Engineering Ionic Liquid Ion Sources for Ion Beam Applications

by

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Abstract

Ionic liquid ion sources (ILIS) are devices capable of producing positive and negative molecular ion beams through field evaporation from room-temperature molten salts. If sufficiently high hydraulic impedance from the liquid-supporting emitter is provided such that the ratio of flow rate $Q$ to liquid’s electrical conductivity $K$ is sufficiently small, a pure ionic regime (PIR) can be achieved, in contrast with traditional electrosprays that produce charged droplets, or mixtures of droplets and ions. The PIR provides high current density from a point source, making ionic liquid ion beams suitable for use in focused ion beam (FIB) applications. The use of ionic liquids in focused ion beams could allow the production of sub-100 nm beams of up to kiloDalton organic ions as well as reactive species, with the possibility of engineering ionic liquid properties for a specific application. In addition, using micro-fabricated and nano-structured emitter arrays operating in the PIR can give access to efficient and compact positive or negative ion sources, for applications from spacecraft thrusters to deep reactive ion etchers (DRIE). There is a need for novel tip geometries and materials that favor the stable formation of a single emission site on the liquid supporting structure, while providing a continuous liquid supply compatible with the PIR.

In this thesis, porous carbon based on resorcinol-formaldehyde xerogels is introduced as an emitter substrate. The target pore sizes and emitter geometries to attain the PIR are obtained through analytical estimates. The carbon xerogel can be shaped to the required micron-sized geometry through mechanical polishing. Time-of-flight mass (TOF) spectrometry is used to verify that charged particle beams produced from the mechanically polished carbon xerogel source, infused with the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF$_4$), contain solvated ions exclusively. In the case of the liquid 1-ethyl-3-methylimidazolium bis(trifluorometrylsulfonyl)imide (EMI-Im), mixed ion-drop operation is obtained.

Laser micro-machining has been validated as a manufacturing technique to shape carbon xerogel into emitters. This technique should allow the production of emitter arrays for DRIE or propulsion applications, and allow the reproducible fabrication of emitters for FIB. Stable emission has been obtained from a laser micromachined tip infused with the ionic liquid EMI-BF$_4$. The results of TOF and retarding potential analysis (RPA) experiments indicate that the emission consists mostly of monomers and dimers, and that a small fraction (< 5%) of the beam might be composed of cluster ions with greater degrees of solvation.

To conclude, the thesis reports on the etching properties of the beams obtained from ILIS, both in the case of traditional externally wetted tungsten sources and with the novel carbon xerogel emitter technology. The W ILIS etches silicon with sputtering rates between 6 and 35 atoms of silicon removed per incident ion at 15 keV irradiation energies, whereas the carbon xerogel ILIS has been used to etch gold, silicon and gallium nitride with sputtering rates in the order of 10 for irradiation energies between 2 and 7 keV.
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Chapter 1

Thesis Motivation

This thesis has the goal of developing Ionic Liquid Ion Sources (ILIS) adequate for use in applications from materials processing to space propulsion. ILIS produce positive or negative ion beams from the electrified meniscus of a room-temperature molten salt, or ionic liquid. The access to a large variety of ion species from ionic liquids makes ILIS attractive for several technologies.

One of the key potential applications of ILIS is Focused Ion Beam (FIB) technology, a crucial tool for the semiconductor industry and for micro and nanofabrication research and analysis. The beams from these ion sources have optical qualities that make them amenable for focusing. There is a large variety of ionic liquids available in the literature, as well as the possibility of engineering liquids for specific applications. ILIS could provide monoatomic reactive species as well as kilodalton molecular ions, and be used to diversify FIB applications, which are restricted to a few elements from the limited number of ion sources available in the literature. This chapter gives an overview of the state-of-the-art in FIB, including a discussion of the capabilities of the ion sources proposed to date, and motivates the use of ILIS as an alternative to expand the applications of the FIB technique. Beyond FIB, ILIS may be used for reactive etching of substrates by firing the reactive ion beam directly onto the material, or be used as compact and efficient sources of ions for space propulsion applications.

In this thesis, we motivate the need for novel emitter configurations that could support ILIS operation in regimes adequate for focusing and other applications. Chapter 2 discusses the theory and state-of-the-art of these ion sources to motivate why new configurations are needed, while chapters 3 through 5 explain the design, fabrication and characterization of ILIS based on porous carbon xerogel. Chapter 6 describes the use of ILIS for reactive ion etching.
1.1 Overview of Focused Ion Beam Technology

In the FIB technique, a beam of ions is obtained from an ion source, and then directed to an optical column containing apertures, electrostatic lenses and deflectors, that narrow the beam to nanometer dimensions and direct it to a substrate for patterning, as shown in Fig. 1-1. FIB systems were developed in the late 1970's and 1980's and have become ubiquitous in semiconductor manufacturing and in micro and nanofabrication, as they can be used for micro-machining, lithography, microscopy, spectrometry and direct ion implantation.

FIB systems have the capability to remove material from a sample by sputtering and to add materials by ion induced reactions in the sub 100-nm scale [85, 121], making them ideal for micro-machining. These capabilities have been extensively exploited for integrated circuit (IC) failure analysis and modification, in which manipulation of features of a few 10's of nm must be performed [83, 85]. An example of a via milled into an IC is shown in Fig. 1-2(a); the FIB can be used to remove faulty connections, and in the presence of a suitable precursor-gas, to deposit material to create new interconnects or insulating layers. Another major use of FIB is the preparation of samples for transmission electron microscopy (TEM) [77]. A TEM sample must be thinned to
less than 100 nm in order to be electron transparent, which is achieved by removing the material around the sample through ion-induced sputtering. An example TEM specimen fabricated with FIB is shown in Fig. 1-2(b).

FIB is also used to pattern directly on samples (direct-write ion beam lithography, see for instance the review in reference [53]), and has the advantage of allowing the creation of three-dimensional structures (see, for instance, Fig.1-2(c)). Furthermore, modern photolithography would not be possible without FIB micro-machining. Photolithography masks consist of chromium patterns on glass, fabricated using electron beam lithography. The electron beam lithography process is prone to imperfections due to shot noise, which result in defects in the chromium pattern. These defects are corrected using FIB, which removes excess material from the mask and uses ion-induced deposition to complete gaps [3, 94]. Ion beams are also being considered for the patterning of sensitive media in high-resolution lithography, as ions do not suffer from the proximity effects hindering electron beam lithography [79, 4].

FIB can also be used for spectrometry and microscopy. As the ion beam scans a sample, ions and electrons are produced. The sputtered ions can be sent to a mass spectrometer for elemental analysis, in a technique called secondary ion mass spectrometry (SIMS) [111]. Since the ion beam removes material gradually from the sample, it is possible to profile the composition along the depth of the sample. The SIMS technique thus allows obtaining both lateral and depth composition information. The electron signal produced as the FIB scans the target can be used to create a sample image. The recent development of the helium ion microscope (HIM) [123] has provided an imaging tool with sub-nm resolution with a number of advantages over scanning electron microscopes. An example of an image obtained using HIM is shown in Fig. 1-2(d). FIB systems can also be used to locally modify the composition of a sample through direct ion implantation. For instance, quantum wells can be created in GaAs by localized implantation of aluminum ions [41].

It is evident that FIB systems are versatile and are useful for research and industrial applications. The next section reviews the available ion sources that can be used in FIB, in order to understand the limitations of the current technologies and motivate the use of ILIS in this area.
Figure 1-2: FIB applications (a) Via milled by FIB into a 32 nm IC [114] (b) TEM lamella milled by FIB [77] (c) Microfluidic channel patterned using FIB [86] (d) Helium ion microscope image of a hydroxyapatite crystal showing large depth of field [7]
1.2 Ion Sources for FIB

1.2.1 Ion Source Requirements

FIB ion sources must satisfy several operational and optical requirements. Operational properties include beam stability and lifetime, while optical properties such as brightness and energy spread determine the attainable probe size, which is usually defined as the smallest beam diameter that contains 50% of the current.

Source lifetime and stability are key demands for FIB implementation. FIB systems are complex machines with ultra high-vacuum systems, specimen stages and delicate optics. It is desirable for a source to have lifetimes greater than hundreds of hours in order to minimize source replacement and the exposure of these systems to contamination. Furthermore, the beam from the ion source must be positioned “precisely in relation with the elements of an optical system” [83] for adequate focusing, which means that the beam should not drift during operation. The ion current stability is an important requirement for FIB machines [119]. The precise stability requirements depend on the desired application. For example, lithography applications, where the size of the feature depends on the current dose [53], have more stringent requirements on the source stability than imaging applications, where beam current fluctuations average during image acquisition [50]. Typical commercial systems operate with current variations of 1-2% per hour [119].

FIB systems strive for minimizing the probe size \( d \) while maintaining a current density in the probe that is high enough for the required application. The probe size depends on several parameters from the ion source and the optical system, and can be calculated from the contributions of the lens magnification on the source size and the chromatic and spherical aberrations of the optical system. The following analysis, including equations 1.1 - 1.4, is based on reference [85].

For a perfect, symmetric Einzel lens, the probe size would be simply given by the lens magnification \( M \) of the source size \( D \):

\[
d_D = MD
\]  

(1.1)

Lenses, however, have aberrations that increase this theoretical size. A lens focuses particles that are coming further from its optical axis more strongly than the particles coming close to it, an effect known as spherical aberration. The spherical aberration depends on the current accepted from the beam, \( I \) (note this might be different than the current emitted from the source, as we may limit the current accepted into the optical system using defining apertures, see Fig. 1-1), as
well as on the current angular spread $\frac{dI}{d\Omega}$, where $\Omega$ is the unit solid angle. We assume a constant $\frac{dI}{d\Omega}$ for this analysis. The spherical aberration also depends on the lens magnification and the lens spherical aberration coefficient $C_s$, and its contribution to the probe size is given by

$$d_s = \frac{I^{3/2}}{2} \frac{C_s}{[\pi M^2 \frac{dI}{d\Omega}]^{3/2}}$$  \hspace{1cm} (1.2)

Chromatic aberration is also an important contribution to the probe size. Einzel lenses traditionally used for FIB will focus a particle depending on the particle’s energy, so if particles come at different energies from each other, the lens will focus them on a different spot, resulting in a larger beam size. Ideally, an ion source emits all particles at an energy $W$. However, due to the physics of ion emission, some particles come at energies slightly different from the main energy peak. Let $\Delta W_{1/2}$ be the full-width-at-half-maximum of the energy distribution. The chromatic aberration contribution to the probe size is given by

$$d_c = I^{1/2} \left( \frac{\Delta W_{1/2}}{W} \right) \frac{C_c}{[\pi M^2 \frac{dI}{d\Omega}]^{1/2}}$$  \hspace{1cm} (1.3)

where $C_c$, the chromatic aberration aberration coefficient, quantifies the spreading effect for a given lens. Adding up the contributions from equations 1.1, 1.2, and 1.3 in quadrature, the probe size is given by

$$d^2 = \frac{I^3}{4} \frac{C_s^2}{[\pi M^2 \frac{dI}{d\Omega}]^3} + I \left( \frac{\Delta W_{1/2}}{W} \right)^2 \frac{C_c^2}{[\pi M^2 \frac{dI}{d\Omega}]^2} + M^2 D^2$$  \hspace{1cm} (1.4)

From 1.4, we observe that reducing the current will lead to a smaller probe size, but doing so is not always practical. Material removal applications require high current densities in the sample to reduce the processing time, and in microscopy, higher currents improve the signal available for image acquisition. Thus, the source should have optical properties that will favor a smaller probe size without resorting to strong current reductions. The two figures of merit that measure the viability of focusing of an ion source are its energy spread ($\Delta W_{1/2}$) and brightness. From equation 1.4 it is evident that the smaller the energy spread, the better the resolution of the FIB system at higher currents. The value of $\Delta W_{1/2}$ must be minimized [119], and should be restricted to less than 10 eV. The brightness of the source is given by

$$\beta = \frac{4I_b}{(\pi \alpha_o D)^2}$$  \hspace{1cm} (1.5)
where the current $I_b$ is the total current produced from a source size $D$, sprayed it into a cone with half angle $\alpha_0$, or into a solid angle $\Omega = 2\pi (1 - \cos \alpha_0) \approx \pi \alpha_0^2$. Brightness affects the probe size through the beam angular spread, current density and source size. The higher $\beta$, the better probe size and current that can be achieved; it is usually required that $\beta > 10^6$ A cm$^{-2}$ sr$^{-1}$ [50].

There are a few ion source candidates for FIB operation, and we discuss Liquid Metal Ion Sources (LMIS) and Gas Field Ionization Sources (GFIS) in detail, as they are used in commercially available systems capable of sub-100 nm patterning. Other less developed ion sources are also reviewed.

### 1.2.2 Liquid Metal Ion Sources

LMIS are the most common sources for FIB, due to their high-brightness and reliability [40]. Ion emission from liquid metals was observed in 1975 by Krohn and Clampitt [59, 18], and the first focusing column using an LMIS was demonstrated by Seliger in 1979 [106, 107].

The ion production mechanism in LMIS is field evaporation from liquid metals. To achieve ion evaporation, a tungsten tip that has been sharpened to a radius of curvature of $\sim 10$ $\mu$m is covered with a molten liquid metal. The tip, or emitter, is in contact with a liquid reservoir. The tip is placed in front of a metallic plate with an aperture in it, the extractor, as shown in Fig. 1-3. The emitter extractor assembly is placed in vacuum. By applying a potential difference of ten or more kV between the emitter and the extractor, the electrostatic pressure overcomes the surface tension forces on the liquid, and the liquid surface evolves into a conical structure known as a Taylor cone [115]. At the apex of the Taylor cone, the electric field is of the order of several V/nm, which triggers direct ion evaporation from the liquid metal surface.

![Figure 1-3: (a) LMIS basic setup (b) Gallium ion source in operation (from [40])](image)

Several ion species can be produced from LMIS. Metals used in LMIS must have low vapor pressures for vacuum operation as well as low melting points, since operation at high temperatures can lead to reactions with the substrate and also promote the evaporation of neutrals. Sources
It is possible to obtain other elements that have high vapor pressure at their melting point such as B, As, Si, Ge if an alloy source is used, in which case the optical column will contain a Wien filter that separates and selects ion species based on their masses [85]. By far, the most widely used source in FIB is the Ga\textsuperscript{+} LMIS. The W support emitter is relatively easy to fabricate, the Ga interacts well with this substrate, and the source operates at room temperature, while being reliable, long-lived, and stable.

Ga\textsuperscript{+} LMIS have attributes that allow them to be routinely focused to sub-100 nm dimensions [40]. The Ga\textsuperscript{+} source emits currents of several \(\mu\text{A}\), although they are usually operated at 2 \(\mu\text{A}\) in order to minimize the energy spread, which increases at higher currents. At this current, the source has a current angular spread of 20 \(\mu\text{Asr}\textsuperscript{-1}\) and a minimum energy spread of 5 eV. The ion emission area at the apex of the Taylor cone is approximately 5 nm in diameter, but due to space charge effects from the high current density near the emission site, the beam spreads through Coulombic interaction, and the effective emission site is 50 nm in diameter. Using these values, LMIS brightness is estimated to be \(10^6 \text{Acm}^{-2}\text{sr}^{-1}\). The smallest probe size demonstrated, using state-of-the-art optics, is 5 nm [40].

Ga\textsuperscript{+} LMIS FIB systems are the tool for creating nanostructures through both subtractive and additive processes. The large sputter yield\textsuperscript{1} of Ga\textsuperscript{+} ions allows removing material for patterning of nanoscale holes, arrays and channels; the etching process can be accelerated using reactive-gas assistance. Ga\textsuperscript{+} beams are routinely used to perform ion implantation and growth of 3D structures with gas-assisted ion induced deposition. An extensive review of FIB uses of Ga\textsuperscript{+} is found in [120], and reference [121] includes a list of different chemistries for material removal and deposition with FIB.

Despite their widespread use, Ga\textsuperscript{+} FIB systems have key limitations. When patterning at scales below 30 nm, the focused beam has tails that perform undesired modification in the edges of the fine structures being created. In addition, Ga\textsuperscript{+} ions can lead to sample contamination, which is not acceptable in some applications, as the implanted Ga can affect both electrical and magnetic properties of a device [119]. Alloy sources can be used instead, but they are not as easy to implement and are not as widely available as the basic Ga\textsuperscript{+} FIB.

\textsuperscript{1}Sputtering yield is defined as the ratio of the number of atoms removed from the sample to the number of incident ions.
1.2.3 Gas Field Ionization Sources

Gas Field Ionization Sources produce beams of ions from noble gases by virtue of field ionization [83]. The basic GFIS setup is shown in Fig. 1-4. A sharpened needle (usually tungsten), with a radius of curvature of ~100 nm, is placed in front of an extractor. A voltage difference of a few kV is applied between the emitter and the extractor, so that fields in the order of 10 V/nm are achieved at the tip. A gas (usually noble) is introduced near the tip, in order to supply the particles to be ionized. The emitter must be cooled cryogenically in order to increase the density of atoms available for ionization. Once an atom is in the vicinity of the tip, it is possible for the atom to be ionized by quantum mechanical tunneling of the electron into the metal, as the energy barrier has been distorted by the electric field. The resulting positive ions are accelerated away from the tip by the electric field. Several ion beams are obtained, one from each emitter atom involved in ionization.

FIB systems using GFIS had been demonstrated in the 1970s by the groups led by Levi-Setti [29] and Orloff and Swanson [84]. Probe sizes of 50 nm with currents of 10 pA were demonstrated [85]. Nonetheless, these ions sources were difficult to maintain, had current fluctuations if any impurities were present in the source gas, and the current densities achievable were too low in comparison with the LMIS, so they were not implemented widely in FIB [119]. In the past 10 years, however, improvements in the tip construction and geometry have allowed the commercial availability of these sources in FIB systems.

In a generic GFIS, the tip is roughly a few hundreds of atoms in diameter, and the ionization of the gas is distributed between all these atoms, as shown in Fig. 1-5. However, by sharpening the tip to be only three atoms at the apex, it is possible to concentrate the total gas supply to these three atoms instead of the hundreds of atoms in the blunter tip [123]. Such a tip can be produced
reliably and can last months in operation. Using He, the source produces three main beamlets, of which one is selected for focusing. The source size is approximately 3 Å, and the current density is 2.5 μA sr⁻¹, giving a brightness of 4 ⋅ 10⁹ A cm⁻² sr⁻¹. In addition, the source has an energy spread of less than 1 eV; these properties allow it to be focused to an ultimate spot size of 0.25 nm.

This improved He⁺ source has been implemented in FIB as an ultra-high resolution microscopy tool. Scanning electron microscopes have probe sizes of down to 1 nm, but incident electrons will interact with the sample through an extended volume and produce signals from an area larger than the probe size. The helium ion beam, instead, will stay relatively collimated as it penetrates into the sample, thanks to the much larger mass of the helium ions. Therefore, the helium ion beam produces signals from a smaller area than electrons would, and this allows the production of images with improved resolution [50].

HIM has additional benefits of elemental contrast and large depth of field (the image in Fig. 1-2(d) is from a HIM). An example comparing images from an SEM and HIM is shown in Fig. 1-6.

Besides He⁺, Ne⁺ beams can be produced with GFIS; the optical properties and stability of the neon source are slightly worse than those of helium, but spot sizes of a nm can still be achieved [96]. The focused He⁺ and Ne⁺ ion beams can be used to pattern materials at scales not accessible by LMIS; it is much easier to produce sub-10 nm structures using these GFIS, as LMIS FIB require dedicated optics to achieve the smallest probe sizes, and because of the beam tail effects mentioned above. Neon is more efficient than helium in sputtering due to its larger mass and is preferred for
nano machining applications [65]. The commercial availability of these GFIS tools has triggered research into many applications, including spectrometry [26] and lithography [125]. Despite their resolution capabilities, He\(^+\) and Ne\(^+\) systems are limited in their throughput for machining applications, as the current achieved in the probe cannot exceed 30 nA, and because He\(^+\) and Ne\(^+\) ions are not as efficient as Ga\(^+\) in material removal. GFIS FIB systems are also quite complex, as they require both cryogenic cooling, high-purity gases and ultra-high vacuum operation.

1.2.4 Other Ion Sources

Alternative technologies for FIB, including plasma ion sources, electrolyte ion sources and laser-based ion sources have been mentioned in the literature. These systems cannot yet reach the same level of resolution of LMIS/GFIS, but they can be of advantage in applications requiring rapid milling or other ion species.

- **Inductively Coupled Plasma (ICP) Source.** In ICP sources, a plasma is created inductively by an RF antenna, and ions are extracted from the plasma chamber through an aperture of 200 \(\mu\)m in diameter [108]. Beams of Ar\(^+\) can be produced, with a brightness of 4590 Acm\(^{-2}\)sr\(^{-1}\) and an energy spread of 7 eV, as well as Xe\(^+\) beams with brightness of 10500 Acm\(^{-2}\)sr\(^{-1}\) and spread of 10 eV. These sources have current densities of several mA sr\(^{-1}\), considerably larger than those of Ga\(^+\) LMIS, but the low value of the brightness results from the effective source size of \(\sim 10 \ \mu\)m. ICP sources cannot compete with the Ga\(^+\) LMIS in producing small beam sizes, although ICP sources are capable of producing sub-100 nm probes, albeit at limited probe currents. ICP sources do become useful, however, if probe sizes of several hundreds of nm are...
desired (for instance, for removal of bulk material). In this case, the ICP can give much larger current densities than a Ga+ LMIS thanks to the superior current emitted. The larger current density, coupled with the sputter yield of heavy ions like Xe+, is beneficial for rapid milling applications. Furthermore, ions like Ar+ or Xe+ do not have the same issues with contamination as Ga+.

- **Multicusp Plasma Ion Source.** A source of this type was described by Scipioni et al. [104]. A plasma is formed in a 50 cm³ volume by a filament discharge, with electrons confined by a multicusp magnetic field, and the ion beam exits through a 1 mm diameter aperture. Beams of inert ion species such as Kr+, Ne+, and He+ have been produced by this source, although their brightness does not exceed 2000 Acm⁻²sr⁻¹ and so sub-100 nm probes are impractical.

- **Penning Type Plasma Ion Source.** Guharay et al. [44] developed a Penning surface plasma source capable of producing both positive or negative ions. The authors report H⁻ beams with brightness of 5 × 10⁴ Acm⁻²sr⁻¹, with less than 3 eV energy spread. This source has the unfortunate need for pulsed operation and has not been developed further, but is one of the few ion sources of relatively high-brightness capable of producing negative ion species, which, as will be explained later, could be beneficial for applications where charging of samples is not desired.

- **Solid Electrolyte Ion Sources.** Escher et al. [28] demonstrated an ion source based on the solid electrolyte (AgI)₀.₅(AgPO₃)₀.₅. In the solid electrolyte, mobile ions (such as Ag⁺ for Escher’s source) can move freely; by shaping the electrolyte as a sharp tip and placing it in front of a metallic extractor, it is possible to extract the mobile species by applying a voltage difference of several kV. The source tested by Escher et al. could sustain µA over several days. These sources have not been developed further, but could potentially provide many other species, such as Cu⁺, F⁻, O²⁻ and H⁺, by choosing an appropriate electrolyte.

- **Laser based ion sources.** It is possible to produce ion beams for FIB by photoionization of laser cooled atoms [47]. Focused ion beams of chromium and lithium have been obtained from Magneto Optical Trap Ion Sources (MOTIS) [110, 57]. In this device, neutral atoms are confined and cooled using a magnetic field and lasers (the magneto-optical trap), where they are photo ionized and subsequently accelerated into a focusing column. MOTIS have a small energy spread (<1 eV), but are limited in their brightness, as the currents obtained from the system are limited by the slow diffusion rate of atoms to refill the ionization region. To avoid this limitation,
Alternative devices are being researched in which the atoms are not confined, but rather, a slow moving atomic beam is laser cooled, compressed, and then photo ionized to produce an ion beam of improved quality [56, 126, 116].

From this survey of ion sources for FIB, it is clear that although several ion species are accessible, not all are easy to implement nor have optical performances comparable to LMIS and GFIS. There is also a need for ion sources capable of providing a greater variety of ion species, especially negative ions.

1.3 Ionic Liquid Ion Sources as an alternative for FIB

ILIS have been recently proposed as ion sources for FIB [66, 136]. These sources produce ion beams by field-evaporation from room-temperature molten salts, or ionic liquids. These substances are mixtures of positive and negative ions, which can be organic molecules or inorganic monoatomic species. Ionic liquids have non-measurable vapor pressures, low surface tensions, and conductivities of the order of 1 S/m, which makes them capable of being electrostatically stressed to trigger ion evaporation. An example ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF4), is shown in Fig. 1-7(a).

In ILIS, the ionic liquid wets a micro-tip emitter, and the liquid is subjected to a potential of 1-2 kV with respect to a downstream metallic extractor (Fig. 1-7(b)). The liquid is stressed into a sharp meniscus. At the apex of the deformed meniscus, electric fields of the order of 1 V/nm trigger ion evaporation from a point source. The brightness of ILIS has been estimated to be of the order of 10^6 Acm^-2sr^-1 [136, 89], which is competitive with LMIS. Furthermore, the beams from ILIS contain highly mono energetic ion populations with energy spreads of 7-8 eV [66, 68], and potentially less if filtering is used [30]. Thus, the focusing of these ion sources into sub-100 nm
spots should be feasible.

The details of ILIS implementation, such as micro-tip geometries and liquids tested, are exhaustively reviewed in Chapter 2. The following is a general motivation for the use of ions from ILIS in FIB:

1. Since the ionic liquid contains cations and anions, ILIS are capable of producing either positive or negative ion beams, by simply reversing the polarity of the applied potential. The ease of access to negative ion beams is almost unique to ILIS, and their use in FIB could bring advantages in the processing of non-conducting samples, which are prone to charging when irradiated with a positive ion beam [45]. Secondary electrons are produced as a result of ion beam irradiation, and since the sample is non-conductive, a net positive charge builds on the substrate which distorts the electric field and affects the imaging or fabrication process. Electron flooding systems are usually required to avoid charging in dielectric samples. If negative ions are available, it may be possible to irradiate these samples in such a way that the arrival of negative ions balances the secondary electron production.

2. ILIS could be used to produce a novelty of ion species not accessible from other source technologies. There are hundreds of ionic liquids being researched as solvents for chemical synthesis and for use in electrochemical systems such as batteries and super capacitors [134]. Given the large variety of anions and cations in the literature, ILIS could potentially provide focused probes of ion species tailored for specific applications by simply choosing a liquid with the desired ion species.

For instance, ILIS could produce heavy molecular ions that could be used for surface smoothing or lithography. What is more, many ionic liquids include reactive species (e.g. BF$_4^-$, HF$^-$, I$^-$, Cl$^-$), which could be useful for micro-machining. If using reactive ions in etching applications, a combination of physical erosion from the incident ions with chemical reactions at the surface could enhance the etching rates. In FIB, it is common practice to introduce reactive gases such as XeF$_2$ near the specimen. The gases react readily with the sputtered material under the ion beam influence, creating volatile species that are readily removed by the vacuum system and prevent redeposition, effectively accelerating the milling process. This is depicted in Fig. 1-8 (a),(b). If using ILIS beams with reactive species, there is no need for introducing reactive gases in the chamber to achieve large milling rates (Fig. 1-8(c)). Thus, using an ILIS could eliminate the need of introducing assistive reactive gases in other FIB
Figure 1-8: (a) Pure mechanical sputtering (b) Mechanical sputtering with reactive bass assistance (c) ILIS milling with reactive ions does nor require gas assistance

systems, which is expensive, cumbersome, but necessary to accelerate the processing speeds.

ILIS reactive etching was demonstrated in 2010 [88]. The beam obtained from the liquid EMI-BF₄ are capable of etching silicon at rates faster than typical Ga⁺ mechanical sputtering at an energy of 15 keV. The sputtering yield was measured to be from 5 to 35 atoms of silicon removed per incident ion, compared to yields of 2 for Ga⁺ ions at the same energy. These results are included in this thesis, and are presented in more detail in Chapter 6.

3. ILIS operation is simpler than LMIS/GFIS, as ILIS emit at room temperature with lower extraction potentials, and no need for ultra-high vacuum.

These novelties should make ILIS ideal candidates for FIB utilization. However, ILIS must satisfy requirements beyond adequate energy spread and brightness to be successfully implemented with FIB optics. The source should reproducibly produce an ion beam that is emitted straight, i.e., have on-axis emission, as well as operation lifetimes of several hundred hours. As will be discussed in Chapter 2, conventional ILIS technology does not meet the lifetime and on-axis emission requirements. As new ILIS technologies are developed, it is of utmost importance to guarantee that the emitters operate in the pure ion regime (PIR) with no intervening droplets. Operation in a mixed ion-drop regime results in non-ideal optical properties that make the source less amenable for focusing. Therefore, this thesis will design, fabricate and test alternative configurations of ILIS that could be implemented successfully in a focusing column.

1.4 Thesis Scope and Outline

The main goal of this thesis is the demonstration of a new emitter technology that is compatible with focused ion beam implementation. Chapter 2 reviews the basic physics of ILIS and the previous efforts on the development of ILIS technology, and explains the need for new configurations of ILIS
compatible with FIB. Chapter 3 gives an outline of the approach for source design, the substrate selection, and the manufacturing process to produce a prototype emitter. This work has identified carbon xerogels as an adequate substrate for ILIS emitters, and test emitters of this material were produced by mechanical polishing. Chapter 4 presents the emission characteristics of the prototype emitters. In Chapter 5, the implementation of the carbon xerogel ILIS is revisited, and laser micro-machining is validated as a suitable manufacturing technique. The emission from the laser micro-machined carbon ILIS is characterized. Chapter 6 shows the irradiation results obtained with tungsten and carbon xerogel ILIS, demonstrating the capability of ILIS for reactive etching. Chapter 7 concludes with a summary of the contributions of the thesis and a discussion of the focusing prospects of this technology.
Chapter 2

Theoretical Background and Literature Review

This chapter covers the fundamentals of emission from ionic liquid ion sources in Section 2.1 and then reviews the ILIS technology researched to date in Section 2.2.

The theoretical framework starts with a review of the onset conditions required to trigger the deformation of a liquid meniscus into an emitting structure, through an estimation of the startup voltage, in Section 2.1.1. Once a sufficient electrostatic traction is applied to a liquid meniscus, the liquid will deform into a stable emitting structure. In the case of liquid metals or electrolyte solutions, the emitting meniscus resembles a Taylor cone. The chapter includes a review of the fundamentals of Taylor cones in Section 2.1.2, and then briefly motivates the different operation regimes observed in liquid metals, electrolyte solutions and ionic liquids in Section 2.1.3. Ionic liquids may operate in a mixed ion-droplet or a purely ionic regime (PIR). Recent numerical investigations [20] indicate that the shape of the electrified meniscus in the case of pure ion emission from ionic liquids differs strongly from the classical Taylor cone approximation. These simulations indicate the existence of an upper limit to the size of a liquid meniscus that can support the PIR, and motivate the role of a high hydraulic impedance in accessing the PIR.

The chapter then includes a review of ILIS emitter technologies and different ionic liquids used to date, as well as the focusing efforts on ILIS, to motivate the need for novel emitter technologies that will be compatible implementation in FIB and other applications.
Figure 2-1: (a) Prolate spheroidal coordinate system. Surfaces of constant $\eta$ are prolate hyperboloids, surfaces of constant $\xi$ are prolate spheroids. (b) Setup geometry: tip is defined by $\eta_0$ hyperboloid, extractor is the $\eta = 0$ surface.

2.1 ILIS Basic Physics

2.1.1 Onset of Electrospray Phenomena: Startup Voltage

A fundamental feature of electrospray devices is the non-linearity in current as a function of voltage. It is generally observed that as the voltage is increased, the current is zero until a threshold voltage, that we call $V_{\text{start}}$, is reached. This voltage can be calculated as done in reference [74]. $V_{\text{start}}$ depends on several factors, including the tip radius of curvature $R_c$, the tip to extractor distance $d$, the size of the wet features on the tip surface, as well as on the ionic liquid’s surface tension $\gamma$. We will calculate the startup voltage both in the case where the liquid supporting structure is perfectly wetted (which is done in Ref. [74]), and also for the case in which the emission comes from a meniscus that partially covers the emitter tip (which requires a minor modification). This calculation will be used later in the thesis to estimate the size of the emitting menisci tested in this work.

$V_{\text{start}}$ can be estimated by solving for the electric field in the surface of the tip, which is assumed to have a hyperboloid shape, and finding the condition for which the electric pressure balances the surface tension force of the wet feature on the tip surface. The electric field can be approximated by solving Laplace’s equation in the prolate spheroidal coordinate system. This coordinate system $(\eta, \xi, \phi)$ consists of confocal hyperbolic and spherical surfaces, as shown in Figure 2-1(a), which can be described in terms of cylindrical coordinates $(R, z, \phi)$ as follows

$$\eta = \frac{1}{a} \left( \sqrt{R^2 + (z + a/2)^2} - \sqrt{R^2 + (z - a/2)^2} \right)$$  \hspace{1cm} (2.1)
Here, $a/2$ is the location of the focus of the hyperbolas and ellipses. If the emitter surface is assumed to be an hyperbola with $\eta = \eta_0$, it can be shown that $\eta_0 = (1 + \frac{R_c}{d})^{-1/2}$ and $a = 2d\sqrt{1 + \frac{R_c}{d}}$. The extractor plate is the $\eta = 0$ surface. This geometry is shown in Figure 2-1(b).

To solve for the potential $\Phi$, we solve Laplace’s equation. The potential is assumed to depend only on $\eta$, and so Laplace’s equation becomes

$$\frac{\partial}{\partial \eta} \left( (1 - \eta^2) \frac{\partial \Phi}{\partial \eta} \right) = 0$$  \hspace{1cm} (2.3)

The potential is $\Phi = V$ for $\eta = \eta_0$ and zero on the extractor. Using this boundary conditions, the potential is given by

$$\Phi = V \frac{\text{atanh}(\eta)}{\text{atanh}(\eta_0)}$$  \hspace{1cm} (2.4)

Then, the electric field is given, in cylindrical coordinates, by

$$E = -\nabla \Phi = - \left( \frac{\partial \Phi}{\partial R} \hat{R} + \frac{\partial \Phi}{\partial z} \hat{z} \right) = - \frac{V}{\text{atanh}(\eta_0)(1 - \eta^2)} \left( \frac{\partial \eta}{\partial R} \hat{R} + \frac{\partial \eta}{\partial z} \hat{z} \right)$$  \hspace{1cm} (2.5)

Where

$$\frac{\partial \eta}{\partial R} = \frac{R}{a} \left( \frac{1}{\sqrt{R^2 + (z + a/2)^2}} - \frac{1}{\sqrt{R^2 + (z - a/2)^2}} \right)$$  \hspace{1cm} (2.6)

$$\frac{\partial \eta}{\partial z} = \frac{1}{a} \left( \frac{(z + a/2)}{\sqrt{R^2 + (z + a/2)^2}} - \frac{(z - a/2)}{\sqrt{R^2 + (z - a/2)^2}} \right)$$  \hspace{1cm} (2.7)

To find the startup voltage of the ILIS, we solve for the voltage for which the electrostatic pressure is equal to the surface tension pressure of the wet feature. If the tip apex is perfectly wetted (ideal case), the balance condition is

$$\frac{1}{2} \varepsilon_0 E^2(R = 0, z = d) = \frac{2\gamma}{R_c}$$  \hspace{1cm} (2.8)

In this ideal case, the startup voltage is given by

$$V_{\text{start, ideal}} = \text{atanh}(\eta_0)(1 - \eta_0^2) \sqrt{\frac{a^2\gamma}{\varepsilon_0 R_c}}$$  \hspace{1cm} (2.9)
If we assume \( d >> R_c \), the expression in equation 2.9 simplifies to

\[
V_{\text{start, ideal}} = \ln \left( \frac{4d}{R_c} \right) \sqrt{\frac{\gamma R_c}{\epsilon_0}}
\] (2.10)

Now, if the tip is not properly wetted, the startup voltage for emission will be increased from the value in equation 2.9. If we have a small pool of liquid of radius \( r_{\text{pool}} \), located at the tip apex, the startup voltage of the source will be determined by

\[
\frac{1}{2} \epsilon_0 E^2(R = 0, z = d) = \frac{2\gamma}{r_{\text{pool}}}
\] (2.11)

In the more general case, we have

\[
V_{\text{start}} = \tanh(\eta_0) \left( 1 - \eta_0^2 \right) \frac{a^2 \gamma}{\epsilon_0 r_{\text{pool}}}
\] (2.12)

The startup voltage is increased from the ideal case by a factor \( \sqrt{R_c/r_{\text{pool}}} \).

### 2.1.2 Taylor Cones

Once an electrostatic traction has been applied, the electrified meniscus becomes unstable and evolves from a rounded meniscus to a stable cone-like structure. This electrified menisci are usually referred to as a Taylor cones [31]. It is possible to gain insight into the shape of the cone and the electric field distribution through the analysis of Taylor [115]. It is important to note that Taylor's analysis corresponds to an idealized situation, and that actual electrified menisci will deviate from this ideal case, and that the deviation is even more prominent in the case of ionic liquids emitting pure ions.

Taylor's analysis solves for the electric field at the surface of the cone. Consider an infinite cone of half-angle \( \theta_T \), with the origin at the apex of the cone, as shown in Fig. 2-2. We consider three stresses that act on the liquid: (1) the hydrostatic pressure difference with the medium, (2) the surface tension pressure and (3) the electric field stresses. Let \( \Delta p \) be the pressure difference between the liquid and the surrounding medium. The pressure due to surface tension is given by \( P_\gamma = \gamma \kappa \), where \( \gamma \) is the surface tension of the liquid, and \( \kappa_c \) is the surface curvature. A distance \( r \) from the apex of the cone, \( \kappa_c \) is given by

\[
\kappa_c = \frac{1}{r_c} = \frac{\cot \theta_T}{r}
\] (2.13)
The liquid is assumed to behave as a perfect conductor, so that all free charges have migrated to the surface of the conductor. The electric field is normal to the surface of the cone and zero inside the cone. With this assumption, the electrical pressure on the surface of the cone is given by the normal component of the Maxwell stress tensor, \( P_E = \frac{1}{2} \varepsilon_0 E_n^2 \).

Balancing stresses, we obtain

\[
\frac{1}{2} \varepsilon_0 E_n^2 + \Delta p - \frac{\gamma \cot \theta_T}{r} = 0
\]

(2.14)

We assume there is no active pressure feed to the liquid and no pressure drops along the liquid due to viscosity effects, i.e. \( \Delta p = P_{upstream} - ZQ = 0 \), where \( P_{upstream} \) is the back pressure applied to the meniscus, \( Z \) is the hydraulic impedance of the emitter and \( Q \) is the flow rate through the cone (which is zero for the static case). Then, the electric field along the surface of the liquid is given by

\[
E_n = \sqrt{\frac{2 \gamma \cot \theta_T}{\varepsilon_0 r}}
\]

(2.15)

The electric field around the Taylor cone is found next. Assuming no space charge in the region surrounding the cone, the electric potential \( \Phi \) must satisfy Laplace’s equation:

\[
\nabla^2 \Phi = 0
\]

(2.16)

In the axisymmetric problem, there is no dependence on the azimuthal coordinate \( \frac{\partial}{\partial \phi} = 0 \), and therefore equation 2.16 reduces to

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r \frac{\partial \Phi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Phi}{\partial \theta} \right) = 0
\]

(2.17)
The solution to equation 2.17 is a combination of functions including Legendre functions $Q_\nu, P_\nu$,

$$\Phi = \sum_\nu (A_\nu Q_\nu(\cos \theta)r^{\nu'} + B_\nu P_\nu(\cos \theta)r^{\nu}) + \Phi_0 \quad (2.18)$$

Here, $\nu$ can be any real number, $A_\nu$ and $B_\nu$ are constant coefficients, and $\Phi_0$ is a constant potential dependent on boundary conditions. We note that $P_\nu$ has a singularity for $\theta = \pi$; as this is a region of free space where the potential should be finite, we must impose $B_\nu = 0 \forall \nu$. This potential solution should also be consistent with the electric field at $\theta = \theta_T$, which requires

$$E_n = -\frac{1}{r} \frac{\partial \Phi}{\partial \theta} = \sum_\nu A_\nu Q'_\nu r^{\nu'-1} = \sqrt{\frac{2\gamma \cot \theta_T}{\epsilon_0 r}} \quad (2.19)$$

From here, we find that the only Legendre function permitted is that corresponding to $\nu = 1/2$, which implies the potential is of the form

$$\Phi(r, \theta) = A_{1/2} Q_{1/2}(\cos \theta)r^{1/2} + \Phi_0 \quad (2.20)$$

Since the liquid is considered a perfect conductor, the $\theta = \theta_T$ surface must be an equipotential surface. From equation 2.20, it is evident that $\Phi$ will have some variation through $r$ unless $Q_{1/2}(\cos \theta_T) = 0$, which occurs for a cone half-angle of 49.29°. We note that this half-cone angle is independent of the liquid or the applied potentials.

The Taylor analysis predicts roughly the shape observed for electrified menisci for liquid metal ion sources and most electrosprays, but it is not an exact treatment. The solution for the field in equation 2.15 has a singularity at $r = 0$, which is not physical. At the cone apex, emission of charged particles occurs, giving rise to a flow $Q$ and current $I$. The flow causes the breakdown of the assumption of equipotentiality. Furthermore, the mechanical balance at the interface will be affected by the hydrostatic pressure from any applied backpressure and from hydraulic pressure drop from the flow. The meniscus will in fact have some curvature, deviating from the ideal Taylor solution. The types of particles emitted and the meniscus shape depend on the liquid properties and the flow supplied to the meniscus. The different emission regimes are discussed in the next section.
2.1.3 The emission from electrified menisci

The emitted beam composition and the shape of the meniscus differ substantially depending on the working fluid and the flow conditions imposed on the meniscus.

In the case of LMIS, the meniscus shape is very close to the Taylor cone geometry, with the exception of a small jet protrusion at the apex of the cone. This jet ends in a small hemispherical cap, where the electric field is strong enough to support pure ion evaporation from the liquid metal. As the emission current of the LMIS is increased, the jet elongates in order to sustain the electric field required for evaporation in the presence of strong space-charge [73, 34, 55]. Under high current conditions, the jet may undergo instabilities that trigger the emission of droplets [71, 33].

Electrolyte solutions produce charged droplets and in some cases ions from cone-like menisci. Figure 2-3(a) illustrates the cone-jet regime observed with these solutions, in which the apex of the Taylor cone deforms into a thin jet that eventually breaks into a spray of charged droplets. As the ratio of the liquid conductivity to the flow rate, $K/Q$, increases, the magnitude of the electric field increases and enables the emission of ions from the base of the jet, as illustrated in Figure 2-3(b).

![Figure 2-3: (a) Cone-jet (b) Mixed ion/drop regime](image)

Loscertales and Fernandez de la Mora derived scaling laws for the current emitted in the cone-jet regime in a seminal 1994 paper [32]. The problem is treated as consisting of three domains: the cone, a transition region, and the jet. In the cone, the cross section for transport of mass is large and the velocity of the fluid is slow, thus allowing the liquid to fully relax and behave as a conductor. In this domain, charge is transported by bulk conduction through the cone volume, and surface charge convection contributes little to the current. The static situation breaks down when the liquid’s electrical relaxation time, $\tau_\epsilon = \epsilon \epsilon_0 / K$, becomes comparable to the passage time $\tau_p = r^3 / Q$. Here, $\epsilon_0$ is the permittivity of vacuum and $\epsilon$ the dielectric constant of the liquid. This is a transition region, defined by a characteristic size.
In this transition region, the velocity of the fluid has increased, and the bulk conduction current is gradually transformed into convected surface charge. In the jet domain, convection is the main charge transport mechanism. The jet eventually breaks up into charged droplets.

To obtain the scaling law for the current as a function of the flow rate, one can evaluate the surface charge convection current on the transition region. From equation 2.15 and Gauss' Law, the surface charge $\sigma_s$ at $r = r^*$, is $\sigma_s = \sqrt{2\varepsilon_0\gamma \cot \theta_T / r^*}$. Assuming sink flow, the velocity of the fluid on the surface of the cone at $r^*$ is given by

$$u_s = \frac{Q}{2\pi r^2(1 - \cos \theta_T)}$$

(2.22)

The current, then, is given by $I = 2\pi r^* \sin \theta_T \sigma_s u_s$, or

$$I = \sqrt{\frac{2\sin \theta_T \cos \theta_T}{(1 - \cos \theta_T)^2}} \sqrt{\frac{\gamma KQ}{\epsilon}}$$

(2.23)

Experimentally, Loscertales and Fernandez de la Mora [32] verified

$$I \sim (\gamma KQ/\epsilon)^{1/2}$$

(2.24)

This scaling law applies well for a range of electrolyte solutions studied, if the emission is stable. The 1994 paper defines the non-dimensional flow parameter $\eta$ as

$$\eta = \sqrt{\frac{\rho KQ}{\gamma \varepsilon_0 \epsilon}}$$

(2.25)

where $\rho$ is the liquid mass density. If the flow rate is reduced so that $\eta$ falls below about 1, the emission becomes unstable.

The scaling fails to predict the $I(Q)$ relation for electrolyte solutions of high conductivity, as was observed by Gamero-Castano [36]. This is due to the appearance of ion evaporation (Figure 2-3(b)), and we now proceed to discuss the circumstances under which ion emission might occur.

In Gamero's work, several solutions of NaI in formamide, of different electrical conductivities, were tested. Once the electrical conductivity of the solution exceeds values of 1 S/m, ions are evaporated from the surface of the meniscus as well as the drops. The author used a combination
of retarding potential analysis and preferential scattering in a gas background to measure the currents of ions generating from the drops independently of the ions originated in the meniscus. For low conductivity solutions, no ion evaporation is observed, and the scaling law \( I \sim Q^{1/2} \) holds. As \( K \) is increased, ion emission might occur directly from the droplets, but this emission does not affect the current scaling as the ion evaporation process occurs once the droplets leave the jet. In the case of the more conductive solutions, the scaling law does not apply completely. For large \( Q \), \( I \) in fact scales as \( Q^{1/2} \), but as \( Q \) is decreased, the current curve has a minimum and then grows as the flow rate is decreased towards the minimum flow rate. This increase in current at the lowest flow rates is attributed to ion evaporation directly from the meniscus, specifically from the base of the jet. The ion evaporation in the droplets and the meniscus is triggered as the electric field exceeds values of \( 1 \) V/nm.

The maximum electric field reached on the meniscus is a function of the liquid’s conductivity \( K \) and the flow rate \( Q \), and in fact scales as

\[
E \sim (K/Q)^{1/6}
\]  
(2.26)

Thus, for higher values of \( K \), \( Q \) may be reduced while keeping \( \eta \) above the minimum required to sustain emission, and at the same time increase \( E \) beyond the threshold for ion evaporation. It is possible to derive this relation in two different ways, as shown by Gamero [36]. First, one can simply note that the maximum electric field must scale with the characteristic meniscus size \( r^* \) as

\[
\frac{1}{2} \varepsilon_0 E^2 = \frac{\gamma}{r^*}
\]  
(2.27)

Using equation 2.21, the scaling of \( E \) in equation 2.26 is obtained. One can also obtain the scaling by calculating the field on the cone and the jet. In a jet where conduction is negligible, the electric field on the jet surface is given, from Gauss’ Law, by

\[
E = \frac{RI}{2Q\varepsilon_0}
\]  
(2.28)

where \( R \) is the local jet radius. Since the jet tapers, the electric field reaches its maximum value at the jet base. The electric field found from the Taylor equilibrium on the cone side is

\[
E = \sqrt{2\gamma \cos \theta_T / \varepsilon_0 R},
\]

where \( R \) is the local radius of the cone \( (R = r \sin \theta_T) \). This expression increases as we approach the jet. The field terms becomes comparable in the transition region.
between the cone and the jet, so that \( R^3 \sim 8 \cos \theta T Q^2 \varepsilon_0 / I^2 \), and \( E^3 \sim \gamma I \cos \theta_T / (\varepsilon_0^2 Q) \). Since \( I \sim (KQ)^{1/2} \), we must have \( E \sim (K/Q)^{1/6} \).

The mixed ion-droplet beams have energy spreads and energy deficits of the order of a few hundred volts. Due to ohmic effects, the voltage varies over the transition region and the jet as the liquid accelerates downstream, and thus the ions are generated for a wide range of potentials. These large energy spreads are unsuitable for focusing; furthermore, the presence of microdroplets in the beam might contaminate focusing elements.

Ionic liquids may operate either in the mixed ion-droplet regime or emit purely ions. In the mixed regime, the length of the jet, the droplet size and the energy spreads are reduced as the flow rate is decreased [37]. If sufficient hydraulic impedance is provided to decrease the flow rate, the ionic liquid meniscus will emit a pure ion beam (this PIR has not been observed with electrolyte solutions). In this PIR, an ionic liquid ion beam is produced with a relatively small energy spread as well as with small energy deficits (\( \sim 7-8 \) eV) that are associated to the energy cost of bringing the ion from the liquid to the gas phase [66]. The pure ion regime is thus ideal for focusing applications.

Recent numerical studies by Coffman [20] reveal that the PIR observed in ionic liquids is accessible only under some specific conditions, and that the meniscus shape supporting pure ion evaporation differs substantially from the classical Taylor geometry. Coffman's simulations solve for the shape of the electrified meniscus of an ionic liquid, that satisfies the mechanical equilibrium between the electric, surface tension and pressure stresses on the liquid-vacuum interface, as a function of several parameters, including the applied downstream electric field, the base size of the meniscus, the hydraulic impedance applied to the flow, and relevant ionic liquid properties, such as conductivity, surface tension, dielectric constant, and solvation energy.

Figure 2-4 shows several ionic liquid menisci profiles as a function of the parameter \( B \) defined by Coffman, which is a non-dimensional length inversely proportional to the base size of the meniscus. The menisci shapes differ significantly from the Taylor cone geometry, due to the presence of a strong hydraulic pressure drop that affects the mechanical balance at the interface. For small menisci, with bases in the order of a few hundred nanometers, the ion emitting meniscus is a slightly deformed rounded structure, with ion evaporation occurring from a large fraction of the surface. As the parameter \( B^{-1} \) is increased, and the menisci size is of the order of few microns, the menisci shape converges to the shape shown in the inset. This meniscus elongates into a small protrusion, with ion evaporation localized at the apex this protrusion. These numerical simulations indicate that conduction is the dominant charge transport mechanism for the PIR of ionic liquids.
Figure 2-4: Meniscus shapes (blue lines) for an ionic liquid operating in the PIR, predicted by the numerical models of Coffman [20]. The black line is the classical Taylor cone geometry. The inset illustrates the limiting geometry as the meniscus base size is increased.

A solution for the meniscus shape exists only for a limited set of parameters, as illustrated in Figure 2-5. This figure shows two solution maps for varying $B$ and applied (non-dimensionalized) electric field $E$, for two different values of hydraulic impedance. The maps show a green area, corresponding to solution regions for ion emitting meniscus. For a given meniscus size, the electric field can be varied over a limited set of values between the onset of emission and before the meniscus becomes unstable. As the meniscus size is increased (larger $B^{-1}$), the range of possible electric fields becomes narrower, indicating that the pure ion mode might not be sustainable with larger meniscus sizes. If the hydraulic impedance is increased, the emitter meniscus size may be increased while still obtaining a wide range of solutions. Coffman’s studies indicate that the meniscus size should be limited to a few micrometers for the PIR to be sustainable, and that the PIR is more easily achievable as the hydraulic impedance of the liquid supplying emitter is increased.

As the goal of this thesis is the development of a source of ions from ionic liquids for FIB and other applications, the next section discusses the instances where the PIR has been observed with ionic liquids.
2.2 Ion Emission from Ionic Liquids

This section reviews the different emitter configurations and materials introduced to sustain pure ionic emission from ionic liquids. Three types of emitter are described in the literature: (1) capillary, (2) externally wetted, and (3) porous, shown in Figure 2-6, which differ on the way the liquid is transported to the emitter apex. The goal is to identify under which conditions the PIR can be achieved for each of these emitter types, and to list the advantages and challenges posed by the different emitter types and substrates used, to ultimately motivate the need for new emitter configurations. Lifetime limitations and mitigation techniques introduced so far are also discussed.

Table 2.1 summarizes the relevant room-temperature properties of the different ionic liquids used in the PIR to date. The abbreviations listed in this table will be used in the remainder of this thesis. The names and formulae of the ionic liquids are listed in table 2.2.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Conductivity [S/m]</th>
<th>Surface Tension [dyn/cm]</th>
<th>Density [kg/m³]</th>
<th>Viscosity [Pa·s]</th>
<th>Electrochemical Window [V]</th>
<th>References</th>
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<tbody>
<tr>
<td>EMI-BF₄</td>
<td>1.36</td>
<td>45.2</td>
<td>1.24</td>
<td>0.038</td>
<td>4.5</td>
<td>[62],[35],[135]</td>
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<tr>
<td>EMI-Beti</td>
<td>0.34</td>
<td>28.7</td>
<td>1.6</td>
<td>0.061</td>
<td>4.1</td>
<td>[62],[78]</td>
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<td>EMI-Methide</td>
<td>0.13</td>
<td>32.4</td>
<td>1.5</td>
<td>0.195</td>
<td>98</td>
<td></td>
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<tr>
<td>BMI-Beti</td>
<td>0.19</td>
<td>27.6</td>
<td>1.51</td>
<td>0.087</td>
<td>98, [62]</td>
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<tr>
<td>DMPI-Beti</td>
<td>0.252</td>
<td>29.7</td>
<td>1.51</td>
<td></td>
<td>98</td>
<td></td>
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<tr>
<td>EMI-GaCl₄</td>
<td>2.2</td>
<td>48.6</td>
<td>1.53</td>
<td>0.013</td>
<td>4</td>
<td>[62],[130],[132]</td>
</tr>
<tr>
<td>EMI-C(CN)₃</td>
<td>2.2</td>
<td>47.9</td>
<td>1.11</td>
<td>0.018</td>
<td>2.9</td>
<td>131</td>
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<tr>
<td>EMI-N(CN)₂</td>
<td>2.8</td>
<td>49.05</td>
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<td>0.017</td>
<td>3.3</td>
<td>38,[62],[131]</td>
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<tr>
<td>EMI-SCN</td>
<td>1.85</td>
<td>41.9</td>
<td>1.11</td>
<td>0.023</td>
<td>2.2</td>
<td>102,[75],[95]</td>
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<td>EMI-Im</td>
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<td>[62],[78]</td>
</tr>
<tr>
<td>BMI-FeBr₄</td>
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<td>47.8</td>
<td>1.98</td>
<td>0.062</td>
<td>62, [133]</td>
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<td>C₆MI-FeBr₄</td>
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<td>0.095</td>
<td>62, [133]</td>
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</tr>
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<td>C₆MI-FeCl₄</td>
<td>0.47</td>
<td>39.4</td>
<td>1.33</td>
<td>0.077</td>
<td>62, [133]</td>
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<tr>
<td>MPI</td>
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<td>1.59</td>
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<tr>
<td>EMI-F(HF)₂₃</td>
<td>10</td>
<td>48</td>
<td>1.13</td>
<td>0.0049</td>
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<tr>
<td>BMI-I</td>
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<td>1.44</td>
<td>1.11</td>
<td></td>
<td>[30],[51]</td>
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</table>

### 2.2.1 Capillary Emitters

In the capillary configuration, the flow rate is usually controlled by applying a back pressure. The hydraulic impedances associated with this geometry are generally small, and the emitting meniscus sizes are often above the limit predicted by Coffman, so capillaries are prone to emit a mixed droplet-ion plume. Nevertheless, capillary emitters can be used to produce beams of pure ions from ionic liquids, but only under very particular conditions, such as high liquid conductivity, surface tension, and flow rates close to the minimum stable flow rate ($\eta \sim 1$).

Pure ionic emission from an ionic liquid was first obtained from capillary sources in 2003 by Romero-Sanz et al. [100]. The authors used a silica emitter of 20 μm inner diameter that was actively fed with the liquid EMI-BF₄. The authors performed time-of-flight (TOF) spectrometry to determine the species composition of the emitted beam at different flow rates. At the highest flow rates, the beam was a mixture of droplets and ions, but as the flow rate was decreased, the drop contribution to the current decreased. Operation in the PIR was only possible at the lowest flow rate for which the emission was steady, but it was nevertheless attainable from a capillary at room temperature.

Reports of PIR emission from other ionic liquids in capillaries soon followed. Romero-Sanz [99] tested the liquid EMI-Beti with a stainless steel capillary 180 μm inner diameter. The liquid EMI-Beti has a low conductivity at room temperature and had mixed regime emission for all flow rates.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMI-BF₄</td>
<td>1-ethyl-3-methylimidazolium tetrafluoroborate</td>
<td>C₆H₁₁N⁺BF₄⁻</td>
</tr>
<tr>
<td>EMI-Beti</td>
<td>1-ethyl-3-methylimidazolium bis(pentafluorosulfonyl)imide</td>
<td>C₆H₁₁N⁺(C₂F₅SO₂)₂N⁻</td>
</tr>
<tr>
<td>EMI-Methide</td>
<td>1-ethyl-3-methylimidazolium tris(pentafluorosulfonyl)imide</td>
<td>C₆H₁₁N⁺(CF₃SO₂)₃C⁻</td>
</tr>
<tr>
<td>BMI-Beti</td>
<td>1-butyl-3-methylimidazolium bis(pentafluorosulfonyl)imide</td>
<td>C₈H₁₅N⁺(C₂F₅SO₂)₂N⁻</td>
</tr>
<tr>
<td>DMPI-Beti</td>
<td>1,2-dimethyl-3-propylimidazolium bis(pentafluorosulfonyl)imide</td>
<td>C₈H₁₅N⁺(CF₃SO₂)₂N⁻</td>
</tr>
<tr>
<td>EMI-GaCl₄</td>
<td>1-ethyl-3-methylimidazolium tetrachlorogallate</td>
<td>C₆H₁₁N⁺GaCl⁻</td>
</tr>
<tr>
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<td>C₆H₁₁N⁺C(CN)₃⁻</td>
</tr>
<tr>
<td>EMI-N(CN)₂</td>
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<td>C₆H₁₁N⁺N(CN)₂⁻</td>
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<td>C₆H₁₁N⁺SCN⁻</td>
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<td>EMI-Im</td>
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<td>C₆H₁₁N⁺(CF₃SO₂)₂N⁻</td>
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<tr>
<td>BMI-FeBr₄</td>
<td>1-butyl-3-methylimidazolium tetrabromidoferate</td>
<td>C₉H₁₉N⁺FeBr₄⁻</td>
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<td>C₁₀H₂₀N⁺FeBr₄⁻</td>
</tr>
<tr>
<td>BMI-MI-FeCl₄</td>
<td>1-hexyl-3-methylimidazolium tetrachloroferate</td>
<td>C₁₀H₂₀N⁺FeCl₄⁻</td>
</tr>
<tr>
<td>MPI</td>
<td>1-pentyl-3-methylimidazolium tris(pentafluorosulfonyl)trifluorophosphate</td>
<td>C₉H₁₇N⁺(C₂F₅)₃PF₃⁻</td>
</tr>
<tr>
<td>EMI-F(HF)₂,₃</td>
<td>1-ethyl-3-methylimidazolium fluorohydrogenate</td>
<td>C₆H₁₁N⁺F(HF)₂,₃</td>
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<td>BMI-I</td>
<td>1-buthyl-3-methylimidazolium iodide</td>
<td>C₈H₁₁N⁺I⁻</td>
</tr>
</tbody>
</table>

tested at this temperature, but, as the capillary is heated, the conductivity is increased and the emission starts to be dominated by ions, eventually reaching the PIR at low flow rates. As the temperature is increased further, the PIR can be achieved at higher flow rates. Additional tests by Romero-Sanz [98] show a similar trend for a handful of ionic liquids (EMI-Im emits pure ions at 82 °C, EMI-Methide at 216 °C, BMI-Beti at 204 °C, and DMPI-Beti at 212 °C). Conductivity is a strong function of temperature, and it seems that as the liquid conductivity is increased through the temperature, the more readily the PIR is reached.

Garoz et al. [38] studied the emission of over a dozen ionic liquids from capillary emitters, and found that the PIR requires not only high liquid conductivity but also high surface tension. In these tests, it was determined that the liquids EMI-GaCl₄, EMI-C(CN)₃ and EMI-N(CN)₂ sustain pure ionic emission at room temperature; these ionic liquids have both excellent conductivity and surface tension. However, liquids with even higher conductivities but poorer surface tensions operate in the mixed regime. For instance, EMI-Im does not emit a pure ion beam at temperatures at which its conductivity is significantly larger than the room-temperature value for EMI-BF₄, and this is attributed to its inferior surface tension. The ionic mode could not be obtained with EMI-BF₄ in Garoz’s study, but this might have been due to the lower hydraulic impedance of the 40 μm capillary used in these experiments, compared to the one used in [100]. The larger capillary may
not have allowed the necessary reduction of the flow rate for PIR.

The group led by Shea at Ecole Polytechnique Federale de Lausanne (EPFL) has worked on capillary emitter arrays for space propulsion and obtained PIR under certain conditions. On 2009, this group developed 24 μm diameter silicon capillary emitters filled with 5 μm diameter silica microspheres, with the intention of increasing the hydraulic impedance of the emitters. The PIR was achieved in these capillaries with EMI-BF$_4$ [60]. However, this capillary configuration was abandoned due to reproducibility considerations [103], and thus the EPFL group has been testing silicon capillaries of smaller diameters in order to increase the emitter hydraulic impedance. Recent tests on a silicon 8 μm diameter capillary show PIR operation from the liquid EMI-SCN [102], but these results could not be extended to capillary arrays operating with the same liquid, nor is the PIR achieved with EMI-BF$_4$.

Capillary emitters can be used to produce a single emission site operating in the pure ionic regime, but this can only be achieved at room temperature from ionic liquids of high conductivity and high surface tension. This configuration has some additional drawbacks: the flow rate must be actively controlled to achieve small flow rates and obtain the PIR, and these devices are prone to failure due to bubble formation and clogging.

2.2.2 Externally Wetted Emitters

Externally wetted emitters were introduced in 2004 by Lozano and Martinez-Sanchez [69]. This emitter configuration was inspired by the LMIS source geometry, were the molten metal covers a roughened tungsten tip. The emitter of Lozano and Martinez-Sanchez consists of an electrochemically sharpened tungsten needle, which was denominated ILIS. The emitter has been treated to roughen the surface and create grooves that allow transport of the liquid from the emitter shank towards the tip apex, see for instance Figure 2-7. This configuration does not require active feeding as a capillary; instead, the flow is controlled by the hydraulic impedance of the emitter and the conductivity of the ionic liquid.

This externally wetted tungsten configuration has been tested with a number of ionic liquids, with PIR operation first verified with the liquid EMI-BF$_4$ [69]. In contrast to capillary emitters, the PIR is readily achieved with ILIS for all liquids tested at room temperature, regardless of the liquid conductivity. For instance, EMI-Im, which emits a mixture of ions and droplets from capillary emitters at room temperature [37, 98], emits only ions when sprayed from ILIS [66]. Castro [17] verified that the liquids C$_6$MI-FeBr$_4$, C$_6$MI-FeCl$_4$, BMI-FeBr$_4$, C$_6$MI-FeCl$_4$, all of relatively poor
conductivity, achieve the PIR with ILIS. The liquids EMI-GaCl$_4$, EMI-C(CN)$_3$ and EMI-N(CN)$_2$, which emit ion plumes from capillaries, also emit ions from ILIS. Larriba [61] tested the liquids MPI and EMI-Beti, and concluded it is possible to produce beams containing kilodalton ions from these liquids, with no intervening droplets. ILIS have also been tested for operation in the PIR with liquids containing highly reactive ion species, such as EMI-F(HF)$_2$$_3$ [112] and BMI-I [30].

The current emitted by ILIS depends on several factors. The current emitted by externally wetted tungsten sources increases with the liquid conductivity. At room temperature, the current varies from a few nA (for instance with MPI) to a few hundred nA with the most conductive liquids tested. Castro [16] determined that increasing the radius of curvature of the emitter increases the current obtained from the ion source, through reductions to the emitter hydraulic impedance. Castro verified that emitters with radius of curvature between 2.5 and 60 μm could operate in the PIR with the liquid EMI-C(CN)$_3$.

Several emitter materials besides tungsten have been used in the externally wetted configuration. For instance, Courtney [22] demonstrated pure ionic emission with the liquid EMI-Im on an electrochemically etched nickel emitter (see Fig. 2-8). Emitter arrays have also been fabricated by patterning silicon substrates using reactive ion etching through photo definable masks [122, 39, 49]. Silicon is not well-wetted by ionic liquids, and so the emitter surfaces must be treated to achieve wicking of the liquid along the tip surface. Velasquez-Garcia [122] and Gassend [39] used different types of plasma etching to obtain a black silicon surface on the emitter arrays. The ionic liquid can then flow along the emitter surface by capillarity in the black silicon. (see Figure 2-9). Gassend
verified that such emitters can operate in the PIR using the liquids EMI-BF$_4$ and EMI-Im. Nevertheless, the emission from these arrays is not constant over time, as the emitters eject drops when operation is started due to over-wetting and then suffer depletion as the liquid reservoir (on the base of the array) is consumed. Furthermore, the sharp black silicon features are prone to unwanted electron emission. More recent work by Hill [49] has used carbon nanotube (CNT) forests grown by chemical vapor deposition on the silicon surface instead of black silicon (Fig. 2-9). According to the authors, emission in the PIR using the liquid EMI-BF$_4$ was achieved; however, these emitters are also prone to unstable emission due to excess liquid as the emitter is started. What is more, examination of collector plates in front of the silicon arrays shows that some CNTs are pulled from the surface of the emitter electrode by the electric field.

Despite the excellent emission properties of externally wetted sources, their operation is subject to electrochemical degradation (this is also the case for capillary sources, but most mitigation work has been pursued with the externally wetted configuration). As ions are extracted from the liquid
in one emission polarity, counter ions migrate to the surface of the emitter and a double layer of charge starts to build up. If the potential across the double layer exceeds the electrochemical window of the ionic liquid, detrimental reactions occur between the emitter and the liquid, which provoke emission degradation and eventually emitter failure. The first strategy proposed to avoid these reactions was to periodically alternate the emission polarity [67]. Switching the emission polarity depletes the charge of the double layer, while forming another one with opposite charge. Theoretical estimates indicated that the saturation time of the double layer should be of the order of a few seconds, and so a low frequency polarity reversal should be sufficient to avoid electrochemical reactions. This strategy was validated by firing a ILIS wetted with EMI-BF$_4$ while alternating the polarity at 1 Hz for 220 hours, with no signs of emission degradation. Castro [16] tested the alternation approach with other ionic liquids and found that the alternation strategy may not be sufficient to prevent electrochemical degradation from other ionic liquids. The liquids EMI-C(CN)$_3$ or EMI-Im or EMI-GaCl$_4$ emit asymmetrical amounts of currents in each polarity, and even if the polarity is reversed periodically, the double layer charge does eventually build up. Alternation with asymmetric periods in each polarity was proposed to allow stable operation.

In 2012, it was shown that distal electrode contacts could be used to operate externally wetted ILIS for prolonged periods without need for alternating the polarity [11]. In the distal contact approach, the voltage is applied to the liquid through an upstream contact while the emitter is left floating electrically, as show in Figure 2-10. In this case, the double layer responsible for electrochemistry will still form and reactions will occur, but these reactions will occur at the distal electrode, without directly affecting the emission site. Dielectric emitter substrates are preferred as no ohmic voltage drop would occur along the surface of the emitter, but if using conductive substrates, electrochemistry should be prevented as long as the ohmic drop along the tip does not exceed the electrochemical window of the ionic liquid [11].

To validate this approach, two externally wetted emitters, both wetted with EMI-BF$_4$, one having a direct contact and the other having a distal contact, were fired side-by-side during 76 hours. The direct contact tip was etched and roughened during this test, while the distal contact emitter showed no signs of degradation. The images of the emitters pre and post test are shown in Figure 2-11.

Despite the ease of access to the pure ion regime, externally wetted ILIS have stability issues during long-lifetime single polarity operation, even when electrochemistry is mitigated with distal contacts. Externally wetted tungsten oxide emitters, similar to W emitters, were implemented
with distal electrodes and fired towards a Faraday cup for several hundred hours while monitoring the collected current \[89\]. Although the source fired stably for periods of several minutes, the long-term stability was poor, possibly due to an interrupted liquid supply to the emitter caused by the non-perfect wetting of the roughened surface. What is more, externally wetted sources are prone to off-axis emission as well as to operation with multiple emission sites\[89, 91\], due to the fact that the emission is likely originated from a pool of liquid on the side of the emitter rather than from the emitter apex. It is possible to get a tungsten tip that fires on-axis and has a stable liquid supply for many hours, but this is a lottery. As part of the experimental work of this thesis, several externally wetted tungsten emitters were tested with views of implementing them in a FIB column, but their operation was inadequate. Details of these tests are included in Appendix A.

It might be possible to avoid the liquid supply and directivity issues by using an emitter with moderate roughening that allows adequate wetting of the tip surface by a continuous liquid film. Nevertheless, none of the externally wetted configurations tested so far seem to achieve adequate wetting required for stable, on-axis, long-term operation.
2.2.3 Porous Emitters

Porous emitters have been proposed to increase the current emitted from ionic liquid ion sources for high-throughput applications such as space propulsion. This type of emitter has a superior fluid transport to the emission site compared to externally wetted sources thanks to the internal fluid routes. Porous tips have a higher hydraulic impedance compared to capillary sources and rely on passive feeding, and so they can achieve the PIR more readily in comparison. Many of the research efforts on porous ionic liquid ion sources have focused on the fabrication of emitter arrays for thruster applications. The first research efforts aimed at the fabrication of porous metal emitters, which suffered of severe lifetime issues, including electrochemistry and gas discharges. We review the efforts towards preventing porous emitter failure, and then proceed to review the recent work on dielectric porous materials being used for emitter substrates.

Legge [63] fabricated and tested emitters based on porous tungsten substrates, motivated by the success with externally wetted tungsten emitters. Porous tungsten is commercially available and planar emitters were fabricated by electrochemical etching of the substrate through a polyimide mask. An SEM image of a sample emitter is shown in Figure 2-12. This substrate has an average pore size of 500 nm and 80% porosity, and the emitter has an end tip radius of curvature of approximately 5 μm. TOF measurements were performed on the beam of these source using four different ionic liquids: EMI-BF₄, EMI-Im, EMI-Beti and MPI. All the liquids, regardless of their conductivity, can achieve the PIR in the porous metal emitters. Reducing the ionic liquid conductivity results in reductions in the emitted current, in the same way as with externally wetted emitters. However, the current emitted by the porous tip is about an order of magnitude greater than that obtained from externally wetted porous emitters. The authors attribute the increase in current to the higher transport rates supported by porous emitters, although this could also be due to other factors, as discussed next.

Research on porous tungsten emitters was followed with investigations on porous nickel. The electrochemical fabrication of tungsten into emitter arrays was difficult, since the photoresists compatible with the tungsten etching are limited and have poor resolution. There are more etching chemistries and photoresist options for nickel. Courtney developed planar arrays of 480 porous nickel emitter tips using electrochemical fabrication techniques [23] (an example tip is shown in Fig. 2-13). These tips had an average tip radius of 15 μm, with an approximate porosity of 45% and pore radius of 2.5 μm.
As in the work from Legge, higher currents per porous nickel emitter are obtained than with externally wetted ion sources[24]. Courtney mentions that the higher currents from porous metal ILIS could be caused not only by the reduced hydraulic impedance but also be due to the presence of multiple emission sites on each emitter structure [22, 25, 24]. This hypothesis follows from indirect observations of the emission pattern on targets placed in front of the emitter arrays showing several impacts corresponding to each emitter. These measurements were taken with non-ideal nickel emitters, and there has been no direct observation of the multiple emission sites from the porous metal tips, but this scenario is not unlikely considering the wetting characteristics of the ionic liquids on metals. From the SEM images, it can be seen that the liquid is present in the metal pores but that it does not wet the tip entirely, and so it is more likely that multiple emission sites appear instead of a single Taylor cone.

Pure ionic emission has not been verified using the porous nickel emitters. These emitter arrays suffered strong current decays and eventual failure within a few minutes, with evidence of dark solid deposits on the emitter arrays after firing; examples of these deposits are shown in Figure 2-14.
It was initially hypothesized that the porous emitter solid deposits and decay were a result of electrochemical reactions [25, 24]. As externally wetted conductive emitters, porous metal tips are prone to electrochemical decay, but using polarity alternation frequencies of the order of 1 Hz was not sufficient to allow prolonged operation. The models proposed by Lozano in Ref. [67] are not applicable to porous substrates, as they fail to take into account the diffusion of the double layer into the porous bulk. The electrochemistry models for porous tips were revised in reference [11] and it was found that alternation frequencies of the order of 1 kHz would be necessary to avoid electrochemical decay for the currents and geometries involved in porous substrates. However, these timescales are comparable to the scale of formation of the emission site [70] and it is not clear if these alternation frequencies would be compatible with the emission process. Therefore, for long-term operation of porous substrates, distal electrode contacts must be used to avoid electrochemical decay.

Porous emitters were then tested with distal contacts, but the solid deposits on the arrays still formed during operation. Brikner found that the appearance of black deposits and emitter failure were a consequence of electrical discharges between the emitter and the extractor [13, 12]. It was hypothesized that the discharges were produced as trapped gas in the pores of the emitter or residual water in the ionic liquid are released during operation. To test if this was the case, two porous nickel emitters were fired with EMI-BF$_4$, one filled under atmospheric conditions, and the other filled in vacuum with degassed and dried ionic liquid. The operation of the emitters was monitored using a microscope. As expected, the emitter filled in atmosphere showed discharges, during which the ionic liquid was presumably heated to temperatures at which carbonization occurs (see Fig. 2-15(a) and (b)). The emitter filled in vacuum did not present discharges during operation.
and no solid deposits were formed (see Fig. 2-15(c)). Further investigations showed that filling in vacuum does not preclude discharges, and that adequate liquid containment within the pores of the emitter is required for discharge-free operation [12].

The introduction of the distal electrode enabled research into non-metallic porous emitter substrates. The electrochemical fabrication of porous metallic emitter arrays is difficult due to non-uniformity issues [25], and there is a larger variety of dielectric materials that could be used in electrospray applications. Dielectric materials explored as ILIS substrates to date include porous borosilicate glass, soda-lime microspheres, and alumina xerogel. Coffman [19] fabricated micro tips on glass substrates with pores of 2-5 μm with 40% porosity using laser ablation, and obtained emission using EMI-BF₄. A sample borosilicate emitter is shown in Figure 2-16. It seems that these porous borosilicate emitters operate in a mixed drop-ion regime [58], but there are no published reports to date with precise measurements of the beam composition. Xie [127] fabricated porous soda-lime substrates by the sintering of glass microspheres and fabricated a coarse emitter with this substrate. Emission was obtained with EMI-BF₄ with currents of approximately 1 μA. Arestie [2] synthesized porous alumina and as Xie, tested a coarse emitter tip from this material, obtaining currents of up to several μA with EMI-BF₄. It is not known if the soda-lime or xerogel emitters are producing one or several emission sites, and pure ionic regime operation has not been confirmed to date from any of these materials.

The porous ILIS emitters studied to date are not suitable for FIB implementation. The technologies verified to operate in the PIR may produce multiple emission sites. It might be feasible to obtain a single emission site from a porous emitter operating in the ionic regime if the wetting
of the substrate and the hydraulic impedance are controlled. Special precautions with the liquid filling procedure must be taken to ensure the stable operation of these emitters without electrical discharges.

2.2.4 Optical Properties of ILIS and Previous Focusing Efforts

As we have mentioned in the previous section, state-of-the-art ILIS pose some challenges in the operational requirements for FIB, and this thesis aims to create new configurations that could overcome these operational limitations. But assuming a pure ion beam could be reliably produced on-axis, how well could an ILIS be focused? As mentioned in Chapter 1, the two figures of merit for an ion source are its brightness and its energy spread. Here, we discuss the optical properties of the ILIS and some of the focusing efforts performed to date.

The brightness of ILIS has been estimated to be comparable to the brightness of LMIS, of the order of $10^6 \text{ Acm}^{-2}\text{sr}^{-1}$. We have calculated the value of the brightness for an EMI-BF$_4$ ILIS to be $6 \cdot 10^5 \text{ Acm}^{-2}\text{sr}^{-1}$ [89]. This value is found by using equation 1.5, assuming an emission current of 600 nA, a half-angle of 18° [69], and a source size of 20 nm diameter. Space-charge effects are assumed to be small for the current values of ILIS, and so the virtual source size is assumed equal to the emission site area. The emission site radius, $r_m$, is estimated from a pressure balance on the surface of the ion emitting meniscus. The electric field outside the liquid is $E^*$, the value required to obtain ion evaporation. By Gauss’ Law, the electric field inside the liquid, $E_{in}$, must satisfy $\epsilon_0 E^* - \epsilon_0 E_{in} = \sigma$, where $\sigma$ is the surface charge density. We may assume that $\sigma$ is small due to the charge removal from the surface, and that this results in the liquid behaving roughly like a dielectric, with $E_{in} \approx E^*/\epsilon$. Now, the approximate pressure balance on the meniscus gives
\[ \frac{1}{2} \epsilon_0 E^* \epsilon - \frac{1}{2} \epsilon_0 \left( \frac{E^*}{\epsilon} \right)^2 \right) = \frac{2\gamma}{r_m} \]  

which results in

\[ r_m = \frac{4\gamma}{\epsilon_0 E^* \epsilon - 1} \]  

For the surface tension of EMI-BF$_4$, a value of $E^* = 1.56$ V/nm, and a dielectric constant of 12.9 [124], $r_m$ is approximately 10 nm. We note that it may be possible to increase the value of the brightness by choosing liquids of higher conductivity or by heating up the ion source, so as to increase the amount of current emitted by the meniscus. It may also be possible to change the liquid's surface tension to reduce the emission site area.

The other important metric for FIB implementation is the energy spread of the ion source. The ion beams from ILIS contain a number of particle species with different energy distributions. An ionic liquid with anion A$^-$ and cation C$^+$ will produce ion species $(AC)_n A^-$ or $(AC)_n C^+$, in the negative and the positive mode, respectively, and where $n$, the degree of solvation, is the number of neutral clusters attached to the ion. The relative proportion of monomers ($n = 0$), dimers ($n = 1$), trimers ($n = 3$) and larger clusters depends on the ionic liquid, but it is observed in general that the beam is mostly composed of monomers and dimers. Lozano measured the energy profiles of several ionic liquids using a retarding potential analysis. For the liquids EMI-Im and EMI-BF$_4$, a portion of the beam has a energy spread of 6-8 eV, with energy deficits of 6-7 eV [66, 68]. This monochromatic ion population is suitable for focusing.

The beams from ILIS, however, also contain ion populations with a broad energy distribution as well as neutral particles. Some of the heavier ions might break up in flight, resulting in a neutral particle and a lighter ion with a fraction of its original kinetic energy. From retarding potential analysis, it is known that breakup can happen in regions of zero potential as well as in the acceleration zone between the emitter and the extractor [66, 30]. Ideally, all ions should have a final kinetic energy $K = qV_{app}$, where $V_{app}$ is the applied potential and $q$ the ion charge (usually the elementary charge). However, if an ion with degree of solvation $n$ and mass $m_n$ breaks into a neutral and ion with degree of solvation $m$ ($m < n$) and mass $m_m$, at a region with potential $V_0$ (say, in between the emitter and the extractor, where the potential varies from $V_{app}$ to ground), then the final kinetic energy of the ion resulting from breakup will be
\[ K_m = qV_b + \frac{m_m}{m_n} q | V_{app} - V_b |. \] (2.31)

If ions break up in the acceleration zone, their energies can range over a few hundred volts, between \( m_m qV_{app}/m_n \) (if break-up occurs after the heavy ion is fully accelerated) and up to \( qV_{app} \) (if fragmentation occurs immediately after emission, \( V_b = V_{app} \)). The ions resulting from break-up will lead to chromatic aberrations in the beam. In order to focus ILIS optimally, it would be necessary to select exclusively the monoenergetic population of ions in the beam, eliminating neutrals and ion fragments. FIB performance could be further improved by selecting one ionic species within the ion beam. It is likely that different degrees of solvation could have different energy distributions, since the barrier for ion evaporation may differ for the different ion species [136]. Then, the energy spread could potentially be reduced from the 6-8 eV measured so far, by selecting exclusively monoenergetic monomers in the beam for focusing. This may be achieved by using a Wien filter in the path of the beam. The filter is a velocity selector, in which orthogonal electric and magnetic fields are applied normal to the axis of the beam. The magnetic force is \( qvB \), and the electric force is \( qE \); in order for the particles to exit the filter, the two forces must be equal, which means that only particles with \( v = E/B \) will exit the filter. Using this instrument, it might be possible to choose only the monoenergetic monomers, the fastest particles in the beam.

Another scheme for improving the optical quality from ILIS is to choose an ionic liquid that displays less fragmentation. Molecular dynamics simulations have shown that "solvated ions from relatively complex ionic liquids (i.e. those with a large number of atoms per ion) are less likely to fragment than simpler ones, as there are more degrees of freedom in which to dissipate energy without fragmenting" [21]. This hypothesis is supported by experimental observations, which indicate that ionic liquids with small anions, such as BMI-I and EMI-BF4, have a larger current of fragmented ions than ionic liquids with complex anions such as EMI-Im [30, 66, 81].

Sub-100 nm focusing is yet to be demonstrated with ILIS. Zorzos [136] used a single Einzel lens to focus the beam from EMI-BF4, and a minimum probe size of 30 \( \mu m \) was achieved. In this experiment, an aperture was used to limit the current entering into the lens (0.7 nA), but no special filtering schemes were used to select the monochromatic section in the beam. It is likely that chromatic aberration might have hindered the focusing of the beam into smaller sizes, however, as the lens constants were unknown, it is not possible to evaluate the performance of the beam in this set of optics. Yoshida et. al performed a simple focusing test with an array of externally wetted...
silicon ILIS [129]. The array included an extractor plate as well as a lens plate, and the beam was fired onto a target a few hundred \( \mu \text{m} \) away from the source. The authors found that they could change the beam angle from \( 11^\circ \) to \( 7.9^\circ \) by changing the lens voltage from 0 to 5 kV; however, the beam spot was in the order of about 200 \( \mu \text{m} \) for these experiments. There is room for future research in the ultimate focusing capabilities of ILIS.

2.2.5 Available technology is not suitable for FIB

From our survey, none of the emitters produced to date could be implemented reliably in a FIB system. Capillaries have a well define single emission site, but only under very few conditions do they allow the PIR. Externally wetted tips do not guarantee on-axis emission due to poor wetting and the liquid supply fails in prolonged operation, and none of the porous tips developed to date have shown PIR operation from a single emission site. Therefore, in this thesis, we will design a new ion source that favors the consistent formation of a single emission site on axis with operation in the PIR, and characterize the emission of this source to determine if it is suitable for focusing.

2.3 Thesis Approach

In order to produce a source suitable for focusing, the following actions have been taken in this thesis:

1. Estimation of emitter hydraulic characteristics required to achieve pure ionic regime. This estimation should provide target emitter radius, half-angles, and substrate transport properties that guide the selection of emitter substrates and potential manufacturing techniques.

2. Selection of substrate candidates with adequate wetting properties by the ionic liquid, as well as possible geometries for an emitter that favors the formation of a Taylor cone on axis.

3. Selection of a fabrication scheme to construct the emitters specified by the design, and production of several test emitters.

4. Characterization the emission from new emitters, including: current voltage responses, time-of-flight spectrometry, and energy profile measures, which should reveal the composition of the beam as well as its energy spread.

5. Characterization the irradiation of the new ion source on targets, to assess the directionality of the beam as well as the potential surface modification capabilities of the ion source.
Chapter 3

Design and Fabrication of a Prototype Emitter

In this chapter, we describe the design and fabrication process of a prototype emitter. We first list some guiding requirements for the design of the emitter, and proceed to choose an emitter type (porous) and target emitter geometries. The work on different porous substrates and fabrication techniques is described.

3.1 Summary of Emitter Requirements

As mentioned in chapters 1 and 2, a novel ILIS must satisfy several constraints to be adequately focused. The ILIS should operate with a single emission site on-axis, in the purely ionic regime. The current of the emitter should not have more than 5% current fluctuations without voltage regulation, and sustain emission for several hundred hours without electrochemical decay or failures in the liquid supply. Furthermore, the source should not produce electrons in the negative polarity. In order to achieve all these goals, we can list some design requirements on the novel ILIS emitter:

- The emitter should operate in the pure ionic regime with no intervening droplets. In order to favor pure ion regime operation, the emitter hydraulic impedance $Z$ should be higher than $1.5 \cdot 10^{17}$ kg s$^{-1}$m$^{-4}$. The reasoning for this requirement is discussed in section 3.2.
- The emitter shall provide an uninterrupted path for liquid flow from the electrical contact/reservoir to the emission site. If the emitter is externally wetted, the liquid should form a continuous film along the emitter surface, and if the emitter is porous, the porosity
should be uniform or have a minimum at the tip apex.

- To minimize electrochemical decay, the emitter's electrical connection should be a distal contact, with the voltage applied to the liquid while the emitter is electrically floating.
- To avoid electron emission, the emitter substrate should be dielectric; if the emitter is based on a conductive substrate, the emitter should not have any surface features or protrusions with radius of curvature less than 100 nm [25].

### 3.2 Emitter Impedance

For FIB implementation, it is of utmost importance that the emitter produces ions with no intervening droplets. As discussed in chapter 2, operation in the PIR depends on the type of emitter and ionic liquids used. Emitters with higher hydraulic impedance favor the PIR with a larger variety of ionic liquids. The question is, what is the threshold emitter impedance for which the PIR is guaranteed for a given ionic liquid?

We survey several cases from the literature to identify emitter impedances that allow operation in the PIR for passively fed emitters. The survey will be limited to the cases where pure ion emission has been obtained from EMI-BF₄ at room temperature, as this is the liquid that has been tested in the most configurations and for which there is more spectrometry data available. Based on the reported data, a value $Z_{\text{min}} = 1.5 \cdot 10^{17} \text{ kg m}^{-4} \text{s}^{-1}$ is chosen as a baseline minimum for the hydraulic resistance of the emitters designed in this thesis. This bound is not claimed to be the value for which ionic liquid electrospays will transition from the mixed regime to pure ion operation; rather, it is a rough guideline for design.

Externally wetted tungsten emitters operate in the pure ionic regime for virtually every ionic liquid tested, and for tips with different radii of curvature [16]. The impedance of this geometry can be estimated using the formula derived by Mair [72]:

$$Z = \frac{32\mu L_s}{\pi^2 R_s r_g^3} + \frac{64\mu \sqrt{l_{\text{tip}}}}{\sqrt{2} R_c \pi^2 r_g^3}$$

(3.1)

where the emitter consists of a shank of length $L_s$ and radius $R_s$, followed by a parabolic tip of length $l_{\text{tip}}$ and end radius of curvature $R_c$. In this expression, it is assumed that the shank is covered by semicylindrical grooves of radius $r_g$ which are separated by a distance $2r_g$, which are perfectly filled by the liquid. The number of grooves decreases as we approach the emitter apex, where the surface is assumed to be smooth.
From SEM micrographs, we can estimate $L_0 \approx 2$ mm, $R_s \approx 250$ μm and $l_{\text{tip}} \approx 1$ mm. $R_e$ typically ranges between 5 and 60 μm, and $r_s \approx 2$ μm for a microroughened tungsten tip. From these values, the tip impedance is estimated to be of the order of $10^{17}$ kgm$^{-4}$s$^{-1}$. We note that this value is a low estimate of the actual hydraulic resistance of these externally wetted tips. As mentioned in chapter 2, the grooves are not perfectly wetted by the ionic liquid and only a fraction of the emitter surface is covered by the liquid, so the actual impedance might be higher.

Some additional insight can be gained from considering the conditions for pure ion emission in capillary sources, even if they are actively fed and the ionic regime can only be obtained by reducing the back pressure. Romero [100] achieved the pure ionic regime from EMI-BF$_4$, from using a capillary of 10 μm radius. The impedance of Romero’s emitter is estimated to be of the order of $3\cdot10^{18}$ kgm$^{-4}$s$^{-1}$, as calculated from the flow rates and applied pressures reported by the authors. This impedance value therefore should be high enough to sustain pure ionic emission in a passively fed emitter. Krpoun [60] obtained pure ionic emission from EMI-BF$_4$ at room temperature from silicon capillaries filled with silica microbeads. The impedance of these emitters is calculated to be approximately $1.5\cdot10^{17}$ kgm$^{-4}$s$^{-1}$ [103]. The capillaries were actively fed and in the case of EMI-Im they do not seem to emit a pure ion beam [60]; however, the fact that they sustain pure ion emission from EMI-BF$_4$ even when a back pressure is applied hints that $Z = 1.5\cdot10^{17}$ kgm$^{-4}$s$^{-1}$ should be high enough to promote the PIR in passively fed emitters.

From these observations, the design will have a hydraulic impedance higher than the one of the Krpoun emitters to promote pure ion regime operation. If possible, the emitter should be designed to have more flow resistance, of the order of $10^{18}$ kgm$^{-4}$s$^{-1}$, which is closer to the actual value from externally wetted emitters and should enable PIR from liquids with lower conductivities and/or surface tensions than EMI-BF$_4$.

### 3.3 Emitter Design

#### 3.3.1 Emitter Type

For this work we have focused on the development of porous emitters over capillary or externally-wetted emitters.

Capillary emitters have several issues that make them undesirable for the intended application. While capillary emitters should operate with a single Taylor cone well anchored to the capillary tip, this type of emitter does not favor PIR operation. Furthermore, they suffer from clogging, bubbles,
and have increased complexity due to the need to actively control the flow to the emitter.

Externally-wetted emitters have high hydraulic impedances thanks to the limited area for liquid transport, and thus operate in the PIR for almost every liquid tested. For FIB implementation, this type of emitter should be covered by a continuous liquid film in order to achieve the uninterrupted liquid supply to the emitter apex and axial emission. Wetting of a sharpened emitter tip requires the surface to be roughened, as for a perfectly smooth tip, the surface tension of the liquid will prevent it from reaching the apex. It may be possible to produce an externally wetted emitter with a surface roughness such that the tip is uniformly covered by a continuous liquid film, but we have focused this research on porous emitters.

A porous emitter shall enable a continuous flow of liquid from the reservoir to the apex, as there are a number of internal fluid routes over which the liquid can be transported. Furthermore, as will be mentioned in section 3.4, porous substrates have some flexibility in the pore sizes that can be achieved, and thus the pore size can be reduced in order to achieve a higher emitter hydraulic impedance as well as a smoother emitter apex. Porous emitter development should also be beneficial for propulsion applications, in which passive supply of the propellant from the emitter tank to the apex is desired.

### 3.3.2 Geometry selection

In this section, target emitter radius of curvature $R_c$, tip profiles and substrate permeabilities ($\kappa$, m$^2$), are chosen to satisfy the minimum impedance requirement. A porous emitter can be shaped in a variety of geometries, including parabolically shaped tips (with the same profile as the externally wetted tungsten tips), or be conically shaped, with a rounded tip. As the impedance calculation is the most straightforward for conical tips, we will focus this section on the design of a conical emitter. The treatment for other profiles is similar and shall lead to similar requirements on $R_c$ and $\kappa$.

The impedance $Z_{cone}$ of a conical emitter is as a function of its half-angle $\alpha$, height $h$, tip radius of curvature $R_c$ and permeability $\kappa$ (see Fig. 3-1), and can be calculated by making use of Darcy's Law [27]:

$$\bar{q} = -\frac{\kappa}{\mu} \nabla P$$

Here, $\bar{q}$ is the volumetric flow rate per unit surface area (m/s), $\nabla P$ is the pressure gradient,
and \( \mu \) is the viscosity of the ionic liquid. The impedance of the emitter satisfies \( \Delta P = Z_{cone} Q \), so we can find \( Z_{cone} \) by integrating equation 3.2 from the base of the emitter to the apex. We note that

\[
q = \frac{Q}{2\pi r^2(1 - \cos \alpha)}
\]  

(3.3)

Thus, the integration is

\[
\Delta P = \frac{\mu}{\kappa} \int_{r_0}^{r_1} \frac{Q}{2\pi r^2(1 - \cos \alpha)} \, dr = \frac{\mu}{2\pi \kappa} \frac{Q}{1 - \cos \alpha} \left( \frac{\tan \alpha}{R_c} - \frac{\cos \alpha}{h} \right)
\]

(3.4)

And the impedance of the conical emitter is

\[
Z_{cone} = \frac{\mu}{2\pi \kappa} \frac{1}{1 - \cos \alpha} \left( \frac{\tan \alpha}{R_c} - \frac{\cos \alpha}{h} \right)
\]

(3.5)

Knowing the dependance of the impedance on the emitter geometrical parameters, we can estimate the required \( R_c, \alpha, h \) and \( \kappa \) to give \( Z_{cone} \geq Z_{min} = 1.5 \cdot 10^{17} \text{ kgm}^{-4}\text{s}^{-1} \).

In equation 3.5, we note that if \( h/R_c \) is about 10 or higher, the second term contributes little to the total impedance, and the sensitivity of \( Z_{cone} \) to variations in \( h \) is not strong. Typical \( R_c \) used in ILIS are of the order of 10 \( \mu \)m in order to have moderate startup voltages of 1-2 kV, and it is advisable to maintain \( h/R_c \) above 10 in order to have enough amplification of the electric field at the apex with respect to the downstream liquid reservoir [25]. Thus, in our first design iteration, we set \( h = 1 \) mm and proceed to compute \( Z_{cone} \) for different \( \alpha, \kappa \) and \( R_c \).

Figure 3-2 plots the normalized impedance \( Z_{cone}/Z_{min} \) for half-angles of 10° or 20° and for emitter radii of 1, 5, 10 and 15 \( \mu \)m as a function of substrate permeabilities below \( 10^{-13} \text{ m}^2 \). The

Figure 3-1: Conical Emitter Geometry
Figure 3-2: Impedance calculation for conical emitters of different half-angles and $R_c$. The height of the emitter is set to $h = 1$ mm for this computation.

The minimum impedance is indicated by the horizontal dashed line. It is clear that $Z_{cone}$ is the most sensitive to changes in $R_c$ and $\kappa$. Tip radius below 5 $\mu$m bring the impedance above the desired value easily. It can also be appreciated that permeabilities above $10^{-13}$ m$^2$ do not meet the goal for tip radii above 10 $\mu$m. Therefore, the emitters fabricated in this research should have a target tip radius of curvature of 5 $\mu$m as well as permeabilities below $10^{-13}$ m$^2$.

Lastly, the requirements on permeability can be translated into requirements of the substrate pore size $r_p$ and porosity $\phi_p$ (defined to be as the fraction of void volume). As explained by Courtney [25], the permeability of a porous sample can be calculated using the Kozeny-Carman formula [15]:

$$\kappa = \frac{D_{eff}^2}{180} \frac{\phi_p^3}{(1 - \phi_p)^2}$$

where $D_{eff} = 1.74 r_p \phi_p^{3/2}$ is the effective particle size as derived by Glover for a substrate consisting of spherical particles [43]. This relation gives $\kappa = r_p^2(60(1 - \phi_p)^2)^{-1}$. Figure 3-3 plots the maximum pore size as a function of porosity for which the permeability of the substrate is below $10^{-13}$ m$^2$. We can see that pore radii of the order of 1 $\mu$m or less are required to achieve the target substrate permeability.
Summarizing, the emitter should have a target radius of curvature of 5 μm, a cone half-angle of 10° and pore radii of approximately 0.5 μm. There is of course some flexibility in these parameters, but these numbers should guide the selection of porous materials.

### 3.4 Material selection and emitter fabrication

Driven by the requirement of sub-micrometer sized pores and suitable wetting by the ionic liquid, the development efforts have focused on two possible emitter materials: alumina and carbon xerogels.

There is little work on the contact angles of ionic liquids on different substrates. Furthermore, the information is not all consistent as special cares must be taken to appropriately dry the ionic liquids and clean the surfaces before measurements. From the limited data, it is found that ionic liquids tend to have small contact angles on polar surfaces such as silica or soda lime glass substrates and graphite, and wet poorly substrates such as metals, teflon or polyethylene [97, 14, 105, 113]. Therefore, it is expected that substrates such as alumina, glass and carbon will have adequate wetting by the ionic liquid. Porous alumina and carbon may be obtained through the sol-gel processes.

Porous substrates of many different compositions can be produced by chemical sol-gel synthesis, which involves several steps depicted in Fig. 3-4. The first step is the preparation of a nano particle suspension (the sol), to which a catalyst is added. In the presence of the catalyst, the nano particles will attach to each other and grow in size, eventually cross linking to form a gel. The collision and
Add catalyst Supercritical Gelation, ageing Drying Sol Gel Aerogel Conventional Drying Xerogel

Figure 3-4: Sol Gel Process

linking process that first gives rise to a network spanning the container is known as gelation. Further cross linking in the material is usually referred to as aging. At this point, the material consists of a solid network immersed in solvent. The gel may be washed with an organic solvent to exchange the gel liquid and rid the material of impurities and reaction byproducts. The last step is to remove the liquid phase by drying, which leaves what is usually referred to as a green body. The solvent could be allowed to evaporate directly from the liquid phase, in which case the porous network shrinks due to the pull of the surface tension of the liquid as it is removed from the pores. The resulting green body is known as a xerogel. The solvent removal could also be performed by supercritical drying, which prevents shrinking of the porous network, and in this case the green body is called an aerogel.

Before proceeding, we make a small clarification on the common terminology used with porous materials. If the pore size is below 2 nm, the material is microporous. If the pore size is between 2 and 50 nm, the material is mesoporous, and if the pores are larger than 50 nm, the material is described as macroporous [101].

3.4.1 Porous alumina

Porous alumina based on the processes developed by Tokudome and Hartmann [117, 48] was fabricated in the course of this research. As mentioned in chapter 2, Arestie produced such substrates based on a slightly modified recipe from [117] and tested a prototype alumina emitter [2]. Here, we have explored fabrication techniques for shaping the porous alumina substrate into emitter structures. High aspect ratio pillars from alumina that could potentially be shaped into emitters have
Figure 3-5: Porous alumina substrates synthesized by Tokudome [117]

been fabricated. These samples have pore diameters of approximately 1 \( \mu m \) and excellent uniformity. Direct molding is briefly discussed. Further work is required to obtain a reliable fabrication process for this substrate, as there are significant issues with gel drying and sample robustness that prevent it from being shaped as a micro tip.

Mesoporous alumina can be synthesized from a solution of \( \text{AlCl}_3 \) in water and ethanol by using propylene oxide as a catalyst [6]. In this case, the resulting material is a mesoporous solid. Tokudome [117] found that adding a small fraction of polyethylene oxide (PEO) to the starting sol can be used to control the resulting morphology of the xerogel and obtain macro porous structures. PEO induces the formation of phase-separating structures, and as the PEO content is increased, the resulting alumina has larger macropores. This is illustrated in Fig. 3-5. In Arestie’s work, a morphology similar to that shown in Fig. 3-5(b) was achieved.

To produce porous alumina with the target pore size, we have use the steps described below. This recipe is the same described by Arestie, but is included here for the sake of completeness.

1. A base solution is prepared by dissolving 0.5 g of PEO (Sigma-Aldrich) in 40 g of water and 43.4 g of ethanol, and then mixing 43.2 g of \( \text{AlCl}_3 \cdot 6\text{H}_2\text{O} \) (Sigma-Aldrich). This base solution can be stored for months in a sealed container.

2. The gel is prepared in small batches, usually by mixing 10 g of base solution with 3.46 g of
propylene oxide. The resulting mixture is poured into molds which are introduced in a sealed container with an ethanol bath. The containers are then placed in a 40°C oven to gel and age. Propylene oxide is extremely volatile and so the prepared solution should be sealed within a couple of minutes from mixing to prevent propylene oxide evaporation before gelation occurs.

3. The gelation occurs within 15-20 minutes during which the solution transforms from a transparent fluid to an opaque gel. The gel is allowed to age for 24 hours at 40°C.

4. Four solvent exchanges are performed. The containers are opened and the gels are flushed with ethanol and sealed again for 90 minutes. Once this time has passed, the excess ethanol is poured out of the container and the gels are flushed with new ethanol and sealed again for an extra 90 minutes. The process is repeated four times.

5. Once the gel has been washed, the containers are opened and the solvent is allowed to evaporate for 12 hours at room temperature. Then, the dried gel is transferred to the 40 °C oven for an additional 12 hours of drying.

We have used these steps to produce alumina pillars of approximately 1 cm length and 300 μm diameter, as shown in Figure 3-6. To prepare these samples, the mixture of base solution with propylene oxide is introduced into glass hematocrit tubes (550 μm diameter) via capillarity, and then allowed to gel, age and dry as described. The resulting samples have pore diameters of roughly 1 μm as appreciated from the SEM images, and could be very promising if shaped into emitter structures. However, alumina has two issues that hinder emitter fabrication.

The drying process tends to break the fragile alumina network. In fact, the samples in Figure 3-6 are partially damaged at the end of the drying process. Arestie [2] attempted direct molding of the alumina sol-gel into emitter-like structures and small aspect ratio capillaries, but the samples broke during drying. This issue might be avoided by using supercritical drying which avoids shrinkage. Tokudome has reported on the pore sizes achievable in porous alumina aerogels using PEO to control macro porosity [118], and it might be possible to produce porous alumina samples of the intended pore size using this method. Another issue is that the resulting samples are fragile and difficult to handle. The mechanical strength of these porous materials can be improved through sintering as described in [48], but this has not been pursued yet. With stronger structures, it may be possible to perform repeatable mechanical polishing of these alumina pillars into precise tip geometries.
3.4.2 Porous carbon

Emitters based on porous carbon xerogel substrates have been fabricated and tested in this research. These materials were researched by Arestie for the fabrication of high surface area electrodes for electrospray thrusters [2]. The novelty of this work is to use the carbon substrate for the emitters instead of the electrical contact. Two fabrication methods were pursued, direct molding of the sol-gel into emitter profiles, as well as mechanical polishing of xerogel monoliths.

Many routes to synthesize carbon xerogels and aerogels of varying morphologies have been described in the literature, as these materials can be used in applications including hydrogen and electrical storage, desalination and catalysis (see for instance the review by Biener [8]). A popular route to produce the carbon substrates is to take advantage of the polymerization reaction of resorcinol (R) with formaldehyde (F) [1, 82]. This reaction can be triggered using basic catalysts, for example Na₂CO₃ [80], or acidic catalysts, such as acetic acid, as shown by Brandt [10]. The resulting RF xero/aerogel is then pyrolized in an inert atmosphere to produce the carbon xero/aerogel.

In this work, we are using the chemistry and process developed by Arestie [2], based on the work of Baumann [5]. The following process yields an carbon xerogel of 0.5-1 μm pore radius and 60% porosity:

1. To prepare the base solution, 2.46 g of resorcinol (Sigma-Aldrich, 99% purity) are dissolved in 3 g of deionized water. Once the resorcinol is fully dissolved, 3.58 g of formaldehyde 37% in water solution (Sigma-Aldrich) are added to the mixture.

2. To induce gelation, 0.088 g of acetic acid (Sigma-Aldrich, purity ≥99%) are added to the mixture and combined thoroughly. The resulting solution is poured into molds and subsequently sealed.

Figure 3-6: Porous alumina pillars. (a) Samples after drying in hematocrit tubes, tube internal diameter is 550 μm (b) SEM image of pillar (c) SEM detail of porous structure.
3. The gelation and aging process takes several days. The solution is kept at room temperature for 24 hours, and then transferred to a 40°C oven for 24 hours. Then, the sample is moved to 60°C for another 24 hours, and finally transferred to an 80°C oven for 72 hours.

4. The samples may undergo a solvent exchange with acetone. This step is optional and was not performed for any of the samples reported in this document.

5. The RF gel is allowed to dry, first at room temperature for 24 hours, and then at 80°C for 72 hours.

6. The RF samples are placed in tube furnace (Lyndberg Blue Mini-Mite) and pyrolized at 900 °C for three hours under an argon flow of 400 sccm.

We proceed to discuss the emitter shaping methods explored, direct molding and mechanical sharpening.

3.4.3 Direct Molding

RF xerogel emitter-like structures can be produced by direct molding. The sol-gel mixture was poured into hydrophilic poly(dimethylsiloxane) (PDMS) molds that had the shape of a parabolic emitter. These molds were prepared using the PDMS chemistry described by Yao [128], based on the Dow Corning Sylgard 184 base and curing agent kit. Twenty grams of PDMS base are mixed with 2 grams of the curing agent to obtain the polymer, and 0.38 g of poly(dimethylsiloxane)-b-polyethylene oxide (Polysciences) are added to this in order to make the material hydrophilic. The resulting mixture is transferred to a petri dish and degassed. Subsequently smooth tungsten tips with a radius of curvature of 5 μm are introduced upside down into the fluid, as shown in Figure 3-7(a). The fluid with the W tips is then placed in the 80°C oven for about 2 hours to allow the polymer to cure. The W tips can then be removed, leaving behind a void with the desired emitter shape. This void is filled with RF solution and cured using the procedure described above.

Direct molding of RF substrates is feasible using this technique, as shown in Fig. 3-7(b). The resulting geometry replicates with high fidelity the original shape of the mold (Fig. 3-7(c,d)). However, the surface of the resulting RF tip consists of a micro or mesoporous layer which does not seem to absorb ionic liquid or be wetted by it (see Fig. 3-8). The surface is smooth and surface tension prevents the liquid from spreading into the tip.

The formation of a smooth tip can be explained by the effect of the mold on the reaction kinetics. In general, RF xerogel samples are macroporous in their bulk and are surrounded by a
Figure 3-7: Direct Molding of RF xerogels (a) Hydrophilic PDMS mold after curing, with W needle (b) Optical micrograph of RF tip (c) SEM image of W tip used for mold (d) SEM image of resulting RF tip

Figure 3-8: Molded RF tip with drops of EMI-BF\(_4\)
"skin" several micrometers thick. This skin is a layer formed by deposition of the reactants on the mold surface [92]. The skin can usually be easily removed through mechanical abrasion, exposing the macroporous structure beneath. However, if the mold dimensions are reduced, the resulting material morphology is affected by deposition on the mold surface. As the volume to surface ratio approaches the characteristic catalytic penetration depth of the surface, the sol becomes diluted and the RF forms with larger particulates. If the volume to surface ratio is even smaller, the surface's catalytic effect consumes completely the RF groups and the whole of the reactants become deposited on the walls. From cross-section inspection of the molded tips in the SEM, it appears that the entirety of the tip has the same morphology as the surface. Thus, the mold dimensions may not favor the formation of a macroporous network inside the tip. It may be possible to use these molded tips as externally wetted emitters by using chemical treatments or pyrolization to alter the wetting behaviour, although these possibilities were not explored in this work.

3.4.4 Mechanical Polishing

Conical emitters with tip radius of curvature below 10 μm have been fabricated from carbon xerogel by mechanical polishing. The fabrication process consists of four main steps: (1) synthesis of RF xerogel in cylindrical shaped molds, (2) mechanical sharpening of RF cylinders into conical structures, (3) pyrolization and (4) final polish. We note that all polishing steps are dry, no water nor any other sort of lubrication is used.

Cylindrical RF monoliths are synthesized in a polypropylene mold. The cylinder mold has a diameter of 6.35 mm and a height of 25.4 mm. The molds are filled with RF sol, and a stainless steel wire 1 mm in diameter is placed concentrically and 12 mm deep into the cylinder. In this way, when the RF cures, a solid cylinder with a metal shaft for handling is obtained.

Mechanical sharpening is used to shape the cylinder into a cone with target half-angle of 10°. A small chuck has been installed on a Polulu 131 Metal Gearmotor 37Dx57L, so that the shaft of the RF cylinders is clamped by the chuck and the cylinder can be spun at about 60 rpm. A pencil sharpener (Kum Brand, Long Point) is used first to remove the bulk of the material from the cylinder. Then, the cone is polished using sandpaper (grits #1000, 2000 and 3000) supported on a 10° aluminum wedge, as sketched on Fig. 3-9. The tip is then polished with Buehler diamond lapping film (6 μm and 1 μm) to achieve a smoother finish. The cone is then rinsed for 2 minutes in acetone in an ultrasonic bath and dried on a hot plate at 100°C for a few minutes.

The sharpened RF xerogel emitters are then pyrolized. The pyrolization process leads to a
shrinkage of approximately 75%. Photographs of a batch of emitters pre- and post- pyrolysis are shown in Figure 3-10. Due to the different thermal stresses of the xerogel and the stainless steel wire, a fraction of the samples broke during pyrolysis. In future iterations, we will use tungsten wire 0.5 mm in diameter to avoid this breakage issues.

The samples were inspected using SEM after the pyrolysis process, and it was found that the emitter apices were covered with particles of a few microns diameter, with the porous xerogel network hidden beneath. An example is depicted of Fig. 3-11. It is uncertain if these particles are contamination from the sanding paper and lapping film, or if they are grown on the RF xerogel during the pyrolysis process. It was attempted to clean some of these tips with ultrasonic baths of acetone and isopropanol, but the tips were damaged by accident during the cleaning process. Nevertheless, it was possible to resharpen the carbon xerogel tips using Buehler diamond lapping
films of 30 μm and 6 μm particle size. The resharpened emitters were washed in isopropanol and acetone ultrasonic baths, for one hour in each solvent, and dried in a hot plate at 100°C for 5 minutes before inspection in the SEM.

Figure 3-12 includes several micrographs of the carbon xerogel tips obtained after resharpening. The carbon emitters have tip radii below 10 μm and a pore size of approximately 1 μm diameter, with half-angles closer to 25-30° than the intended 10°. Some large particulates are still present, but far upstream of the apex, where the samples were not likely repolished. Assuming radii of 6-7 μm, the estimated impedances are roughly $3 \times 10^{17}$ kgs$^{-1}$m$^{-4}$, which is above the minimal impedance required. Thus, we proceed to test the emission of these tips different ionic liquids. The tip tested with the ionic liquid EMI-BF$_4$ is referred as PBF$_4$ in the remainder of the manuscript, and the tip tested with EMI-Im is referred to as PIm.
Figure 3-12: SEM Images of carbon xerogel tips after final sharpening and cleaning. Images (a-c) correspond to one emitter, which we denominate PBF₁, images (d-f) to another, designated PIm
Chapter 4

Prototype Carbon Xerogel Ionic Liquid Ion Source

This chapter presents the emission characteristics of two prototype carbon xerogel emitters, tested with the ionic liquids EMI-BF$_4$ and EMI-Im. The current-voltage responses of the emitters are presented, as well as the results of time-of-flight spectrometry. For both cases tested, once a startup voltage is exceeded, the source operates with a single emission site, and, as the extraction voltage is increased, the source transitions to multiple emission site operation. We discuss some electrochemical degradation issues observed and suggest possible causes and feasible mitigation strategies. The TOF results indicate that the carbon xerogel emitter using EMI-Im operates in a mixed ion-droplet regime, whereas the carbon xerogel emitter with EMI-BF$_4$ operates in the pure ion regime.

4.1 Emitter Characterization Techniques

Several experiments are required to characterize the source current, as well as the beam directionality, energy profile and composition. We first describe the required precautions for the implementation for carbon xerogel emitters and then explain the procedures for current-voltage tests and time-of-flight spectrometry that were performed on the prototype emitters.

4.1.1 Emitter Implementation

Carbon xerogels are conductive substrates, and thus, if the voltage were applied directly to the emitter, electrochemical decay would prevent single polarity operation for more than a few minutes.
Therefore, a distal electrical contact must be used to allow single polarity operation for prolonged periods. The distal electrode should ideally have a large surface area to increase the charging time of the double layer and delay the onset of electrochemistry. In fact, a carbon xerogel monolith with a platinum wire can be used for the tip contact if separated from the carbon emitter by an insulating permeable layer such as glass, as is done with glass electrospray thrusters based on ILIS \cite{2}. For the prototype tests reported in this chapter, we choose a slightly simpler implementation— the electrical contact is a platinum wire, wrapped around the emitter, but electrically isolated from it using fiber glass.

Another important caution for porous emitter operation is the filling procedure. As discussed in chapter 2, porous emitters filled in atmospheric conditions will be prone to electrical discharges as trapped gas is released from the pores. To avoid this issue, it is preferable to fill the emitter in vacuum, with ionic liquid that has been dried and degassed. For all experiments, the emitter is filled by immersing the tip in a crucible of ionic liquid at pressures of approximately 1 μTorr. To avoid any discharges due to inadequate liquid containment, excess liquid on the emitter is removed with a wipe. Images of the prototype emitters with their distal contact and filled with ionic liquid are shown in Figure 4-1.

The emitter filled with liquid is then mounted on a triaxial precision stage and centered in front of an extractor aperture 1.6 mm in diameter. The extractor is followed by another plate that acts as a shield. The shield supports a small magnet that helps to eliminate spurious signals from secondary electron emission resulting from ion beam impingement on the setup surfaces; pictures of the source mounted on the setup for emission are found in Figure 4-2. The source is installed in a vacuum chamber and emission experiments are performed at pressures below 1 μTorr.
4.1.2 Current Voltage Measurements and Time-of-flight Spectrometry Setup

The basic assessment of emitter performance consists on measuring the emitted current, $I_{\text{emitted}}$, as a function of the voltage applied to the tip, $V_{\text{app}}$, with the extractor grounded, to determine the onset voltage, levels of current supplied, and appearance of multiple emission sites. The voltage applied to the emitter is provided by a custom Matsusada AP-3B1-L2 bipolar power supply, which is controlled by a computer. The current provided by the power supply ($I_{\text{emitted}}$) is measured by recording the voltage drop across a 1 MΩ resistor placed in series with the power supply. It is also possible to record the voltage drop through the extractor and thus determine the intercepted current. The readings for $I_{\text{emitted}}$, intercepted current and $V_{\text{app}}$, are recorded by a computer program at a sampling rate of 30 Hz¹.

The beam is directed to a TOF setup to determine the beam composition. The charge-to-mass ratio $q/m$ distribution of the particles in the beam can be determined by measuring the time $t$ it takes the particle to travel a known distance $L$; this time depends on $q/m$ and the energy of the particle. If the particles are assumed to have an energy equal to the applied voltage, we have

$$ t = L \sqrt{\frac{m}{2qV_{\text{app}}}} \quad (4.1) $$

The TOF spectrometer consists of a set of deflector plates, an electrostatic deflection gate, and a channeltron detector (Photonis Magnum 5900), as shown in Figure 4-3. The deflector plates consist of two pairs of parallel planar electrodes 25.4 mm long and separated by approximately 1 cm, which can be used to steer different sections of the beam towards the channeltron by biasing the plates to a few tens of volts (supplied by two Acopian P03-5HP17 and two Matsusada AMS-5B6 power

¹Program is Electrospray Characterizer, by F. Mier Hicks, student in the MIT Space Propulsion Lab. More details of the emitted current measurement circuit may be found in Appendix B.
supplies). To measure the flight time, the beam of particles is deflected away periodically from the channeltron by the electrostatic deflection gate. When the gate is on, no charged particles arrive to the detector. When the deflection is turned off, we measure the current received by the channeltron as a function of time. Faster, lighter particles arrive to the detector first and the current keeps increasing as the slower particles arrive.

The gate consists of several grounded apertures enclosing two electrodes of length 6.25 mm along the path of the beam, biased to ± 950 V, operated at a frequency of 500 Hz. The flight distance is set to \( L = 0.75 \) m. The channeltron front is biased to \( V_{in} \) and the back is grounded (\( V_{out} = 0 \) kV). The channeltron output is directed to a non-inverting amplifier with rise time of less than 300 ns \(^2\). The signal controlling the gate and the amplifier output are recorded by an oscilloscope (Agilent DSO5014A) and averaged over several thousand samples to filter noise.

4.2 Experiments with EMI-Im

Tip PIm was tested for emission with the ionic liquid EMI-Im. Current voltage responses were obtained, and stable emission of a few hundred nanoamperes was obtained in both the positive and negative polarities. In the negative mode, electrochemical effects may provoke instabilities after a few minutes of DC operation. TOF spectrometry indicates that the carbon xerogel emitter infused with EMI-Im operates in the mixed ion-drop regime. The detailed results are presented next.

\(^2\)TOF setup and amplifier designed and constructed by C. Miller, student in the MIT Space Propulsion Lab. Amplifier details can be found in Appendix B
4.2.1 Current-Voltage Curves and Electrochemistry Considerations

The IV response of the emitter was obtained by applying a symmetric triangular voltage signal ranging from 0 V to ±2100 V over a period of 120 s. The results are plotted in Figure 4-4. The top panel shows the voltage applied and the current response as a function of time, while the bottom panel shows the I-V curve extracted from the data in the top panel. Once the source exceeds a threshold voltage \( V_{\text{start}} = 1500 \) V, for this particular implementation, the current increases with the applied voltage. If the voltage is increased beyond 1780 V, the current curve has a discontinuity consistent with the appearance of a second emission site on the emitter. If the voltage is increased beyond 1850 V, there is another discontinuity suggesting that a third emission site appears. These additional emission sites are firing off-axis, as evidenced by the interception of current in the extractor electrode. When the voltage magnitude is decreased, the emission sites have extinction voltages a few tens of volts lower than their startup voltages.

The current-voltage data suggests that the initial emission occurs from a pool of liquid spanning several pores on the tip apex but that does not cover the tip entirely. According to the startup voltage model presented in chapter 2, the startup voltage for a perfectly wetted tip of radius \( R_c = 6 \) μm placed a distance \( d = 500 \) μm away from an extractor plate should be 900 V (see equation 2.10). If the emission was coming from an individual pore of radius \( r_p = 500 \) nm located at the apex of the tip, the startup voltage would be in excess of 3000 V, due to the increased surface tension pressure exerted by the smaller meniscus. The value of 1500 V is consistent with emission from a pool of liquid of approximately 4 μm diameter on the apex of the emitter, according to equation 2.12.

The response of the ion source is characterized further by performing I-V tests with alternating voltage ramps, as shown in Figure 4-5. In this experiment, the first ramp has constant voltage segments of 20 s, and the second ramp has constant voltage segments of 60 s. At applied voltages close to \( V_{\text{start}} \), the source current is unstable. As the voltage is increased and the electrostatic traction increases, these instabilities disappear. There is a current overshoot immediately after the source switches polarity, but the source becomes stable within a few seconds. For example, for a voltage of 1591 V, the source emits 141 nA, with less than 1% variations in the current. As the voltage is increased further, the appearance of additional emission sites is evident as jumps in the current.

The source has instabilities in the negative mode that may be associated with electrochemical
Figure 4-4: (a) Current response of carbon xerogel emitter infused with EMI-Im, subjected to a triangular voltage ramp, as a function of time. The current intercepted in the extractor is represented by the dashed curve (b) Current response as a function of applied voltage.

effects. After prolonged operation in the same polarity, the current in the negative mode suddenly increases beyond the stable level and behaves erratically. In Figure 4-5(b), for the first ramp with a faster alternation frequency, no instabilities are observed in the positive or the negative mode. However, for the second ramp with longer steps, the current becomes unstable in the negative mode, at the higher operation voltages and currents associated with multiple emission sites. The fact that the instabilities are absent when the polarity is alternated at a higher frequency, and that the instabilities are absent at the lower current levels, suggest that the instabilities are associated to a charging mechanism. Detrimental electrochemical reactions will occur if the double layer on the electrode surface is charged beyond the electrochemical window of the ionic liquid. Considering that the charging time of the double layer is proportional to the source current [11, 67], the observed trend of instabilities at higher operation currents is consistent with electrochemistry. At the higher alternation frequencies, the double layer is discharged before it reaches the electrochemical window limit, and the instabilities are avoided. If the electrochemical window limit is exceeded, gas generating reactions in the distal electrode may affect the emission on the tip. Another possible cause of instabilities could be the emission of electrons from a dry feature on the tip; however, since
Figure 4-5: Response of carbon xerogel emitter infused with EMI-Im, subjected to alternating voltage ramps of different alternation frequency.

the source emits comparable levels of current in both the positive and negative mode, the negative mode beam is likely produced by a sharp liquid meniscus without unwanted electron evaporation.

4.2.2 TOF Results

TOF experiments were performed on the source operating in the positive mode at voltages between $V_{app} = 1516$ V and $V_{app} = 1768$ V, in 25 V increments. The deflector plates in the path of the beam were grounded for this experiment. The voltage applied to the source and the emitted current during the TOF test are plotted in Figure 4-6. The source emits from a single site for all of the voltages tested, except for $V_{app} = 1768$ V, for which the source starts with a single emission site but suddenly a second site appears.

The TOF results are shown in Figure 4-7. The signals have been obtained from the raw data as follows:

1. The amplifier output has a non-zero offset and capacitive coupling effects when the gate is operating but the source is off ($V_{app} = 0$ V). This offset is subtracted from the raw data.

2. After removing the $V_{app} = 0$ V offset, the TOF signal has a nonzero offset when the gate is
on, i.e., a signal is detected in the channeltron when the beam is deflected. This signal likely corresponds to neutral particles generated as a result of fragmentation of ions during flight; these neutrals are unaffected by the gate and will be detected when the gate is on. We thus subtract the offset due to neutrals from the TOF signal.

3. The signals are all normalized to their respective maxima.

The results indicate mixed ion-droplet operation. The signals have sharp steps that are attributed to the emission of solvated ions, along with a “tail”, or a current increase over several hundred microseconds before reaching the maximum, which is attributed to charged drops produced from a cone-jet. The masses and flight times of the positive ions from EMI-Im, assuming particle energies of $V_{app}=1516 \: \text{V}$ and $V_{app}=1768 \: \text{V}$, are shown in Table 4.1. These flight times correspond closely to the times at which the signal increases. It must be noted that the flight times of the ions in the cone-jet regime are increased with respect to the ideal flight time shown in the table, as the ions, which are produced either at the start of the jet or from Coulombic explosions in the droplets, will have an energy deficit of the order of 100-300 V due the ohmic voltage drop along the jet [37]. Particles arriving with flight times in the excess of 100 $\mu\text{s}$ and up to 400 $\mu\text{s}$
Figure 4-7: Normalized TOF spectrometry signals for different operation voltages of the carbon xerogel emitter infused with EMI-Im. The signal at 1768 V was acquired once the second emission site had appeared. Note the channeltron voltages are set to $V_{in}$=-1.5 kV, $V_{out}$=0 kV.

Table 4.1: EMI-Im Ion Flight Times

<table>
<thead>
<tr>
<th>Ion</th>
<th>Mass (a.m.u.)</th>
<th>q/m [C/kg]</th>
<th>TOF, $V_{app}=1516$ V [µs]</th>
<th>TOF, $V_{app}=1768$ V [µs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMI$^+$</td>
<td>111</td>
<td>$8.68 \times 10^5$</td>
<td>14.6</td>
<td>13.7</td>
</tr>
<tr>
<td>(EMI-Im)EMI$^+$</td>
<td>502</td>
<td>$1.92 \times 10^5$</td>
<td>31</td>
<td>28.8</td>
</tr>
<tr>
<td>(EMI-Im)$_2$EMI$^+$</td>
<td>893</td>
<td>$1.08 \times 10^5$</td>
<td>41.4</td>
<td>38.4</td>
</tr>
</tbody>
</table>

correspond to droplets with $q/m$ ranging from $2 \times 10^4$ to $1 \times 10^3$ C/kg, assuming an energy deficit of 200 V with respect to the applied voltage. This charge to mass ratios correspond to droplet radii between 2 and 14 nm, if the droplets are assumed to be charged to the Rayleigh limit. The exact determination of the charge to mass ratio and droplet size distribution of the beam would require retarding potential analyzer measurements to determine the energy of the particles; however, these data demonstrate the presence of droplets in the emission from EMI-Im.
4.3 Experiments with EMI-BF$_4$

Tip PBF$_4$ was tested for emission with the ionic liquid EMI-BF$_4$. Current voltage responses were obtained, and stable emission of a few hundred nanoamperes was obtained in both the positive and negative polarities, with emission responses very similar to those obtained with traditional externally wetted tungsten tips. In the negative mode, electrochemical effects in the distal electrode may provoke instabilities after a few minutes of DC operation. TOF spectrometry indicates that the carbon xerogel emitter infused with EMI-BF$_4$ operates in the pure ion regime. Some of these results were reported in reference [90].

4.3.1 Current-Voltage Curves and Electrochemistry Considerations

Triangular voltage signals and alternating voltage ramps are applied to the distal contact of tip PBF$_4$ to determine the source response. Figures 4-8(a),(b) show a sample voltage signal and the corresponding emitted current response from the emitter.

The onset voltage for these tests is ±1535 V. As with PI, this value of $V_{\text{start}}$ indicates that the initial emission occurs from a pool of liquid spanning several pores on the tip apex but that does not cover the entire apex. The startup voltage for a perfectly wetted tip of radius $R_c = 7 \, \mu\text{m}$ placed 500 \(\mu\text{m}\) away from an extractor plate should about 1063 V, according to equation 2.10. If the emission was coming from an individual pore of radius $r_p = 500 \, \text{nm}$ located at the apex of the tip, the startup voltage required would be almost 4000 V. The value of 1535 V is consistent with emission from a pool of liquid of approximately 7 \(\mu\text{m}\) diameter on the apex of the emitter, as estimated using equation 2.12.

The I-V response of the emitter (Fig. 4-8(c)) was obtained by plotting the average current for each of the voltages tested in the ramp of Figure 4-8(a),(b). Several emission regimes can be distinguished. First, the source emits intermittently at voltages close to the startup voltage. When $V_{\text{app}}$ is increased, the source emission becomes uninterrupted, with the current increasing as the voltage is incremented. There is a current overshoot immediately after the voltage is switched, and the source reaches a stable current level within a few seconds. This overshoot is also observed on externally wetted emitters [70]. The current levels of this emitter are of the same order as those of externally wetted emitters [69], and the slope in current vs. voltage of the carbon xerogel emitter is almost the same as that of an externally wetted tungsten tip (0.383 nA/V vs. 0.375 nA/V). When $V_{\text{app}}$ is increased beyond a certain level (2000 V in this particular implementation), the current
Figure 4-8: (a) Sample voltage profile and (b) corresponding current response from carbon xerogel emitter infused with EMI-BF₄. (c) Current-voltage profile. (d) Samples of constant voltage operation.
shows a clear step, which indicates the appearance of a second emission site on the emitter apex.

The source displays short-term stability in the intermediate voltage range (current signal has no drops, and only one emission site is observed). Figure 4-8(d) shows two-minute intervals of operation of the source, one in the positive and another in the negative polarity. The variation of current (standard deviation/mean) for these samples is less than 0.01, suggesting an adequate liquid supply to the emission site.

The source presents some instabilities after prolonged constant voltage operation in the negative regime, which, as with tip PIm, are also attributed to electrochemistry in the distal electrode contact. Figure 4-9 shows the current obtained from the source for alternating voltage tests, for different magnitudes of $V_{app}$ and different alternation periods. The tests reported in this figure were performed with a different source-extractor configuration from the one used in Figure 4-8, and thus the startup voltage is somewhat higher but the source behavior is very similar otherwise. In Figures 4-9(a)-(c), the source is subjected to a square wave voltage waveform, alternating between $V_{app} = \pm 1788$ V, and with periods of 60, 180 and 600 s, respectively. This voltage is close to the startup voltage of the configuration, and so the source current presents some current drops. For the faster alternation frequencies, there are not any sudden increases in the magnitude of the emitted current; however, for the test at a prolonged period, sudden, erratic increases are detected in the negative emitted current. These instabilities are indicated with the red arrows in the figure. Figure 4-9(d) shows the current response when the source is alternated with a 180 s period between $V_{app} = \pm 1920$ V, and then the voltage is increased to $V_{app} = \pm 1970$ V. At the lower voltage and current, the source presents no instabilities for this alternation frequency, whereas for the higher operation current, instabilities are present in the negative mode.

The instability occurrence is dependent on the alternation period and has a faster onset for higher emission currents, suggesting an electrochemical mechanism as with tip PIm. With EMI-BF$_4$, electrochemical reactions lead to gas generation in the negative mode [67], and so it is likely that the reactions in the distal electrode may affect the porous emitter. In the positive mode, solid deposits are created on the electrode, which would affect the source emission in the long term but do not seem to alter the immediate emission characteristics of the positive mode. It is believed that the electrochemistry occurs on the platinum wire distal contact, and that the conducting tip is not subject to reactions. If there was a direct contact to the carbon tip (say, if the fiber glass had a gap where the Pt wire touches the carbon directly), electrochemistry on the porous network near the emitting apex would occur within ms, due to the slow diffusion of the double layer onto the
Figure 4-9: Current response of carbon xerogel emitter EMI-BF₄ when subjected to a square wave voltage waveform (a) $V_{app} = \pm 1788 \text{ V}, \text{60 s period}$ (b) $V_{app} = \pm 1788 \text{ V}, \text{180 s period}$ (c) $V_{app} = \pm 1788 \text{ V}, \text{600 s period}$. In panel (d), the source is subjected to two periods with $V_{app} = \pm 1920 \text{ V}$, 180 s period, before being tested over two periods with $V_{app} = \pm 1970 \text{ V}$, 180 s period.
porous network [11]. Using the models of Ref. [67], we estimate the time it takes for the Pt distal contact to reach the 2.25 V electrochemistry onset to be of the order of a minute, for an emission current of 200 nA, which is comparable to the onset times observed in the experiments.

4.3.2 TOF Results

TOF experiments were performed for different positive operation voltages of the tip PBF4. The deflectors were used to direct the beam towards the channeltron and perform sampling from several sections of the beam. The voltages of the deflectors, $V_1$ and $V_2$, applied as shown in Figure 4-10(a), were changed over a few tens of volts. A detailed scan was performed at $V_{app}=1818$ V, while shorter scans were performed at $V_{app} = 1718, 1769, 1869$ and 1920 V. These measurements were performed over periods of several hours (the 1818 V test was a 3 hour continuous run) without any significant changes in the emission current.

A coarse map of the beam was produced for $V_{app} = 1818$ V. In this case, $V_1$ was varied between 0 and 80 V, in 10 V increments, and for each $V_1$ value, $V_2$ was varied between -140 and 60 V, in 10 V increments. A beam profile is constructed from the maximum signal detected in the channeltron for each pair $(V_1, V_2)$, as shown in Figure 4-10(b).

(a) \hspace{2cm} (b)

Figure 4-10: (a) Deflector Voltage Configuration- beam goes into the page. (b) Coarse beam profile at $V_{app} = 1818$ V, obtained by varying the voltage applied to the deflectors in the path of the beam and recording the intensity of the signal at the channeltron. $V_2$ is varied while maintaining $V_1$ constant to produce each cross-section. Signal intensities have been normalized by the maximum intensity detected at $(V_1, V_2) = (10, -90)$ V.
Table 4.2: EMI-BF$_4$ Ion Flight Times for $V_{\text{app}} = 1818$ V

<table>
<thead>
<tr>
<th>Ion</th>
<th>Mass (a.m.u.)</th>
<th>$q/m$ [C/kg]</th>
<th>TOF [µs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMI$^+$</td>
<td>111</td>
<td>8.68$\times$10$^5$</td>
<td>13.3</td>
</tr>
<tr>
<td>(EMI-BF$_4$)EMI$^+$</td>
<td>309</td>
<td>3.11$\times$10$^5$</td>
<td>22.3</td>
</tr>
<tr>
<td>(EMI-BF$_4$)$_2$EMI$^+$</td>
<td>507</td>
<td>1.9$\times$10$^5$</td>
<td>28.5</td>
</tr>
<tr>
<td>(EMI-BF$_4$)$_3$EMI$^+$</td>
<td>705</td>
<td>1.36$\times$10$^5$</td>
<td>33.6</td>
</tr>
<tr>
<td>(EMI-BF$_4$)$_4$EMI$^+$</td>
<td>903</td>
<td>1.36$\times$10$^5$</td>
<td>38.1</td>
</tr>
</tbody>
</table>

Figure 4-11 shows sample TOF traces obtained with the source operating at $V_{\text{app}} = 1818$ V. All signals have been processed using the steps outlined in Section 4.2.2, and each signal has been normalized to its own maximum. The insets of each panel show the beam profile for the given $V_1$ and show the relative intensity of each signal compared to the maximum signal in the scan. TOF profiles are shown only for the strongest signals detected. For larger deflections, a non-zero signal is detected in the channeltron. However, the TOF experiments at these small signals have artifacts (such as artificial spikes at the ion arrival times) that are non-physical, and so the analysis is restricted to the stronger signals for which artifacts are absent.

The TOF results indicate that the carbon xerogel infused with EMI-BF$_4$ emits a purely ionic beam. The current signals show clear steps at the times corresponding to the monomer EMI$^+$, the dimer (EMI-BF$_4$)EMI$^+$ and the trimer (EMI-BF$_4$)$_2$EMI$^+$ (see Table 4.2). In between steps, a gradual increase in current can be observed. This signal corresponds to ions resulting from fragmentation events. An ion resulting from fragmentation is faster than its parent ion, but slower than the unfragmented ion of the same degree of solvation.

Some of the signals show particles arriving at 50 µs, which may correspond to larger clusters of ions. However, after this flight time, no more increases are detected in the signal up to 460 µs (the plots are illustrated for up to 100 µs, but the signals stay constant after this point). There seems to be no current associated to microdroplets.

Traces from the experiments at $V_{\text{app}} = 1718, 1769, 1869$ and 1920 V display pure ionic behavior as well. For the scans at these voltages, $V_2$ was held fixed either at 0 or -100 V, and $V_1$ was varied between -10 and 100 V. The TOF traces from different sections of the beam are shown in Figure 4-12. All signals have been processed using the steps outlined in Section 4.2.2, and each signal has been normalized to its own maximum. The insets of each panel show the beam profile for a set $V_2$, and show the relative intensity of each signal compared to the maximum signal in the scan at the given $V_{\text{app}}$. Again, the steps in current are observed at the times expected for ion arrival, and there are no droplet signals.
Figure 4-11: Time-of-flight profiles for different locations over the cross sections of the beam, with the source operating at $V_{app}=1818$ V. Insets show the beam profile along the linear scan for each $V_1$. The maximum signal was obtained for $(V_1, V_2) = (10, -90)$ V, in panel (b). Note the channeltron voltages are set to $V_{in}=-1.5$ kV, $V_{out}=0$ kV.
Figure 4-12: Time-of-flight profiles for different operating voltages. The insets show the current profile as the beam is scanned ($V_2$ is kept constant, grounded, while $V_1$ is varied). Each inset is normalized against the maximum signal of the scan at the given $V_{app}$. 
It is possible to estimate the hydraulic impedance of the carbon xerogel emitter operating with EMI-BF$_4$ from the slope of the I-V data, $s = \Delta I/\Delta V$, and using the beam composition from the TOF results. The hydraulic impedance is related to the flow rate and driving pressure as $Z = \Delta p/\Delta Q$. The change in flow rate can be related to the change in current, and similarly the driving pressure can be computed from the change in operation voltage.

The change in flow rate with current can be estimated from the composition of the beam, and is given by

$$\Delta Q = \Delta I \sum f_i (m/q)_i$$

Here, $f_i$ and $(m/q)_i$ is the fraction of the current carried by each type of ion and the respective mass to charge ratio.

Now, the pressure driving the flow, $\Delta p$, must be computed as a function of the tip voltage $V$. The meniscus has the electrostatic and surface tension pressures acting upon its surface. Most of the electric field pressure is used to overcome the surface tension, but the excess electric field force is used to drive the flow. The electrostatic pressure is estimated with the prolate-spheroidal model of the electric field on the surface of the tip (see Section 2.1.1). We will consider the case where the emission comes from a feature of radius $r_{ch}$ located at the apex of the tip of radius $R_c$ (in Section 4.3.1, we had estimated $r_{ch} = 3.4 \mu m$ on a $R_c = 7 \mu m$ tip from the experimental starting voltage).

The electrostatic pressure, at any operation voltage $V$ is given by

$$P_E = \frac{\epsilon_0 E^2}{2} = \frac{1}{2} \frac{4V^2/a^2}{\text{atanh}^2(\eta_0)(1 - \eta_0^2)}$$

where $a$ and $\eta_0$ are geometrical constants defined by the geometry of the tip and extractor (the exact expressions for $a$ and $\eta_0$ are on Section 2.1.1). This pressure $P_E$ consists of the pressure required to overcome the surface tension, $2\gamma/r_{ch}$, and the excess driving the flow:

$$P_E = \frac{2\gamma}{r_{ch}} + \Delta p$$

The voltage $V$ is some value $\Delta V$ above the startup voltage, this is, $V = V_{\text{start}} + \Delta V$. For the onset condition, we have

---

3 This estimation procedure was suggested by Dr. Carmen Guerra.
Thus, we can rewrite the electric pressure from equation 4.3 as

\[ P_E = \frac{2\gamma}{r_{ch}} \left( 1 + 2 \frac{\Delta V}{V_{start}} + \left( \frac{\Delta V}{V_{start}} \right)^2 \right) \]  

(4.6)

We may neglect the second order term in equation 4.6, and using equation 4.4, we obtain

\[ \Delta p \approx \frac{4\gamma \Delta V}{r_{ch} V_{start}} \]  

(4.7)

Combining equations 4.2 equation 4.7, the impedance \( Z \) is given by

\[ Z = \frac{4\gamma \rho}{r_{ch} V_{start} \sum f_i (m/q)_i} \]  

(4.8)

To calculate \( Z \), we use \( s = 0.383 \) nA/V and \( V_{start} = 1535 \) V. If we take the beam to be composed of half monomers and half dimers, the hydraulic impedance is computed \( 5.14 \cdot 10^{19} \) kgm\(^{-4}\)s\(^{-1}\); if we assume 50% monomers, 40% dimers and 10% trimers, the hydraulic impedance is \( 4.7 \cdot 10^{19} \) kgm\(^{-4}\)s\(^{-1}\). We note that this \( Z \) is significantly higher than the value estimated from the geometrical parameters of the conical tip and the porous substrate. The model we have used is an estimation, and the prolate-spheroidal geometry may not illustrate accurately the electrostatic pressure increases in the apex of our conical emitters. The higher value of \( Z \) is probably due to the fact that the emission site probably covers only partially the emitter apex, and this reduced meniscus base size increases the hydraulic impedance.

### 4.4 Discussion

The results indicate that the pure ion regime can be achieved with a porous carbon xerogel emitter and the ionic liquid EMI-BF\(_4\). In the case of the liquid EMI-Im, which has a poorer conductivity and surface tension, the flow restriction from the carbon xerogel tip is not sufficient to eliminate the droplet component of the beam. The baseline impedance was based on experimental evidence from the ionic liquid EMI-BF\(_4\). This impedance limit may be sufficient for EMI-BF\(_4\), but not for the liquid EMI-Im, which is less viscous and might need more flow restriction from the carbon structure to guarantee a flow rate compatible with the PIR. However, it may be possible to produce the pure
ion regime from carbon tips infused with EMI-Im, as the hydraulic impedance may be increased by making the tips sharper and reducing the pore size or porosity of the substrate.

The emission from both ionic liquids is stable in the positive mode, and the instabilities in the negative mode are most likely provoked by electrochemistry. The observations suggest that these carbon xerogel emitters must be implemented with high surface area electrodes with charging times of several hours, in order to avoid triggering reactions that may upset the emission.

Several improvements must be performed in the fabrication and implementation of the carbon xerogel into emitter tips. The prototype emitters were shaped manually into micrometer tips, and this process lacks yield and repeatability. Additionally, the tips were loaded with liquid by immersing and removing an unknown amount of liquid from the tip. A more repeatable implementation would fill the emitter with a previously measured amount of ionic liquid. In the next chapter, laser micromachining is demonstrated as a manufacturing method for carbon xerogel ILIS tips, which should improve the repeatability of the emitters. The next chapter also describes a new design for the emitter implementation, with an integrated reservoir that permits the precise filling of the porous tip.
Chapter 5

Laser-Micromachined Carbon Xerogel Ionic Liquid Ion Source

In this chapter, we describe a novel implementation of the carbon xerogel ILIS. A new design for the source, including a reservoir with distal electrode contact, is presented in Section 5.1. The carbon xerogel is formed into a micrometer sized tip using laser micromachining. Section 5.2 describes the process used to pattern the carbon xerogel as well as a detailed justification for the fabrication process. Section 5.3 then describes the implementation and characterization of the source infused with EMI-BF₄, including current-voltage curves, stability measurements, and results from time-of-flight spectrometry and retarding potential analysis. The source operates in the pure ionic regime, with possible large clusters of ions being produced in addition to monomers and dimers.

5.1 Revised Emitter Design

For optimal long-term operation, the carbon xerogel ILIS should be in contact with a reservoir that replenishes the ionic liquid consumed by the tip. For this reason, the carbon xerogel ILIS is implemented in a cylindrical teflon container, as shown in Figure 5-1.

The teflon cylinder has a cavity that fits the cylindrical piece of carbon xerogel with the carbon tip, as well as another cavity that contains the distal contact and acts as a reservoir. In order to isolate electrically the distal contact from the carbon piece containing the tip, a piece of fiber glass is used as a spacer. The fiber glass provides wicking from the reservoir to the porous carbon structure.

The distal electrode in the reservoir should have a high surface area to increase the electrical
charging time of the double layer and delay the onset of electrochemistry. The carbon xerogel substrate used for the tips can in fact be used for the electrode material. For typical emission conditions used with ILIS, the carbon xerogel electrode has a charging time in the order of several tens of hours per gram of carbon [76]. For the tests described in this chapter, the distal electrode was a platinum wire, as a carbon electrode was not available at the time of assembly, but ideally a carbon xerogel electrode should be used.

The carbon xerogel tip is fabricated by laser micro machining. As can be observed in the figure, the piece of carbon xerogel holding the tip has a base that fits into the teflon container. The other end of the piece is trimmed to a smaller diameter (about 1.6 mm) in order to reduce the amount of material that needs to be removed during the laser machining process. Once the piece has been trimmed, the thinner end is exposed to a laser beam to ablate material selectively around the center of the structure, leaving behind a micro-tip emitter structure of roughly 300 μm height. The following section describes in detail the formation of tips using laser micromachining.

5.2 Laser Micromachining Process

The laser machining process is described as follows: Section 5.2.1 explains the process used to prepare the carbon pieces for laser machining, Section 5.2.2 describes the laser tool in detail, and Section 5.2.3 describes the process used to select the laser conditions for tip fabrication as well as the results from the fabrication process.

The goal of the laser machining process is to produce a carbon tip with a radius of curvature $R_e \leq 10 \, \mu m$ and at least 100 μm tall. As discussed in Chapter 3, the hydraulic impedance of the
emitter is a strong function of the tip radius of curvature, and values of $R_e$ below 10 $\mu$m help bring the hydraulic impedance above the design target. The tip height should be at least a factor of 10 greater than the tip radius to provide sufficient electric field amplification at the tip with respect to the base substrate [25], and so the minimum height required is 100 $\mu$m. However, it was noted that the sharpening schemes used for the machining process removed about 100 $\mu$m of material per pass, and most often we used three passes to produce emitters of approximately 300 $\mu$m height, which should have a higher impedance thanks to their superior aspect ratio.

### 5.2.1 Preparation of Carbon Pieces

The carbon xerogel piece for the tip is prepared for laser machining as follows. First, the carbon xerogel is synthesized into cylinders 3.5 mm in diameter and about 25 mm long. The cylinders are then cut to a length of approximately 5 mm using a razor blade. The piece is brought to a 4.6 mm length by polishing the ends to a flat finish using a 6 $\mu$m Buehler diamond film. The pieces are subsequently washed in ultrasonic baths of acetone and isopropanol, for half an hour in each solvent. The pieces are dried in a hot plate at 150°C during 5-10 minutes to remove the solvents.

The clean piece is installed in the laser, and a small square mark (~400 $\mu$m by ~400 $\mu$m) is etched on one of the flat ends. This square mark is concentric with the cylinder, and serves as an alignment mark later in the process. The edges of the marked side of the cylinder are sanded off using 2500 grit sandpaper and 6 $\mu$m Buehler film, leaving the end of the piece with a ~1.6 mm diameter by 2.3 mm long cylinder. The piece is washed again in solvents and dried before the machining of the emitter structure.

### 5.2.2 Laser Micromachining Instrument

The laser facility in the Space Propulsion Laboratory consists of a KrF excimer laser, a set of optics to shape, direct and focus the beam, and a micropositioning stage for the sample. The system, shown in Figure 5-2, was custom made by Photomachining Inc. of New Hampshire.

The KrF laser produces a 248 nm beam, with a 17 ns pulse at a frequency between 1 and 300 pulses/s. The laser pulse peak energy can be varied between 200 and 300 mJ per pulse. The beam is guided by a set of mirrors and transfer optics towards the sample. The path of the beam is illustrated with the dashed line in Figure 5-2(a). First, the beam passes through a collimator before being masked by a reticle, as depicted in Figure 5-2(b). The available reticles are circular apertures of 0.017", 0.0325", 0.052", 0.078" and 0.106" diameter. The masked beam is then reflected upwards,
Figure 5-2: Laser Micromachining Setup: (a) Optical Bench with guiding optics and sample stage, dashed line indicates beam path (b) Reticle location (c) Imaging lens and sample stage. Note the sample stage is in the loading position in this image, and the sample is moved underneath the lens for machining.
towards mirrors mounted on a vertical breadboard that guide the beam towards the imaging lens, which is placed directly above the sample (see Figure 5-2(c)). The imaging lens is a 44 mm diameter spherical lens with a focal length of 100 mm.

The location of the breadboard mirrors can be adjusted to change the beam demagnification and beam fluence (energy per pulse per unit area, J·m⁻²) on the sample. The demagnification, \( D \), is given by

\[
D = \frac{\delta_1}{\delta_2} = \frac{O}{I}
\]  
(5.1)

where \( \delta_1 \) and \( \delta_2 \) are the object and image size, respectively, \( O \) is the distance between the object (the reticle) and the lens, and \( I \) is the distance between the lens and the image, as shown in Figure 5-3. The fluence on the sample, \( F_1 \), is also modified by changing \( O \), since \( F_1 \) depends on the demagnification as

\[
F_1 = F_0 D^2 (1 - L_f)
\]  
(5.2)

Here, \( F_0 \) is the fluence of the beam before the lens, which is fixed by the reticle mask and the laser energy, and \( L_f \) is the percent energy loss through the lens (about 5%, although the loss may increase over time due to wear in the mirrors [93]). For this laser setup, \( D \) can take values between 10 and 25.

The last component of the system is the micropositioning stage. A pattern is created in the material by rastering the target under the fixed laser beam. This motion table consists of three linear stages to adjust the \( x, y, \) and \( z \) position of the sample, as well as a rotary stage. It is important to find the focal height of the beam with a sacrificial substrate (usually kapton) before patterning any sample, and then to place the surface of the sample at this height using the \( z \) stage.
The detailed sample preparation and stage calibration process is described in the tool manual.

To pattern a carbon xerogel tip, adequate laser operating parameters must be chosen. The parameters that can be varied are the beam energy, the pulse repetition rate, the reticle mask, the demagnification, and the stage velocity. In addition to an adequate set of laser parameters, a writing pattern (commands for movement of the sample stage) is required. To produce the emitters used in this thesis, the following parameters were used: energy of 200 mJ, a repetition rate of 200 Hz, the 0.052" reticle, \( D = 25.2 \), a stage velocity of 500 \( \mu \text{m/s} \), and a set of hexagonal lines to cut material selectively around the center of the carbon tip. Section 5.2.3 justifies the selection of this laser operating conditions and explains in detail the design of the writing pattern.

5.2.3 Selection of Laser Operating Conditions

The fabrication of carbon xerogel tips was done for a fixed laser energy of 200 mJ and repetition rate of 200 pulses/s, which are the default values of the tool. For the tip fabrication experiments reported in this thesis, the laser demagnification was kept fixed at 25.2.\(^1\) Given these fixed parameters, a stage speed must be chosen, then a reticle must be selected for the given stage speed, and then a number of tests are performed to identify a suitable movement pattern for the stage.

The stage speed was set to 500 \( \mu \text{m/s} \), or a spacing between spots of 2.5 \( \mu \text{m} \). Note that the repetition rate and stage velocity can be interchangeably varied, as what ultimately matters is the spacing between laser spots. This stage speed was selected after a series of experiments where a three line test pattern was produced. The test pattern dimensions are shown in Figure 5-4. The stage speed was varied between 500, 1000 and 2000 \( \mu \text{m/s} \) with the 0.017" and 0.0325" reticles. The resulting lines in the carbon xerogel are inspected with a scanning electron microscope, as shown in Figure 5-5. Ideally, adjacent laser spots should overlap in order to produce continuous lines in the carbon xerogel, and thus guarantee that feature edges will be smooth. The line edge roughness is the smallest for the 500 \( \mu \text{m/s} \) case.

\(^1\)It is possible that a different demagnification might be required to reproduce the results due to some alignment issues encountered after the fabrication of emitters was completed- this is discussed at the end of this section.
Figure 5-4: Test Pattern Dimensions

Figure 5-5: Comparison of different reticles and stage speed etching effects on the carbon xerogel. The red arrows in panel (a) show the defects in the lines caused by the acceleration of the stage at the beginning of each line, which are present for all panels.
The 0.052" reticle was selected for patterning of the emitter tips. The 0.078" reticle was also used with encouraging results. To choose a reticle, the test pattern is written into the carbon xerogel using the 0.017", 0.052", 0.078" and 0.106" diameter reticles, for a fixed stage speed of 500 \( \mu m/s \). The scanning electron micrographs of the resulting lines are shown in Figure 5-6. Figure 5-7 is a three dimensional map of the patterned carbon surface obtained with a Keyence optical microscope. The larger the reticle, the larger the beam spot in the sample, resulting in greater spot overlap. This results in wider and deeper cuts into the carbon. The approximate line widths and maximum line depths are given in Table 5.1. The line depth is obtained from the optical microscope image—due to artifacts in the image acquisition, the depth measurement is only a rough guideline. Note that the cuts with the 0.0325", 0.052" and 0.078" reticles leave the xerogel adjacent to the line unaffected, whereas there is significant redeposition in the surface of the xerogel adjacent to the line cut with the 0.106" reticle, as well as some breakage. Thus, to have an increased etching rate while maintaining the integrity of the material, the 0.052" and 0.078" reticles could be used.

![Figure 5-6: SEM images of test patterns on carbon xerogel created with different reticle masks. Note the bottom row figures have different scale bars.](image)
Figure 5-7: 3D reconstruction of the carbon surface patterned using different reticles. The top left, top right, bottom left and bottom right test patterns were created using the 0.0325", 0.052", 0.078" and 0.106" reticles, respectively.

<table>
<thead>
<tr>
<th>Reticle</th>
<th>Line Width [μm]</th>
<th>Max. Line Depth [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0325&quot;</td>
<td>37</td>
<td>26</td>
</tr>
<tr>
<td>0.052&quot;</td>
<td>56</td>
<td>40</td>
</tr>
<tr>
<td>0.078&quot;</td>
<td>84</td>
<td>60</td>
</tr>
<tr>
<td>0.106&quot;</td>
<td>103</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1: Line width and depth for tests of Figures 5-6 and 5-7

With the stage speed and laser reticle selected, a stage movement pattern must be designed and tested. Patterns of hexagonal lines were used to remove the material around the center of the carbon xerogel piece. The pattern may be repeated several times to remove additional material and increase the aspect ratio of the tip structure; the height of the sample may also be adjusted between passes, and we refer to the change in stage height as Δz.

The patterns used consist of a “main” material removal pattern and a set of sculpting lines. The main pattern consists of three sets of parallel lines spanning the area of a circle of radius R, placed a distance d apart from each other. The lines are placed at 0°, 60° and -60°. At the center of the pattern, a hexagon of apothem a is left unpatterned. Two of these patterns were tested, the first with \((R, a, d) = (850, 75, 25)\) μm and then with \((R, a, d) = (860, 60, 20)\) μm. These patterns are illustrated in Figure 5-8. The spacings between lines, of 25 and 20 μm, were chosen according to the etching results in a single line. Since the 0.052” reticle creates lines slightly wider than 50 μm,
adjacent lines should overlap when placed at or less than 25 μm apart. The apothems were chosen so that some material would be left behind in the center of the pattern.

The main pattern usually results in structures several tens of micrometers thicker than the target design, and so “sculpting” lines are introduced in the pattern. These sculpting lines are executed at the end of each pass, once the main pattern removes the bulk of the material surrounding the center. Figure 5-9 shows two examples of the sculpting lines tested to form the tips. Table 5.2 summarizes the different combinations of main patterns and sculpting lines that were tested to form tip structures.

Two precautions were taken when programming the movement of the sample stage. First, the pattern is programmed so that the lines are etched in a boustrophedon, i.e., the laser travels in opposite directions on alternate lines, to minimize the cutting time. If the laser were to cut all lines in the same direction, the patterning time would be approximately doubled due to the travel time from the end of one line to the beginning of the next one. With the boustrophedon pattern, a pass of the \((R, a, d) = (850, 75, 25) \, \mu m\) pattern takes 15 minutes, and the \((860, 60, 20) \, \mu m\) pattern requires 20 minutes per pass. The second precaution is that all laser lines begin cutting on the edge of the pattern. This precaution was implemented since the laser stage has some acceleration artifacts, and the beginning of the lines are cut at a slightly slower rate than the rest of the lines (see for instance Figure 5-6). This is specially important for the lines in the center of the pattern, which should end at the edge of the hexagon.

Figure 5-8: Cutting pattern geometries, where the origin is defined as the center of the carbon piece to be etched.
The first sharpening experiments were performed with the \((R, a, d) = (850,75,25) \mu m\) main pattern. Table 5.3 summarizes the results of the resulting structures after using schemes P1 and P2. Pattern P1, with the main pattern \((R, a, d) = (850,75,25) \mu m\) and no sculpting lines, was tested first. The pattern was repeated three times without changing the \(z\) position of the stage \((\Delta z = 0 \mu m)\). The result is a carbon xerogel hexagonal structure, 408 \(\mu m\) tall and with an apothem of approximately 56 \(\mu m\), as measured with an optical microscope. Since this pillar is much thicker than the target structure, sculpting lines were added to the design. Scheme P2, with sculpting lines 56 \(\mu m\) away from the pattern center, helps to reduce the width of the hexagonal pillar from 56 \(\mu m\) to approximately 20 \(\mu m\). Increasing the number of P2 passes from three to four increases the height of the tip structure but does not result in any significant additional sharpening. Note that changing \(\Delta z\) by as little as 1 \(\mu m\) between passes molds the tip into a spherical cap with a radius of curvature closer to the target.
<table>
<thead>
<tr>
<th>Pattern</th>
<th>Resulting structure</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1, 3 passes, $\Delta z=0 , \mu m$</td>
<td>$h = 408 , \mu m$</td>
<td>Apothem $= 56 , \mu m$</td>
</tr>
</tbody>
</table>
| P2, 3 passes, $\Delta z=0 \, \mu m$ | $h = 418 \, \mu m$ | $R_e \approx 21 \, \mu m$ | • Blunt tip  
• $R_e$ too large |
| P2, 3 passes, $\Delta z=0 \, \mu m$ | $h = 408 \, \mu m$ | $R_e \approx 18 \, \mu m$ | • Blunt tip  
• $R_e$ too large  
Sculpting lines at 56 $\mu m$ help reduce size of structure, but structure is still blunt. |
| P2, 4 passes, $\Delta z=0 \, \mu m$ | $h = 480 \, \mu m$ | $R_e \approx 17 \, \mu m$ | • Blunt tip  
• $R_e$ too large  
Additional passes of scheme P2 increase structure height but do not result in additional sharpening. |
| P2, 4 passes, $\Delta z=1 \, \mu m$ | $h = 480 \, \mu m$ | $R_e \approx 11 \, \mu m$ | • Rounded tip  
• $R_e$ is 1 $\mu m$ larger than target  
Adjusting $\Delta z$ in between passes helps with tip rounding and reduction of the apex size. |

Table 5.3: Laser patterning results for different patterning strategies, using a main pattern of $(850,75,25) \, \mu m$ and sculpting lines at $56 \, \mu m$. 

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Different sculpting schemes were tested next to reduce the radius of curvature of the resulting structure. These experiments are summarized in Table 5.4. Scheme P3, with sharpening lines at 53 \( \mu \text{m} \) from the center, results in a tip structure of 17 \( \mu \text{m} \) radius if \( \Delta z = 0 \); however, these sharpening scheme is unreliable, since it might result in breakage of the tip structure. It is hypothesized that the breakage may be caused by the hasty removal of material on the thin pillar, and that gradual sharpening may help forming the rounded apex. However, the use of schemes P4 and P5, with gradual cuts using sculpting lines at 56, 55, 54, 53 \( \mu \text{m} \) and at 54, 52, 50 and 48 \( \mu \text{m} \) does not result in structures with \( R_c \) below 10 \( \mu \text{m} \). Adding extra sharpening lines even closer to the apex, as with scheme P6, results in breakage.

To achieve a structure with the desired radius of curvature, a main patterning scheme that results in an initially smaller hexagonal pillar should be used. Table 5.5 shows the results obtained using the \((R, a, d) = (860, 60, 20) \mu \text{m}\) pattern. The main pattern alone (scheme P7), used with the 0.052" reticle, results in a hexagonal pillar of apothem 46 \( \mu \text{m} \) after three passes. Thus, sharpening lines at 48, 46, 44 and 42 \( \mu \text{m} \) are included to remove the material to form a sharp tip; the stage height is adjusted by \( \Delta z = 1 \mu \text{m} \) to round the apex. This scheme (P8) results in tips with radii within the target, as shown in the table. Two test structures were produced repeatably with this patterning scheme. The \((R, a, d) = (860, 60, 20) \mu \text{m}\) pattern was used with the 0.078" reticle with encouraging results, as shown in the bottom row of the table. After three passes, a tip with an aspect ratio of 43 is obtained. Although the tip radius is not within the target, it is possible that reducing slightly the apothem of the main pattern, changing \( \Delta z \), or using sharpening lines with the 0.078" reticle, could result in tips with the desired radii and with improved aspect ratio.

Three device tips were prepared using the following process: three passes with \( \Delta z = 1 \mu \text{m} \), with the main pattern of \((R, a, d) = (860, 60, 20) \mu \text{m}\) and sharpening lines at 48, 46, 44 and 42 \( \mu \text{m} \) per pass. The device tips, denominated L1, L2 and L3, are shown in Figure 5-10. We note there is some variability in the tip geometry, with the radius of curvature varying between 5 and 11 \( \mu \text{m} \). Nonetheless, the results are within or very close to the target and these tips could be implemented as an ILIS emitter. Furthermore, the half-angle of these emitters is 7-8°, which should be favorable to increase the hydraulic impedance of the emitter. This work demonstrates it is possible to use a 248 nm laser for the creation of sub-10 \( \mu \text{m} \) \( R_c \) tips with heights above 300 \( \mu \text{m} \). Using additional pattern passes or a larger reticle could increase the aspect ratio of these structures. This fabrication method should be amenable for the reproducible fabrication of emitters for FIB applications, and can be exploited for the fabrication of emitter arrays for DRIE or space thrusters.
<table>
<thead>
<tr>
<th>Pattern</th>
<th>Resulting structure</th>
<th>Conclusion</th>
</tr>
</thead>
</table>
| P3, 3 passes, $\Delta z=0$ $\mu$m | $h = 412 \mu$m $R_c \approx 17 \mu$m | • Rounded tip  
• $R_c$ too large  
Closer sharpening lines, at 53 $\mu$m, do not necessarily result in smaller tip apices. |
| P3, 3 passes, $\Delta z=0$ $\mu$m | $h = 410 \mu$m $R_c \approx 18 \mu$m | • Tip truncated  
Pattern P3 is not repeatable and might result in tip breakage. |
| P4, 4 passes, $\Delta z=1$ $\mu$m | $h = 285 \mu$m $R_c \approx 13 \mu$m | • Rounded tip  
• $R_c$ too large  
Gradual cut with sharpening lines at 56, 55, 54 and 53 $\mu$m does not result in breakage, but apex is larger than target. |
| P5, 3 passes, $\Delta z=1$ $\mu$m | $h = 285 \mu$m $R_c \approx 13 \mu$m | • Rounded tip  
• $R_c$ too large  
Gradual cut with sharpening lines at 54, 52 and 50 and 48 $\mu$m does not result in breakage, but apex is larger than target. |
| P6, 3 passes, $\Delta z=1$ $\mu$m | $h = 410 \mu$m $R_c \approx 18 \mu$m | • Tip truncated  
Additional sharpening line at 44 $\mu$m from center results in tip breakage. |

Table 5.4: Laser patterning results using a main pattern of (850,75,25) $\mu$m and different sets of sculpting lines.
<table>
<thead>
<tr>
<th>Pattern</th>
<th>Resulting structure</th>
<th>Conclusion</th>
</tr>
</thead>
</table>
| P7, 3 passes, \(\Delta z=0\) \(\mu m\) | \(h = 346\) \(\mu m\) Apothem \(\approx 46\) \(\mu m\) | - Hexagonal pillar  
- Pillar width too large  
Main pattern \((860,60,20)\) requires sharpening lines. |
| P8, 3 passes, \(\Delta z=1\) \(\mu m\) | \(h = 318\) \(\mu m\) \(R_c \approx 6\) \(\mu m\) | - Rounded tip  
- \(R_c\) within target  
Three passes of scheme P8 with \(\Delta z = 1\) \(\mu m\) result in desired feature. |
| P8, 3 passes, \(\Delta z=1\) \(\mu m\) | \(h = 316\) \(\mu m\) \(R_c \approx 6\) \(\mu m\) | - Rounded tip  
- \(R_c\) within target  
Scheme P8 is repeatable. |
| P7, 3 passes, \(\Delta z=0\) \(\mu m\), Note we used the 0.078” reticle. | \(h = 608\) \(\mu m\) \(R_c \approx 14\) \(\mu m\) | - Rounded tip  
- \(R_c\) too large  
The use of a larger reticle doubles the height of the resulting tip and might be useful to produce higher AR structures. |

Table 5.5: Laser patterning results using a main pattern of \((860,60,20)\) \(\mu m\) and different sets of sculpting lines.
Figure 5-10: Laser-cut carbon xerogel emitters (a,d) Tip L1, height is 323 μm, $R_c \approx 6$ μm (b,e) Tip L2, height is 310 μm, $R_c \approx 5$ μm. Note the laser did not cut completely the carbon around the emitter, probably as the piece was originally not sufficiently sanded. (c,f) Tip L3, height is 323 μm, $R_c \approx 11$ μm

For further work in the laser micromachining of carbon into emitter tips, it will be necessary to monitor periodically the beam fluence on the sample using a power meter. After the test emitters shown in Figure 5-10 were fabricated, the laser gas chamber was refilled and the mirrors were realigned. The laser was then used to study alternate patterning schemes with the 0.078” reticle, but it was noted that the etching rates of the carbon were increased and that there was breakage of the tip structures. To understand the cause of this difference in etching, test patterns were written into the carbon using the 0.0325”, 0.052” and 0.078” reticle for demagnifications of 25.2, 20.84 and 19.7. The results of this experiment are shown in Figure 5-11. For the larger demagnifications (and hence larger beam fluences, recall equation 5.2), the xerogel shows signs of breakage outside of the pattern, specially for the larger reticle. Reducing $D$ mitigates this issue. This experiment suggests the existence of threshold dose (J/m²) above which the material breaks. During the pattern exploration and test tip fabrication, this breakage did not occur, likely due to aging of the laser gas, or to misalignment of the mirrors provoked by vibrations of the laser stage.
Figure 5-11: Test patterns on carbon xerogel, using the 0.0325”, 0.052” and 0.078” reticle for D=25.2, 20.84 and 19.7. Patterns made after laser refill and realignment.
5.3 Emitter Implementation and Characterization

Tip L3 was used for characterization experiments with the liquid EMI-BF$_4$. The tip was implemented with a teflon reservoir as described in Section 5.1. The teflon was machined in a lathe, taking caution to clean the cutting tools from any oil residues. The machined teflon piece was then washed in ultrasonic baths of acetone and isopropanol for 30 minutes each. The distal electrode consisted of a platinum wire, which was pressure fit through the back end of the teflon container.

The container and the emitter are filled with ionic liquid with previously degassed ionic liquid, using the following steps:

1. Using a micropipette, 5.3 $\mu$L of liquid were inserted into the reservoir section of the teflon container. This volume of liquid was estimated from optical microscope measurements of the teflon container.

2. A piece of fiber glass (VWR 691 Microfibre) is cut into a circle of approximately 3 mm diameter and then placed inside the teflon container, just above the reservoir. The fiber glass should aid the transport of the liquid from the reservoir into the carbon piece.

3. Using a micropipette, 16.6 $\mu$L of liquid are inserted into the teflon container. This is the volume of liquid that should fill the porous carbon volume, which was estimated from optical microscope measurements of the carbon piece.

4. The carbon piece is carefully inserted into the teflon container.

5. The assembly is left for an hour to allow wicking of the ionic liquid into the structure. At the end of this hour, it was noted that some excess ionic liquid (a few $\mu$L) was left around the emitter base, which we presume is liquid that was not fully inserted into the reservoir. This excess liquid was removed with the micropipette.

The emitter, in its teflon container, is then installed in a PEEK holder that is attached to a triaxial precision stage. The same extractor and shield assembly used in Chapter 4 are installed in front of the emitter, as shown in the photographs of Figure 5-12. The emitter is centered in front of the extractor aperture. The emitter-extractor setup is mounted in the vacuum chamber with the TOF spectrometer setup, and brought to pressures below 1 $\mu$Torr for firing tests.
5.3.1 Current Voltage Responses and Source Stability

The emitter, infused with the liquid EMI-BF$_4$, was operated in the positive and the negative polarities, using the same setup described in Chapter 4. Figure 5-13 shows an applied voltage signal and the corresponding current response. The positive voltage was increased from 1720 V to 2000 V in 20 V steps, and then decreased back to the lower voltage. An analogous ramp was performed in the negative mode. Figure 5-14 shows the current voltage curves obtained from the average voltages and currents for each of the steps in Figure 5-13.

The source has a startup voltage of approximately ± 1720 V. The source emits intermittently at voltages close to the start voltage. As the magnitude of the voltage is increased, the emission becomes stable. Current levels of 300 nA are observed once the source is stable, which are consistent with operation from a single emission site. As the voltage is increased, the current can by increased up to 550 nA before a discontinuity in the current is observed. This discontinuity is likely caused by the appearance of a second emission site. On the ramp down, this second emission site displays an extinction voltage lower than its onset voltage. On the negative ramp, a similar behavior is observed. Note that the current levels obtained in the positive and negative polarities are both of the same magnitude, which indicate that the negative emission originates from a liquid meniscus and not from electron emission. If a sharp, dry feature on the apex was emitting electrons, an exponential rise in current with the applied voltage would be observed in the negative mode.

The startup voltage indicates that the emission is coming from a pool of liquid spanning several pores on the apex of the emitter. If the liquid covered the whole apex of the tip (from SEM images, $R_e = 11 \, \mu m$), the startup voltage should be approximately 1200 V for a tip-extractor distance of 500 $\mu m$, according to the model in Chapter 2. The startup voltage of 1720 V is consistent with a wet feature of radius 5.5 $\mu m$ on the tip of the emitter.
Figure 5-13: (a) Voltage applied and (b) current response

Figure 5-14: Current-voltage response of laser micromachined carbon xerogel ILIS
The stability of the ion source was evaluated by monitoring the signal in the channeltron collector for voltages close to the startup voltage. Figure 5-15 shows the voltage applied and the corresponding current response for a test where the voltage was gradually increased from 1718 V to 1789 V. The current data in this figure are obtained by measuring the voltage drop across a resistor placed in series with the power supply. When the source is close to the startup voltage, the source emits at a stable current level for a few hundred milliseconds, and then drops to zero for several tens to hundred milliseconds before emission starts again. As the voltage is increased, the current pulses last longer and eventually the current becomes continuous. This current measurement, however, has a limited time resolution (data is acquired only every 30 ms by the computer interface), and might not capture faster instabilities in the emission process. Therefore, stability measurements are taken with the channeltron detector to verify that the current from the source indeed becomes stable. For each of the voltages shown in Figure 5-15, the current measured in the channeltron is monitored through the amplifier. The amplifier signal is recorded every 320 μs by the oscilloscope. The channeltron and amplifier have a response time of less than 100 ns, and thus any faster instabilities might be detected. Figure 5-16 shows samples of the channeltron signal acquired using the amplifier over 10 s samples. The signal level of the pulses remains constant as the voltage is increased, but the duty cycle of the pulses increases. The source instabilities seem to occur over the scale of several tens to hundred of milliseconds, which is consistent with the resistor measurement on the emitted current. Once the source reaches a higher operation voltage, the current in the channeltron is steady.

Figure 5-15: Response of tip L3 infused with EMI-BF$_4$ at voltages close to the startup voltage. (a) Voltage signal applied and (b) corresponding current response
Figure 5-16: Amplifier signal of current measured by the channeltron for the voltages applied in Figure 5-15. The data in this plot are taken every 320 µs.
The laser micromachined carbon xerogel ILIS displays some instabilities in the negative mode which are likely caused by electrochemical reactions in the distal electrode. The current magnitude in the negative mode starts to increase erratically after prolonged DC operation in the negative mode. These instabilities are more likely to occur at higher operation currents and for lower alternation frequencies between the positive and the negative mode. An example of these instabilities is shown in Figure 5-17. Here, an alternating voltage ramp is applied to the source. In the first ramp, source is alternated between the negative and the positive mode every 120 s, and for the second ramp the alternation period is reduced to 40 s. For the faster ramp, no instabilities are observed, not even at the higher currents associated to the two emission sites. However, for the longer ramp, the emission in the negative mode presents instabilities at the higher current associated to the second emission site. This behavior is very similar to the response from the mechanically polished carbon xerogel emitters discussed in Chapter 4, and is consistent with the charging of the distal contact to the electrochemical window limit. Even if a distal contact has been used, any gas generating reactions in the liquid surrounding the platinum electrode might affect the beam emission in the negative mode.

![Figure 5-17: Alternating voltage ramps and current response.](image)
Despite the presence of instabilities in the negative mode, the positive mode operation is repeatable. Figure 5-18 shows the current response of the source over several positive voltage ramps. In between the positive voltage ramps, the source is operated for about a minute in the negative mode. On each pass, the current of the source is practically the same for voltages between 1840 and 1960 V. For the lower voltages currents, there is some slight variation in the computed current due to the current drops caused by insufficient electrostatic traction.

5.3.2 Time-of-flight Spectrometry and Retarding Potential Analysis

TOF spectrometry was used to determine the composition of the particles in the beam. The setup is the same one described in Chapter 4, with the exception that the deflector plates were removed for these tests. Therefore, the TOF signals obtained with this emitter correspond to a fraction of the beam that was aligned with the channeltron detector.

Figure 5-19 shows the TOF signals obtained at different operation voltages. For these experiments, the gate was turned on at $t = 0 \mu s$. At $t = 0$, all the current is collected, and then the current drop is measured as function of time. The raw signals have a non-zero, constant offset.
in the current detected at the channeltron even when the beam has been deflected. This offset is presumed to be due to neutral particles in the beam, and so, to process the data, the neutral particle offset is removed and then the signal is normalized. The normalized signals show clear steps at about 13 and 22 μs, which correspond to monomers and dimers in the beam (the exact arrival time varies for each operation voltage, with faster particle arrivals for the higher operation voltages). The signal drops from 4 % to the noise level between 33 μs (the trimer arrival, although the step is not clear) and about 55 μs. This small signal may correspond to clusters of ions with degrees of solvation between 4 and 9.

Figure 5-19: TOF profiles for laser-micromachined carbon xerogel emitter operating with EMI-BF₄. The legend indicated the value of $V_{app}$ for each curve. At 1981 V, the source has 2 emission sites.
The beam energy distribution was characterized through retarding potential analysis (RPA). The RPA setup is illustrated in Figure 5-20. In these experiments, the beam is fired towards a Faraday cup placed behind a set of retarding grids. If the bias of the retarding grids, \( V_{RP} \), exceeds the energy of the particle in the beam, the particle cannot reach the collector. Therefore, by varying the retarding potential and measuring the current arriving to the Faraday cup, it is possible to obtain the beam energy distribution.

![Figure 5-20: Retarding Potential Analysis setup](image)

The instrument consists of seven grids followed by a Faraday cup. The first grid is a 90% transparent tungsten mesh, which is grounded and located approximately 25 mm downstream from the extractor. The next five grids are the retarding grids, which consist of 76 \( \mu \text{m} \) diameter parallel tungsten wires, spaced 0.76 mm apart, with a 90% transparency for each grid. The voltage applied to the grids (\( V_{RP} \)) is supplied by a Matsusada AMS-5B6 bipolar power supply controlled by an Agilent 33220A signal generator. \( V_{RP} \) is monitored directly with a 100:1 high voltage probe connected to the oscilloscope. The last grid before the Faraday cup is a tungsten mesh biased to a potential \( V_{SE} \), set in our experiments to -25 V. The function of this last grid is to suppress spurious current signals due to secondary electron emission from the Faraday cup. The Faraday cup is connected to a current amplifier (Keithley 428, gain set to 1E6), whose signal is recorded in an oscilloscope.

To perform RPA experiments, the source is held at a constant voltage, and a high voltage triangular wave, varying between 0 and a voltage of slightly greater magnitude than \( V_{app} \), is applied to the retarding grids, at a period of 10 s. The current signal from the Faraday cup is processed using a low pass filter and a sorting algorithm. The signals are then normalized to the maximum signal detected in the collector. The results from the experiments at different operation voltages of the source are shown in Figure 5-21.
The results from Figure 5-21 are a coarse measurement of the beam energy distribution, as there are several artifacts that can be attributed to the instrument. First, for retarding potentials of about $0.05V_{app}$, an increase in the current collected is detected, probably due to a focusing effect from the retarding grids. Furthermore, the instrument introduces an artificial spread in the energies detected due to geometrical effects. An ion with energy $qV_0$ should ideally be stopped by a potential barrier $V_{RP} = V_0$. However, an ion of energy $V_0$ coming at an angle $\theta$ with respect to the optical axis will be deflected by a potential $V_{RP} = V_0 \cos^2 \theta$. Then, since the RPA instrument is capturing the whole beam, the current drops corresponding to monochromatic ion populations will have an artificial spreading. For instance, in Figure 5-21, there is a current drop close to the applied potential that likely corresponds to the ions that have been fully accelerated, but this drop occurs over a significant range of voltages. Finally, in the negative mode, a spike in the RPA signal is seen after the artificial step at $0.05V_{app}$. This spike is an artifact of the secondary electron suppression grid, since it is not observed when $V_{bias} = 0$ V. This artificial spike is observed in the experiments with the carbon xerogel ILIS as well as with externally wetted emitters being studied with the same instrument\(^2\).

\(^2\)C. Miller, personal communication
Table 5.6: Kinetic energy fractions after fragmentation for EMI-BF$_4$ in the field-free region, $V_b = 0$

<table>
<thead>
<tr>
<th>$n \rightarrow m$</th>
<th>Positive Mode</th>
<th>Negative Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 $\rightarrow$ 1</td>
<td>0.36</td>
<td>0.3</td>
</tr>
<tr>
<td>3 $\rightarrow$ 1</td>
<td>0.218</td>
<td>0.18</td>
</tr>
<tr>
<td>3 $\rightarrow$ 2</td>
<td>0.609</td>
<td>0.59</td>
</tr>
<tr>
<td>4 $\rightarrow$ 1</td>
<td>0.157</td>
<td>0.127</td>
</tr>
<tr>
<td>4 $\rightarrow$ 2</td>
<td>0.438</td>
<td>0.418</td>
</tr>
<tr>
<td>4 $\rightarrow$ 3</td>
<td>0.72</td>
<td>0.709</td>
</tr>
<tr>
<td>5 $\rightarrow$ 1</td>
<td>0.122</td>
<td>0.099</td>
</tr>
<tr>
<td>5 $\rightarrow$ 2</td>
<td>0.34</td>
<td>0.324</td>
</tr>
<tr>
<td>5 $\rightarrow$ 3</td>
<td>0.56</td>
<td>0.549</td>
</tr>
<tr>
<td>5 $\rightarrow$ 4</td>
<td>0.78</td>
<td>0.774</td>
</tr>
</tbody>
</table>

Taking into account these artifacts, it is possible discern some of the physics of the ion beam from the RPA data. As well as the current drop due to the ions coming close to the full accelerated potential, there are signatures that indicate the fragmentation of solvated ions in the beam. As mentioned in Chapter 2, these fragmentation events have been observed in ILIS [66, 30]. The energy of a fragmented ion is a fraction of the kinetic energy of the parent ion, with an extra contribution if the break-up occurred in a region of non-zero potential. Recall that if an ion with degree of solvation $n$ and mass $m_n$ breaks into a neutral and an ion with degree of solvation $m$ ($m < n$) and mass $m_m$, at a region with potential $V_b$ (such as the region between the emitter and the extractor, where the potential varies from $V_{app}$ to ground), the final kinetic energy of the ion resulting from breakup will be

$$K_m = qV_b + \frac{m_m}{m_n} q |V_{app}-V_b|.$$  \hspace{1cm} (5.3)

Thus, a fragmented ion will be stopped at a potential $V_{RP} = K_m/q$. In the figure, distinct current drops can be observed at $V_{RP} \approx 0.36V_{app}$ and $V_{RP} \approx 0.3V_{app}$ in the positive and the negative mode, respectively. These retarding potentials correspond to the fragmentation of dimers into monomers after the beam has been fully accelerated, as indicated by Table 5.6. There is a continuous current drop between the $2 \rightarrow 1$ retarding potential and the main current drop, which indicates that fragmentation is occurring in between the emitter and the extractor. The RPA signals show a particle population coming at low energies, between $0.1V_{app}$ and the $2 \rightarrow 1$ retarding potential. These signals may be caused by fragmentation of cluster ions (with 4-9 neutrals attached) into monomers. This would be consistent with the TOF results that show a small component of cluster ions in the beam.
5.4 Discussion

Laser micro-machining has been validated as a manufacturing technique to shape carbon xerogel emitters with tip radii of 10 μm or less. This technique should allow the production of emitter arrays for DRIE or propulsion applications, and allow the reproducible fabrication of emitters for FIB.

Stable emission has been obtained from a laser micromachined tip infused with the ionic liquid EMI-BF$_4$. The source emits stably currents between 300 and 500 nA; if the voltage is increased further, a second emission site is activated. The results of TOF and RPA experiments indicate that the emission consists mostly of monomers and dimers, and that a small fraction (< 5%) of the beam might be composed of cluster ions with greater degrees of solvation.

The emitter shows some instabilities after prolonged DC operation in the negative mode, which may be eliminated through the use of a high-surface area distal electrode instead of a platinum wire distal contact. Despite the instabilities in the negative mode, the positive mode operation is stable and reliable, and in the next chapter, this ion source is used to irradiate substrates and evaluate the potential of the carbon xerogel ILIS beam for surface modification.
Chapter 6

Substrate Irradiation by ILIS

ILIS are attractive for FIB and general material processing applications, such as deep reactive ion etching, due to the capability of modifying a surface with the ILIS beam. As mentioned in Chapter 1, there is a large selection of beam compositions thanks to the many available ionic liquids and the possibility of engineering new molten salts with the desired properties for individual applications. This chapter reports irradiation experiments performed with two types of ionic liquid ion sources. Section 6.1 describes irradiation experiments on silicon using the externally wetted tungsten ILIS configuration. The ILIS, using EMI-BF$_4$ and operating at 15 keV beam energy, is capable of etching silicon with enhanced sputtering yields thanks to the reactivity of the ions present in the beam. These results were published in 2010 in reference [88], and have motivated the continued research of ILIS for FIB. To evaluate the patterning potential of the carbon xerogel ILIS, the laser-micromachined emitter described in Chapter 5 has been also used for irradiation experiments, detailed in Section 6.2. The carbon xerogel ILIS operating at energies between 2 and 7 keV is capable of etching gold, silicon and GaN. The sputtering yields on these materials at these irradiation conditions are calculated.

6.1 Irradiation of silicon with externally wetted W ILIS

The patterning capabilities of externally wetted W ILIS were studied with a series of experiments in CNRS-LPN, in Marcoussis, France. Externally wetted tungsten ILIS emitters were fabricated there, and implemented in an ion gun geometry to elevate the beam energy and perform irradiation experiments in silicon. Here, the basic setup is described and then the experiments performed are listed. The silicon substrates were etched after the irradiation tests. With the etched depth...
information, it is possible to calculate the sputtering yield of ILIS ions on silicon.

The experimental setup is shown in Figure 6-1. The setup consists of an ion gun, with the externally wetted W tip enclosed by an extractor electrode, and a sample holder placed 4 cm away from the gun exit. The W tip is installed in contact with a W loop reservoir. The tip and reservoir are loaded with ionic liquid by immersing in a crucible of EMI-BF$_4$ under high vacuum conditions. Once installed in the gun, the ILIS is operated and the target is irradiated for 30 minutes at constant current.

![Figure 6-1: Experimental setup for W ILIS irradiation tests. (a) SEM image of W ILIS tip used at LPN, with a loop reservoir (b) Diagram and (c) photograph of setup in vacuum chamber.](image)

The emitter and extractor are biased independently to increase the energy of the beam, $E_{beam}$. The voltage applied to the emitter, $V_{tip}$, is fixed, while the voltage applied to the extractor, $V_{extractor}$, is controlled by a power supply with voltage regulation to keep the emitted current constant. The emission voltage is given by $V_{emission} = V_{tip} - V_{extractor}$. These voltages are illustrated in Figure 6-2. The extractor power supply will respond to changes in the tip voltage to achieve the required emission voltage for the preset current. If the sample is at ground potential, the landing energy of the beam is $E_{beam} = eV_{tip}$, where $e$ is the elementary charge. For all substrate irradiation experiments, the sample is held at ground potential. It must be noted that the W ILIS is contacted directly for these experiments (distal contacts had not been introduced then) and operated in the positive DC mode only, and so electrochemical effects limit the lifetime of the source.

To determine the surface modifications caused by the ion exposure, copper grids (diameter 3 mm, 200 μm mesh) may be attached to the silicon surface. This copper grid acts as a mask whose pattern is transferred onto the sample with a 1:1 ratio. The silicon samples are monocrystalline, P-doped < 100 > type. After the exposure, the mask is removed and resulting pattern in the sample is profiled with a Dektak stylus profilometer to determine if the beam exposure results in deposition or etching of the substrate. The surface may also be studied with an atomic force microscope to
Figure 6-2: Definition of operation voltages for irradiation experiments.

evaluate the roughness quality of the irradiated surface.

Table 6.1 lists the experimental conditions used for the three irradiation experiments with the W ILIS. Note that the W ILIS was operated at 10 and 1 μA current levels, which are significantly higher than the typical currents of a few hundreds of nA typically obtained with the externally wetted configuration. This current levels are accessed by operating the W ILIS at an extraction voltage a few hundred volts higher than the startup voltage. The first two experiments were performed with one emitter, and a new W tip was used for the third experiment, since the first emitter was displaying decay signs after the two high current irradiations.

Table 6.1: List of Irradiation Experiments with W ILIS

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$V_{\text{tip}}$ [kV]</th>
<th>$V_{\text{ext}}$ [kV]</th>
<th>$V_{\text{sample}}$ [kV]</th>
<th>$E_{\text{beam}}$ [keV]</th>
<th>Time [min]</th>
<th>Current [μA]</th>
<th>Copper mask?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>15</td>
<td>12.5</td>
<td>0</td>
<td>15</td>
<td>30</td>
<td>10</td>
<td>No</td>
</tr>
<tr>
<td>Silicon</td>
<td>15</td>
<td>12.5 to 12</td>
<td>0</td>
<td>15</td>
<td>30</td>
<td>10</td>
<td>Yes</td>
</tr>
<tr>
<td>Silicon</td>
<td>15.09</td>
<td>13.5</td>
<td>0</td>
<td>7.01</td>
<td>30</td>
<td>1.05</td>
<td>Yes</td>
</tr>
</tbody>
</table>

In the first irradiation experiment, a bare silicon wafer was exposed with a beam energy of 15 keV and current of 10 μA for 30 minutes. A photograph of the silicon surface after irradiation is shown in Figure 6-3. A clear, symmetric beam impact of approximately 39 mm diameter can be distinguished on the surface. The beam divergence angle is estimated to be 24.5° from this impact.

A second wafer, covered with copper grids, was irradiated under similar conditions, in order to determine the nature of the beam impact observed in the first experiment. The extractor voltage varied from 12.5 kV to 12 kV from the beginning to the end of the test to sustain the 10 μA emission. A photograph of the wafer after beam exposure is shown in Figure 6-4. As in the first experiment, a clear beam impact can be distinguished. Upon removal of the copper grids, it was observed that the mask pattern was transferred cleanly onto the silicon substrate. By using a stylus profilometer, we measured 17±0.9 nm deep holes carved into the silicon target through
the mask, demonstrating that the ILIS irradiation is capable of etching silicon. The profilometer measurements were complemented with atomic force microscopy measurements in the tapping mode\textsuperscript{1}. A root mean square (rms) roughness of 0.33 nm was measured on a 100 μm\(^2\) sample of the etched surface. The native roughness of the masked surface is 0.32 nm, showing that the etching process leaves the surface with a roughness comparable to that of the native surface.

\textsuperscript{1}measurements performed by N. Gogneau of LPN-CNRS

A third irradiation experiment was performed at 1 μA emission current, with 15 keV beam energy for 30 minutes. A clear beam impact was observed after the experiment, and the beam half-angle was found to be approximately 20° for this emission current. The copper mask pattern was transferred into the silicon target, as shown by the optical microscope images of Figure 6-5. Profilometer measurements indicate that the silicon is etched by 24±5 nm on the areas exposed to the beam.
Figure 6-5: Results of 15 keV, 1 μA ILIS irradiation. (a) Optical microscope image of pattern transferred onto the silicon surface after the copper grid was removed. (b) Detail of the transferred structure, revealing transfer of submicron details from the copper grid. Figure taken from reference [88].

The sputtering yield (number of target atoms remove per incident ion) can be calculated from the measured etch depths and the beam spreading. The sputtering yield $Y$ is given by the ratio of atoms removed to the ion dose over a reference area, $Y = N_r/D_{ref}$. For this calculation, we use a reference area of $A_r = 1 \mu m^2$. The number of removed atoms is given by

$$N_r = \frac{n_c A R \rho N_A}{A} \quad (6.1)$$

where $n_c$ is the number of atoms in the crystal cell (1 for elemental samples), $d$ is the etched depth, $\rho$ is the target density (2329 kg·m$^{-3}$ for Si), $N_A$ is Avogadro’s number, and $A$ is the sum of the atomic masses of the atoms in the unit cell of the target (28 g/mol for Si).

The total ion dose on the sample is $It/e$, where $I$ is the irradiation current, $t$ the irradiation time, and $e$ the elementary charge. To calculate the ion dose over the reference area, we assume a parabolic current density distribution over the impact. This parabolic distribution has been observed with externally wetted W ILIS sources [87, 68]. For the 10 μA experiment, the dose per unit area at the center of the impact is estimated to be $1.34 \cdot 10^8$ ions/μm$^2$ (±5%). For the 1 μA test, the dose is $3.38 \cdot 10^7$ ions/μm$^2$ (±5%). Then, the sputtering yield is calculated to be 6 silicon atoms removed per incident ion for the 10 μA test, and 35 for the 1 μA experiment. This sputtering yields are significantly higher than those caused by pure mechanical sputtering. For instance, the sputtering yield of Si for irradiation with Ga$^+$ at 30 keV beam energy is 2 [85]. There must be some chemical enhancement in the etching process.

To understand the mechanism of the etching process, the surface of the silicon irradiated at 10 μA without copper grids was studied by X-ray photoelectron spectroscopy.\footnote{Measurements performed by P. Jegou of the Laboratory of Chemistry of Surfaces and Interfaces of France’s CEA,} The XPS results
indicate the appearance of Si-C and Si-N bonds on the irradiated surface. The relative intensity of the B 1s to F 1s peaks is 1.5 instead of 4, indicating some removal of the fluorine species. It appears that the molecular ions in the beam fragment into radical species when they impact the surface with a high kinetic energy. Free radicals of C and N may react with the surface atoms, while fluorine radicals may create volatile species that enhance the etching rate.

These experiments demonstrate the capability of ILIS to etch silicon at enhanced rates thanks to the reactive ion species contained in the ion beam. This capability may be exploited to increase throughput in FIB applications, or that arrays of ILIS may be used as deep reactive ion etchers.

6.2 Irradiation with carbon xerogel sources

The laser-machined carbon xerogel emitter tested in Chapter 5 has been implemented at MIT in an ion gun geometry traditionally used in FIB, provided by LPN-CNRS. The beam energy can be raised to up to 25 keV with this configuration, and so we use this platform to test the irradiation effects from the carbon xerogel ILIS. These experiments are performed at variable beam energies and on different substrates, including sputtered gold on silicon, silicon and gallium nitride. The end goal is to determine the deposition or etching rates in the target, and to assess the surface modification capabilities of the novel carbon xerogel configuration.

Section 6.2.1 describes the ion gun setup and the voltage arrangements used to increase the beam energy in these experiments. Section 6.2.2 describes the results of the irradiation experiments.

6.2.1 Experimental Setup and Test Description

In the irradiation experiments, the ion gun with the carbon xerogel ILIS is fired towards a target covered with a copper mask. The target is irradiated for several minutes while keeping the current constant with voltage regulation. The shadow mask is removed and resulting pattern in the sample is profiled to determine if the beam exposure results in deposition or etching of the substrate. Figure 6-6 shows a diagram and a photograph of the experimental setup.

The ion gun consists of a vacuum feedthrough with an emitter holder, around which an extractor electrode is installed. The extractor electrode used for these tests is a 1.45 mm diameter aperture, placed approximately 2 mm away from the carbon xerogel tip. The emitter is aligned visually in the center of the extractor aperture. The ion gun is installed in the test vacuum chamber pointing and analyzed by Dr. Stephane Guilet of LPN-CNRS
Figure 6-6: (a) Diagram of the ion gun setup for irradiation experiments with carbon xerogel ILIS (b) Photograph of setup in vacuum chamber. Note the target holder is rotated and is in the inspection position. For the beam exposure, the target holder is rotated so that the samples are placed normal to the ion gun.

downwards, towards a plate holding several irradiation targets. The target holder holds up to four samples. The holder is mounted in a manual translational stage, so that the targets might be irradiated consecutively without breaking vacuum. The target holder can also be rotated in front of the ion gun. In the figure, the target holder is at the inspection position, but for irradiation tests, the targets are placed normal to the ion gun. The target holder is placed either 10.7 or 23 mm away from the ILIS tip.

As with the W ILIS experiments, the emitter and extractor are biased independently to increase the energy of the beam, $E_{beam}$. All experiments are restricted to the positive mode operation of the ILIS (due to the electrochemistry effects in the negative mode, discussed in Chapter 5). The voltage applied to the emitter's distal electrode, $V_{tip}$, is controlled by a power supply with voltage regulation to keep the emitted current constant. The voltage applied to the extractor is $V_{extractor}$.
Table 6.2: List of power supplies and other instrumentation

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Power Supply</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{\text{tip}}$</td>
<td>FUG HCP 8-4000</td>
<td>0-40 kV</td>
</tr>
<tr>
<td>$V_{\text{extractor}}$</td>
<td>Matsusada AMS-5B6 / Bertan 205B-10R</td>
<td>-5 to 5 kV / 0 to 10 kV, 1 kV steps</td>
</tr>
<tr>
<td>$V_{\text{sample}}$</td>
<td>Keithley 6517 Electrometer</td>
<td>-100 to 100 V</td>
</tr>
</tbody>
</table>

and the emission voltage is given by $V_{\text{emission}} = V_{\text{tip}} - V_{\text{extractor}}$. These voltages are the same ones illustrated in Figure 6-2. Table 6.2 lists the power supply models used in these experiments. If the extractor potential is increased, the tip’s power supply will provide more voltage to achieve the required emission voltage for the preset current. If the sample is at ground potential, the landing energy of the beam is $E_{\text{beam}} = eV_{\text{tip}}$, where $e$ is the elementary charge. For all substrate irradiation experiments, the sample is held at ground potential.

The setup includes two magnets placed beneath the target holder. Originally, the setup did not have any magnets in the assembly. However, when it was attempted to increase $V_{\text{extractor}}$ above 1.2 kV, the emission of the source became unstable, with variations in the power supply voltage of the order of ±50 V when the current is set to 0.34 μA. This instability occurred only if the target was placed directly in front of the ion gun. With the target holder placed away from the gun, it was possible to set $V_{\text{extractor}} = 5$ kV, giving $V_{\text{tip}} = 6.98$ kV for an emission current of 0.34 μA. The instability, therefore, must be caused by the target holder, and it is hypothesized that secondary electrons produced in the target may be affecting the emission process. For the lower values of $V_{\text{tip}}$ (lowest landing energies), the electric field may not be sufficient to draw secondary electrons towards the tip; however, as $V_{\text{tip}}$ is increased, the electric field increases, and the secondary electrons may be drawn by the voltage gradient from the target towards the extractor and the tip, disturbing the emission process. It is possible to trap some of these secondary electrons using a small magnetic field, and so two magnets are attached the backside of the target holder. The magnetic field on the target is ~ 80 Gauss. The sample holder was initially placed 11.6 mm away from the emitter tip, but it was moved farther away from the tip, to a tip-target distance of 23 mm, in order to reduce the electric field that attracts the electrons towards the tip. With the magnets in place and the larger tip-target distance, it is possible to obtain stable operation at increased beam energies.

The target holder is connected to a Keithley 6517 electrometer, which is used to monitor the current on the target. This current measurement includes the impinging ion current as well as the current caused by secondary electron emission. The electrometer may be used to apply a small potential to the target.
The targets selected for the irradiated experiments are sputtered gold on silicon, silicon and gallium nitride. The gold target consists of a 100 nm layer of gold on 10 nm of titanium, both sputter coated on a silicon surface. This substrate was chosen as the gold surface is relatively easy to sputter and should provide strong contrast [40]. The uncoated silicon samples are P-type (Boron) < 100 > single side polished wafers, provided by University Wafer. This silicon type is the same used for the irradiation experiments performed previously with externally wetted tungsten ILIS [88], and so it is tested again to compare the irradiation effects from the different ILIS configurations. The GaN samples consist of a 4 µm epitaxial layer of GaN grown on single side polished sapphire, also provided by University Wafer. GaN is a material with excellent thermal and mechanical stability [9], and it is of interest to assess if the ILIS beam containing reactive species might accelerate the etching of this "hard" material.

The mask used for irradiation consists of a 3 mm diameter copper grid, with a 150 µm square mesh, provided by SPI Supplies. The copper grid is attached to the sample with two or three drops of silver colloidal suspension (SPI Supplies). After irradiation, the copper grid is removed. The surface protected by the copper grid serves as a control to evaluate the effects of irradiation on the exposed areas. The patterned surface is scanned with a profilometer (Veeco Dektak 150) or with an atomic force microscope (AFM, Agilent Instruments 5500) to measure the effects of irradiation.

### 6.2.2 Experimental Results

Table 6.3 summarizes the irradiation experiments performed with the carbon xerogel ILIS. The emission voltage of the ILIS is approximately 2 kV for the range of emission currents for which the source is stable. The extractor is operated at 0, 1.5, and 5 kV in order to obtain beam energies of approximately 2, 3.5, and 7 keV. The samples are irradiated for 20 to 30 minutes while holding the emission current constant at 350 or 450 nA. All experiments are performed at room temperature and at pressures below $1 \cdot 10^{-7}$ Torr.

In all experiments, after removal of the copper mask, a pattern is imprinted on the target material. All resulting patterns, except for the GaN irradiated at 2.06 keV, were characterized with a stylus profilometer or the AFM. All experiments display etching of the material, and in the case of gold irradiated at 2.06 keV, some deposition is observed at the center of the impact. The optical microscope images and profilometer results for the gold are presented first. We then discuss the results for silicon and finally for the gallium nitride tests. The experimental observations are followed by a calculation of the sputtering yields and a discussion of the ILIS performance.
Irradiation of Gold Substrates

A total of four irradiations were performed on gold substrates using the carbon ILIS, two at 2.06 keV beam energy, one at 3.78 keV, and the last one at 7.05 keV. The first irradiation at 2.06 keV was done with the shorter tip-target distance of 10.7 mm and no magnets in the setup. The other three experiments were conducted with the tip-target distance of 23.3 mm and using magnets to suppress secondary electron emission from the target.

For the first experiment at 2.06 keV, the gold substrate covered with a copper mask was irradiated with a beam current of 0.34 μA for 20 minutes, with the sample placed 10.7 mm away from the tip. For this experiment, the Bertan power supply was used to provide $V_{\text{extractor}}$. This extractor power supply was initially set to 0 kV, but eventually the display read 0.013 kV during emission. This voltage difference was probably caused by secondary electrons impinging upon the extractor. The tip voltage did not vary during the experiment, indicating a stable emission process. After the experiment, a clear mark was discernible in the gold substrate, as shown in Figure 6-7. As seen in the microscope images, the grid pattern left on the gold has a central area that appears to consist of a deposited film, surrounded by an etched area. The thickness of this center section has not been measured. The profile of the outer section shows the periodic pattern of the copper grid. The scan also reveals some curvature caused both by the native curvature of the sample and by leveling artifacts of the profilometer software. There are several sharp peaks in the profile, present both in the irradiated and unirradiated areas, which are probably caused by silver glue particulate contamination upon removal of the copper grid. The profile shows that trenches of a few nanometers were etched into the gold outside of this center area.

The high energy experiments were attempted next, and due to the issues with secondary electron emission described in Section 6.2.2, the magnets and longer tip-target distance (23.3 mm) were
introduced into the setup. The Matsusada AMS-5B6 power supply is used to modify the extractor voltage. Since the setup was altered, the 2.06 keV irradiation was performed again with the modified setup, at a current of 0.45 μA for 30 minutes. The results of this 2.06 keV irradiation are shown in Figure 6-8. There are two distinct features in the exposed gold surface. First, the copper grid pattern was transferred to the substrate, with the exposed surface being etched. The profilometer scan shows that depth etched into the gold is approximately 10.4±2.3 nm. Second, there is a distinct circular feature of approximately 1.9 mm diameter towards the side of the silicon grid. Profilometer measurements indicate that this circular feature is deposited material roughly 10 to 20 nm thick.

It is hypothesized that the deposit observed at this irradiation energy is caused by low energy neutral particles present in the beam. As discussed in chapter 5, the retarding potential analysis shows the fragmentation of ions in the acceleration zone in between the emitter and the extractor. If an ion breaks into a neutral and another ion soon after emission, the resulting neutral is not accelerated further by the extraction potential. Thus, the ion beam contains neutral particles with energies as low as a few electron volts. Direct visualization experiments performed on externally wetted tungsten sources demonstrate that the neutral particles are concentrated at the center of the ion beam [91]. Thus, it is possible that the low energy neutral particles concentrated in the center of the beam may be deposited onto the sample. This deposition competes with the mechanical
Figure 6-8: Irradiation results in gold at 2.06 keV, at 0.45 μA and a tip-target distance of 23.3 mm
(a) Sample photograph (b) Optical microscope image of features created into the sample after
removing the copper grid. The mask pattern is transferred, and a clear, circular deposit is formed
close to the grid shadow. (c) Profilometer results. Scan performed along arrow direction in image
(b), just outside the center section of the impact.

and chemical sputtering caused by the high energy ions in the beam, and the deposition disappears
at the edge of the impact, where the neutral particle population is smaller. Furthermore, the
deposition constitutes a small fraction of the total flow rate obtained from the ion source. From
the volume of the deposit and irradiation time, we estimate a deposition flow rate of 3.15 fL/s,
whereas the flow rate from the ion source is of the order of 850 fL/s. This small fraction could be
linked to the fraction of low-energy neutrals in the beam.

Higher energy irradiations on gold, at beam energies of 3.78 keV and 7.06 keV, were also
performed with the carbon xerogel ILIS. The beam current was held constant at 450 nA for half an
hour. Figure 6-9 shows the results from these experiments. In both cases, the copper mask pattern
was cleanly transferred onto the copper substrate. As the energy of the beam is increased, the
optical contrast on the pattern increases. The profilometer scans have the periodic pattern of the
copper grid. Large spikes are again observed, but these are attributed to particle contamination
from the silver glue used to attach the grids. The profilometer data indicate that the gold was
etched 17.6±2 nm for the 3.78 keV irradiation, and 41.1±5.7 nm for the 7.06 keV experiment. For
these experiments, no deposition was detected on the samples.
Figure 6-9: Irradiation results in gold at different energies. (a,d) Optical microscope image of imprinted patterns, the black arrows indicate the location and direction of profilometer scan. (b,e) Optical microscope image of pattern details. (c,f) Profilometer results. In image (c), between about 1400 µm and 2200 µm in the horizontal direction, the stylus tip is going over an unirradiated area, thus giving a roughly constant signal before returning to the periodic section pattern again.
Irradiation of Silicon Substrates

Silicon samples were irradiated at 2.06 keV, 3.61 keV and 7.01 keV using the carbon xerogel ILIS. For these irradiation experiments, the tip target distance was set to 23.3 mm and magnets were used to suppress secondary electron emission from the target. The emission current was held constant at 450 nA for 30 minutes in each case.

The irradiation experiments all result in etching of the silicon samples. The optical images and profilometer scans of the patterns on the silicon after the removal of the copper mask are shown in Figure 6-10. The contrast between the irradiated and non-irradiated surfaces is stronger with increasing beam energy. The profilometer scans all show the periodic pattern due to the copper grid, and show that the silicon is etched for the three irradiation energies. The average trench depth is 3±1.19 nm, 14.2±1.6 nm, and 26.5±1.4 nm for the 2.06, 3.61 keV and 7.01 keV irradiations, respectively. No additional features that could be linked to deposition are observed on the silicon surfaces.

A high resolution optical microscope image of the 7.01 keV test (Figure 6-11) shows the silicon surface in the edge between the covered and irradiated surfaces. The line edge roughness of the copper grid has been replicated with submicrometer accuracy.

Irradiation of Gallium Nitride Samples

Two irradiations were performed onto GaN samples, the first at 2.06 keV and the second at 3.57 keV. The beam current was held at 450 nA for half an hour in both cases. For both experiments, the silicon grid pattern was transferred onto the surface, as shown in Figure 6-12. The GaN samples show excellent optical contrast between the irradiated and unexposed areas, and the circular beam impact can be distinguished in the photographs. The copper mask was located towards the edge of the beam impact for these experiments. Only the 3.57 keV sample has been profiled, and this study was done with the atomic force microscope. The result of the AFM scan is shown in Figure 6-13. The yellow region in the image corresponds to the area that was masked by the copper grid, while the red section was exposed to the ILIS beam. There is a step between the surfaces, indicating that the exposed GaN was etched by 12±3.5 nm. The AFM reveals that the etched surface has an RMS roughness of 4 nm, whereas the native surface displays a roughness of 2 nm.
Figure 6-10: Irradiation results in silicon at different energies. (a,d,f) Optical microscope images of imprinted patterns. The black arrows indicate location and direction of profilometer scans. (b,e,h) Optical microscope image of pattern details. (c,f,g) Profilometer results.
Figure 6-11: Optical microscope image of imprinted pattern on silicon sample, with $E_{\text{beam}}=7.01$ keV. The top left area was covered by the copper mask.

Figure 6-12: Irradiation results in GaN at different energies. The energy is indicated in each figure. (a,d) Photographs of beam impact on GaN sample. (b,e) Optical microscope image of imprinted pattern after removal of copper mask. (c,f) Optical microscope image of pattern details.
Figure 6-13: AFM map of GaN surface- the yellow, higher surface is the GaN that was covered by the copper mask, while the red surface is the surface that was exposed to the ILIS beam. The white features are attributed to dust contamination.

**Determination of Sputtering yields**

With the knowledge of the etched depths on the samples, it is possible to calculate the sputtering yields of the materials under ILIS irradiation if the ion dose on the sample is known. To compute the ion dose, the beam profile and the beam half-angle are required. The ILIS beam is assumed to have a parabolic distribution, as determined by previous studies with externally wetted emitters [68, 87].

To obtain the beam spreading, the beam half-angle is measured at low energy, and a geometric scaling is used to obtain the beam half-angle at higher energies.

The beam half-angle was measured by scanning a 250 μm diameter, 44 mm long tungsten wire in front of the ion gun and measuring the current collected by the wire. The wire was placed approximately 21 mm away from the ILIS tip. Using this probe, the beam half-angle for the beam current of 450 nA and $E_0 = 2.04$ keV beam energy was measured to be approximately $\alpha_{E_0} = 20^\circ$.

To obtain the beam half-angle at higher energies, we assume that the additional electric field serves to accelerate the ions axially but does not alter their radial velocity, and so the beam half-angle at a beam energy $E$, $\alpha_E$, is related to the beam angle at $E_0$ as

$$\frac{\tan \alpha_E}{\tan \alpha_{E_0}} = \sqrt{\frac{E_0}{E}}$$  \hspace{1cm} (6.2)
For instance, the beam half-angle at 3.78 keV is 14.7°, and at 7.01 keV is 10.88°. With these beam angles, the doses on the sample can be computed. Since the copper grills were visually aligned beneath the ion gun, the exact location of the mask within the beam impact is unknown (at least for the Si and Au substrates). Thus, the dose is calculated in a 1 μm² reference area both at the center of the beam and at a location 1.5 mm from the edge of the beam. With the two dose values, it is possible to get a lower and an upper bound on the sputtering yields on the materials.

The sputtering yield is calculated using the equations defined in Section 6.1 with the adequate physical constants for each of the materials. The minimum possible sputtering yield is that of the center of the beam, and it may be more, up to the value calculated near the edge, if the copper mask was off-center. Table 6.4 summarizes the sputtering yields calculated for the different experiments, gold, Si and GaN.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>E_{beam} [keV]</th>
<th>Depth Etched [nm]</th>
<th>Center Dose [ions/μm²]</th>
<th>Edge Dose [ions/μm²]</th>
<th>Y_{center}</th>
<th>Y_{edge}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>2.06</td>
<td>10.5±2.3</td>
<td>4.70·10⁷</td>
<td>1.55·10⁸</td>
<td>13.28</td>
<td>40.3</td>
</tr>
<tr>
<td>Gold</td>
<td>3.78</td>
<td>17.6±2.1</td>
<td>9.49·10⁷</td>
<td>4.08·10⁸</td>
<td>10.99</td>
<td>25.52</td>
</tr>
<tr>
<td>Gold</td>
<td>7.06</td>
<td>41.1±5.74</td>
<td>1.61·10⁸</td>
<td>9.00·10⁷</td>
<td>15.11</td>
<td>27</td>
</tr>
<tr>
<td>Silicon</td>
<td>2.09</td>
<td>3.03±1.2</td>
<td>4.77·10⁷</td>
<td>1.58·10⁷</td>
<td>3.17</td>
<td>9.58</td>
</tr>
<tr>
<td>Silicon</td>
<td>3.61</td>
<td>14.17±1.7</td>
<td>8.24·10⁸</td>
<td>3.48·10⁷</td>
<td>8.61</td>
<td>20.4</td>
</tr>
<tr>
<td>Silicon</td>
<td>7.01</td>
<td>26.47±1.4</td>
<td>1.6·10⁸</td>
<td>8.91·10⁷</td>
<td>8.28</td>
<td>14.8</td>
</tr>
<tr>
<td>GaN</td>
<td>3.57</td>
<td>12±3.5</td>
<td>8.15·10⁴</td>
<td>3.4·10⁴</td>
<td>26.3</td>
<td>62.5</td>
</tr>
</tbody>
</table>

### 6.2.3 Discussion

The beam from the carbon xerogel ILIS has been used to etch silicon, gold and gallium nitride samples, with some deposition observed in gold at the lowest energy tested.

The sputtering yields observed in the three materials, with irradiation energies between 2 and 7 keV, are high compared to the sputtering yields obtained with gallium at higher energies. For reference, with Ga, the sputtering yields on Si at 10 and 30 keV are 2.22 and 2.72, respectively [64]. The sputtering yield of Ga on gold at 30 keV is 14.7 [85], and the sputtering yields of Ga on GaN are between 5 and 7 for irradiation energies between 14 and 70 keV [109]. The competitive sputtering yields of the ILIS beam on the three materials may be attributed to the reactive species contained in the beam.

The etching is thought to be a combination of mechanical sputtering with chemical effects. As the molecular ions arrive on the substrate, the kinetic energy of these ions causes the dislocation of surface atoms from the target, as well as the breakage of the chemical bonds in the incident
ion. The resulting free radicals may create new bonds on the sample surface. Some of the fluorine radicals may react with the sputtered particles to create volatile species that accelerate the material removal. Yoshida [133] has recently performed 5 keV irradiation experiments on Si using a silicon emitter ILIS with the ionic liquid EMI-BF$_4$. In Yoshida’s tests, a mass spectrometer detects SiF gases produced as the silicon sample is irradiated, confirming the role of fluorine in the reactive etching of Si by the ILIS beam.

The differences in deposition and sputter yields between the materials may be attributed to the different chemical interactions of each substrate with the ILIS beam. The fact that deposition is observed on the gold and not on the other substrates at the 2 keV energy may be due to the different reactivity of this relatively inert substrate with the incident beam.
Chapter 7

Conclusions

Ionic Liquid Ion Sources have been studied for their use in focused ion beams, space propulsion and material processing applications. The main contribution of this thesis is the design, construction and characterization of a carbon xerogel ILIS emitter aimed at overcoming the limitations posed by previous configurations of ILIS. This chapter summarizes the specific contributions of this thesis and proposes future venues for investigation.

7.1 Thesis Contributions

The thesis contributions are the following:

1. Using analytical models of the emitter hydraulic impedance and guidelines from previous literature, we have estimated porous substrates morphologies and target emitter dimensions to favor the pure ion regime with the liquid EMI-BF$_4$. It is estimated that pore sizes below 1 $\mu$m are required for PIR operation with this liquid.

2. Porous carbon based on resorcinol-formaldehyde xerogels has been introduced as an emitter substrate. The carbon xerogel can be shaped to the required micron-sized geometry through mechanical polishing.

3. Time-of-flight mass spectrometry has been used to verify that charged particle beams produced from the mechanically polished carbon xerogel source, infused with the ionic liquid EMI-BF$_4$, contain solvated ions exclusively. In the case of EMI-Im, mixed regime operation is observed.
4. Laser micro-machining has been validated as a manufacturing technique to shape carbon xerogel into emitters. This technique should allow the production of emitter arrays for DRIE or propulsion applications, and allow the reproducible fabrication of emitters for FIB.

5. Emission has been demonstrated from a laser micromachined tip infused with the ionic liquid EMI-BF$_4$. The results of TOF and RPA experiments indicate that the emission consists mostly of monomers and dimers, with a fraction of the beam composed of cluster ions.

6. The capability of ILIS to etch materials has been demonstrated for two ILIS configurations using the ionic liquid EMI-BF$_4$. In the case of externally wetted W ILIS, silicon etching with sputtering yields of 6 and 35 were observed for irradiation at 15 keV beam energy. The laser-micromachined carbon xerogel ILIS has been used to irradiate silicon, gold and GaN samples at beam energies between 2 and 7 keV, with etching observed in all three substrates at all energies tested. The reactivity of the ions in the beam enhances the etching process through the creation of volatile species that aid in material removal.

7.2 Suggestions for Future Work

Further experimental investigations are required to fully validate the carbon xerogel emitter for use in FIB and other applications. For instance, the carbon xerogel ILIS should be tested with high surface area carbon electrodes to verify stable operation in the negative mode. Once the source is implemented with an adequate distal electrode, the long-lifetime performance of the source can be evaluated in the positive and the negative mode through several hundred hour continuous runs. The carbon xerogel tip should also be tested in a FIB column to determine if the beam can be operated stably at the increased energies used in FIB, of the order of 20 keV.

There is room to explore more versions of the carbon xerogel ILIS. Many more ionic liquids can be tested in this configuration to assess if the pure ionic regime may be obtained. In this thesis, mixed-droplet regime operation was observed with the ionic liquid EMI-Im, but it may be possible to achieve the PIR with this liquid infused on a carbon tip if a carbon substrate with smaller pore sizes is used. For FIB in particular, it may be of interest to use ionic liquids that are less prone to fragmentation than the ionic liquid EMI-BF$_4$. The observed fragmentation in the beam may increase the chromatic aberration contribution of the lens to the probe size, and thus it is ideal to minimize the beam fragmentation if possible. As reactive etching has been demonstrated with
EMI-BF₄, it would be useful to study the patterning capabilities of ILIS using alternative reactive species, with ionic liquids such as BMI-I or EMI-Cl.

7.3 Prospects for an ILIS FIB and other applications

The field of ILIS FIB is just beginning. Recently, focusing of the ILIS into a sub-micrometer sized spot was demonstrated, and the beam was used to perform ion microscopy. In this test, an externally wetted W ILIS (provided by the author) was tested with a proprietary ionic liquid supplied by M. Vaultier of the Bordeaux Institute of Molecular Sciences. The tip was tested at an energy of 20 keV and at an emission current of 3 μA. This is a preliminary result, but it demonstrates that it is indeed possible to focus the beam produced by an ILIS and perform ion microscopy.

Figure 7-1: Secondary electron micrograph generated by a focused ILIS beam. Imaged sample is a gold checkerboard pattern on silicon. Figure courtesy of J. Gierak, LPN-CNRS.

Future work should investigate the use of alternative configurations, such as the carbon xerogel emitter, and other ionic liquids. Future research should explore the ultimate resolution limits of ILIS in FIB, the stability of the ion source for FIB patterning, and the potential use of the focused ILIS beam for etching, deposition, SIMS, and microscopy.

Besides FIB, the possibility of using ILIS for reactive etching is very attractive. ILIS arrays
could be used as a compact source of reactive ions to provide etching, without the need for hazardous reactive gases typically used in DRIE applications. The porous carbon xerogel emitter arrays could also be potentially implemented as electrospray thrusters, with the possibility of obtaining the elusive pure ion regime and achieve efficient propulsion with specific impulses in excess of 3000 s.
Appendix A

Test with Externally Wetted W ILIS at LPN-CNRS

This appendix describes experimental work performed with externally wetted W ILIS at the Laboratory for Nanostructures and Photonics in Marcoussis, France. Externally wetted W tips may operate with the required stability and single site emission, although for a limited amount of time (a few minutes of a few hours) before emission becomes unsteady. W tip operation is unrepeatable, as it is not possible to predict if the source apex is wetted and will operate properly. These tests are reported with the purpose of illustrating the hardships incurred when trying to use this type of emitter in FIB, and to motivate the development of new ILIS pursued in this thesis.

The goal of the experiments at LPN is to implement the ILIS in a high-resolution FIB system developed at CNRS-LPN, the NanoFIB system. The nanoFIB typically uses a gallium ion source and has an optical column based on the design discussed in reference [42]. This system counts with ion microscopy capabilities and has been used for sub 10 nm fabrication [40]. In order to implement an ILIS in this system, the source must contain the liquid within the tip structure, i.e., no droplet ejection from the emission site nor from the reservoir or emitter shank. Also, the emission must come from a single point on the emitter apex, and be within 10 degrees from the system axis, in order to allow the beam to exit the ion gun and go into the focusing column. It is also required that the emitter has stable DC current operation (regulated current operation with voltage variations of no more than ±50 V) during at least one hour so that focusing tests may be performed.

Given these requirements, the ion source must be qualified before installation in the delicate
NanoFIB system. Four W emitters were tested to measure their stability, directivity, and lifetime. The emitters are first used in basic characterization tests, where a sample is irradiated for a few minutes to produce an impact and assess the quality of the emission. The emitters are then installed in a nanoFIB ion gun to produce a high energy ion beam and verify the quality of the source in this high-energy regime, before installing in the nanoFIB system. Section A.1 explains the qualification tests in detail, including the emitter preparation procedure, the emission trends, current-voltage curves, and high-energy tests in the gun setup. An externally wetted tungsten emitter was installed in the nanoFIB system to try to perform ion microscopy, and the results and challenges faced in this process are described in Section A.2.

A.1 Experimental Results: Emitter Qualification Tests

A.1.1 Qualification Test Equipment and Overview

This section describes the preparation protocol and the experimental setups used for each tip, and presents the main experimental results with each of these emitters. The qualification process included basic irradiation experiments in a test chamber and installation in a ion gun for IV curve acquisition and high-energy experiments.

The emitters are installed in source holders compatible with the NanoFIB system and introduced into a test chamber where they can be annealed, filled with ionic liquid in vacuum and subsequently fired in basic irradiation tests. The test chamber for these experiments has three key components: (1) a linear stage on which the tip is mounted, and moved up and down (2) a crucible holder, where the ionic liquid is degassed and into which the tip is lowered, and (3) a grounded aluminum plate that rotates horizontally and which can be placed in between the source and the crucible once the tip has been filled. This aluminum plate acts as an extractor electrode, and samples may be placed on top of the aluminum plate for irradiation tests, or the aluminum target may be irradiated directly. The setup diagram is shown in Figure A-1. The power supply used for annealing is an OPEA-800 that can supply 0-10 A, and the source is biased with a FUG HCP 8-40000 (0-40 kV, 0-200 μA). The power supply voltage can be controlled and recorded digitally.

The ion gun consists of a special feedthrough on which the source can be mounted and then enclosed by an extractor electrode, which has a 2.5 mm diameter aperture. The source and extractor can be biased separately and both voltages can be computer controlled. To perform tests with the ion gun, the linear stage is removed from the test vacuum chamber and the gun is put in its place.
The beam from the ion gun can be used to irradiate samples placed on the movable aluminum plate.

Four W emitters were used in irradiation experiments, and three of them were tested in the ion gun. IV curves were obtained, and high-energy experiments were performed to test the ion sources at beam energies of 18-20 kV to determine if the beam exits the gun and if the source is stable in the high-energy regime.

### A.1.2 Emitter preparation

The four W tips tested are referred to as W1, W2, W3, W4. All except tip W2 were installed in the ion gun for IV tests and high energy experiments.

Tips W1 and W2 were fabricated at MIT, and tips W3 and W4 were fabricated at LPN, following the preparation procedure of reference [69]. The emitters are fabricated by electrochemically sharpening a 0.5 mm diameter W wire in a NaOH (1N) solution. The shaped wire is then dipped in a hot solution of 9 g of K$_3$Fe(CN)$_6$ in 25 mL of NaOH (1N). This treatment creates micron sized grooves along the surface, which enable wetting of the emitter structure by the ionic liquid. The images of the emitters’ apices and their respective radius of curvature are included in Figure A-2(a)-(d).

The micro roughened tips are installed in the LPN source holder with a W loop reservoir, as shown in Figure A-2(e). The loop is made with 0.25 mm diameter W wire and is 1.5 mm in
diameter, except for tip W2, for which the loop had a diameter of 1.75 mm. For all tips, the distance from the top of the reservoir to the emitter apex is 2.5 mm. The voltage in all cases is applied directly to the emitter and the loop, there is no distal contact. The assembled emitter is cleaned by boiling in trichloroethylene and washing in ultrasonic baths of acetone and isopropanol. The emitter is placed in the test chamber, where it is annealed by passing a current of 5-6 A through the loop for two minutes, in order to eliminate contaminants from the tip surface. The annealed emitters are allowed to cool for a minimum of an hour before being submerged in ionic liquid. Tips W1, W2, and W4 were tested with the ionic liquid EMI-BF$_4$, and tip W3 was tested with the ionic liquid EMI-GaCl$_4$.

![Figure A-2](image-url)  
Figure A-2: (a) Tip W1 SEM image, $R_c = 2\mu$m (b) Tip W2 SEM image, $R_c = 2\mu$m (c) Tip W3 optical microscope image, $R_c \approx 5\mu$m (d) Tip W4 SEM image, $R_c = 5\mu$m (e) Tip W3 in LPN source holder, with W loop reservoir.

Each emitter is tested after wetting by irradiating a target (an aluminum plate or a gold-coated Si wafer) for several tens of minutes and observing the resulting impact(s), as depicted in Figure A-3. The current is set to a fixed value and the required voltage is recorded digitally to assess the stability of the ion source. If the directivity and stability of the source are deemed adequate, the tip is installed in the ion gun, as shown in Figure A-4, for IV tests and high energy experiments. Before installing in the gun, additional liquid is applied to the loop reservoir with a syringe, as it is not possible to completely submerge the loop after annealing in the test chamber.
Figure A-3: Examples of irradiation tests with tip W2 (a) Multiple site emission, three impacts on target (b) After rewetting, irradiation gives single impact on target.

Figure A-4: Installation of tip W3 in gun. (a) Tip in gun (b) Extractor mounted around tip (c) Gun in test chamber pointing towards target.
Emission trends

Table A.1.2 summarizes the results from the experiments with the W emitters, including the startup voltages, directivity, voltage stability and lifetime of the sources tested. This table includes observations from the irradiation experiments as well as observations from the tests in the ion gun. We can observe the following trends with W emitters:

- The W tips have startup voltages between 1.27 and 2 kV for currents between 60 and 100 nA. Most irradiation experiments (performed for currents between 80 and 200 nA) have adequate voltage stability with less than 50 V standard deviation in the extraction voltage, and result in a single impact which is off-axis by 7-20°. Ideally the emitted beam should be on-axis, but it shall be possible for the beam to exit the ion gun for off-axis emission below ~10°. Only tip W2 was deemed inadequate for gun tests due to directivity, as its beam was off by 10-20°, whereas the other tips were off by roughly 10°. The non-ideal directivity of the W tips may be due to non-perfect wetting of the ionic liquid on the tungsten substrate (as observed in scanning electron micrographs of wet W tips, see for instance [91]) and the non-ideal symmetry of the W apices.

- The W tips can be expected to operate stably between 0.5 and 4.5 hours at 80-200 nA before emission degradation- this is, the sudden increase of several hundred volts in the extraction voltage, or the appearance of voltage oscillations\(^1\). The voltage increase or oscillations indicate that the liquid supply to the emitter has been depleted and emission must occur from points upstream from the emitter apex. This is plausible as the ionic liquid most likely does not form a continuous film of liquid on the W needle, but forms pools or isolated streams along the tip surface. When one of these liquid paths dries up, emission at a given current requires a larger voltage to stress the liquid at sites farther upstream in the tip. Besides the liquid supply issues, factors such as backspattering from the extractor/target and electrochemical reactions between the liquid and the emitter affect the emission lifetime. The degradation of the ionic liquid is evident after a few hours of testing, with the ionic liquid becoming darker after a few hours of operation.

- The W emitters have emission from multiple sites in some tests, as revealed from multiple impacts on the target (see for instance Figure A-3(a)). For these tests, the operation voltage increased from the initial value of ~1.5 kV to up to 3 or 4 kV. These multiple emission sites

\(^1\)An oscillation is defined as an increase (or decrease) in voltage of more than 100 V followed by a decrease (increase) in voltage of more than 100 V over the span of a minute or less.
Figure A-5: Test at 1 μA current with Tip W1. Liquid Film seems to be pulled over the W tip after large extraction voltage is applied.

and increased voltages indicate that emission is not occurring from the tip apex, but rather from several upstream locations when the apex is not properly wet. It is possible to recover single impact operation at moderate voltages after recycling the ion source (washing, annealing and rewetting) or after redipping in the ionic liquid.

- Voltage increases may sometimes result in operation stabilization. In a handful of experiments, it was observed that the voltage increased by a few hundred volts over an interval of a few minutes from the initial operation voltage, but suddenly the voltage dropped within a few seconds and the source became stable. This spontaneous stabilization is due to the pull of liquid towards the emitter apex due to electrostatic traction at the increased operation voltage. In a particular test, the source was set to operate at 1 μA, and the power supply was allowed to supply up to 6 kV. In this case, the extraction voltage exceeded 5 kV for a few seconds before suddenly dropping to about 3 kV. It was observed that a film of liquid was created over the emitter, as seen in Figure A-5. Even if voltage increases may sometimes lead to voltage stabilization, it is not always the case. In most experiments where the sources did not emit as desired, voltages of up to 3 or 4 kV were not sufficient to stabilize the source. The stabilization after high-voltage operation is more of an indication of the limited liquid supply to the emitter apex with the W tips- ideally, a fixed voltage close to the startup potential should suffice to support the currents without need of an additional electrostatic pull to bring the liquid to the apex.
<table>
<thead>
<tr>
<th>Tip</th>
<th>W1 Liquid</th>
<th>W2 Liquid</th>
<th>W3 Liquid</th>
<th>W4 Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Startup Voltage</td>
<td>1.27 kV for 70 nA for first test outside gun, 1.4 kV is lowest operation voltage in ion gun, for 250 nA</td>
<td>Initially 1.8 kV, but after rewetting 1.4 kV</td>
<td>Observe 160 nA emission for 1.65 kV outside gun, 200 nA for 1.9 kV inside gun</td>
<td>Observe 100 nA emission for 1.9 kV, in ion gun.</td>
</tr>
<tr>
<td>Directivity/ Multi-cone emission</td>
<td>Variations of less than 50 V for most tests at 100-300 nA. At 1 μA, almost always observe variations greater than 100 V and oscillations.</td>
<td>Variations of less than 50 V for tests at 80-100 nA after rewetting</td>
<td>For 200 and 400 nA, voltage varies by less than 50 V. If the current is taken above 600 nA, source shows hysteresis, requiring several hundred volts more emission voltage</td>
<td>Voltage varies by less than 50 V for currents below 200 nA. After 1 μA operation, 100-200 nA operation requires 3+ kV instead of ~2 kV (hysteresis). Possible to obtain 2.5 kV emission at 100-200 nA after overnight pause.</td>
</tr>
<tr>
<td>Voltage Stability</td>
<td>Right after wetting new tip, discharge 0.81 mC before voltage increases abruptly. This is the equivalent of 135 min. operation at 100 nA. For tests after applying liquid to the loop and installing in the ion gun, voltage destabilizes after 1.7 mC are discharged, or the equivalent of 290 min. at 100 nA. For test where the liquid seems to be pulled to the tip at 1 μA operation, can operate stably at 205 nA for 34 min.</td>
<td>Tested for 273 min. at 80-100 nA without appreciable deterioration. Did not test further due to poor directivity.</td>
<td>Tested at 200-1000 nA without large voltage oscillations until 1.4 mC were discharged, or the equivalent of 113 min. operation at 200 nA</td>
<td>Tested at 100-200 nA for 24 min. in irradiation test. For gun tests, discharge 0.63 mC (105 minutes at 100 nA), with source functional afterwards but showing hysteresis.</td>
</tr>
</tbody>
</table>
A.1.3 Current-Voltage (IV) Curves

Current-voltage curves of the emitters were obtained once they were installed in the ion gun. The extractor was kept grounded for these experiments. Figure A-6 shows the average voltage required for Tips W1, W3 and W4, obtained for currents between 100 nA and 1 µA. The horizontal error bars correspond to the standard deviation in the required voltage. For tip W1, two separate scans were performed while increasing the current, and no decreasing scan was performed. For tips W3 and W4, the IV data was obtained by increasing and decreasing the current in one scan.

The IV curves reveal different operation regimes. Low-current (<400 nA) operation is relatively stable, with voltage deviations of about 50 V or less and linear increases in current as the voltage is increased. As larger currents are demanded, there is a change in the slope in the IV curve, indicating additional emission sites are activated from further upstream on the emitter apex [91, 89]. Operation above 600 nA is unstable as revealed by the larger deviations in the voltage, and almost always has undesired voltage oscillations.

The IV curves also demonstrate hysteresis, as illustrated in Figure A-7. The source starts emitting current at a given startup voltage, depending on the liquid surface tension and the tip geometry. As the voltage is increased, the emission current increases linearly. Eventually, there is a change in the slope $dI/dV$, and the emission current flattens even if more voltage is applied. This flattening reveals that emission current is limited by the liquid supply. The hysteresis is related to the fact that the emission current requires a higher voltage in the ramp down process than in the ramp up process. For Tip W1, the required voltages for each current increase by 100-300 V from one pass to the other, whereas for tips W3 and W4, the emission voltage increases by several hundred volts after operation at 1 µA. The high-current operation seems to deplete the emitter apex from liquid, as low-current operation after the high-current regime requires more voltage than originally applied. Also, (for tip W4) the beam exits the ion gun for currents at or below 200 nA in the ramp-up process but not after the high-current operation. This indicates that the emission site moves further upstream in the needle after high-current operation, and the beam is more off-axis and intercepts the extractor.

The large voltage changes between ramps in the IV data indicate that the W emitter liquid supply is limited. Operation above 400 nA is unstable and depletes the emitter apex of ionic liquid.
Figure A-6: IV Curves (a) Tip W1 with EMI-BF$_4$. Black curve is first pass, blue curve is second pass, both increasing from smallest to highest current. Note that in first pass operation at 100 and 150 nA was unstable, but source stabilizes after a “voltage pull” (b) IV curve for tip W3 with EMI-GaCl$_4$, first ramp up from 200 nA to 1 µA and then decrease towards 200 nA again (c) Tip W4 with EMI-BF$_4$, first ramp up from 100 nA to 1 µA and then decrease towards 100 nA again.
A.1.4 Elevated Beam Energies Tests

For FIB implementation, it is necessary to increase the beam energy $E$ to reduce the effects of chromatic aberration on the probe size, which scale as $\Delta E/E$, where $\Delta E$ is the beam energy spread. For a source/extractor arrangement as shown in Figure A-8, the energy of the beam is given by $qV_{source}$, where $q$ is the charge of the ion species ($q = 1$ for all cases studied here). To increase the beam energy, $V_{source}$ is increased by elevating the extractor voltage while sustaining the same emission voltage to sustain the desired current.

The nanoFIB system has been optimized for a 30-40 keV beam energy, which is achieved by holding the extractor at a 20 kV potential (restricted to this value due to insulation requirements) and using a 10-20 kV emission voltage for the gallium LMIS. It is thus desired to operate the ILIS in the ion gun configuration at an energy of 30-40 keV. Nevertheless, due to the smaller emission voltages of ILIS (2-3 kV) and the limit on the extractor voltage, the beam energy cannot be as high. For ILIS tests, the extractor voltage is set to a target 15 kV so that the beam energy is $\sim$18 keV. To reach this high-energy regime, the source is set to emit with the extractor grounded.
and then the extractor voltage is increased to 15 kV, with the source power supply increasing the voltage accordingly to sustain the prescribed current. For the ramp-up process, the source emission current is set to 1 μA, in order to allow the current-regulated power supplies to increase the voltage quickly. Once the extractor is at the desired voltage, a smaller emission current is imposed. The emitter stability is assessed from the recorded currents and voltages, and the experimental setup is checked visually to verify that no liquid spills occur during this high-energy test ramp-up or tests.

Three emitters were tested in high-energy experiments, with the following results:

- **Tip W1:** This tip was operated at 17 keV beam energy. Figure A-9 shows the source and power supply voltages, extraction voltage and emitter current for a high-energy test with this source. It was possible to increase the extractor potential to 15 kV with the source emitting 1 μA. Once at 15 kV, the emission current was set to 205 nA with a stable extraction voltage of 2007±60 V for 34 minutes. After this time, the extraction voltage increased beyond 4 kV, indicating the apex had been depleted of ionic liquid. This tip was tested again in the high-energy regime several times to try and determine if the beam was exiting the ion gun, but the extraction voltages kept increasing after each test and the source stability degraded severely, with voltage oscillations observed for almost all currents. The tip was thus discarded for FIB implementation.

- **Tip W3:** several attempts were made to increase the beam energy with this source, but it was not possible to reach the target voltages. The source potential could not be increased beyond 10.4 kV. As the extractor was brought from 0 to ~7 kV, the source power supply increased the voltage to sustain the ~4 kV extraction voltage for the emission current; however, as the extractor voltage was increased beyond 7 kV, the source voltage stayed at 10.4 kV with the recorded emission current fixed at 1 μA, even if the extraction voltage is not enough to sustain this emission current. The power supplies were verified to work properly after this test, and so it is presumed that there was some insulation problem with the installation of this source, and that a leakage current is induced at this top-up voltage. An irradiation test was attempted with the extractor at 5 kV, but this experiment was unsuccessful because the source became unstable and because the beam did not exit the ion gun due to source misalignment. The emitter was discarded for FIB implementation.

- **Tip W4:** This tip was operated with a 18.5 keV beam energy. The extractor was brought to 15 kV while emitting 1 μA and then the source was set to a 100 nA emission current. The
extraction voltage for the 100 nA current increased after the 1 μA operation and the beam was not exiting the gun in this test. After an overnight pause, the source was operated at 100 and 200 nA with the extractor grounded and at reduced extraction voltages. In this low-energy test, the beam did exit the gun. It is likely that the high-current emission depleted the apex and that the emission during the high-energy test was coming from an upstream site. The tip apex was probably partly replenished by capillarity after the overnight pause and it was possible to recover directivity. This ion source was chosen as a candidate for FIB tests, with the restriction of operation currents in the 100-400 nA range. Although the ramp-up process will be a few minutes longer, the current restrictions should prevent depletion of the source.

The high-energy tests demonstrate it is possible to bring the ILIS beam energy to 17-18.5 keV. No liquid spills were detected by visual inspection of the experimental setup after any of these experiments. Tip W4 was the only qualified emitter for FIB experiments, and the results of the nanoFIB tests with tip W4 are described in the next section.
A.2 Experimental Results: FIB Experiments

Tip W4 was installed in nanoFIB system for focusing experiments, with the goal of producing a secondary electron image via scanning ion microscopy from the ILIS beam.

The nanoFIB ion gun consists of the ILIS and an encasing extractor electrode similar to the one used in the qualification tests. The nanoFIB extractor has a 2 mm diameter aperture, and the tip is centered approximately 2 mm away from the extractor plane. The emitter inside the gun can be seen in Figure A-10(a). The extractor was enclosed in an additional aluminum structure (see Figure A-10(b)) to prevent any liquid from contaminating the nanoFIB column. The ion gun was then installed on top of the nanoFIB optics column, depicted in Figure A-10(c). This column is similar to the design described in Ref. [42], and consists of the ion gun, a limiting aperture (in this case 50 μm in diameter), two lenses, and stigmator and deflector electrodes. The focused beam is scanned over a sample and the secondary electron signal is recorded by a detector.

![Figure A-10: (a) Tip W4 installed in nanoFIB ion gun (b) Ion gun is covered with additional enclosure to prevent liquid spills into nanoFIB column (c) NanoFIB column schematic, figure modified from Ref. [40]](image)

For the imaging tests, the system was evacuated to below 8E-8 mbar, and the source was set to emit at 0.22 μA with the extractor grounded and a source voltage of 1.85 kV. The extractor
voltage was then gradually raised to 18 kV while the source power supply increased the voltage accordingly to sustain the 0.22 μA current. Once at 18 kV, the source voltage was approximately 19.8 kV, although it varied by several tens of volts. The source voltage was not recorded digitally for this test so it is not possible to quantify the stability of the extraction voltage.

With the source emitting, the ion gun was aligned mechanically and the lens voltage was varied until a signal could be detected in the secondary electron image. Two electron signals were recorded, one with the source emission current of 0.17 μA and the other with the source emission current of 0.29 μA, shown in Figure A-11(a) and (b), respectively. In both cases the source voltage was approximately 20 kV and the condenser lens was set to 11.86 kV. Each image is 2048 × 2048 pixels, acquired over 10 s.

![Figure A-11: Secondary electron images produced by scanning ILIS beam](image)

From the streaked pattern of these images, it can be deduced that the source emission was intermittent. The length of each emission pulse can be estimated from the images, as each pixel is recorded over approximately 2.4 μs. The greyscale image can be translated to an intensity signal between 0 (black) and 1 (white) to obtain the electron signal as a function of time. Samples of the secondary electron signal during a span of 100 ms are shown in Figure A-12 for each of the two tested currents. We assume the source is emitting if the secondary electron signal is greater than
0.95. From the figure, it can be appreciated that the pulses of emission last a few milliseconds, and that the pulses at 0.29 μA are more frequent than for the 0.17 μA case. Overall, the beam is “on” for 4.7% of the time at the 0.17 μA current, and 6% of the time at the 0.29 μA current.

Figure A-12: Normalized secondary electron signals for (a) beam emission current at 0.17 μA and (b) beam emission current at 0.29 μA. The 100 ms samples correspond to 4200 pixels, or two lines of the images in Figure A-11

The intermittent emission pattern observed is not adequate to perform ion microscopy, and it was attempted to operate the ion source at other currents to obtain stable emission, but this was not possible. It is likely that this intermitted emission pattern was caused by a poor liquid supply to the tip apex.
Appendix B

Circuit Diagrams

This appendix includes the diagrams of the circuits used for data acquisition. For the current-voltage measurements, we use a custom power supply, based on the Matsusada AP-3B1-L2. The power supply has been modified to include a circuit that measures the current drop through a resistor placed in series with the power supply, which can be used to monitor the current emitted by the ion source. This circuit is shown in Figure B-1. The voltage drop through the resistor is measured by a voltage buffer followed by an isolation amplifier with a 10X gain. In this way, we can connect the voltage measurement to sensitive electronics, such as a DAQ rack or oscilloscopes, without exposing the electronics to the high voltages applied to the tip.

The TOF measurements (performed in the positive mode exclusively) were performed using a non-inverting amplifier to convert the current signal from the channeltron into a voltage signal. The circuit diagram for the amplifier is shown in Figure B-2. This instrument has a response time of 58 ns [81].
Isolated current measurement

Voltage follower OP07

10x gain isolation amplifier

OP07CP

R1 100 kΩ

R2 10 kΩ

R3 4.3 V

R4 1 MΩ

SW1

HV1 in

Connect known resistor between HVOut and Ground to calibrate gain

Figure B-1: Current Measurement Circuit, courtesy F. Mier Hicks
Figure B-2: Non-inverting amplifier circuit, from ref. [81]
Bibliography


