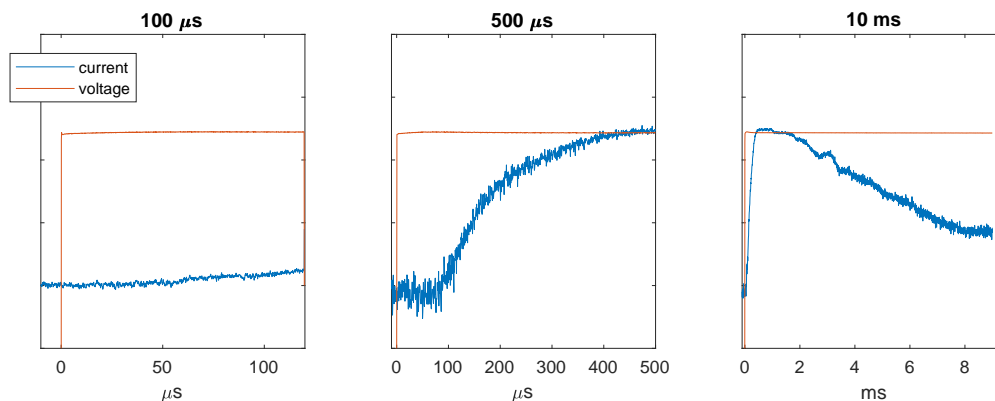
were observed.

Figure 10. Current emitted at start-up as detected by the CEM.

.

B. Mass Spectra

The transient TOF approach was used to probe the ion mass spectra at various pulse time delays from start-up. For these tests, an emitter array was attached to a propellant tank filled with EMI-BF4 in a thruster configuration. Test conditions are provided in Table 1. All transient firing was performed with a +/-1500 V square wave at 1 Hz. Note that in these tests, a 1 μs pulse width was used, which could lead to slight horizontal skewing of the distribution as depicted in Fig. 4(b). The steady state firing data was collected separately after much of the propellant had been depleted and was emitting lower currents ($\sim$ 20% of the current during transient data collection).

Table 1. Experimental conditions for transient TOF temporal emission scan.

time delay (ms)	$I_{emitted}$ (μA)	pulse width	cycles averaged ($no.$)
1	45	1 μs	256
2	57	1 μs	256
10	40	1 μs	256
100	45	1 μs	256
250	47	1 μs	256
steady	10	5 ms	2064

Fig. 11 shows the TOF spectrum recorded at five different times across the firing period: 1, 2, 10, 100, and 250 ms, along with the steady firing TOF result for comparison. Along the right vertical axis, the percentage of larger particles (flight times $> 100\ \mu s$) are listed. This represents the proportion of the sampled current that is made of very large ion clusters (m>2700 amu) and droplets. Results may indicate a change in mass spectra across the firing period, particularly near start-up where a substantial population is predicted to be high mass particles.
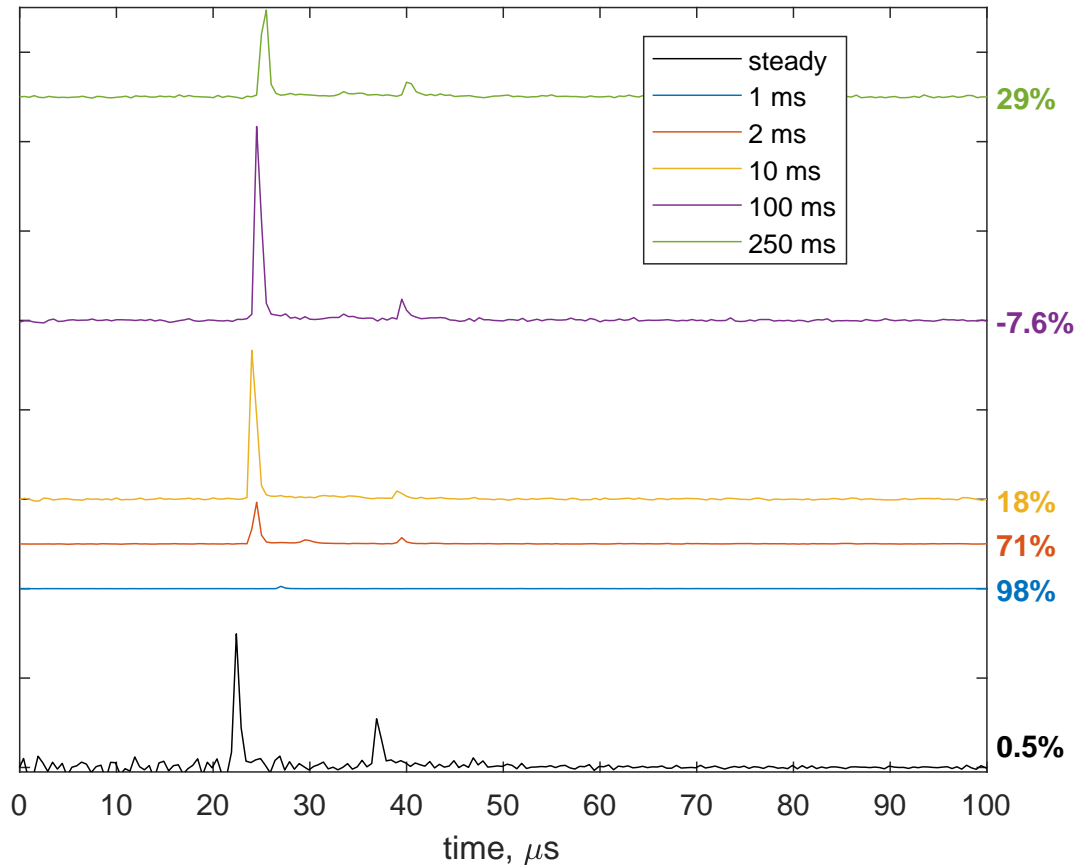

Figure 11. TOF spectra recorded at various delays from start-up.

.

Another way to view the data is to integrate the transient TOF curves so that they resemble the traditional TOF curve (an inverse cumulative distribution function). This view is presented in Fig. 12 with (a) a close-up view of the ion flight times and (b) the full time captured. When a source is operating in or close to the pure ion mode, very few features will be visible at the 0-500 μs time-scale shown in Fig. 12(b). The substantial currents observed here for the low times (1-2 ms) indicate the beam may be composed primarily of high mass particles. Additionally, these two curves do not asymptote to zero indicating that very large mass particles may be emitted at start-up, extending even beyond what is captured here.

V.   Conclusions and Future Work

As a result of this work, the first measurements of porously-fed ionic liquid ion beam composition during start-up transients have been performed. First, the approach to recording transient time-of-flight mass spectra is validated against traditional, steady-state measurements. Then, the transient approach is used to probe the emission characteristics of a thruster arrays at various time delays from start-up when fired in a repeating (square wave) pattern. These tests support the hypothesis that the mass composition of the ion
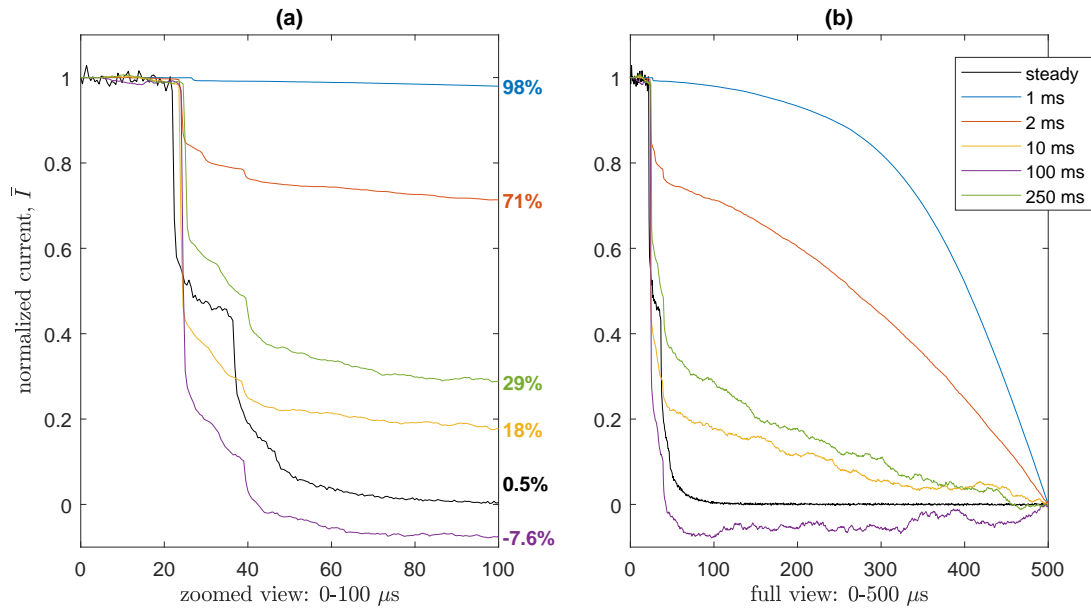
Figure 12. Integrated transient TOF curves

.

beam varies during different periods of the firing cycle. In particular it was found that the ion beam near the beginning of the firing period contains more high mass particles than the beam in the middle or near the end of the firing period. Further characterization is necessary to understand the mechanisms behind these variations.

This information provides new insight into flight-relevant operational modes of electrospray thrusters. An understanding of plume composition dynamics will help to predict thruster performance and optimize efficiency. Information about the evolution of the plume immediately following emission onset will also serve to inform dynamic modeling of the physical processes.

The data presented here represent the initial testing and proof of concept of a new mass spectrometry technique that enables measurements of the beam at different points in its evolution from start-up. While reasonably good agreement is demonstrated between transient results that have settled to a constant current and steady-firing results, further investigation and comparison between the approaches is warranted. The next stage in this investigation will involve improving measurement resolution with increased averaging and further investigation of the 1-10 ms start-up period. An important next step will be to obtain high resolution measurements of the emitted current in coordination with time-of-flight data, especially in the region immediately following start-up.

Acknowledgements

References

[1] Perez Martinez, C. S., *Engineering Ionic Liquid Ion Sources for Ion Beam Applications by*, Ph.D. thesis, Massachusetts Institute of Technology, 2016.

[2] Thompson, S. and Prewett, P., "The dynamics of liquid metal ion sources," *Journal of Physics D: Applied Physics*, Vol. 17, 1984, pp. 2305–2321.

[3] Lozano, P. and Martinez-Sanchez, M., "On the dynamic response of externally wetted ionic liquid ion sources," *Journal of Physics D: Applied Physics*, Vol. 38, 2005, pp. 2371–2377. doi:10.1088/0022-3727/38/14/011.

[4] Lozano, P. and Martínez-Sánchez, M., "Ionic liquid ion sources : suppression of electrochemical reactions using voltage alternation," *Journal of Colloid and Interface Science*, Vol. 280, No. 1, 2004, pp. 149–154. doi:10.1016/j.jcis.2004.07.037.

[5] Krejci, D., Mier-hicks, F., Thomas, R., Haag, T., and John, N., "Emission Characteristics of Passively Fed Electrospray Microthrusters with Propellant Reservoirs," *Journal of Spacecraft and Rockets*, Vol. 54, No. 2, 2017, pp. 447–458. doi:10.2514/1.A33531.

[6] Miller, C. and Lozano, P., "Measurement of the Fragmentation Rates of Solvated Ions in Ion Electrospray Thrusters," 07 2016. doi:10.2514/6.2016-4551.

[7] Freeman, D. S., *Design and Manufacture of the Next Generation of Ion Electrospray Thrusters*, Master's thesis, Massachusetts Institute of Technology, Cambridge, MA, 6 2019.

[8] Miller, C. E., *On the Stability of Complex Ions in Ionic Liquid Ion Sources*, Master's thesis, Massachusetts Institute of Technology, Cambridge, MA, 6 2015.