

# Ion production from LiF-coated field emitter tips

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Ion emission has been obtained from a LiF-coated tungsten field-emitter tip. Ion formation is thought to be caused by the high electric field experienced by the LiF. At the time of emission the electric field at the surface of the LiF is calculated to be on the order of 100 MV/cm. Inside the LiF the field is on the order of 10 MV/cm. These fields exceed the value needed to produce bulk dielectric breakdown in LiF. The surface field is of sufficient magnitude to produce ion emission by field evaporation from the crystal surface. Even prior to dielectric breakdown, precursor processes can lead to ion formation. Electric-field-stress fragmentation of the LiF layer is thought to occur, followed by ionization of the fragments.

## I. INTRODUCTION

The mechanism of ion production from electric-field-stressed LiF-coated porous stainless steel surfaces is of interest since such ion sources are used routinely at Sandia National Laboratories on the Particle Beam Fusion Accelerator II (PBFA II) and on the PI 110 accelerator to produce intense, pulsed lithium ion beams.<sup>1,2</sup> In these accelerators, the anode is bombarded by electrons with energies of millions of electron volts during the ion-formation time. It is commonly assumed that these electrons are necessary for the production of ions, although their precise role has never been established for LiF. Results from the PI 110 accelerator have indicated that the electron energy deposition is not sufficient to melt or vaporize the LiF. Instead, ion formation seems to be associated with the geometry-related electric-field enhancement of the porous substrate.<sup>3</sup> Alkali ion emission from LiCl, NaCl, and KCl in the presence of electric fields of about 2 MV/cm at temperatures in excess of 200 °C have been reported previously.<sup>4,5</sup> Here, we report on an experiment to measure ion production from room-temperature LiF as a function of electric-field strength at the anode in an environment where the electron flux to the anode is negligible. We then consider several field-related mechanisms that may explain ion formation.

## II. EXPERIMENT

The anode was prepared by coating tungsten field-emitter tips with LiF, as shown schematically in Fig. 1. The radii of the tungsten tips were on the order of 50–100 nm. LiF was vapor deposited onto the tips. The thickness of the LiF coating ranged from 9 to 150 nm. Ion emission was obtained by applying a dc voltage to the anode surface. The voltage increased at a rate of 100 V/s. A negative extracting electrode was located about 0.5 nm from the tip. Ion current was observed on a channel electron multiplier array (CEMA) detector and recorded in real time on a video system.

Our primary objective was to determine the electric field at the surface of the LiF when ion current commenced. Knowledge of the tip geometry and its field-ion imaging properties allowed us to establish a relationship between the

applied voltage and the electric field at the emitter tip. The average electric field at the tip is related to the voltage by  $E = V/\kappa r$ , where  $r$  is the tip radius and  $\kappa$  is a geometry-dependent factor that indicates the departure from spherical symmetry. The factor  $\kappa$  can be determined by imaging the tip in a helium atmosphere. It is known that an average electric-field strength of 4.5 MV/cm is required to field ionize He and to obtain a field-ion image. Knowing the tip radius and the applied voltage, the geometric factor  $\kappa$  for the bare tip is obtained. Here, we have assumed that the coated tip has the same value of  $\kappa$  as the uncoated tip. The tip radius and the LiF layer thickness were obtained by examining transmission electron micrographs of the coated needles, one of which is shown in Fig. 2. Because of surface roughness, the electric field at any given point on the surface of the LiF will be greater than the average electric field calculated in this manner.

In these experiments, as the voltage was increased ion emission began sporadically and faintly, then became spatially uniform. The voltage we have chosen as characteristic of ion emission is that associated with spatially uniform emission from the tips. The emission remained uniform for a period of time on the order of second, after which it rapidly diminished and recommenced, in a burstlike manner. In Table I we list geometric parameters for three of the tips used in

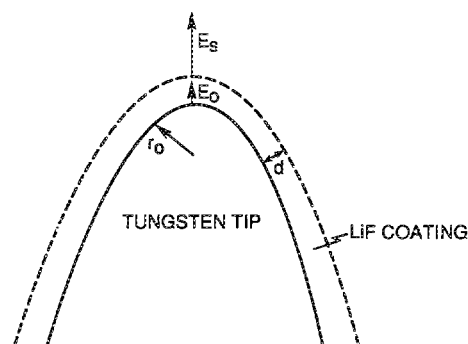


FIG. 1. Schematic representation of the LiF-coated tungsten field-emitter tip.

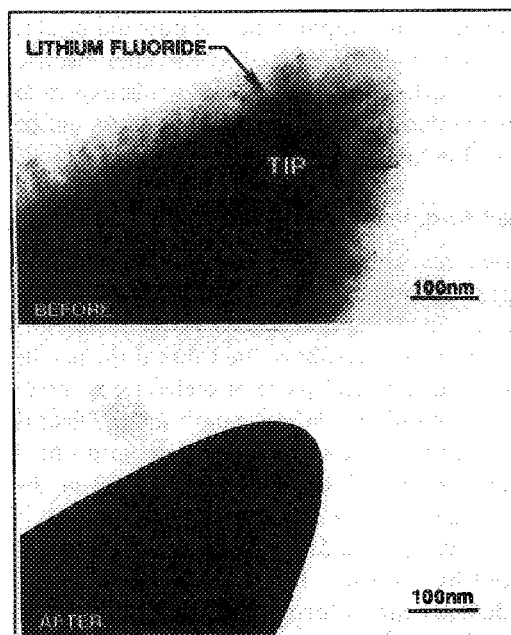


FIG. 2. Transmission electron micrograph of a LiF-coated tungsten field-emitter tip, before and after application of the field. Note the roughness of the surface of the LiF. After application of the field, the LiF is removed from the surface.

the experiments, and the voltage at which uniform emission occurred for each of these tips. Also tabulated are the calculated values of the electric field at the surface of the LiF and inside the LiF at the tungsten interface. The electric field at the position  $r$  outside the LiF is given by

$$E_{\text{out}} = [\epsilon r_0 / (\epsilon r_0 + d)] V / \kappa r, \quad (1)$$

where  $\epsilon$  is the value of the dielectric constant ( $\epsilon = 9$  for LiF),  $V$  is the applied voltage  $r_0$  is the radius of the tungsten tip, and  $d$  is the thickness of the LiF layer. Inside the LiF, the electric field is given by Eq. (1) divided by  $\epsilon$ . As seen in Table I, the field at the surface of the LiF,  $E_s$ , is on the order of 50–100 MV/cm, neglecting surface roughness of the LiF coating. The field in the LiF at the tungsten boundary,  $E_0$ , is on the order of 10 MV/cm.

We note that the electric field at the negative extracting electrode is related to the field at the tip roughly by a factor of  $r_0^2/r^2$ , where  $r$  is the “radius” of the electrode. Using  $r_0 \approx 100$  nm and  $r \approx 1$  mm, for  $E = 100$  MV/cm the field at the negative electrode is on the order of volts per centimeter, which is far below the threshold for field emission of elec-

TABLE I. Values of the tungsten tip radius,  $r_0$ , LiF layer thickness,  $d$ , geometric factor,  $\kappa$ , and the voltage  $V$  at which uniform ion emission occurred for three of the tips used in the experiments. Also shown are the calculated values of the electric field at the LiF surface,  $E_s$ , and the electric field in the LiF at the tungsten tip radius,  $E_0$ .

Tip no.	$r_0$ (nm)	$d$ (nm)	$\kappa$	$V$ (kV)	$E_s$ (MV/cm)	$E_0$ (MV/cm)
5	26	9	6.2	2.2	94	14
3	92	70	2.4	3.8	89	17
1	35	16	9.5	2.5	49	8

trons. Thus, high-energy cathode electrons can be neglected in this experiment.

### III. THEORY

The mechanism for ion production is clearly related to the electric field. Here, we will consider three possible field-dependent mechanisms for producing ions: Direct field evaporation of the  $\text{Li}^+$  from the LiF surface (Sec. III A), dielectric breakdown in the bulk of the LiF (Sec. III B), and electric-stress-induced fragmentation of the LiF, (Sec. III C).

#### A. Field evaporation

Field evaporation is the thermally activated escape of an ion over the lattice potential energy barrier. The rate of escape  $R$  is given by  $R = \nu e^{-Q/kT}$ , where  $\nu$  is a temperature-dependent attempt frequency,  $Q$  is a field-dependent activation energy,  $k$  is Boltzmann's constant and  $T$  is the temperature.<sup>6</sup> For our purposes, we will assume that the condition for field evaporation is that  $Q = 0$ , i.e., when the probability for escape is unity. For an ionic crystal in the presence of an external electric field,  $Q$  can be approximated as the sum of the cohesive energy per ion due to the Coulomb interaction and the potential energy term associated with the electric field:

$$Q \approx (A_s e^2 / 4\pi\epsilon_0 a) - E_s e x, \quad (2)$$

where  $A_s$  is the surface Madelung constant,  $e$  is the electron charge,  $E_s$  is the surface electric field,  $\epsilon_0$  is the permittivity of free space, and  $a$  is the distance between nearest neighbors in the LiF crystal lattice (assumed to be the same before and after application of the electric field), and  $E_s e x$  is the electrostatic potential energy of the Li ion at position  $x$ , where  $x$  is measured with respect to the position nearest the  $\text{F}^-$  ion. We have neglected polarization effects and the repulsive core-core potential energy. For LiF  $a \approx 0.2$  nm and the bulk value of the Madelung constant is 1.75.<sup>7</sup> For a particular site on the surface, the Madelung potential is a fraction of the bulk value. A typical surface consists of large smooth regions, that end in ledges, which themselves may end in kinks. In Fig. 3, atoms are shown occupying positions in the surface (1), in a ledge (2), at a kink (3), and in a self-adsorbed site on the surface (4).<sup>8</sup> The coordination number, i.e., number of nearest neighbors, is different for each of these positions. The ratio of the surface Madelung potential to the bulk value for sites (1)–(4), respectively, is 0.948, 0.897, 0.5, and 0.038 for an unrelaxed crystal.<sup>9</sup> There are many surface sites with values between those for sites (3) and (4). It is thought that evaporation proceeds in a step-wise manner, with atoms moving from sites with higher coordination numbers to those with lower coordination numbers. Under normal conditions, the atom enters into the vapor phase from the self-adsorbed site.<sup>8</sup>

Setting  $Q = 0$  and  $x = a$  in Eq. (2), we find that only about 24 MV/cm is needed to field evaporate an ion from a self-adsorbed site on the surface, compared to about 300 MV/cm needed to remove an ion from a position at a kink on a ledge.<sup>10</sup> Since atomic-scale roughness could easily increase the field by a factor of 3, we suspect that our fields could

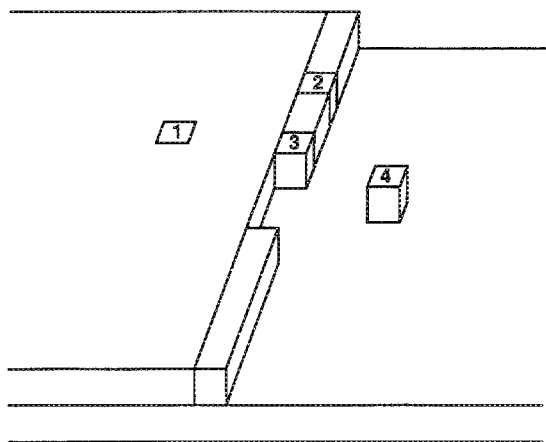


FIG. 3. A typical surface consists of large smooth regions, known as terraces, ending in ledges, which themselves may end in kinks. Atoms are shown occupying positions in the surface (1), in a ledge (2), at a kink (3), and in a self-adsorbed site on the surface (4).

produce field evaporation of ions located at kinks. Certainly, we have sufficiently strong fields to field-evaporate ions from the self-adsorbed sites and many other surface sites.

### B. Dielectric breakdown

Dielectric breakdown refers to the destruction of the lattice structure as a result of temperature increases caused by current conduction in a dielectric.<sup>11</sup> There are many theories to describe the events that lead to the occurrence of dielectric breakdown, all of which require a sufficient population of electrons in the conduction band of the dielectric. The theories differ in the mechanisms proposed for populating the conduction band.

Dielectric breakdown can result from electron avalanche when the electric field in the bulk is sufficiently high that an energetic free electron (in the conduction band) gains enough energy between collisions with valence electrons to knock other valence electrons into the conduction band. In the case of LiF, where the fluorine occurs as a negative ion, an avalanche could proceed by the reaction  $e^- + F^- \rightarrow F + 2e^-$ . After  $n$  generations the number of electrons will be  $2^n$ . For the avalanche process to proceed to breakdown, many electron mean-free paths are required. Experiment indicates that the breakdown field strength of bulk LiF is about 3 MV/cm.<sup>12</sup> This value is compatible with a theoretical description of dielectric breakdown proceeding by the avalanche process.<sup>13</sup> In thin films, where there are fewer electron mean-free paths, the breakdown field strength is higher. Here, the mechanism for populating the conduction band may be field emission of electrons from the valence state.<sup>14</sup>

Even prior to producing bulk breakdown, these processes could result in a lattice of  $Li^+$  and neutral F in the vicinity of the conduction path or on the surface. Field evaporation of  $Li^+$  then could occur from this region at a much lower value of the electric field than for the direct field evaporation discussed previously. If lithium ions are produced by the field evaporation process in this manner, we would expect to see few fluorine ions, if any. However, if the process

proceeds to breakdown, and vaporization of bulk material is produced, this vapor could be ionized in the high electric field near the anode surface. In this case, we would expect to see both lithium and fluorine ions. Neutral species would be difficult or impossible to detect.

### C. Field-induced fragmentation

High electric stress can cause fragmentation of the dielectric along grain boundaries or other crystal imperfections. The electric field strength at the surface of the dielectric fragment will be enhanced above the value at the needle tip. For example, if a spherical piece of dielectric is introduced into a region of uniform field strength  $E_0$ , the field is distorted in the region of the sphere. The maximum field strength at the surface of the dielectric is given by  $E_{max} = E_0(3\epsilon/\epsilon + 2)$ , where  $\epsilon$  is the dielectric constant.<sup>15</sup> For LiF, where  $\epsilon = 9$ ,  $E_{max} \approx 2.5E_0$ . The field inside the fragment is enhanced by the same factor. If the fragment is charged, the enhancement factor will be even greater. The enhanced surface field will increase the probability of direct field evaporation of surface ions. The enhanced interior field will expedite dielectric breakdown processes and electron tunneling. Also, a charged fragment will be unstable when the repulsive coulomb energy exceeds the cohesive energy. If the charge is distributed uniformly on the surface, using the fact that the cohesive energy of each LiF pair is 10.5 eV,<sup>7</sup> it is easy to show that a spherical cluster of  $N$  atoms is unstable when the fractional ionization  $f$  satisfies  $f > \sqrt{1.43/N}$ .

Thus, for a number of reasons, the fragment is a more probable source of ions than the original surface.

## IV. DISCUSSION

The data presented here do not permit unambiguous determination of which of these mechanisms is responsible for the production of ions in this experiment. As shown in Table I, the surface electric field is estimated to be near 100 MV/cm, assuming a smooth LiF surface. Transmission electron micrographs show that the surface is rough. Such roughness could easily produce local fields several times higher, sufficient to directly field evaporate Li ions from many surface sites on the LiF crystal. Within the LiF, the field is estimated to be on the order of 10 MV/cm, which is higher than the bulk breakdown field for LiF. Processes leading to dielectric breakdown certainly occur at these fields. If field-induced fragmentation occurs, all field strengths are increased significantly for the fragment, rendering all means of ion production more probable. The burstlike nature of the emission leads us to expect that fragmentation, followed by a breakdown phenomenon of some sort, is occurring.

In conclusion, we have determined that ion emission from LiF can occur solely as a result of high electric field stress. Although we have not been able to unambiguously determine the field-related mechanism responsible for producing ion current, we believe that field-induced fragmentation and dielectric breakdown are likely to occur. Field intensities are also sufficient to directly field evaporate  $Li^+$  from a number of surface sites. A measurement of the emit-

ted ion species would help to determine the mechanism, as we would expect a pure Li beam from field evaporation and a beam of Li and F ions from dielectric breakdown-induced vaporization. In experiments on particle beam accelerators, high-energy electrons strike the ion-emitting surface. The effect of these high-energy electrons impinging on the LiF surface could be determined by using an electron gun aimed at the tip in our experimental setup.

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