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Nanoelectrospray aerosols from microporous polymer wick sources

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Nanoelectrospray aerosols were formed from microporous polymer wick sources. Current-voltage characteristics were measured as a function of solution electrical conductivity and surface tension and two distinct electrospray modes were observed. In the first mode, when the maximum capillary flow rate through the wick exceeds the electrospray flow rate, a single electrospray forms from a droplet at the end of the wick. In the second mode, when the maximum capillary flow rate is less than the electrospray flow rate, a multitude of microscopic nanoelectrospray sources are formed from within the surface of the wick tip. © 2009 American Institute of Physics.

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Electrospray aerosols of charged liquid droplets are employed in applications such as analytical chemistry, particle generation, coatings, space propulsion, and particle ionization.^{1–7} Typically, an electrospray is formed from an electrically conducting liquid inside of a capillary needle placed at a high potential. The small dimension of the needle increases the electric field magnitude at the liquid surface and a conical protrusion known as a Taylor cone is formed at the liquid surface through a competition between the applied electric force and the liquid surface tension. Although several distinct electrospray modes have been identified and studied,^{8,9} the so-called cone-jet mode, where a continuous jet of charged liquid emerges from the tip of the Taylor cone when the applied electric force overcomes the liquid surface tension, is the most important for fine aerosol generation. The charged liquid jet is inherently unstable and an aerosol is formed when the jet breaks up into a plume of charged liquid droplets with an initial diameter of just a few microns.¹⁰

An important breakthrough in the development of electrospray sources was the introduction of the so-called nanoelectrospray (NanoES) source.¹¹ In the NanoES source, the diameter of the capillary is reduced by over an order of magnitude (from about 100 μm to just a few microns). Consequently, the liquid flow rate and initial droplet diameter are reduced, which is advantageous in applications such as mass spectrometry where complete solvent evaporation is required. However, due to the very small diameter of the NanoES orifice, these sources can become blocked by any small particles suspended in the liquid. More recently, polymer monolith (PM) sources have been reported for applications in mass spectrometry and microfluidics.^{12,13} PM sources are formed within the orifice of a microcapillary tube using an *in situ* polymerization reaction resulting in a plugged but porous opening in the end of the capillary tube from which an electrospray aerosol can be formed. Because there are multiple liquid pathways, PM sources are less susceptible to clogging but the fabrication process is relatively cumbersome.

Recently we reported on the development of electrostatic precipitators where the particle ionization is accomplished by

charge transfer from aqueous electrospray aerosols emitted from an array of porous synthetic polymer wick sources.^{5–7} Figure 1 is a photograph showing a 1 mm diameter cylindrical polymer wick from Porex Corporation consisting of a polyester/polyethylene blend with a void volume of 60%–70% and a pore size of between 20 and 40 μm . These low-cost, fully wettable, wicking materials are used commercially in devices such as writing instruments, air fresheners, ink jet printers, filters, and medical testing kits and are readily available in a variety of geometries and porosities. Capillary action is very strong in these microporous wicking materials and we have found that an electrospray aerosol can be formed from one end of the wick simply by placing the opposite end into a liquid, thus eliminating the need for a syringe pump or other means to initiate and sustain the liquid flow.

The current-voltage characteristics of aqueous electrospray aerosols produced from a 1 mm diameter Porex polymer wick source were measured as a function of liquid viscosity, surface tension, and electrical conductivity. The surface tension and electrical conductivity of the electrospray liquid was varied by adding either an ethanol cosolvent or a common surfactant to distilled water. Table I lists the room temperature surface tension, viscosity, and electrical conductivity of each solution evaluated in this study. Ammonium lauryl sulfate (ALS) was used as a surfactant at concentrations ranging from 0.1% to 1% by weight. Solution data for pure ethanol and pure water is provided in the table as a reference, but no electrospray aerosols were tested from these pure liquids. Both the ethanol cosolvent and the ALS

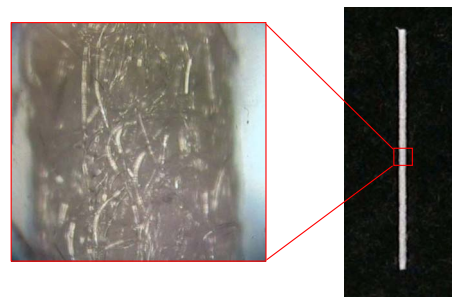


FIG. 1. (Color online) Image of a 1 mm diameter Porex wick.

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TABLE I. Conductivity, surface tension, and viscosity data for the electro-spray solutions. Note that conductivity was not measured for pure ethanol.

Solution	Conductivity ($\mu\text{S}/\text{cm}$)	Surface tension (dynes/cm)	Viscosity (centipoise)
100% H ₂ O	1.5	71.97	1.00
100% EtOH	NA	21.3	1.04
10% EtOH	1.0	39.0	1.23
0.1% ALS	240	44.1	1.03
0.2% ALS	450	33.1	1.01
0.5% ALS	821	29.4	1.04
1% ALS	1412	28.2	0.97

surfactant reduced the water surface tension without significantly affecting the viscosity. The ALS surfactant also significantly increased the electrical conductivity of the liquid.

Figure 2 is a plot of the electro-spray current versus the applied voltage for a 1 mm diameter Porex wick inserted into a 10:1 distilled water/ethanol solution. A positive voltage was applied to the wick and the current was measured from a grounded counter electrode located 1 cm from the wick tip. The electro-spray current initiates at a voltage of about 6.2 kV and then increases and levels off at about 150 nA. Between 6.5 kV and 8 kV the electro-spray current is nearly independent of the applied voltage and this is a well-known characteristic of the cone-jet mode of electro-spray. Above an applied voltage of 8 kV, the current increases rapidly indicating the initiation of corona ionization.

Figure 3 is a plot of the electro-spray current versus the applied voltage for the four ALS surfactant solutions ranging in concentration from 0.1% to 1% by weight in distilled water. The electro-spray initiation voltage decreases monotonically from 5.2 kV for the 0.1% solution to 4.3 kV for the 0.5% and 1% solutions. The current for the 0.1%, 0.2%, and 0.5% concentrations then increases and levels off near 360 nA. However, the range of voltages over which the electro-spray current is relatively independent of the applied voltage (i.e., the cone-jet region) is small in comparison to the ethanol solution and decreases with increasing solution conductivity (or ALS concentration). In fact, for the 1% ALS concentration the cone-jet plateau region, if present, is not clearly discernible in the data of Fig. 3. The voltage at which the electro-spray current begins to increase rapidly indicating

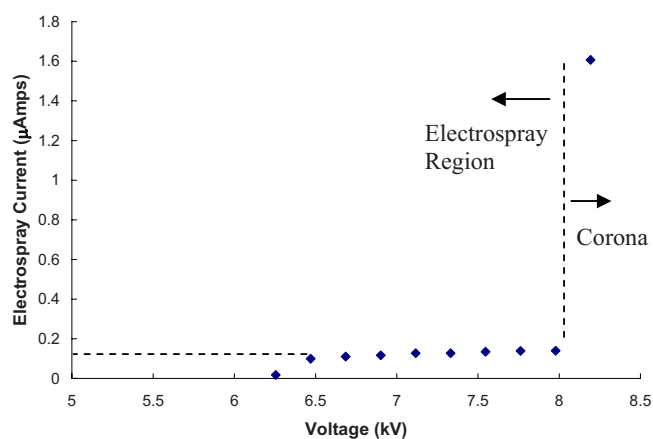


FIG. 2. (Color online) Current vs voltage for a single Porex nozzle electro-spraying a 1/10 ethanol/water solution.

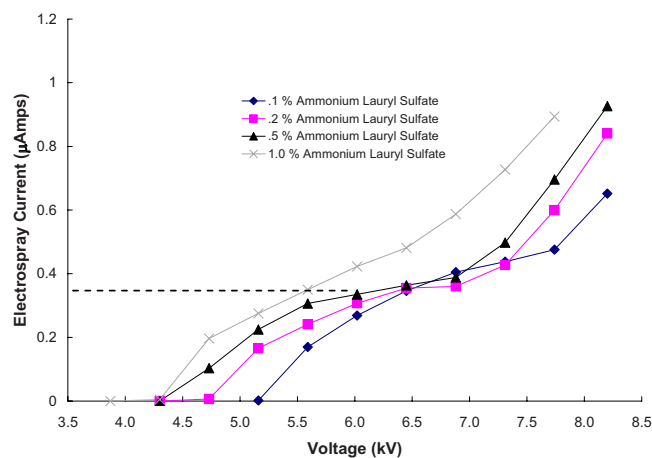


FIG. 3. (Color online) Electro-spray current vs applied voltage for four different ALS concentrations (0.1%, 0.2%, 0.5%, and 1.0%).

the onset of corona ionization also decreases monotonically with increasing ALS concentration.

Because no pumps were used to control the liquid flow rate through the wick, the flow rate is limited only by capillarity, resulting in two possible electro-spray modes from the polymer wick sources. The first mode is shown in Fig. 4(a) and occurs when the maximum rate of capillary flow within the wick is larger than the rate at which the electro-spray aerosol removes the liquid. In this case, a single cone-jet is observed to form from a large fluid droplet formed at the end of the wick and the function of the wick is simply to replenish the liquid removed from the droplet by the electro-spray. The second mode, illustrated in Fig. 4(b) occurs when the maximum possible rate of capillary flow within the wick is less than the rate at which the electro-spray aerosol removes the liquid. In this case the fluid droplet at the wick tip rapidly depletes, but the electro-spray current remains and is produced instead by a multitude of microscopic cone-jets emerging from the porous surface of the wick tip [not visible in Fig. 4(b)]. The base diameter of the microscopic Taylor cones is of the order of a few microns, and while the spray from any one cone is periodically interrupted while the fluid replenishes the average overall electro-spray current is steady due to averaging over a multitude of microscopic electro-spray sources. This second mode, which occurs only when the wick body restricts or limits the liquid flow rate, is not observed in conventional electro-spray sources but has distinct advantages for fine aerosol generation and mass spectrometry and is essentially equivalent to multiple parallel NanoES sources.

In the absence of an externally applied pressure gradient, the rate at which a fully wettable liquid travels through a porous material by capillarity is described by Washburn's equation as¹⁴

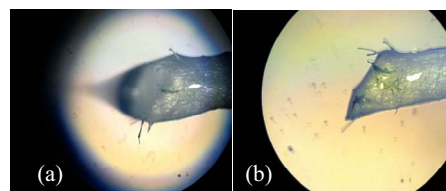


FIG. 4. (Color online) Optical microscope image of wick electro-spray aerosol in (a) mode 1 and (b) mode 2.

$$L^2 = \gamma Dt / 4\eta, \quad (1)$$

where t is the time for a liquid of viscosity η and surface tension γ to penetrate a distance L into a porous material with average pore diameter D . In the experiments reported here the material porosity (D), wick geometry, and liquid viscosity (η) are essentially constant and, therefore, Eq. (1) predicts that the capillary-driven liquid flow rate is directly proportional to the liquid surface tension ($Q \sim \gamma$).

The electro spray current in the cone-jet mode depends on the surface tension, solution conductivity, liquid flow rate, and dielectric constant as given by^{11,15}

$$I = g(\epsilon)(\gamma K Q)^{1/2}, \quad (2)$$

where $g(\epsilon)$ is a function that depends only on the dielectric constant of the liquid. Because the liquid evaporation rate from the side of the wick cylinder is on the order of the electro spray flow rate, we do not have an accurate and independent measurement of the electro spray flow rate for the data shown in Figs. 1 and 2. Nevertheless, Eqs. (1) and (2) can be used to interpret the nested I - V curves of Fig. 2.

If we assume that the liquid flow rate is governed by capillary forces according to Eq. (1) and is proportional to the surface tension, the electro spray current from Eq. (2) will then be proportional to the product of the surface tension and the square root of the conductivity as

$$I = g(\epsilon)C\gamma(K)^{1/2}, \quad (3)$$

where C is a parameter that depends on the wick porosity (D), length (L), cross-sectional area (A), as well as the solution viscosity (η) and is essentially constant in the experiments reported here. Based on the surface tension and conductivity data given in Table I and assuming that the dielectric constant does not change significantly for the four ALS solutions, Eq. (3) predicts that the cone-jet mode electro spray current for the 0.2%, 0.5%, and 1% ALS solutions normalized to the 0.1% solution are 1.03, 1.23, and 1.5, respectively. This result correctly predicts the ratio of the mea-

sured electro spray currents near the onset of the cone-jet plateau in Fig. 3, which occurs near an applied voltage of 6 kV.

In conclusion, an array of NanoES aerosols was formed from the surface of a porous polymer wick source when the rate at which liquid is removed by the electro spray aerosol exceeds the maximum capillary flow rate through the wick. That is, when the wick restricts or limits the electro spray flow rate. The maximum flow rate through the wick can be controlled and is a function of the wick porosity, liquid surface tension, and viscosity. NanoES wick sources can potentially be used in mass spectrometry, microfluidics and aerosol generation.

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¹J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong, and C. M. Whitehouse, *Science* **246**, 64 (1989).

²A. J. Rulison and R. C. Flagan, *J. Am. Ceram. Soc.* **77**, 3244 (1994).

³A. E. Seaver and C. J. Eckhardt, U.S. Patent No. 4,748,043 (31 May 1988).

⁴C. Bartoli, H. von Rohden, S. P. Thompson, and J. Blommers, *J. Phys. D* **17**, 2473 (1984).

⁵G. Tepper, J. Fenn, R. Kessick, D. Pestov, and J. Anderson, Proceedings of the Sixth IEEE Conference on Nanotechnology, 2006 (unpublished), Vol. 2, p. 781.

⁶G. Tepper, R. Kessick, and D. Pestov, *J. Appl. Phys.* **102**, 113305 (2007).

⁷G. Tepper and R. Kessick, *J. Aerosol Sci.* **62**, 604 (2008).

⁸M. Cloupeau and B. Prunet-Foch, *J. Aerosol Sci.* **25**, 1021 (1994).

⁹A. Jaworek and A. Krupa, *J. Aerosol Sci.* **30**, 873 (1999).

¹⁰A. M. Ganan-Calvo, J. Davila, and A. Barrero, *J. Aerosol Sci.* **28**, 249 (1997).

¹¹M. Wilm and M. Mann, *Anal. Chem.* **68**, 1 (1996).

¹²T. Koerner, K. Turck, L. Brown, and R. D. Oleschuck, *Anal. Chem.* **76**, 6456 (2004).

¹³P. Wang, Z. Chen, and H. Chang, *Electrophoresis* **27**, 3964 (2006).

¹⁴E. W. Washburn, *Phys. Rev.* **17**, 273 (1921).

¹⁵L. T. Cherney, *J. Fluid Mech.* **378**, 167 (1999).