

# Voltage Controlled Dual Mode of Ionic Liquid Electrospray

IEPC-2017-349

*Presented at the 35th International Electric Propulsion Conference  
Georgia Institute of Technology • Atlanta, Georgia • USA  
October 8 – 12, 2017*

Yuntao Guo<sup>1</sup>, Zhiwen Wu<sup>2</sup>, Wang Liu<sup>3</sup>, Shipeng Li<sup>4</sup> and Noman Hossain<sup>5</sup>  
*Beijing Institute of Technology, Beijing, 100081, China*

**Abstract:** In this paper, an electrospray prototype with ionic liquid as propellant is established, and stable spray is realized in wide voltage range. It is found that two electrospray modes, mixed mode and ion mode can be realized simultaneously by adjusting the voltage. The influence of the voltage on the spray mode is analyzed theoretically. These two modes can be distinguished in terms of in the current - voltage relationship, specific charge and images. The experimental results show that low flow rate and high voltage are beneficial to produce ions with high specific charge, which is very important for optimizing the performance of ionic liquid ion source.

## Nomenclature

$e$	= elementary charge
$E$	= electric field
$f(\epsilon)$	= empirical constant dependent of $\epsilon$
$G(E)$	= the reduction in $\Delta G$ due to the presence of the electric field
$h$	= Planck's constant
$I$	= current
$j(E)$	= ion current density
$k$	= Boltzmann's constant
$K$	= conductivity
$q/m$	= specific charge
$Q$	= flow rate
$r$	= distance between the local site and the tip of Taylor cone
$T$	= absolute temperature
$u$	= atomic mass unit
$\alpha$	= half angle of the Taylor cone, usually taken as $49.29^\circ$
$\gamma$	= surface tension coefficient
$\Delta G$	= Gibbs free energy required to bring an ion from the liquid into the gas
$\epsilon_0$	= vacuum permittivity
$\epsilon$	= relative permittivity
$\rho$	= density
$\sigma$	= surface charge density

---

<sup>1</sup> PhD student, School of Aerospace Engineering, guoyt@bit.edu.cn.

<sup>2</sup> Associate professor, School of Aerospace Engineering, bitwzw@bit.edu.cn.

<sup>3</sup> Master, School of Aerospace Engineering, liuw@bit.edu.cn.

<sup>4</sup> Associate professor, School of Aerospace Engineering, lsp@bit.edu.cn.

<sup>5</sup> PhD student, School of Aerospace Engineering, knoman.edu@yahoo.com.

## I. Introduction

Electrospray is widely applied in mass spectrometry<sup>1</sup> and electric propulsion<sup>2</sup>. With the development of Cubesats, the demand of micro-thrusters is higher, such as high precision thrust adjustment, high efficiency, low power consumption. Electrospray is used to produce micro Newton levels of thrust for both of the colloid thruster and field emission electric propulsion (FEEP) thruster, so it is suitable for the propulsion system of Cubesats. However, the traditional colloid thruster has the disadvantage of low specific impulse, and FEEP needs high voltage to make the liquid metal ionization. In recent years, many researchers have developed an ionic liquid ion source (ILIS), some of which have been used as propulsion system of Cubesats<sup>3,4</sup>, it shows great potential. The ionic liquid is molten salt which is liquid at room temperature. It has the advantages of high conductivity, low saturated vapor pressure and good stability, which makes it suitable for a propellant. Some researchers believe that it can work in colloid mode or pure ion mode<sup>5,6</sup>, and set up some models for simulations<sup>7,8</sup>. As far as our knowledge, the problem of voltage controlled ionic liquid electrospray in two modes has not been researched.

In this study, the relationship between the mode of the ionic liquid electrospray and the applied voltage is studied. We compared the current-voltage relationship and the specific charge in two modes, analyzed the principle of different modes, and observed the morphology of liquid surface in two modes to verify the hypothesis. The results have important significance for the study of high efficiency ILIS.

## II. Experiment and measurement methods

Figure 1 shows the schematic diagram of our experimental prototype and measurement instruments, we use capillary made up of stainless steel (outer diameter is 0.7mm, inner diameter is 0.15mm) as the emitter, copper plate as the extractor (with an aperture of 8mm in diameter) and the collector. The distance between the emitter and extractor is approximately 3mm. We take positive mode in our routine experiments, i.e. the emitter is attached positive high voltage, while the extractor and the collector are grounded. We use high precision micro syringe pump to control a stable flow rate of propellant, picoammeter to measure the total current from extractor and collector, high speed camera and high magnification microscope to observe the state of electrospray.

All the experiments were completed at atmospheric pressure, maybe the results could be less directly applied to electric thruster, the aim of this study is to investigate the relationship between the applied voltage and electrospray mode, and seek for the optimal condition of high efficiency emission.

In our typical experiment, we set up the prototype, set the parameter of the instrument, then started the pump and

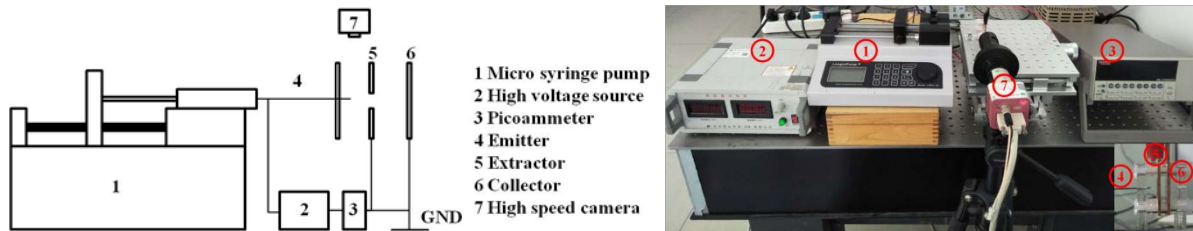


Figure 1. Schematic diagram of experimental prototype and measurement instruments.

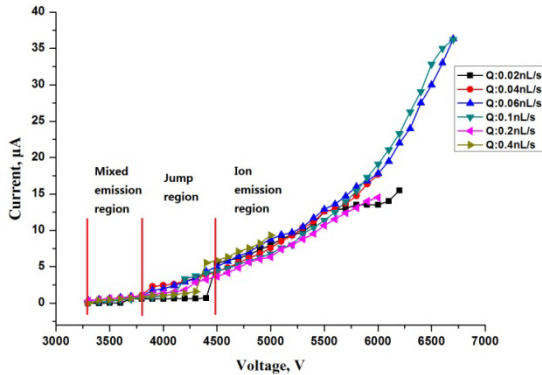
increased the voltage step by step, observed the morphology of liquid surface at the emitter tip, and recorded the current displayed on the picoammeter. We increased the voltage until discharge happened between the emitter and the extractor, and then finished the experiment. The flow rate was from 0.02nL/s to 0.4nL/s. Usually, the start voltage was about 3300V, when a Taylor cone formed and a current signal appeared. Each time we changed the voltage or flow rate, we waited 1min-2min and then recorded the current to make sure the equilibrium was stable enough.

## III. Results and discussion

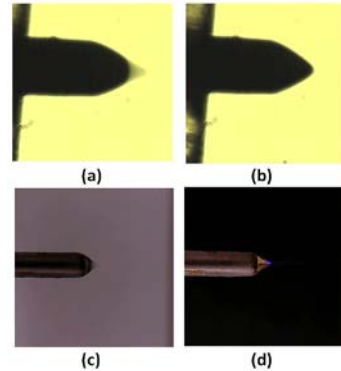
### A. I-V characteristic curve

Fig. 2 illustrates the current voltage relationship in different flow rate conditions. The range of flow rate is between 0.02nL/s, which is near the theoretical minimum flow rate<sup>9</sup>, and 0.4nL/s. We find the same I-V relationship in the range of experiment flow rate conditions, and divide the whole voltage range into 3 regions: the first region (3300V-3800V) named mixed emission region and in this region the current increases slightly with voltage. The second region (3800V-4500V) named jump region, where the current suddenly increases at some voltage,

accompanied by rapid spray sound. The last region (above 4500V) named ion emission region and in this region the current increases remarkably with voltage.



**Figure 2. I-V characteristic curves at different flow rates.**



**Figure 3. Images of two spray modes by high speed camera and high magnification microscope. (Flow rate is 0.4nL/s).**

### B. Images

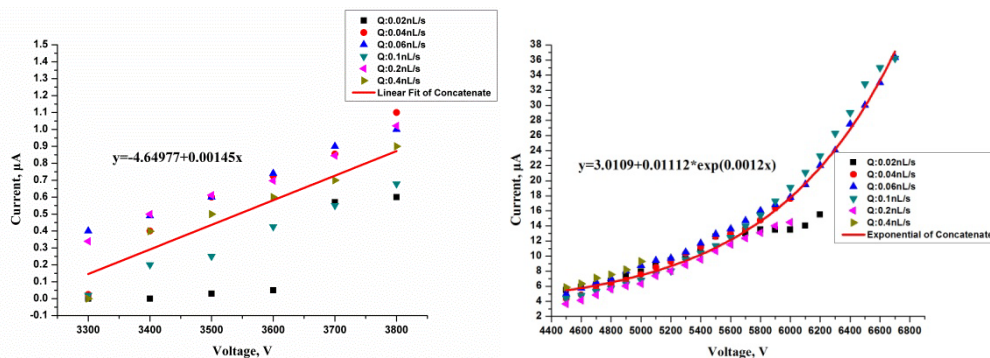
Fig. 3 shows the images of two spray modes which are obvious different in high speed camera and high magnification microscope. In the mixed emission region (Fig. 3a, 3c), the ionic liquid do not completely fill with the tip of the Taylor cone and seemed to be “atomized”. In the ion emission region (Fig. 3b, 3d), the ionic liquid fills the entire Taylor cone and is ionized, with a clear blue plume. It is proved that when the local electrical field reaches the threshold of ionization, the ionic liquid is ionized and accelerated to form a plume under the electric field. We can easily distinguish two spray modes by the photos of camera or microscope.

### C. Characteristic current

Fig. 4 shows the characteristic current curves of two spray modes, we can easily know that in the mixed emission region, the I-V relationship is linearity with the slope is  $0.00145\mu\text{A}/\text{V}$  (Fig. 4 left), it means that the current increases slightly with voltage, this is a little different from the conclusion that the current is independent of applied voltage (as shown Eq.(1))<sup>10</sup> because of the presence of ion emission in the mixed mode in our experiment.

$$I = f(\varepsilon) \left( \frac{\gamma K Q}{\varepsilon} \right)^{1/2} \quad (1)$$

The current generated by ion emission increases as the voltage increases, whereas the proportion of ion emission is very low, so the magnitude of increasement is little. I-V relationship is exponential in the ion emission region, as shown in the right part of Fig. 4. It is consistent with the theory of field evaporation proposed by Iribarne and Thomson in 1976<sup>11</sup>, which gives the ion current density ( $j$ ) as the following function of the local electric field ( $E$ ) of the liquid surface:



**Figure 4. I-V curves of two spray modes. (Left: mixed emission mode. Right: ion emission mode).**

$$j(E) = \frac{kT}{h} \sigma \exp \left[ -\frac{\Delta G - G(E)}{kT} \right] \quad (2)$$

Where  $T$  is the absolute temperature,  $k$  and  $h$  are Boltzmann's and Planck's constants,  $\sigma$  is the surface charge density,  $\Delta G$  is the Gibbs free energy required to bring an ion from the liquid into the gas, and  $G(E)$  is the reduction in  $\Delta G$  due to the presence of the electric field  $E$ . For a liquid of high dielectric constant and a surface with a radius of curvature of several nanometres,  $G(E)$  may be written through the Schottky hump approximation<sup>12</sup> as

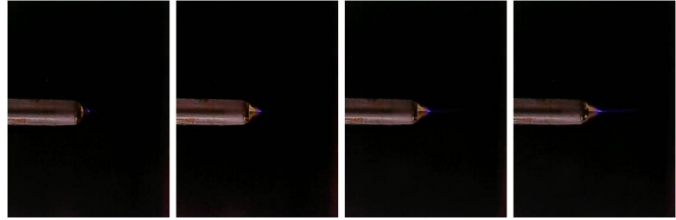
$$G(E) = \left( \frac{e^3 E}{4\pi\epsilon_0} \right)^{1/2} \quad (3)$$

Generally speaking,  $\Delta G$  is on the order of 1-2 eV, we can calculate the threshold value of external field required to initiate ion emission is 0.7 V/nm from Eq. (3). The local electric field of the Taylor cone surface can be described as following Eq. (4) based on the balance of electric field force and surface tension:

$$E = \sqrt{\frac{2\gamma}{\epsilon_0 r \tan \alpha}} = 1.87 \times 10^7 f^{1/3}(\epsilon) \gamma^{1/2} \left( \frac{K}{\epsilon Q} \right)^{1/6} \quad (4)$$

We observed that  $E$  is greater with the smaller  $r$  (that means the closer to the tip of Taylor cone), and the same proportion to the flow rate. In our experiment, the maximum flow rate is 0.4nL/s, then we can get the  $E=0.7$  V/nm, which meets the threshold value.

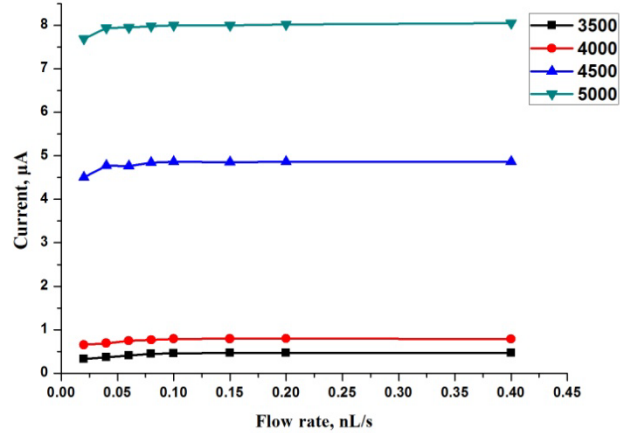
In fact, we observed the ideal phenomenon in the experiment which is consistent with the theory, the ion emission plume at the tip of Taylor cone is more and more vivid with the increase of voltage (local electric field enhancement), indicating that the larger emission current, as shown in Fig. 5.



**Figure 5. The variation of ion emission state at different voltage. (The voltage is 4500V, 5000V, 5200V, 5500V, respectively. Flow rate is 0.4nL/s).**

#### D. Flow rate

Figure 6 shows that the changes of emission current with different flow rates, we can observe that the current is dependent on the flow rate only in mixed emission region (black line 3500V and red line 4000V) between 0.02nL/s and 0.1nL/s, which is similar with the phenomenon of Mora (1994). It means that the presence of the colloid sprays. While in ion emission region (blue line 4500V and green line 5000V), the current is independent on the flow rate. We can also get the same conclusion that the voltage strongly affects the current in the ion emission region but little in mixed emission region.



**Figure 6. I-Q characteristic curves at different voltages.**

#### E. Specific charge

If all the propellants are sprayed in the form of charged droplets, i.e., the colloid mode, the Taylor cone jet current is satisfied Eq.(1), The relation between specific charge, current and flow rate is:

$$\frac{q}{m} = \frac{I}{\rho Q} \quad (5)$$

We can obtain the theoretical maximum specific charge (Rayleigh limit) of the droplets in colloid mode:

$$\left( \frac{q}{m} \right)_{\text{col}} = \frac{f(\epsilon)}{\rho} \left( \frac{\gamma K}{\epsilon Q} \right)^{1/2} \quad (6)$$

According to the literature,  $f(\epsilon)$  is an empirical constant between 15-25 for the liquid with high relative permittivity ( $\epsilon > 40$ ), we set it 20 in this paper to calculate easily. The parameters of the ionic liquid EMIBF<sub>4</sub> used in our experiment are  $\gamma = 0.052 \text{ N/m}$ ,  $\rho = 1294 \text{ kg/m}^3$ ,  $K = 1.3 \text{ S/m}$ ,  $\epsilon = 68$ . The theoretical maximum specific charge in colloid mode under different flow rates can be obtained by entering these parameters into Eq.(6), the results are listed in Table 1.

If the ionic liquid is sprayed in the form of cation monomer (EMI<sup>+</sup>, positive mode), the theoretical maximum specific charge is:

$$\left(\frac{q}{m}\right)_{\text{EMI-m}} = \frac{e}{111u} = \frac{1.6 \times 10^{-19}}{111 \times 1.66 \times 10^{-27}} = 868338 \text{ C/kg} \quad (7)$$

With the same method, we can get the specific charge of cation dimer (EMI(EMIBF<sub>4</sub>)<sup>+</sup>) and trimer (EMI(EMIBF<sub>4</sub>)<sub>2</sub><sup>+</sup>) is 321285 C/kg and 197107 C/kg, respectively. The specific charge data of theoretical and experiment are listed in Table 1 and graphed in Fig. 7, we can see the theoretical maximum specific charge in colloid mode decreasing with the growth of flow rate, while in ion mode keeping a constant. We calculate the specific charge at 3000V and 5000V, respectively, based on the measured currents. We can see the specific charges of experiment are all above the theoretical maximum specific charge of the colloid mode, and decrease with the growth of flow rate, the line of 3500V is closer to the colloid mode line, especially at 0.4nL/s, while the line of 5000V is obviously higher than it. From these data, we get several conclusions as following:

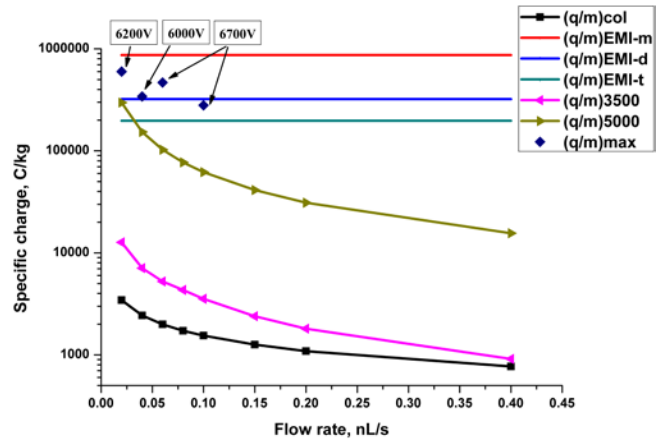
**Table 1. Specific charge data of theoretical and experiment**

Flow rate, nL/s	$(q/m)_{\text{col}}$ , C/kg	$(q/m)_{\text{EMI-m}}$ , C/kg	$(q/m)_{3500}$ , C/kg	$(q/m)_{5000}$ , C/kg	$(q/m)_{\text{max}}$ , C/kg
0.02	3446	868338	12674	297025	598918(6200V)
0.04	2437	868338	7090	153362	340997(6000V)
0.06	1989	868338	5242	102396	467968(6700V)
0.08	1723	868338	4328	77087	-
0.1	1541	868338	3547	61824	279853(6700V)
0.15	1258	868338	2391	41216	-
0.2	1090	868338	1804	30989	-
0.4	771	868338	912	15553	-

(1) The colloid spray and ion emission are all present in the mixed mode, the percentage of ion emission is higher at low flow rate, while the percentage of colloid spray is higher at large flow rate.

(2) Ion emission plays a dominant role in ion mode (at high applied voltage), but not a monomer ion, most of ions are dimer, trimer and multimer. The specific charge is higher at low flow rate, which means higher specific impulse and efficiency.

(3) We got the optimal results in different flow rate and applied voltage in our experiments, e.g., 0.02nL/s at 6200V, 0.04nL/s at 6000V, 0.06nL/s and 0.1nL/s at 6700V, all of them are between the monomer and dimer. The most one is 0.02nL/s at 6200V, which efficiency is about 70%. It is shown that high ion emission efficiency could be attained at low flow rate and high voltage. This conclusion is very useful for designing of high efficiency liquid ion electric propulsion thruster in the future (including colloid and FEEP thruster).



**Figure 7. Specific charge of two spray modes with different flow rates.**

#### IV. Conclusion and future work

We realized stable electrospray in a wide range of voltage (from 3300V to about 6000V), using ionic liquid EMIBF<sub>4</sub> as propellant, and can easily change two spray modes by adjusting the applied voltage, i.e. mixed emission mode and ion emission mode. When the flow rate is 0.02nL/s and the voltage is 6200V, we can get the optimal ion

emission efficiency close to 70%. The required minimum theoretical flow rate of electrospray using EMIBF<sub>4</sub> is as low as 0.0186nL/s, and such a low flow rate means higher thrust adjustment accuracy. Some work is planned to do in future, including a series of experiments in vacuum chamber, and directly determinate the specific charge of the plume by mass spectrometry.

### Acknowledgments

This work is supported by National Natural Science Foundation of China (No.11672039) and Research Foundation of Beijing Institute of Technology (No.20160142002). We would like to express our gratitude to Dr. Katharine Smith (The University of Manchester) for some useful discussions and advices.

### References

- <sup>1</sup>Fenn, J. B., Mann, M., Meng, C. K., Wong, S. F., Whitehouse, C. M., "Electrospray Ionization for Mass Spectrometry," *science*, Vol. 246, No. 4926, 1989, pp. 64-71.
- <sup>2</sup>Guerragarcia, C., Krejci, D., Lozano, P., "Spatial uniformity of the current emitted by an array of passively fed electrospray porous emitters," *Journal of Physics D Applied Physics*, Vol. 49, No. 11, 2016, pp. 115503.
- <sup>3</sup>Krejci, D., Lozano, P., "Scalable Ionic Liquid Electrospray Thrusters for Nanosatellites," AAS GNC Conference, 2016.
- <sup>4</sup>Krejci, D., Mier-Hicks, F., Fucetola, C., Lozano, P., Hsu, A., Martel, F., "Design and Characterization of a Scalable ion Electrospray Propulsion System," International Electric Propulsion Conference, Hyogo-Kobe, Japan, 2015.
- <sup>5</sup>Romero-Sanz, I., Bocanegra, R., Fernandez De La Mora, J., Gamero-Castan O, M., "Source of heavy molecular ions based on Taylor cones of ionic liquids operating in the pure ion evaporation regime," *J Appl Phys*, Vol. 94, No. 5, 2003, pp. 3599.
- <sup>6</sup>Marcuccio, S., Giusti, N., Pergola, P., "Slit FEEP Thruster Performance with Ionic Liquid Propellant," AIAA/ASME/SAE/ASEE Joint Propulsion Conference, San Jose, CA, 2013.
- <sup>7</sup>Lastow, O., Balachandran, W., "Numerical simulation of electrohydrodynamic (EHD) atomization," *J Electrostat*, Vol. 64, No. 12, 2006, pp. 850-859.
- <sup>8</sup>Borner, A., Li, Z., Levin, D. A., "Prediction of Fundamental Properties of Ionic Liquid Electrospray Thrusters using Molecular Dynamics," *The Journal of Physical Chemistry B*, Vol. 117, No. 22, 2013, pp. 6768-6781.
- <sup>9</sup>Alexander, M. S., Smith, K. L., Paine, M. D., Stark, J. P. W., "Voltage-Modulated Flow Rate for Precise Thrust Control in Colloid Electrospray Propulsion," *J Propul Power*, Vol. 23, No. 5, 2007, pp. 1042-1048.
- <sup>10</sup>De La Mora, J. F., Loscertales, I. G., "The current emitted by highly conducting Taylor cones," *J Fluid Mech*, Vol. 260, No. 1, 1994, pp. 155.
- <sup>11</sup>Guerrero, I., Bocanegra, R., Higuera, F. J., Fernandez De La Mora, J., "Ion evaporation from Taylor cones of propylene carbonate mixed with ionic liquids," *J Fluid Mech*, Vol. 591, 2007.
- <sup>12</sup>Loscertales, I. G., Fernández De La Mora, J., "Experiments on the kinetics of field evaporation of small ions from droplets," *The Journal of Chemical Physics*, Vol. 103, No. 12, 1995, pp. 5041-5060.