The Use of Ionic Liquid Ion Sources (ILIS) in FIB Applications

by

Anthony Nicholas Zorzos

Submitted to the Department of Aeronautics and Astronautics in partial fulfillment of the requirements for the degree of Master of Science in Aeronautics and Astronautics at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Abstract

A new monoenergetic, high-brightness ion source can be constructed using an arrangement similar to liquid metal ion sources (LMIS) by substituting the liquid metal with an ionic liquid, or room temperature molten salt. Ion beams produced by these ionic liquid ion sources (ILIS) have energy deficits and distributions that closely resemble their metallic counterparts, with the exception that, if needed, they can be stably operated at current levels as low as a few nA. ILIS sources are here presented as having two further key advantages: (1) the ability to obtain both positive and negative ion beams, and (2) the ability to produce very diverse molecular ions in terms of their masses, compositions and properties, due to the fact that the number of available ionic liquids is large. In this thesis an overview of ILIS sources is presented, as well as preliminary results of their performance in a FIB column.

Thesis Supervisor: Paulo Lozano
Title: Professor
Acknowledgments

First and foremost I recognize my advisor and mentor, Professor Paulo Lozano. During my time at MIT he has demonstrated wisdom and humanity alongside his obvious brilliance; I consider myself lucky if only a small bit of that mojo rubs off on me. I have been and always remain his loyal minion. I also recognize Professor Martinez-Sanchez and the rest of the Space Propulsion Laboratory for their unwavering assistance with my academic efforts.

Of a categorically different flavor, I note my parents: my ontological Creation was somewhat of a help in forming a Master’s thesis. Finally, and most earnestly, I praise the never-ending support of my fiancee.
Contents

1 INTRODUCTION .................................................. 15
   1.1 Focused Ion Beam Overview ............................. 15
   1.2 Focused Ion Beam History and Development ........... 17

2 LIQUID METAL ION SOURCES VS. IONIC LIQUID ION SOURCES 19
   2.1 Liquid Metal Ion Sources ............................... 19
   2.2 Ionic Liquid Ion Sources ............................... 20
   2.3 Ionic Liquid Ion Sources in Focused Ion Beam Applications 24

3 ELECTROSPRAY CHARACTERISTICS .......................... 30
   3.1 Electrospray History .................................... 30
   3.2 Electrospray Applications .............................. 31
   3.3 Basic Physics ............................................ 31
      3.3.1 Relaxation Time .................................... 31
      3.3.2 Taylor Cone Formation .......................... 33
      3.3.3 Emitted Current and Starting Voltage .......... 35
      3.3.4 Field Evaporation .................................. 37
      3.3.5 Electrospray Emitter Types ..................... 39
4 Focused Ion Beam Column

4.1 Column Outline ............................................. 46
  4.1.1 Emitter and Extractor Assembly .................... 46
  4.1.2 Electrostatic Lenses .................................. 48
  4.1.3 Deflection Plates .................................... 49
  4.1.4 Collector Assembly .................................... 49

5 Experimental Techniques ............................ 51

  5.1 Time-of-Flight Mass Spectrometry ..................... 51
  5.2 Wire-Grid Detector ...................................... 54
  5.3 Vacuum System and Lab Facilities ..................... 54

6 Experimental Results ................................ 59

  6.1 Experimental Overview ................................ 59
  6.2 Single Emitter Performance ............................ 59
    6.2.1 EMIF2.3HF ......................................... 60
    6.2.2 BMI-I .............................................. 62
  6.3 Performance in FIB Column ............................. 65
    6.3.1 Probe Size and Lens Potential ................... 66
    6.3.2 Ion Fragmentation and Energy Consistency ....... 67
  6.4 Electrochemical Issues ................................. 70
    6.4.1 Potential Solutions to the Electrochemical Decay Issue 71
    6.4.2 Bipolar Electrospray ............................... 73
    6.4.3 Dielectric Bipolar Electrospray ................... 73

7 Conclusions and Future Work ........................ 78

  7.1 Future Work ............................................. 78
7.2 Conclusions
List of Figures

1-1 The three main sections of the Focused Ion Beam (FIB) system: the ion source, the electrostatic optics, and the substrate target. 16

2-1 Theoretical performance of an ILIS optical column. 28

3-1 Schematic of standard capillary emitter setup. 34
3-2 Schematic of Taylor cone parameters. 35
3-3 Diagram of coordinate system. 37
3-4 Model of ion evaporation. 39
3-5 Electrospray emitter types: A. capillary emitter, B. internally wetted porous emitter, C. externally wetted emitter 40
3-6 Diagram of electrochemical etching system. A voltage is supplied between the needle and surrounding stainless steel cylinder in a NaOH liquid bath. 42
3-7 System setup for needle-tip annealing. 43
3-8 Needle tip emitter SEM. 44
3-9 Needle tip emitter SEM. 45

4-1 The FIB column experimental setup is composed of an externally wetted source, extractor, aperture, einzel lens, deflection plate assembly, wire-grid detector, and collector plate. 47
4-2 Emitter and extractor assembly. ........................................ 48

5-1 Time-of-flight (TOF) system composed of ion source, electro-
static gate, and faraday-cup collector. ................................. 52

5-2 Characteristic current landscape for time-of-flight data. .... 53

5-3 A schematic of the model parameters. ............................... 55

5-4 Wire-grid current landscape. ......................................... 56

5-5 Stainless steel vacuum chamber. .................................... 57

5-6 Electronic systems. ..................................................... 58

6-1 TOF spectrum for $EMIF_{2.3HF}$ in the positive polarity, nor-
malized to unity. .......................................................... 63

6-2 TOF spectrum for $EMIF_{2.3HF}$ in the negative polarity, nor-
malized to unity. .......................................................... 64

6-3 $BMI-I$ synthesis setup, including: reflux condenser, round
bottom flask, bubbler, argon gas lead, crystal dish, hot plate,
thermometer, magnetic stirrer, and reagents. ....................... 65

6-4 TOF spectrum for $BMI-I$ in the positive polarity, normalized
to unity. Vertical markers represent ion masses up to one degree
of solvation to neutral, N. ............................................. 66

6-5 TOF spectrum for $BMI-I$ in the negative polarity, normalized
to unity. Vertical markers represent ion masses up to three
degrees of solvation to neutral, N. .................................. 67

6-6 The current signal as the beam is passed over a single wire. By
fitting the theoretical model of a circular beam passing over the
wire, the beam size in this case is found to be 30 $\mu$m. ........ 68

6-7 The focused spot size is determined for different lens potentials. 69
6-8 Diagram of double-layer buildup along ionic liquid-tungsten interface. ........................................ 71
6-9 Electrospray response to polarity reversal. ......................... 72
6-10 Diagram of physical emitter A) without polarity alternation, and B) with polarity alternation. ............... 75
6-11 Setup for bipolar electrospray. ........................................... 76
6-12 Long-term current test with initial dynamic behavior. ...... 77
6-13 Long-term current test with emission stabilization. .......... 77
7-1 Outline of Wien filter. ...................................................... 79
7-2 Outline of full FIB column cage, to which the Wien filter is directly integrated. All elements are mounded on 1/8” alumina rods. ................................................................. 80
List of Tables

2.1 Various Ionic Liquids. ........................................ 23

5.1 SPL Electronic Systems. ................................. 56

6.1 Permutations of possible positive ion species. ............ 61

6.2 Permutations of possible negative ion species. ............ 62
Chapter 1

INTRODUCTION

1.1 Focused Ion Beam Overview

Focused Ion Beam (FIB) technology can be classified into two separate categories: lithography and microscopy. The general definition of lithography, coming from the Greek *litho* meaning *stone* and *grapho* meaning *to write*, involves the transfer of a pattern onto a substrate. Microscopy, coming from the Greek *micro* meaning *small* and *scopy* meaning *to look*, involves the “probing” of an arbitrary substrate or surface to gather information on certain of its characteristics. These general definitions of lithography and microscopy apply to systems of any scale, from the nano to the cosmo. However, in the modern age, the trend has been for the increasing miniaturization of technology, and for this endeavor FIB systems are necessary and useful. Applications include FIB-microscopes, micro-machining, ion-etching, ion-milling, ion-beam induced deposition, Transmission Electron Microscopy (TEM) preparation, and photo-mask repair. Because of the broad range in applications, FIB systems are absolutely crucial in the semiconductor industry, and a great deal of
interest in them has grown in that community.

The FIB system can be decomposed into three main sections: the source, the optics, and the target, as shown in Figure 1-1. The source is where the ions are generated. As described below, there have been many different types of ion sources over the history of FIB systems. The optics is where the ion beam is manipulated using electromagnetic lens systems; this is where the ion beam is "focused" and directed. The target is the substrate-of-interest, where the ion beam interacts with a material. The type of reaction depends on a host of system parameters, and those parameters are trained by the desired application. This description is a skeleton of FIB systems, outlined here in box-diagram form, as simplified as possible. Each section is a complex field in and of itself, and is treated so in the community at large. Although this study involves and depends upon all three sections, the main thrust, or emphasis, lies with the ion source.

![Figure 1-1: The three main sections of the Focused Ion Beam (FIB) system: the ion source, the electrostatic optics, and the substrate target.](image-url)
1.2 Focused Ion Beam History and Development

[1] The original creation and development of FIB systems was based on, and influenced by, scanning electron technologies and ion thrusters for space propulsion. Starting in the 1960’s, systems capable of spot sizes (the “spot” being the footprint of the focused ion beam on the target) on the order of 100 nm at a few pA [2] were developed. The ion sources at this time were low-brightness plasma sources. Later in the 1960’s, the importance of high-brightness sources and low-aberration optical systems for high-resolution capabilities was demonstrated [3]. In the early 1970’s, gas field ionization sources (GFIS) were used to produce spot sizes on the order of 50 nm at a current of 10 pA by Levi-Setti of University of Chicago and Orloff/Swanson of the Oregon Graduate Center. Regardless of the small probe size, GFIS were abandoned because of (1) the low ion current, and (2) the problematic need to cryogenically cool the source. In its place came liquid metal ion sources (LMIS), invented in England in 1975 by Clampitt. It was not until 1982 (Jergenson) that a long-lived stable LMIS was developed. Following this, Levi-Setti, alongside Seliger and Ward, developed a high-resolution tool for microscopy and surface analysis. From this point, FIB research expanded dramatically. At IBM Wagner began to develop FIB systems as a tool for mask repair [4]. Gamo, Wang, and Ahmed (of Japan, HRL, and Cambridge respectively) built mass-separated filtration systems for FIB columns. Ishitani (1987) of Hitachi developed the method of using FIB systems as a tool for integrated circuit cross sectioning. In 1988 Sudraud at CNRS combined a FIB column with a scanning electron microscope (SEM) to create the first dual-beam system capable of microcircuit surgery. Smith
has explored new plasma source configurations for applications requiring high currents and ion sources other than Gallium.

By far, the most common ion sources in FIB columns today are LMIS. The purpose of this study is to propose ionic liquid ion sources (ILIS) as a potential ion source. However, we first must what LMIS are, what ILIS are, and how ILIS can potentially overcome the inherent limitations of LMIS.
2.1 Liquid Metal Ion Sources

Ionic liquid ion sources (ILIS) are among the most recent additions to the list of charged particle FIB sources suitable for applications in the analysis and processing of materials [5,6]. These devices were originally developed (and still are) as space propulsion micro-engines and were inspired by the well-known liquid metal ion sources (LMIS). In LMIS, metals at a temperature slightly higher than their melting points coat a sharp conductive needle. A voltage difference of the order of a few kilovolts is applied between the needle tip and a downstream aperture electrode typically located within a distance comparable to a few needle diameters. When the electrostatic force on free charges in the conductive liquid is higher than the surface tension of the liquid film covering
the needle, the free surface evolves into a dynamically stable conical structure known as a Taylor cone [7], thus producing ion beams of extraordinarily high brightness. LMIS have played a critical role in FIB applications; they have been used in ion lithography, ion etching, ion implantation, ion microscopy, and as a generic tool in micro- and nano-manufacturing. There are, however, a few limitations intrinsic to LMIS. Except for metals like In or Ga, most sources work only at very high temperatures, thus introducing some difficulties in the source implementation and operation, as the thermal evaporation rate of neutrals increases and chemical reactions with the needle material (usually tungsten) may occur. High temperatures also have an impact in the random thermal motion of ions, which decrease the beam quality. These thermal and compatibility issues mean that only a relatively small number of metallic elements and alloys can be successfully used in FIB from LMIS. In addition, operation as outlined above is possible only in the positive polarity, emitting only positively charged metallic ion beams.

2.2 Ionic Liquid Ion Sources

ILIS working mechanisms are very similar to those of LMIS. The main distinction is that ionic liquids (IL) are used in ILIS. The recent discovery of ILs represented a breakthrough in many areas, especially in those involving chemical engineering processes. These substances, also known as room-temperature molten salts, are composed of non-solvent mixtures of complex organic and inorganic cations and anions. These ions are large enough to produce a poorly coordinated mixture that remains in the liquid phase at moderate temperatures. Some of them display super-cooling tendencies in which they remain as
liquids well below their nominal freezing points. Just as their inorganic cousins (simple salts like NaCl, KBr, etc.) at their melting points (typically > 850° C), they exhibit appreciable electrical conductivity at room temperature, making them suitable for electrostatic deformation and subsequent Taylor cone formation. ILs are thermally stable over a wide range of temperatures (they do not boil, but decompose at temperatures ~ 250-500° C) and are apparently non-toxic. They have received much attention for many applications with green standards, such as in the synthesis and catalysis of chemical reactions. Another research area for ILs involves their use in electrochemical systems, such as high energy density super-capacitors. Their attractiveness in this area relies on the size of their electrochemical window (i.e., the maximum potential difference sustainable by the liquid before electrochemical reactions are triggered), which is higher than in conventional aqueous solutions. In addition to these characteristics, ILs possess the important property of extraordinarily low vapor pressures at their melting points. This allows their use in high vacuum equipment in open architectures such as liquid-coated needles.

In 2003, the group led by Prof. Juan F. de la Mora of Yale University [8] demonstrated that pure positive ion emission is possible using the ionic liquid EMI-BF$_4$ (1-ethyl-3-methyl imidazolium tetrafluoroborate) with capillary emitters, and proved that an initially droplet-rich regime transitions at low flow rates to a purely (singly charged) ionic mode. More recently, it was found that pure ion emission from other ionic liquids is not possible using capillary emitters. In contrast, every ionic liquid tested so far using an externally wetted configuration on a solid needle produces streams of pure ions [9]. However, it was also found that emission from capillary and externally wetted ILIS is seriously compromised due to the electrochemical decomposition of the ionic
liquid when the counterions that are not extracted in the beam are attracted
to and accumulate on the needle surface, thus creating a double-layer charge
structure when the image charges in the needle material are taken into account.
Electrochemical reactions can be avoided altogether if the charging time of this
double-layer structure is long enough to actively stop its growth [5]. This de-

dpends on the magnitude of the potential difference across the double layer
required for electron transfer (the electrochemical window) and the device ca-
pacitance. Before the voltage reaches the critical value for decomposition, the
polarity of the power supply is reversed to discharge the double layer while
creating a new one with the opposite charge. The electrochemical window of
ionic liquids is typically 2-4 volts on each polarity and consequently the al-
ternation frequency is relatively low. Stable emission has been demonstrated
for at least ~200 hours with a frequency of 1 Hz. By increasing the device

capacitance (for instance, by increasing the liquid-solid contact area), emitters
can be operated for extended periods of time (> 100 hr) at frequencies as low
as 0.3 mHz.

The emission characteristics of an externally wetted EMI-BF$_4$ ILIS have
been established by time-of-flight spectroscopy showing that (EMI-BF$_4$)$_n$EMI$^+$
ions with molecular masses of 111 (n = 0) and 309 (n = 1) amu respectively,
are emitted in the positive cycle, while negative (EMI-BF$_4$)$_n$BF$_4^-$ ions with
masses 87 (n = 0) and 285 (n = 1) amu are emitted in the negative mode
[6]. The currents of both beams are close to ±200 nA at a voltage of about
±1.8 kV. Angular emission properties of ILIS show that beams spread at half-
angles smaller than 18° from the centerline. Ion beams from another ionic
liquid (EMI-Im) have been studied as well [10]. In addition to solvated ions
with a structure similar to that found in EMI-BF$_4$, measurements using a
retding potential analyzer (RPA) show that little energy of the order of $\sim 7$ eV (energy deficit) is spent in creating the ions, which are emitted with narrow distributions ($\sim 7$ eV FWHM = full width at half maximum).

One of the most important advantages of ILIS over other ion sources is the availability of ionic liquids of different properties. There are hundreds of ionic liquids described in the literature so far [11], with many more amenable for synthesis. Almost every possible ion, positive and negative, can be found in one of these liquids. Some of them, like EMI-BF$_4$, have inorganic molecular anions, and some have massive organic anions, like in EMI-Im. Others include atomic species, such as I$^-$ and Cl$^-$. The variety is immense [9, 11, 12], and so is the potential to produce ion beams tailored to every possible application.

In addition, ILIS is unique in that negative ions from a point source can be obtained. Negative ions like those described above could be beneficial in applications requiring reactive species, or to mitigate substrate charging problems without recourse to electron flooding [13]. Ionic liquids used and characterized by this lab, as well as others, are shown in Table 2.1.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMI-BF$_4$</td>
<td>1-ethyl-3-methylimidazolium tetrafluoroborate [14]</td>
</tr>
<tr>
<td>EMI-IM</td>
<td>1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) [15]</td>
</tr>
<tr>
<td>EMI-Beti</td>
<td>1-ethyl-3-methylimidazolium bis(pentafluoroethyl) sulfonium imide [9]</td>
</tr>
<tr>
<td>C$_5$MI-(C$_2$F$_5$)$_3$PF$_3$</td>
<td>1-methyl-3-pentylimidazolium tris(pentafluoroethyl) trifluorophosphate [9]</td>
</tr>
<tr>
<td>C$_4$mim-I</td>
<td>1-butyl-3-methylimidazolium iodide [11]</td>
</tr>
<tr>
<td>EMIIF:2.3HF</td>
<td>1-ethyl-3-methylimidazolium fluorohydrogenate [16]</td>
</tr>
<tr>
<td>EMI-GaCl$_4$</td>
<td>1-ethyl-3-methylimidazolium gallium tetrachloride [17]</td>
</tr>
<tr>
<td>EMI-N(CN)$_2$</td>
<td>1-ethyl-3-methylimidazolium dicyanamide [18, 19]</td>
</tr>
<tr>
<td>EMI-C(CN)$_3$</td>
<td>1-ethyl-3-methylimidazolium tricyanomethanide [18]</td>
</tr>
<tr>
<td>BMI-FeBr$_4$</td>
<td>1-butyl-3-methylimidazolium iron tetrabromide [20]</td>
</tr>
<tr>
<td>C$_6$MI-FeBr$_4$</td>
<td>1-hexyl-3-methylimidazolium iron tetrabromide [20]</td>
</tr>
<tr>
<td>C$_6$MI-FeCl$_4$</td>
<td>1-hexyl-3-methylimidazolium iron tetrachloride [20]</td>
</tr>
</tbody>
</table>
2.3 Ionic Liquid Ion Sources in Focused Ion Beam Applications

The quality of the beam probe (the beam projected area on the target surface) depends on the properties of the ion-optical system and the beam itself. It is imperative in many applications (micro- and nano-manufacturing, scanning microscopy, etc.) for the probe size to be as small as possible. This size, or circle of least confusion, will be determined by the different aberrations introduced by the optical system [21, 22].

Even in the ideal case of monoenergetic paraxial beams, and in the absence of other aberrations, the smallest probe will be determined by the physical size of the source, \( D \). This is known as the source limit of an optical system, contributing with a diameter \( d_0 = M D \). Reducing the magnification, \( M \), is not always a practical option to obtain smaller probes because the increase in probe diameter due to spherical and chromatic aberration at reduced \( M \) offsets gains in smaller \( d_0 \) under many operating conditions. Source size is obviously an important limitation for plasma-based FIB systems, where the ionization region is contained in a non-negligible volume. In field ionization/evaporation sources, the region where ions are produced is extremely small in comparison, and in many cases is regarded as a virtual point source.

The source size of LMIS was a topic of intense discussion for a considerable amount of time, until Driesel, et al. [23] were able to resolve the free surface on the liquid metal cone apex using transmission electron microscopy (TEM). Direct observations plus theoretical estimates were combined to reach a consensus on the shape and size of the ion-emitting source. It is now well-accepted that the source in LMIS is formed by a semispherical cap at the end
of an elongated protrusion issuing from the Taylor cone apex with a diameter that varies from about 1 nm to more than 50 nm, depending on the intensity of the emitting current. Sizes of that order should be expected in ILIS since the physical mechanisms responsible for ion emission are similar in both cases. A simple scaling from Schottky’s field-enhanced thermionic emission relation can be made to estimate the relative sizes of LMIS and ILIS sources:

\[ j = \varepsilon_0 E_n \frac{kT}{h} \exp \left[ -\frac{1}{kT} \left( \frac{q^3 E_n}{4\pi\varepsilon_0} \right) \right] \]  

(2.1)

where \( j \) is the current density, \( E_n \) is the electric field normal to the liquid surface, \( q \) is the ion charge (Ze), \( k \) is Boltzmann’s constant \( (1.38 \times 10^{-23} J/K) \), \( \varepsilon_0 \) is the permittivity of vacuum \( (8.854 \times 10^{-12} \text{F/m}) \) and \( G \) is the solvation energy of the bound ion. As can be seen from the expression above, copious ion emission is triggered when the normal electric field satisfies \( E_n \approx \frac{4\pi\varepsilon_0 G^2}{q} \), with \( G \) given in eV. This electric field is also responsible for producing the required force that sustains the curvature of the semispherical cap, therefore \( E_n \propto \frac{\gamma}{D} \), where \( \gamma \) is the liquid surface tension.

Ionic liquids and liquid metals have very different physical and electrical properties. However, according to the model above, the relevant quantities that determine the source size are the surface tension and solvation energy. Under these conditions, the relative source sizes should be approximately related by,

\[ \frac{D_{il}}{D_m} \approx \frac{\gamma_{il}}{\gamma_m} \left( \frac{G_m}{G_{il}} \right)^4 \]  

(2.2)

The surface tension of metals is in most cases (except for Cs) about an order of magnitude larger than that of ionic liquids. Determination of solvation energies is considerably more difficult, theoretically and experimentally. Data
quoted in the literature vary significantly from author to author, but in general, values in metals are typically about two to three times that of evaporation of molecular ions from liquid surfaces. The preceding rationalization allows us to estimate size ratios \( \frac{D_u}{D_m} \) from about 2 to 8. The purpose of this argument is not to give a quantitative measure of the source size in ILIS, but to justify our initial assumption of sizes comparable to LMIS. More comprehensive models, or direct visualization, would be required to establish the size and shape of the ion emission region in ILIS.

The ultimate objective of the ion optical system is to compress as much current as possible into the smallest achievable area. An important figure of merit of FIB ion sources is therefore the angular brightness, or angular current density \( \frac{dI}{d\Omega} \), which characterizes the beam current emitted as a function of the solid angle projected from a virtual point source. The angular brightness is related to the beam current by \( I = \int \left( \frac{dI}{d\Omega} \right) d\Omega \). Taking \( \frac{dI}{d\Omega} \) as constant (assuming uniform profile) and from the definition of solid angle \( \Omega = 2\pi (1 - \cos \theta) \), we get \( I \approx \pi \alpha_0^2 \left( \frac{dI}{d\Omega} \right) = \pi M^2 \alpha^2 \left( \frac{dI}{d\Omega} \right) \) after integrating between zero and the (small) beam source angle \( \alpha_0 \), and making use of einzel type optics (\( \alpha \) is the beam target angle). When including contributions from spherical and chromatic aberrations, the probe size \( D \) can be written as,

\[
d^2 = I^3 \frac{C_s^2}{\left( \pi M^2 \left( \frac{dI}{d\Omega} \right) \right)^3} + I \left( \frac{\Delta W_{1/2}}{W} \right)^2 \frac{C_c^2}{\pi M^2 \left( \frac{dI}{d\Omega} \right)} + M^2 D^2. \tag{2.3}
\]

Even sources with extremely high angular brightness would perform poorly in FIB applications if the energy spread \( \Delta W_{1/2} \) is also high. The relevant figure of
merit to be maximized is what is known as the chromatic angular intensity [24],

$$\Phi = \frac{dt}{d\Omega} \left( \frac{\Delta W_\theta}{2} \right)^2$$  \hspace{1cm} (2.4)

High $\Phi$ requires not only high brightness, but also low energy spread. In LMIS, both the angular brightness and the energy spread increase roughly linearly with current. Given the square dependence on the denominator in $\Phi$, this means that one would want to operate at the lowest possible currents. In fact, the best performance would occur for currents $< 1 \mu A$. The problem for LMIS is that it becomes very difficult to obtain stable emission at such low currents. Fortunately, there is an atypical kink in the angular intensity at currents between 1 and 5 $\mu A$, producing a local maximum in $\Phi$ [21]; this is the optimal point of operation.

In contrast, ILIS nominally work stably at considerably lower currents than LMIS. It is relatively easy to obtain currents between 10 and 1000 nA. The angular brightness increases in that range (the emission angle does not grow as fast as the current itself) while the energy spread remains practically constant [10]. Given these low currents, most of the time FIB ILIS would operate in the chromatic aberration regime, or even in the source limit regime.

Determination of the optical properties for ILIS requires a detailed calculation of the aberration coefficients. This depends on the geometry of the column and on the beam properties for a particular source. Nevertheless, it is possible to estimate the individual contributions from data available in the literature. For example, Figure 2-1 shows an estimate of the probe size as a function of probe current for a single lens ILIS column with $M = 1$ operating at 600 nA and 18° beam half angle, which for a uniform distribution gives
\( \frac{dl}{dh} = 2 \mu_A \text{sr} \). The FWHM is 7 eV and the column energy is 3 keV. The source is assigned an assumed (constant) diameter of 10 nm and aberration coefficients (constant as well) estimated from [22]. Even though the values are somewhat on the conservative side, the estimates are encouraging. The probe current density for a 50 nm diameter would reach a value of 152 \( \frac{A}{cm^2} \).

![Figure 2-1: Theoretical performance of an ILIS optical column.](image)

It must be stressed that the purpose of this work is to propose a novel ion source and test its feasibility as such. A limited in-house fabricated column serves this test of feasibility; it does not serve, however, a direct test of the proposed source’s performance as a tool in lithography and microscopy. For this reason certain column-dependent parameters are not precisely characterized.
As mentioned, electrospray is the fundamental mechanism behind ion emission from an ionic liquid. To predict and analyze how ILIS behaves in a FIB column, it helps to first understand electrospray physics in depth.
Chapter 3

ELECTROSPLAY
CHARACTERISTICS

3.1 Electrospray History

The electrospray phenomenon was first observed by John Zeleney in 1914, when he empirically observed the onset of a stable cone-jet liquid surface (later to be known as the Taylor cone) under a strong externally applied electric field [25]. It was not until 1964, however, that a theoretical model was developed by G.I. Taylor to explain the onset of a Taylor cone [7]. The model was based on the balance of electrostatic traction forces and surface tension. Although further advances in the theoretical understanding of electrosplay have been made since then, this model still serves as a foundational physical understanding. Throughout the 1960’s, electrospray was strongly considered and researched as an alternative to ion-engines in the field of space propulsion [26]. At the time, it was realized such a replacement was not viable due to the charge-to-mass ratio of the emitted particles. As a result, research on electro-
spray lay relatively dormant for nearly two decades. Research, however, saw a new dramatic expansion in the late 1980’s and 1990’s with the developments made by John Fenn and the synthesis of new ionic liquids. John Fenn successfully utilized electrospray as a mass spectrometry tool in the bio-sciences, and for his efforts, in 2002 was awarded the Nobel Prize. [27].

3.2 Electrospray Applications

Electrospray sources have found applications in a variety of fields, even though, as stated, they did not find a place in space propulsion in the 1960’s. However, with the aforementioned progress, promising and successful research has started again on electrospray thrusters [28]. Spearheaded by John Fenn in the late 1980’s, electrospray sources are now regularly used in the biological sciences as an *indispensable* mass spectrometry tool [27]. They have been used in thin-film deposition [29], painting [29], and even in the creation of uniform nanofibers in a process known as electrospinning [30]. Most importantly, it is the purpose of this study and hope of this author to see electrospray sources applied to the field of FIB technologies [31].

3.3 Basic Physics

3.3.1 Relaxation Time

A Taylor cone results from a balance between electrostatic forces on the fluid and the surface tension of the liquid. Where and on what the fluid rests, and how it is supplied, will be discussed in Section 3.3.2. Before getting to electrospray-specific theory, a more general physical understanding must be
established. For a liquid subject to an external electric field, the following relation holds,

$$E_n^l = \frac{1}{\epsilon} E_n^g.$$  \hspace{1cm} (3.1)

where $E_n^l$ is the electric field with the liquid surface, $E_n^g$ is the electric field outside the liquid surface, and $\epsilon$ is the dielectric constant. This relation only holds for liquids treated as dielectrics. Because the liquids of interest often have high dielectric constants, the difference between internal and external fields can be quite large.

Of critical importance to understanding the dynamics of Taylor cone formation is the concept of charge relaxation. This is a measure of how the charges dynamically redistribute in the fluid given certain finite mobilities. The conductivity, $\kappa$, is taken as,

$$\kappa = ne \left( \mu^+ + \mu^- \right),$$  \hspace{1cm} (3.2)

where $(\mu^+ + \mu^-)$ is the lumped mobility and $ne$ is the charge density. The free surface charge density accumulation rate is given by,

$$j = \kappa E_n^l.$$  \hspace{1cm} (3.3)

Using Gauss’ Law, the free surface charge density is given by,

$$\sigma_f = \epsilon_0 E_n^g - \epsilon \epsilon_0 E_n^l.$$  \hspace{1cm} (3.4)
By combining equations 3.3 and 3.4 the following equation is established,

\[ \frac{d\sigma_f}{dt} + \frac{\kappa}{\varepsilon\varepsilon_0} \sigma_f = \frac{\kappa}{\varepsilon} E_n^g. \]  

(3.5)

The important element of this equation is the quantity \( \frac{\varepsilon}{\varepsilon_0}^{-1} \), known as the relaxation time. The relaxation time dictates what the time scale is for fluid-response to the applied electric field. For instance, how a stable Taylor cone will respond when the externally applied voltage is changed, or switched, is directly related to this quantity. By extension, the relaxation time is critically important for FIB applications, as will be explained.

### 3.3.2 Taylor Cone Formation

Figure 3-1 shows the setup of a standard capillary-tip electrospray. The conducting fluid (in this case an ionic liquid) is passed through a sharpened needle while a potential is applied between an extractor and an emitter. The electrostatic traction forces on the liquid tend to deform it into a conical structure. Under certain conditions, a stable Taylor cone is established [7,32]. The Taylor cone is distinctly characterized by a conical shape, stable configuration, and emission from the apex. There are several unique emission regimes: droplet, ion, and droplet+ion. This is described in more detail in Sections 3.3.4 and ??.

However, for the purposes of this study, the pure ionic regime is most relevant. There are also several unique emitter types, of which the capillary is only one. This will be discussed in detail in Section 3-5.

Figure 3-2 is a simple schematic of an established Taylor cone, where \( \alpha_T \) is the Taylor cone angle, and \( r \) is the radial distance from the apex along the
cone. For a liquid with surface tension, $\gamma$, the normal electric field is given by,

$$E_n = \sqrt{\frac{2\gamma \cot \alpha_T}{\epsilon_0 r}}. \quad (3.6)$$

This relation is established by equating the electric traction, $\frac{1}{2}\epsilon_0 E_n^2$, and the surface tension, $\frac{2}{R_c}$, where $R_c$ is the radius of curvature relative to the cone axis. The Taylor cone is an analytical result found by solving Laplace’s equation for the potential distribution on the liquid surface; the angle is found to be 49.29°.

As the liquid’s local fluid residence time (a function of distance to the apex) becomes comparable with the relaxation time, the charges can not redistribute
to counter the external electric field. The electrostatic/surface tension balance is then broken and a cone-jet geometry is established. For droplet and ion emission regimes, the fundamental physics behind Taylor cone formation is similar. It is the behavior of the liquid after the formation that distinguishes the two regimes.

### 3.3.3 Emitted Current and Starting Voltage

The emitted current is related to the conductivity, $\kappa$, surface tension, $\gamma$, and the flow rate, $Q$, by,

$$ I = \frac{f(\epsilon)}{\sqrt{\epsilon}} (\gamma \kappa Q)^{\frac{1}{2}}, $$

where $f(\epsilon)$ is a fluid-dependent parameter. This relation has been established experimentally; a detailed derivation can be found in [7, 33]. Of note is the current independence on viscosity, electric field, and emitter geometry.

The starting voltage for a capillary emitter is found by calculating the necessary field to overcome the surface tension forces on the liquid surface. For
the following derivation, spheroidal prolate coordinates are used. A potential
difference, $V_A$, is applied between an emitter and extractor separated by a
distance, $h$. The coordinate transformations are given by,

\begin{align*}
x &= a \sinh \mu \sin \nu \cos \theta \\
y &= a \sinh \mu \sin \nu \sin \theta \\
z &= a \cosh \mu \cos \nu.
\end{align*}

(3.8) (3.9) (3.10)

The parameters are shown in Figure 3-3; $\theta$ is the azimuthal angle around the
z-y intersection line. Under this coordinate transformation, Laplace's equation
is written as,

$$\frac{d}{d\mu} \left[ (1 - \mu^2) \frac{d\phi}{d\mu} \right] = 0.$$  

(3.11)

The boundary conditions for the emitter are, $\phi(\mu_0) = V_A$, and the extractor,
$\phi = 0$. The solution is given by,

$$\phi = V \frac{\tanh^{-1} \frac{\mu}{\mu_0}}{\tanh^{-1} \frac{\mu}{\mu_0}}$$  

(3.12)

Via several manipulations [7], the electric field at the emitter tip is given by,

$$E = \frac{2V}{R_c \ln \frac{4h}{R_c}}.$$  

(3.13)

The emission will occur when the electrostatic forces match the surface tension
forces,

$$\frac{1}{2} \varepsilon_0 E^2 = \frac{2\gamma}{R_c}.$$  

(3.14)
Plugging in Equation 3.13, the starting voltage is found as,

\[ V_s = \sqrt{\frac{\gamma R_c}{\epsilon_0}} \ln \frac{4h}{R_c}. \]  

(3.15)

Figure 3-3: Diagram of coordinate system.

### 3.3.4 Field Evaporation

As discussed in Section 3.3.2, there are distinct modes of operation for electrospray. This section pertains to the regime of ionic emission. As demonstrated by Equation 3.6, the electric field on the surface of the Taylor cone is related to distance from the apex; the field increases with proximity to the apex. At some distance to the apex, the field is sufficiently strong to surpass the ionic
free energy. If this distance is greater than the distance at which the cone would transition to a jet, the electrospray will operate in a purely ionic mode. Assuming full charge relaxation, the current emitted per unit area is given by [7],

\[ j = \epsilon_0 E_n \frac{kT}{h_p} e^{-\frac{\Delta G - G(E)}{kT}}, \]  

(3.16)

where \( h_p \) is Planck’s constant, \( \Delta G \) is the free energy of solvation, and \( G(E) \) is the free energy reduction for a given electric field.

To further understand the quantity \( G(E) \), begin with the model shown in Figure 3-4. An ion, \( +q \), being pulled from the liquid surface by electric field, \( E \), is pulled back by its own virtual image, \( -q \). The force on the ion is then,

\[ F = -\frac{q^2}{4\pi\varepsilon_0 (2x)^2} + qE. \]  

(3.17)

The energy necessary to bring the charge to position, \( x \), is,

\[ W = \int_x^{+\infty} F(x)dx \]  

(3.18)

Assuming zero field at infinity, the potential energy is then given by,

\[ W = -\frac{q^2}{16\pi\varepsilon_0 x} - qE_n x. \]  

(3.19)

The maximum of this potential function is,

\[ W = -\left(\frac{q^3 E_n}{4\pi\varepsilon_0}\right)^\frac{1}{2}. \]  

(3.20)

This is known as the Schottky depression and can be substituted back into Equation 3.16. When \( G(E) \) becomes comparable to \( \Delta G \), significant ion emis-
sion occurs. When the two quantities are identical, the necessary electric field can be solved for as,

\[ E_n = \frac{4\pi\varepsilon_0 \Delta G^2}{q^3}. \]  

For many electrospray solvents, field evaporation occurs as a field strength of 1-2 V/nm [34]. This field strength corresponds to a \( \Delta G \) of 1.2-1.7 eV.

![Image of ion evaporation model](image)

Figure 3-4: Model of ion evaporation.

### 3.3.5 Electrospray Emitter Types

For an electrospray emitter to perform well two services must be provided. It must provide fluid flow to the end, or tip, and locally enhance the field
Emitter types can be characterized in three different categories: capillary, porous, and externally wetted emitters, shown separately in Figure 3-5.

Figure 3-5: Electrospray emitter types: A. capillary emitter, B. internally wetted porous emitter, C. externally wetted emitter

The liquid flow in capillary emitters is maintained either by a pressure feed or capillary forces. Because this geometry is characterized by large flow rates it usually engenders droplet-mode operation. Porous emitters employ sharpened needles composed of a porous material. This porosity yields significantly higher flow rates and emitted ion current. Given the tip porosity, there is a degree of uncertainty as to where the Taylor cone is established. It is very important for FIB applications that the Taylor cone is axially symmetric relative to the system.
Externally wetted emitters provide fluid flow to the needle tip via surface wetting. They are solid and their surface is treated to aid in the wetting process. The Taylor cone is established on the needle apex and ion-regime emission is highly probable. The fabrication of the externally wetted emitter is a multi-stage process.

**Externally Wetted Emitter Fabrication**

The fabrication process of externally wetted needle emitters is a three-stage process: needle sharpening, annealing, and chemical micro-roughening.

The needle shaping and sharpening begins with cutting 5 cm length pieces of 0.02” diameter straight tungsten wire. These individual pieces are then electrochemically etched in a NaOH solution, as shown in Figure 3-6. In the electrochemical reaction the cathode is a 1.5” diameter stainless steel cylinder, and the anode is the centered tungsten wire. This step in needle fabrication can be decomposed into two separate tasks: cutting and shaping. The dynamics of the electrochemical etch and the shape of the final product depends on the voltage amplitude between the anode and cathode, as well as the type of voltage: DC or AC. Optimal results were realized by (1) cutting the wire with a 30 V AC immersion, followed by (2) shaping the tip with a 120 second immersion at 2.5 V AC. The cutting is made possible by the liquid surface meniscus interaction with the tungsten surface. The resultant needle has a radius of curvature too small for electrospray operation. A needle too sharp makes fluid flow to the apex difficult; a needle too dull can yield operation in the droplet-ion regime. The target tip radius of curvature is 10-20 μm. As stated, this is accomplished through a low-voltage immersion. The electrochemical reaction is strongest at the geometrically sharpest regions of the
needle, the tip. Therefore, the low-voltage immersion has the desired dulling affect.

![Diagram of electrochemical etching system](image)

Figure 3-6: Diagram of electrochemical etching system. A voltage is supplied between the needle and surrounding stainless steel cylinder in a NaOH liquid bath.

The electrochemical etch has the effect of smoothing the needle where the reaction occurs. The act of annealing, heating over long periods of time, re-establishes the surface boundary grain conditions on the tungsten surface. The annealing system diagram is shown in Figure 3-7. The needle is spot welded to a 0.01” diameter, 3 cm long tungsten filament, across which 4 V AC is applied. The electrical heating is maintained for 5 minutes in vacuum, followed by 15 minutes of cooling in vacuum.

The surface of the tungsten needle is further treated by a chemical micro-roughening procedure. The roughened surface of the tip aids in fluid transport to the apex. A heated solution of NaOH and potassium ferricyanide is used. First the NaOH solution is heated to 90° C. The potassium ferricyanide is added until saturation occurs. Saturation is apparent when a thin film occurs on the surface of the liquid. The solution is then heated to 95-98° C, and the
needle is immersed for 120 seconds. The needle is then cleaned in an acetone bath, dried with an inert gas, and coated with an ionic liquid. The ionic liquid protects the tungsten surface from atmospheric interaction. Figures 3-8 and 3-9 show scanning electron microscope images of a well-fabricated externally wetted (with EMI-BF₄) emitter under different magnifications.
Figure 3-8: Needle tip emitter SEM.
Figure 3-9: Needle tip emitter SEM.
Chapter 4

Focused Ion Beam Column

4.1 Column Outline

The FIB column experimental setup, as shown in Figure 4-1, is composed of a source, extractor, aperture, einzel lens, deflection plate assembly, wire-grid detector, and collector.

4.1.1 Emitter and Extractor Assembly

A detailed description of emitter type and fabrication method is described in Section 3.3.5. The tip, externally wetted, is brought to a certain potential relative to a grounded extractor. The extractor position and size will affect electrospray dynamics and operation. For this study the extractor has a diameter of 1.8 mm and is held 1 mm downstream. The extractor hole is beveled outward relative to the emitter tip to minimize ion impingement, as shown in Figure 4-2. Immediately downstream relative to the extractor is a beam-limiting aperture, 1.5 mm in diameter and 40 mm distant. This aperture serves to limit the radial span of the beam passing through the subsequent
Figure 4-1: The FIB column experimental setup is composed of an externally wetted source, extractor, aperture, einzel lens, deflection plate assembly, wire-grid detector, and collector plate.

lens assembly, hence controlling certain inherent radial-dependent aberrations, as further described in Section 2.3.

Also shown in Figure 4-2 is the assembly designed to supply liquid to the emitter. It is composed of a pressure-fit holder for the needle and a liquid reservoir chamber, through which the needle is passed. The reservoir chamber cylinder is 2 mm in diameter, 5 mm long, and made of stainless steel. Given the emission rates, the reservoir chamber provides a sufficient amount of liquid for indefinite operation.
4.1.2 Electrostatic Lenses

The electrostatic optical assembly in the FIB column is responsible for focusing the ion beam. There are a variety of different electrostatic lens designs. In this study an einzel lens is utilized. An einzel lens is a three cylindrical element lens. The potential gradients through which the ion beam passes leaves the beam's axial momentum unchanged while providing a momentum exchange in the radial direction, hence the focusing effect.

The einzel lens is analogous to an optical lens. In an optical lens, the photons pass through a refraction gradient and are focused accordingly; in an electrostatic lens, the ions pass through a potential gradient. As in optics, the electrostatic lens suffers from inherent aberrations, as discussed in Section 2.3.
4.1.3 Deflection Plates

The deflection plate assembly is the element responsible for directing the focused ion beam to a certain two-dimensional location on the target. The assembly provides a uniform electric field through which the ions pass. An electric potential is applied across two sets of stainless steel parallel plates, each set corresponding to a certain orthogonal direction. The plates are 1” long, 0.5” wide, and separated by 1”. All such experiments are performed with a scanning frequency of 2 mHz, corresponding to a scanning speed of 6.25 μm/s.

4.1.4 Collector Assembly

The collector assembly is composed of two separate entities: a wire-grid detector and a faraday cup. The wire-grid detector is placed several millimeters in front of the faraday cup. It is composed of a parallel array of tungsten wire, and placed 9 mm from the deflection plates. The wires have a diameter of 75 μm and are spaced by 750 μm. As will be discussed in Section 5.2, the shape of the signal collected as the focused ion beam passes over a wire will yield information on the probe size. The ion beam is scanned over the wire-grid detector by applying a ramp potential to the deflection assembly. A ramp function yields linear uniform motion of the beam across the detector. The amplitude of the ramp potential dictates the range the probe passes over and the frequency of the scanning rate. The faraday cup, connected to an ammeter, is a metallic structure designed to collect the remaining ion flux.

Without beam manipulation, the collector current is measured to be 0.7 nA with an emitter current of 200 nA. To verify this is the expected throughput,
given the system geometry, the following geometric argument is used for an assumed uniform distribution,

\[ I_C = I_B \frac{1 - \cos \theta_A}{1 - \cos \theta_B}, \]  

(4.1)

where \( \theta_A \) is the geometric half-angle of the aperture with respect to the needle tip, \( \theta_B \) the divergence angle of the ion beam, \( I_C \) the collector current, and \( I_B \) the source current. From the system dimensions \( \theta_A \) is 1.1°; \( \theta_B \) is taken to be 18° [6]. From this, the expected collector current is 750 pA, which compares with the measured 700 pA. Potential explanations for this slight discrepancy are (1) current interception by the wire-grid, and (2) secondary emissions from the collector. It is therefore shown, the aperture is the current-limiting step for this system; there is no further attenuation for nearly all of the beam.
Chapter 5

Experimental Techniques

5.1 Time-of-Flight Mass Spectrometry

When an ion is evaporated from the FIB source it gains an energy of \( q\phi \), where \( q \) is the ion charge and \( \phi \) is the potential difference between the source tip and extractor. In reality, there are certain energy losses associated with the ion evaporation process and the emitted energy is different. However, for the current study, it has been shown [10] the energy losses are insignificant. When equating to the kinetic energy of the ion, the charge-to-mass ratio is then found as,

\[
\frac{q}{m} = \frac{1}{2} \frac{v^2}{\phi},
\]

(5.1)

where \( m \) and \( v \) are the ion’s mass and velocity, respectively. Evidently, given a potential drop, the specific charge of an ion can be found by isolating its velocity. This is precisely what the time-of-flight (TOF) methodology employs. Furthermore, if single ionization, \( q = e \), is assumed, the ion mass is,

\[
m = \frac{2e\phi}{v^2},
\]

(5.2)
The single ionization assumption is valid given the usual energy levels utilized in ILIS electrospray systems.

![Figure 5-1: Time-of-flight (TOF) system composed of ion source, electrostatic gate, and faraday-cup collector.](image)

The single-gate TOF system is composed of an ion source, an electrostatic gate, and a faraday cup collector, Figure 5-1. The distance between the gate and the collector is known to be $L$. In the gate's open state the beam passes unimpeded. In its closed state the beam is stopped entirely. The velocity of an ion species is found by monitoring the collector current following the closing (or opening) of the gate. Specifically, the current characteristic of relevance is a drop (or rise), for that corresponds to the ions between the gate and collector. Furthermore, multiple drops (or rises) in the current landscape correspond to multiple ion species of different velocities. As an example, consider Figure 5-2. Assigning the gate closing $t = 0$, $\Delta t_1$ corresponds to the termination of a faster moving ion species and $\Delta t_2$ to the termination of a slower moving species. The distinct species' velocities are simply $v_1 = \frac{L}{\Delta t_1}$ and $v_2 = \frac{L}{\Delta t_2}$. The
species' masses are then,

\[ m_1 = \frac{2e\phi \Delta t_1^2}{L^2}, m_2 = \frac{2e\phi \Delta t_2^2}{L^2}. \]  

(5.3)

Hence the spectrum of masses in the ion beam is realized. Furthermore, the relative contributions, \( f_1 \) and \( f_2 \), to the total beam makeup from the distinct species is given by,

\[ f_1 = \frac{I_1}{I_t}, f_2 = \frac{I_2}{I_t}, \]  

(5.4)

where \( I_1, I_2, I_t \) are shown on Figure 5-2.

Figure 5-2: Characteristic current landscape for time-of-flight data.
5.2 Wire-Grid Detector

As discussed in Section 4.1.4, the wire-grid detector is an element designed and used for characterizing the ion beam probe size.

For an ion beam with a circular cross section of diameter $d$ passing over a metal wire of greater diameter, the model for wire current is,

$$I = I_{BG} + \frac{I_B}{\pi} (\theta - \cos \theta \sin \theta) ,$$

(5.5)

where $I_{BG}$ is the background current, $I_B$ the beam current, and $\theta$ the angle shown in Figure 5-3, which is related to the distance, $x$, the beam has passed over the wire by,

$$x = \frac{d}{2} (1 - \cos \theta) .$$

(5.6)

A probe size, $d$, is found by fitting the model parameters to the electric current landscape acquired on the tungsten wire. As an illustration, see Figure 5-4. The shown landscape with the plateau region manifests only if the probe size is smaller than the wire size. This is true for the current study. The main fitting parameter, $d$, corresponds to the width of the transient region. The parameter $g_0$ corresponds to the width of the wire, and is used as a consistency check. Also, from the given landscape the background current, $I_{BG}$, and the beam current, $I_B$, are acquired.

5.3 Vacuum System and Lab Facilities

The vacuum chamber used in all testing is a cylindrical stainless steel chamber with inner diameter of 20 cm and length of 50 cm, shown in Figure 5-5. An extended region, 5.6 cm inner diameter and 36.5 cm length, is integrated on the
end of the chamber to increase accuracy in TOF experiments. Initial roughing is established with a Varian SD-40 mechanical pump, while normal vacuum operation is established with two Varian V-70 turbopumps. All experiments are performed at $10^{-6}$ torr. The chamber has an access hatch, a viewing window, and many feedthroughs to provide electrical connections. Feedthroughs include three MHV coax connectors, two high voltage feeds, and a multi-pin connector. The electronic systems used are shown in Figure 5-6 and outlined in Table 5.1.
Figure 5-4: Wire-grid current landscape.

Table 5.1: SPL Electronic Systems.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Model/Brand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oscilloscope</td>
<td>Agilent Infinium 54835A</td>
</tr>
<tr>
<td>Function Generator</td>
<td>Agilent 33220A</td>
</tr>
<tr>
<td>Electrometers</td>
<td>Keithley 6517</td>
</tr>
<tr>
<td></td>
<td>Keithley 6514</td>
</tr>
<tr>
<td></td>
<td>Meterman 37XR</td>
</tr>
<tr>
<td>HV Power Supplies</td>
<td>Matsusada AMS-5B6</td>
</tr>
<tr>
<td></td>
<td>Bertan 205B-05R</td>
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<tr>
<td></td>
<td>Bertan 205B-10R</td>
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<tr>
<td></td>
<td>Acopian P03-5HP17</td>
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<tr>
<td>Pulse Generator</td>
<td>BNC-555</td>
</tr>
<tr>
<td>Pulse Amplifier</td>
<td>DEI PVM-4210</td>
</tr>
</tbody>
</table>
Figure 5-5: Stainless steel vacuum chamber.
Figure 5-6: Electronic systems.
Chapter 6

Experimental Results

6.1 Experimental Overview

All experiments are performed in MIT’s Space Propulsion Laboratory. This chapter is separated into three sections. First, a single emitter is operated separately from the FIB column. Several new ionic liquids, specially suited for use in FIB applications, are tested and characterized. Second, the performance of the emitter module in a FIB column is presented. Lastly, a novel emitter design is proposed and tested as a solution to certain issues mentioned below.

6.2 Single Emitter Performance

One of the advantages of ILIS is the multitude of available species. A specific application requires a specific type of ion emission. The variety of ILIS serve that requirement. Two newly developed ionic liquids show promise: $EMIF_{2.3}HF$ and $BMI - I$. Both liquids are shown to emit the highly reactive negative atomic ion species $F^-$ and $I^-$, respectively. For reasons outlined
in Section 2.2 these ion beams are highly desirable.

The following ion beam characterizations are performed by the TOF method explained in Section 5.1.

6.2.1 EMIF2.3HF

The tested supply of ionic liquid EMIF2.3HF was synthesized and donated by Professor Rika Hagiwara of Kyoto University. Figures 6-1 and 6-2 show the TOF spectra for two acceleration voltages in the positive and negative polarity. At time zero, the beam deflector halts the steady flow of ionic current to the detector. Each step on the current profile corresponds to a particular ion species.

In previous studies it is found that ion species, generally represented as $[A^+]$ or $[B^-]$, are emitted with the general solvation form $[A^+B^-]_n[A^+]$ and $[A^+B^-]_n[B^-]$ in the positive and negative mode, respectively. $[A^+B^-]_n$ is a bulk neutral and the degrees of solvation are $n=0,1,2,3...$ with 0 and 1 being the most frequently observed. The fluorohydrogenated ionic liquid is composed of the cation EMI and a mixture of HF-based anions of the form $F(HF)_k$, where $k$ is 2 and 3 in the liquid phase with an average composition given by $k=2.3$. The solvated species would therefore have the generic form $[EMI - F(HF)_i]_jEMI^+$ in the positive mode and $[EMI - F(HF)_i]_jF(HF)_k^-$ for negative ions. Tables 6.1 and 6.2 list the ionic masses that result from the different combinations of the sub-indices $(i,j,k)$ for positive and negative ions. These tables show those ions matching the experimental data. The relative number ratio is a non-dimensional factor dictating what portion of the total beam current is due to a certain mass species. Mass species with an asterisk for the relative number ratio are detectable but non-quantifiable due to such slight
current drops. Some of the solvated ion combinations, such as (3,1,1), (2,1,2) and (1,1,3) are degenerate, and therefore cannot be distinguished in the data. There are a few potential sources for the width of the TOF waves observed in Figures 6-1 and 6-2, ranging from the finite response time of the amplifier to the possibility of some degree of energy spread in the beam. Previous results with other ionic liquids have established the energy distributions are quite narrow, but it will be required to verify this important property for this fluorohydrogenated ionic liquid.

Table 6.1: Permutations of possible positive ion species.

<table>
<thead>
<tr>
<th>i</th>
<th>j</th>
<th>Mass (amu)</th>
<th>Relative number ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>0</td>
<td>111</td>
<td>0.38</td>
</tr>
<tr>
<td>0</td>
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<tr>
<td>1</td>
<td>1</td>
<td>261</td>
<td>*</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>281</td>
<td>*</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>301</td>
<td>0.03</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>411</td>
<td>0.04</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>451</td>
<td>*</td>
</tr>
</tbody>
</table>

Even though k=2 and 3 in the liquid phase, some of the $F(HF)_k$ ions in the pure negative and solvated forms have k=0 and 1. This could be of interest in FIB applications, as highly reactive $F^-$ ion beams could be produced. It is also interesting to note the overall emitted mass in both the positive and negative modes are of about the same order, and on average with ions heavier than 100 amu. Finally, there are still some unexplained masses arising in the positive mode (19, 33 amu), which do not correspond to those listed in Tables 6.1 and 6.2. Doubly charged ions at full energy would appear to have lower masses than their singly charged counterparts, however, these masses do not match, therefore multiple charged ions is an unlikely explanation of these signals. Interestingly, one of the observed masses hypothetically would corre-
Table 6.2: Permutations of possible negative ion species.

<table>
<thead>
<tr>
<th>i</th>
<th>j</th>
<th>k</th>
<th>Mass (amu)</th>
<th>Relative number ratio</th>
</tr>
</thead>
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<tr>
<td>x</td>
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<td>0</td>
<td>19</td>
<td>0.03</td>
</tr>
<tr>
<td>x</td>
<td>0</td>
<td>1</td>
<td>39</td>
<td>0.08</td>
</tr>
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<td>x</td>
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<td>2</td>
<td>59</td>
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dpond to $F^+$ or $HF^+$ ions. Such assignation appears unlikely in ILIS sources, nevertheless, confirmation using complementary analysis tools to measure the energy properties of individual ion signals would still be required.

6.2.2 BMI – I

BMI – I Synthesis

The general process of ionic liquid synthesis is the combination of equimolar amounts of 1-Methylimidazole and an Alkyl Halide of choice, such as Butyl
Figure 6-1: TOF spectrum for EMI$F$2.3$HF$ in the positive polarity, normalized to unity.

Iodide (1-Iodobutane) for BMI$-I$. The reaction of 1-Methylimidazole and 1-Iodobutane, 1:1.4 in volume, is endothermic; therefore, heat must be applied over extended time periods for the reagents to react. The mixture is heated to 70° C for three days, taking care to use an entirely dehydrated system. Ethyl acetate is added to the resultant liquid until two distinct liquid phases form, the top layer being unreacted elements. After separation, excess ethyl acetate must still be removed, for some will remain dissolved within the ionic liquid. This is achieved through a vacuum induced outgassing procedure, making sure the toxic ethyl acetate is not released to atmosphere. The synthesis setup is shown in Figure 6-3.

BMI$-I$ synthesis was performed by UROP student Enrique Cintron.
**BMI – I Results**

Using the same setup as for the *EMIF2.3HF* ionic liquid, the TOF spectra for *BMI – I* in the positive and negative mode is presented in Figures 6-4 and 6-5 respectively, where the data is normalized to unity. Potential levels are 2400 V for the positive polarity and -2300 V for the negative. This ionic liquid is composed of the cation *BMI* and the anion *I*. The solvated species has the generic form \([BMI – I]_nBMI^+\) in the positive mode and \([BMI – I]_nI^-\) in the negative mode.

Figure 6-4 clearly shows the presence of two distinct ion species: the non-solvated species *BMI*\(^+\) and the singly solvated species \([BMI – I]BM{I}^+\). Figure 6-5 is relatively unclear in its presentation. The data is more susceptible to
the amplifier noise because the current level at the detector is significantly less.
However, apart from the electronic noise, there are apparent manifestations of
nonsolvated, singly solvated, and even higher, solvated species.

6.3 Performance in FIB Column

The single ILIS electrospray emitter source is tested as an integrated element
in a FIB column, designed and fabricated in-house. Column optimization was
not belabored, for the emphasis of this study did not lie there. The results
presented for column operation are more proof-of-concept than demonstration
of optimal operation. For the latter effort the source module will be integrated
Figure 6-4: TOF spectrum for BMI – $I$ in the positive polarity, normalized to unity. Vertical markers represent ion masses up to one degree of solvation to neutral, N.

into a pre-existing, professionally developed column. All column experiments are performed with the ionic liquid $EMI – BF_4$.

6.3.1 Probe Size and Lens Potential

By fitting Eqn. 5.5 to the wire-grid experimental results shown in Figure 6-6, with $d$ as the fitting parameter, a probe size of approximately 30 $\mu m$ is found, with a 1.5 mm apperture. As predicted, when the probe is passed over the wire of larger diameter, a flat region to the current profile is observed. The expected length of this region, taking into account the wire diameter and probe size, is 45 $\mu m$; the measured length of 43 $\mu m$ is consistent.
Given the narrow energy distribution of the primary ion beam [10], it is expected the range of potentials over which the lens focuses the beam is equally narrow. The above analysis is applied to cases of different lens potential, and the results are presented in Figure 6-7. Lens potentials outside of the [-1.995 kV, -1.999 kV] range yield probe sizes arbitrarily larger than the wire diameter of 75 \( \mu \text{m} \).

### 6.3.2 Ion Fragmentation and Energy Consistency

In the negative mode, the emitted beam is composed of both the single ions \( \text{BF}_4^- \), and the solvated species \( \text{EMI-BF}_4)_n\text{BF}_4^- \) [10]. In regions where the
Figure 6-6: The current signal as the beam is passed over a single wire. By fitting the theoretical model of a circular beam passing over the wire, the beam size in this case is found to be 30 μm.

Potential changes, such as between the emitter tip and extractor or inside the einzel lens, there is the possibility of molecular fragmentation of solvated ions. This introduces a population of particles with lower energies. These particles will be scattered away by the einzel lens, contributing to the background current. The beam probe scanned over the wire should consist almost exclusively of non-fragmented high-energy ions. To check for consistency between the observed beam energy and the energy associated with non-fragmented ions, a relation between deflection distance at the target and ion energy is used here. Let \( h \) be this deflection distance, \( V_d \) the potential between deflection plates, \( V_e \) the emitter potential, \( z \) the distance between the deflection electrodes, \( x_0 \)
the length of the deflection electrodes, and $w$ the distance from the deflection electrode to the wire-grid detector. With these parameters, it follows that,

$$V_{dh} = \frac{V_d}{4v_z} x_0 (x_0 + 2w).$$

(6.1)

Inferring $h$ from the distance between wires, $V_e$ is back-solved to be -1.58 kV, which is close to the operating voltage of -1.56 kV. Therefore, it is concluded the focused beam is of the highest energy species as discussed in [10]. This assessment, however, does not dictate what the mass composition of the focused beam is; it could be composed of singly, doubly, or even higher solvated ions, none of which would be a product of fragmentation. Being so different in nature, it is possible these families of ions would also have different, although
close, beam energies. This energy spread in the un-filtered beam is a potential explanation of the discrepancy between the probe sizes plotted in Figure 2-1 and the experimentally found 30 μm.

With the previously assumed source diameter of 10 nm, the brightness of the source, normalized to source area and beam voltage, is estimated to be $527 \frac{A}{cm^2srV}$. The published normalized source brightness of Ga⁺ LMIS is 100 $\frac{A}{cm^2srV}$ [31]. Given the source area of 10 nm is an estimate, it can only be said these two figures are comparable.

Depending on the source potential, the ionic liquid source will emit either positive or negative ions. For reasons outlined in Section 6.4 it is of benefit to have a FIB column capable of both positive and negative emission. ILIS are unique in this sense. However, there are inherent limitations preventing the use of ILIS in either polarity for extended periods of time. The issue is electrochemical decay.

### 6.4 Electrochemical Issues

During the electrospray emission process there is a constant rate of charge accumulation in the liquid, simply as a result of opposite charge emission. The buildup induces the formation of a charge double layer between the tungsten needle and the ionic liquid, as shown in Figure 6-8. Over time the electric potential amplitude induced by this double layer grows. At some threshold potential an electrochemical reaction occurs between the metallic needle and liquid. Through this process the chemical makeup of the ionic liquid is altered and the electrospray operation is irrevocably disrupted. This electrochemical issue is inherent to the electrospray setup and must be contended with.
6.4.1 Potential Solutions to the Electrochemical Decay Issue

The characteristic time scale of electrochemical decay is theoretically estimated as

\[
t_w = \epsilon \epsilon_0 \frac{V_w A}{I \delta},
\]

where \(\epsilon\) and \(\epsilon_0\) are permittivity constants, \(V_w\) is the electric potential established across the charge double layer, \(A\) is its surface area, \(\delta\) is its spatial extent, and \(I\) is the characteristic current. For the systems being addressed, this comes to approximately 10 seconds. Therefore, alternation of the emission polarity with a period under this time will relieve the charge double layer.
before the electrochemical threshold is reached. The Taylor cone emission response time to polarity reversal is remarkably fast, as shown in Figure 6-9. Figure 6-10 demonstrates the success of this method. Part A shows the emitter after 5 hours of operation without polarity reversal. During this 5 hour period there is a steady decrease in emitter performance, eventuating in a totally disfunctional emitter. There is an apparent discoloration, a manifestation of the electrochemical decay. Part B shows the identical system after 200 hours of operation with a polarity alternation at a frequency of 1 Hz. There is no discoloration and the emission behavior is unaffected [6].

![Figure 6-9: Electrospray response to polarity reversal.](image)

The failure of this method comes from its complexification of long term FIB applications. A given application requires a polarity of one type for a certain amount of time. When double-layer "relief" is required, the emission polarity is reversed while the beam is blocked for the discussed period of time. Often, however, periods of many hours or even days are required. For such requirements, including, for instance, large-pattern mask repair, electrochemical reaction would occur far before polarity reversal.
6.4.2 Bipolar Electrospray

A "bipolar electrosray," brain-child of Professor Martinez-Sanchez of MIT, is a novel system designed to eliminate the charge double-layer prior to formation. Figure 6-11 shows the basic setup. A wetted tungsten double-tipped centerpiece, fabricated in an identical manner as a single tip, floats electrically isolated. A large potential is applied between the two extractors, one being grounded. A potential between the initially charge-neutral centerpiece and non-grounded extractor eventuates in stable ion emission, upon which a large opposite potential is formed between the centerpiece and grounded extractor, yielding oppositely charged ion emission. Any charge buildup on the centerpiece results in a larger ion emission of that polarity. Therefore, the centerpiece is necessarily charge neutral. No charge double-layer is formed because there is no charge buildup to begin with.

Initial fabrication and testing of this system is performed with a tungsten centerpiece. However, electrochemical reaction behavior is still observed over the course of a few hours. While electrochemical decay is postponed, it still occurs. The local charge diffusion at the tip is not great enough to avoid the electrochemical threshold. The entire centerpiece is net-neutral, but locally at the tip apex a double-layer strong enough to trigger electron transfer is formed.

6.4.3 Dielectric Bipolar Electrospray

By fabricating the double-tipped centerpiece from a dielectric material, the electrochemical decay is altogether avoided, regardless of local charge double-layer formation. Experimentally, a centerpiece is fabricated from porous alu-
mina. It is a double-cone shape, 1/8” in diameter and 1 cm long. It is soaked through with ionic liquid. Figures 6-12 and 6-13 shows results from long-term testing of the system. For approximately the first hour there is still a dynamic current decay behavior. Uniquely, however, this system settles at a stable current, albeit low, for extended periods of time.
Figure 6-10: Diagram of physical emitter A) without polarity alternation, and B) with polarity alternation.
Figure 6-11: Setup for bipolar electrospray.
Figure 6-12: Long-term current test with initial dynamic behavior.

Figure 6-13: Long-term current test with emission stabilization.
Chapter 7

Conclusions and Future Work

7.1 Future Work

The emission beam is composed of ions of a variety of energies, masses, and velocities, as described in Section 6.3.2. From the perspective of a FIB column’s ability to focus the beam, this is an undesirable characteristic. Any attempt at focusing, electrostatic or magnetic, is hampered by ionic species diversity. In fact, as discussed previously, the aberration of a focusing element is proportional to the level of diversity in the beam. Therefore, the optimal ion beam is composed of ions of equal energies, masses, and velocities. This can be achieved through ion filtering.

Ion filters are well-established elements used to selectively isolate species depending on energy, mass, or velocity; there exist energy filters, velocity filters, and energy filters. Due to the relationship between energy, mass and velocity within an ion beam, only two distinct filters are necessary to select a characteristically unique composition. Any one filter used by itself potentially yields redundancies in the other quantities.
The first ion filter we have attempted to fabricate is an $E \times B$ filter, also known as a Wien filter. Its fabrication and operation is profoundly simple. Its operation involves perpendicular electric and magnetic fields, and the incident ion velocity is orthogonal to both. Only the ions subject to equal magnetic and electric forces pass through the filter. Because the magnetic force is velocity-dependent, the Wien filter itself is a velocity filter, filtering out ions with velocities different from $v_w = \frac{E}{B}$. See Figure 7-1. The balance of forces operates in one direction, that of the electric field. Because of this, inherent to the Wien filter, is a velocity-based astigmatism engendering a broadening of the focal spot in one dimension.

The next phase of our work involves the testing of this Wien filter for velocity resolution/selectivity and improvement in spot size. A diagram of our current full system cage, including the directly integrated Wien filter, mounted to a vaccum flange, is shown in Figure 7-2.

As mentioned, from the perspective of beam focusing ability, diverse ion
beam emissions are anathemas. However, from the vantage of general FIB applicability, this is one of the strong advantages of ILIS: the ability to access various species with various characteristics from a single source. However, the possibility of harnessing this strength-in-diversity is only made possible with a matched ion filtration system.
7.2 Conclusions

ILIS sources are presented as having several key advantages over other ion sources. (1) They can be stably operated at current levels as low as a few nA, lessening the effect of certain system aberrations. (2) Because the liquid is exclusively formed by positive and negative ions, it is possible to change the polarity of the ion beam simply by reversing the power supply. (3) The number of available ionic liquids is extraordinarily large. This means ILIS can produce very diverse atomic and molecular ions in terms of their masses, composition and properties. (4) Some of the negative ions in ILIS are reactive species that could be used for enhancing etching rates in several applications without recurring to chemical assistance.

The experimental results presented here demonstrate the feasibility of using these sources in a FIB column. The emitted ion beam is focused down to a spot size of 30 $\mu$m, and that figure should improve by introducing optical devices traditionally utilized in commercial columns, such as energy and mass filters. Such filters would also make it possible to select application-specific ions from the beam. A separate method of improving the spot size currently being pursued is the simple lessening of the beam-defining aperture. As previously mentioned, this moves to lessen certain radial-based aberrations inherent to the focusing element. Compared to current aperture sizes used in mature FIB columns, the aperture in this work is orders of magnitude larger; we expect to see comparable levels of improvement in spot size upon switching.
Bibliography


