Parameters affecting electrospray performance of hot-embossed open-channel polymer microfluidic chips

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Abstract. We investigate the effect of chip tip-to-counter electrode spacing (gap), channel-size aspect ratio, onset voltage on electrospray ionization (ESI) performance of embossed polymer microfluidic chips. Planar polymer substrates were hot embossed using an electroformed tool and a laser machined tool. The embossed microchips were tested for successful ESI demonstration with minimum sample consumption and high throughput. Factors influencing the stability of electrospray were analyzed by a series of experiments. Theoretically and experimentally, it was observed that the distance of the microchannel tip to the counter electrode directly relates to the onset voltage applied. Furthermore, the overall pattern observed is the decrease in Taylor cone size with a decrease in channel dimensions. The total ion current was analyzed as a function of time and onset voltage at various gaps. Five electrospray modes, namely, drop mode, pulse mode, Taylor-cone jet mode, multijet mode, and oscillating jet mode recorded at the open channel tips were identified and the electrospray cycle investigated. These results are in good accordance with theory, and comparisons are drawn with the findings of other researchers.

Subject terms: electrospray; hot embossing; microfluidics; Taylor cone formation; polymers; electroforming process; laser machining process.

Paper 09093PPR received Apr. 30, 2009; revised manuscript received Dec. 10, 2009; accepted for publication Dec. 17, 2009; published online Mar. 9, 2010.

1 Introduction

The electrospray ionization mass spectrometry (ESI-MS) process involves the emission of a pressurized liquid from a capillary at the input of a mass spectrometer. At the capillary exit, the liquid is subjected to an electrical potential, and the high electrical field generated induces charges on the surface of the liquid in the area of the spray tip. The spraying of the fluid substance in the vicinity or area of the spray tip generally occurs when the coulombic forces are strong enough to overcome the surface tension forces present in the liquid. This spray occurs in the form of a thin jet of liquid at the tip of the Taylor cone. Electrospray (ES) has advantages over other atomization methods due to monodispersity of droplets sizes, flexibility to generate droplet of different sizes, compatibility, flexibility, and ease of operation. Because of its unique features, there are many applications of ES, which include nanomaterial processes, and development of dimensionless parameters that further work is necessary, including elucidation of the effect of space charges, quantification of the electric field in the vicinity of the nozzle during the dynamic spraying processes, and development of dimensionless parameters that may be used to simplify understanding. Hence, electrostatic spraying of conductive liquids into a nonconductive medium remains a rich field for continued research. Much of the work has been aimed at developing stable spraying systems for particular applications and understanding qualitatively the many modes of ES. Work by Tsouris et al. examined the effect of several controlling variables,
including the geometry of the nozzle from which the fluid is sprayed, the flow rate of the fluid, and the conductivity of the continuous phase. In their experimental investigations, Tsouris et al. found that the key to electrostatic spraying is the electric stress on the fluid-fluid interface. A strong electric stress can render the interface unstable and, thus, can result in the emission of fine droplets or bubbles. It was reported that the electric stress on the fluid interface under an electric field plays a major role in electrostatic spraying. Many groups have fabricated ESI interfaces on microchips using glass, silicon, and plastic as the substrate materials. Previous methods such as attachment of a nanospray tip to the microchannel exit, has yielded promising experimental results; however, extensive work is required to fabricate and manufacture the chip. This approach, although successful, is not compatible with mass production processes. It may also be difficult to avoid a dead volume at the interface between the chip and the spray capillary. Undesired wetting at the contact between the capillary and the microchannel resulted in the formation of a liquid dead volume. The issues with conventional ESI-MS systems include the contamination and clogging of the microchannel tip due to the electrochemical process at the emitter tips. Moreover, the difference in material used for capillary attachments and microchips can vary the repeatability of ES demonstration. Furthermore, bubbles were sometimes formed at a high rate at the junction between the feed capillary and microchips, severely disturbing the ES. In open-channel flow, there is less susceptibility to bubble formation for liquid flow in the microchannels and during the filling of the microwells. However, the trade-off for this design is the enhanced evaporative loss of the fluid samples, especially for liquids with high vapor pressure under ambient conditions. The evaporative losses in closed/bonded channel systems is lower; however, the microchannels and reservoirs have a greater propensity to form bubbles during filling. Bubble formation in these bonded systems can impede the capillary flow and can lead to catastrophic failure for fluid actuation in these devices. Also, Banerjee et al. verified from the simulations that the filling action is faster in open-channel systems and consistent with the analytical results.

Extensive literature review showed that the aims of researchers are to obtain more reproducible mass-fabricated devices, to minimize system complexity along with reduction in manufacturing cost and time, and to eliminate dead fluid volume related to the external connections. Hence, to fabricate an ESI-MS chip with single material with no dead volume is significant to the ESI field. The focus is on fabrication of high-performance ESI-MS devices manufactured using mass production techniques, such as hot embossing and injection molding. The polymer microfluidic chips are also easy to align to the orifice of the mass spectrometer because less care is needed to avoid collision and breaking. Different improvements regarding the quality of the emitter tips are proposed in the literature. Reproducible dimensions can be achieved using an enhanced fabrication route based on laser micromachining. More durable coatings have also been reported. Most of these improvements, however, do not solve the basic problems of clogging and the lack of reproducibility that affect the analysis conditions. Using microtechnology techniques, reproducible and ready-to-use high-quality ES tips can be mass manufactured.

In this work, disposable low-cost polymer microfluidic open-channel tips were successfully produced using the hot-embossing technique on polystyrene (PS) and polycarbonate (PC) substrates. The embossed chips were successfully tested for ES demonstration with minimum sample consumption and high throughput as reported in our previous study. Furthermore, the open structure limits the common problems of air bubbles and clogging. This paper aims to extend research in this field by investigating the factors influencing the performance of ES polymer microchips in terms of repeatability, practicality, onset voltages, and functionality. The microchip used in the investigation was designed with minimum complexity to simplify fabrication by having an open reservoir and channel. The design also eliminated dead fluid volume normally due to external connections to the chip by using capillary forces for fluid flow along the microchannel.

ES is very sensitive at the vicinity of the spray tip. Hence, the control of the ES mechanism and reproducibility of ES results with stable and reliable performance has not been achieved. The primary interest to the ES MS practitioners is to control the spray process in order to gain high and stable ion signals. Interesting phenomena take place when high voltage is applied to a conductive capillary/needle containing a polar fluid. As voltage is increased the liquid air interface becomes polarized with an excess ionic charge producing a Taylor cone. In this work, disposable low-cost polymer microfluidic open-channel tips were successfully produced using the hot-embossing technique on polystyrene (PS) and polycarbonate (PC) substrates. The embossed chips were successfully tested for ES demonstration with minimum sample consumption and high throughput as reported in our previous study. Furthermore, the open structure limits the common problems of air bubbles and clogging. This paper aims to extend research in this field by investigating the factors influencing the performance of ES polymer microchips in terms of repeatability, practicality, onset voltages, and functionality. The microchip used in the investigation was designed with minimum complexity to simplify fabrication by having an open reservoir and channel. The design also eliminated dead fluid volume normally due to external connections to the chip by using capillary forces for fluid flow along the microchannel.

The Taylor cone is a very dynamic system that deforms, oscillates, and contains convection flows of charge and mass. It was shown recently by Marginean et al. that Taylor cone deformation plays a central role in the mechanism of electrostatic spraying. Furthermore, the onset voltage required to start jet production is proportional to the square root of the surface tension multiplied by the radius of the capillary orifice. The higher the onset voltage is, the greater are the chances of an electrical discharge. The liquid under the stable ES operation is often observed to form a conic meniscus at the outlet of the capillary, through the apex of which a fine liquid ligament is ejected. This liquid ligament breaks into droplets further downstream to form a dispersed spray. If the liquid is conductive, then the conic meniscus at the outlet of the capillary will deform into a cone under the action of electric force. Taylor proved that the semivertical angle of the cone was 49.3 deg, theoretically and experimentally, and this cone is now called the Taylor cone. Furthermore, Taylor showed that the instability of an elongated drop would not occur unless a pressure difference existed, and it was found that a...
drop, elongated by an electric field, becomes unstable when its length is 1.9 times its equatorial diameter. Cloupeau and Prunet-Foch\textsuperscript{39} studied the droplet size distribution and the effects of flow rate and applied voltage on the ES by using a granulometer. Later, Fernandez\textsuperscript{40} studied the effects of the charged droplets on the Taylor cone.

In this study, ES is produced at the hot-embossed microchannel exit tip without a cover. The hot-embossed microchannel is attached to a hot-embossed open reservoir. In addition, our work contributes to research on ES parameters influencing the initiation and formation of the Taylor cone shape and size for open-channel systems. Formation of the microchannel is important for delivery of the fluid to the tip where the ES forms. The corner of the channel may have significant contribution to the electric double-layer field, subsequently to the fluid flow field for ES formation.\textsuperscript{41} The microchannel must end in a sharp tip to provide a sufficiently high electrical field for producing ES. Any geometrical deformation leads to a nonoptimal Taylor cone configuration during ES.\textsuperscript{42} Shinohara et al.\textsuperscript{43} investigated the influence of hot-embossed bonded channel tip angle on Taylor cone formation. They stated that the success rate of Taylor cone formation increased with decreasing the tip angle ($\alpha$). Arscott et al.\textsuperscript{44} concluded that the performance of nib sources was seen to be linked to the slot dimensions; the smaller slot dimension is, the better the performance of SU-8 micronebs. While a high voltage is applied, a Taylor cone could be formed at the tip.\textsuperscript{13} The size of the cone depends on the geometry and wetted area.\textsuperscript{45} Chiu et al.\textsuperscript{46} investigated the effect of the outside diameter (o.d.) of the tip on the size of the Taylor cone. The relationship between the o.d. of the capillary ($D_o$) and the height of the Taylor cone was plotted and indicates that the geometric shape of the Taylor cone is a strong function of the $D_o$. The larger the capillary is, the bigger the size of the Taylor zones. Kebarle\textsuperscript{47} proposed that the required ES voltage is a function of the radius of spraying capillary as well as the surface tension of the spraying liquid. Using a sequence of snapshots, Wang et al.\textsuperscript{48} showed that the size of the Taylor cone is governed by the tip orifice geometry and the formation of the cone is governed by electrical potential. Wang et al.\textsuperscript{49} suggested that the cone size and shape is also related to the flow rate and the distance between the tip and MS inlet.

Jaworek et al.\textsuperscript{47} classified the electrospray modes into the following two groups:

1. Dripping modes, in which only fragments of liquid are ejected from the capillary outlet by the deformation and detaching of the liquid meniscus. These fragments can be formed as large regular drops (dripping mode), fine droplets (microdripping mode), a single or multiple spindles (spindle and multisindle modes), or irregular fragments of liquids.

2. Jetting modes by which the meniscus elongates into a long fine jet. The jet can be smooth and stable (cone-jet mode) or can move in any regular way: rotate around the capillary axis (precession mode) or oscillate in a plane (oscillating mode). Sometimes a few jets on the circumference of the capillary can be observed (multijet mode). The case when the jet branches are known as a ramified jet.

Researchers have reported spray modes where the liquid meniscus repeatedly forms a transient jet at constant frequency that depends on voltage.\textsuperscript{47,49} The jet formation and collapse occurs on time scales of typically <1 ms; though the time period decreases as the applied field increases.\textsuperscript{39} Sequential phenomena that occur when ES are triggered by sudden voltage steps were also reported by Paine.\textsuperscript{30} Moreover, a number of authors\textsuperscript{30,50,51} have applied voltage pulses of short duration (1–10 ms) to an ES source in an attempt to make ES drop on demand. A final point is the existence of fluctuations in the ion signal even under good conditions, whose origin must lie in the solution parameters governing the spray process.\textsuperscript{12} A conductive liquid at the tip of a wetted needle or a filled capillary will, as the voltage is increased, deform into a cone. Once a threshold voltage (called the “onset voltage”) is reached, the electric stress at the apex of the liquid surface overcomes surface tension and a spray of particles is ejected toward a counter electrode.\textsuperscript{52} Krpouna and Shea\textsuperscript{53} presented a method to quantitatively determine the onset voltage of a single or array of ES taking into account the real emitter-extractor geometry and the surface tension of the liquid. Ieta et al.\textsuperscript{13} investigated the emission frequency of capillary droplets of aqueous ESs near the onset voltage and stated that during ES, the droplets are emitted with a frequency increasing...
with voltage, but it may often be difficult to determine precisely what is the onset voltage. The following sections describes the fabrication of polymer microfluidic chips, testing of microchips for ESI using the microdevice developed, evaluation of performances of PS/PC chips for ESI, and investigation of influence of ES parameters, such as gap, onset voltage, and current on ES emitted from hot-embossed polymer microfluidic chips.

2 Experimental Procedure

2.1 Polymer Microfluidic ESI Tip Preparation

Planar microfluidic ES tips were fabricated using polymer hot embossing with electroformed and laser-machined master tools on PS and PC substrates. For the hot-embossing process, the tool was designed with a microchannel and reservoir feature attached. The master tool is comprised of six radially arranged tools on a single surface to produce multiple chips. Accordingly, six different dimension microchips can be obtained in a single embossing run as reported in our previous study. Figure 2 illustrates the scanning electron microscope (SEM) images of a polystyrene microchip embossed with the laser-machined steel tool. Figure 2(a) shows the top view of embossed reservoir feature attached to the microchannel. Figure 2(b) shows the top view of embossed polymer microchip tip, and Fig. 2(c) shows the side view of the embossed open-channel PS microchip tip. The images show good surface finish and uniformly formed microchannel and reservoir on the polymer microfluidic substrates.

The embossed PS/PC substrates show smooth surfaces and were tested for hydrophilicity by taking the contact angle measurements. The average contact angle measured on the embossed surfaces was $\sim$40 to 42 deg, which indicates that the surface is moderately hydrophilic, and the embossed chips were tested for capillary action using methanol/water (70/30) as the test solution. Fluid is transferred from reservoir to microchannel exit tip as a result of capillary forces and electroosmosis, thus eliminating the need for external pressure devices such as the use of syringe pumps, which are generally used for filling the microchannel/capillary with the fluid sample in the systems reported in the literature. The next step was to test the embossed chips for ES.

2.2 ESI Experiments

For ES chip design, the critical points are the application of the high voltage, ease of operation, and dead volume miniization. To simplify the experiment, the ESI interface developed was operated at atmospheric pressure and room temperature. The design of chip and the ESI device developed simplifies the experiments by the elimination of the use of syringe pumps, which was used in systems reported in the literature. The use of syringe pumps was to force the fluid into the microchannel. This can lead to air-bubble formation in the channel, thereby leading to catastrophic failure of the system. The trade-off for the open-channel system is the evaporation of the fluid in the microchannel. However, 1 $\mu$L of fluid would last for 5 min, as reported earlier, and this is sufficient for MS/MS analysis. Furthermore, the open-channel design of the microchips eliminates the use of processes such as bonding and gluing and their impurities.

In the experiment, the chip is stationary and positioned in front of a movable polished aluminium plate that acts as a counter electrode in the ESI circuit. The plate position relative distance to the microchip tip was adjustable by using a digital vernier and viewed through a microscope. Figure 3 illustrates the experimental setup, ESI circuit, and apparatus used for ES experiments. The inset shows an embossed polymer microchip set for ES testing with a positive electrode (stainless steel wire) inserted into the reservoir and the microchip tip positioned a few millimeters in front of the counter electrode (polished aluminum plate) connected in circuit.

Prior to ES testing, the hot-embossed chips were cleaned in an ultrasonic bath using ethanol for 10 min. A high-voltage power supply was used to provide up to 5000 V dc for the experiments. The positive terminal of high voltage was connected to a stainless steel electrode inserted into the reservoir, and the negative was connected to the multimeter, which was connected in series to the counter electrode (aluminum plate). In the ES experiments, the first step was to set the gap between the channel exit and the counter electrode. Second, a fluid droplet was added to the reservoir by a micropipette and the high voltage was switched on. The fluid solution used for all the ES experiments was methanol/water (70/30). The solution travels from the reservoir to the channel tip by capillary action, and the voltage is increased in increments until ES is initiated at the tip of the channel. The video camera on the microscope recorded the formation of the Taylor cone and ES. The onset and duration of the ES was observed by the measurement of current using a multimeter and the video recording. Fluid accumulated at the aluminum plate as a result of the ES phenomenon. Next, the distance between the channel exit and counter electrode was changed and the same procedure was carried out. A stainless steel electrode wire was selected to reduce contamination and inserted into the reservoir of the chip.

Salata stated that the progress in ES technology would have been impossible without a continuous development of ES apparatus. An example of a state-of-the-art research apparatus has been reported. The combination of hot-embossing fabrication and an open channel provide an improved approach to reduce impurities and simplify manufacture. Fluid flow in the channel is critical for the chip’s performance and capillary action. Several microchips were fabricated and tested, and the ES experimental
results reported. Stable and fine Taylor cones were recorded at the channel exits of hot-embossed PS and PC substrates, as described in Section 3.

2.3 Optical ESI Characterization

ES behavior and Taylor cone geometry were observed under the microscope, with the corresponding total ion current from the emitter exit simultaneously measured. The fluid sample used for all the experiments was methanol/water (70/30). The polymer microchips were set for testing at the desired spacing from the counter electrode. The fluid was added into the reservoir of the microchip by using a micropipette, and the high voltage was switched on. Stable ESs were recorded by using a video and microscope.

3 Results and Discussion

The results of this study are broadly classified into three sections investigating the effects of chip-to-counter electrode spacing (gap), microchannel dimensions in terms of aspect ratio (depth-to-width ratio), and length of microchannel on ESI performance of the microchips. The results show that the observed ESI performance follow expected theoretical trends. The influence of onset voltage on ES modes and the voltage-current characterization is also investigated. Furthermore, the output is compared to and is in good agreement with the findings of other researchers.

3.1 Influence of Gap

The chip tip–to–counter electrode spacing (gap) was set to a desired value. A fluid sample was added to the reservoir using a micropipette. The fluid travels from the reservoir to the tip by capillary action, and the high voltage was switched on. Figure 4 shows microscope time sequence images of the top view of ES at the tips demonstrating an elongating Taylor cone [Figs. 4(a)–4(d)], jet emission elliptical cone [Fig. 4(e)], and cone-jet mode electrospray [Figs. 4(f) and 4(g)] at an onset voltage of 2000 V for a duration of ~3 min at a chip-to-counter electrode spacing of 1.2 mm. When the ESI voltage was applied and slowly increased, the Taylor cone elongated and formed into an elliptically shaped cone. As the voltage was further increased to an onset voltage, the ellipsoid spontaneously changed to a pointed cone and the ES started, as evidenced by the measurement of a jump in ion current between the ESI chip and polished ground plate. Onset voltages of 2000 and 2500 V were measured for 1.2 and 1.4 mm microchip-to–counter electrode spacing, respectively. As the counter electrode spacing increased, the onset voltage increased since the electrical field exhibits a logarithmic dependence on chip tip–plate distance. It was also observed and recorded that as the applied voltage increased and the Taylor cone size decreased, with an associated decrease in jet diameter and jet breakup length. As observed in Fig. 4, the cones are well defined with virtually no lateral dispersion of the fluid at the microchannel exit. Compared to literature, Wang et al. reported threshold (onset) voltages of...
3200 and 3520 V for 1.5 and 2 mm microchip-to–counter electrode spacing and stated that the threshold voltage at 1.5 mm is smaller than that at 2 mm due to the stronger electric field, and as expected, the threshold voltage increases with higher gaps.

A relation giving the dependence of onset voltage $V_{on}$ was given by Smith,\textsuperscript{57} which is as follows:

$$V_{on} = A \sqrt{\frac{2Tc \cos \theta_0}{\varepsilon_0}} \ln \frac{4d}{r_c}$$

where $T$ is the surface tension of the fluid, $\theta_0$ is the half-angle of the liquid cone at the tip of the capillary, $r_c$ is the outer radius of the capillary, $\varepsilon_0$ is the electric permittivity of vacuum, $d$ is the distance between the chip tip and counter electrode, and $A$ is a proportionality constant. As in these set of experiments, $d$ is the variable, and onset voltage varies linearly with the logarithm of chip-to-counter electrode spacing (gap). Therefore,

$$V_{on}(d) = a \ln d + b$$

The experimental data are in agreement with relation (2), as shown in Fig. 5, which shows the measured ES as a function of onset voltage and gap for various chip prototypes. PS and PC substrates were embossed using a laser-machined steel tool and an electroformed nickel tool. Six microchips were obtained in a single embossing run; therefore, more than 24 microchips were tested and evaluated for ES demonstration. It was observed that as the distance between the channel exit and counter electrode increases, the onset voltage also increases. Wang et al.\textsuperscript{13} described using a sequence of snapshots of how the size of the Taylor cone is governed by the tip orifice geometry and the formation of the cone is governed by the electrical potential. In fact, the cone size and shape are also related to flow rate and the distance between the tip and MS inlet.

3.2 Effect of Aspect Ratio (AR)

AR is defined as the ratio of depth of the microchannel to the width of microchannel. Table 1 lists the microchannel dimensions, which were embossed using a laser-machined steel tool and an electroformed nickel tool on PS/PC substrates. These dimensions are reported in our previous study.\textsuperscript{30} Table 1 also records the ES parameters for the PS chip formed using the laser-machined steel tool at a gap of 1.2 mm from the counter electrode, and the images of the Taylor cones with brief comments. Similar results were also observed for various PS/PC substrates formed using the laser-machined tool and the electroformed nickel shim.

The hot-embossed open channel attached to a hot-embossed open reservoir on PS and PC substrates was experimentally observed to be hydrophilic because the fluid is delivered by electroosmosis and capillary forces, and the microchips can demonstrate good ESI performance at relatively low voltages. It was experimentally observed that for an open channel of smaller widths and depths, the narrower the channel is, the better the ES performance at low voltages is. The smaller the microchannel dimensions are, the higher the spray performance is. For a wide channel, the fluid tends to accumulate at the channel tip before it is sprayed. Hence, a bigger Taylor cone formation occurs before initiation of ES. From Table 1, the pattern observed is the decrease in Taylor cone size with a decrease in channel dimensions.

In this work, ES is produced at the open-channel polymer microfluidic chip designed with a microchannel exit angle of 90 deg. Our work is similar to Shiea and Yuan,\textsuperscript{58} who produced electrospray from open-channel exits fabricated by different tip angles. They suggested that there was no significant difference detected in the ion signal stability or the onset voltage of the ES generated from an open channel fabricated with exits sharpened at different tip angles (30, 60, 90, and 120 deg). Shinohara et al.\textsuperscript{43} investigated the influence of a hot-embossed bonded channel tip.
angle on Taylor cone formation. They stated that the success rate of Taylor cone formation increased with decreasing the tip angle \(\alpha\). Arscott et al.\(^{44}\) concluded that the performance of nib sources was seen to be linked to the slot dimensions; the smaller slot dimension is, the better the performance of SU-8 micronibs is. While a high voltage is applied, a Taylor cone could be formed at the tip.\(^{13}\) The size of the cone depends on the geometry and wetted area.\(^{45}\) Chiou et al.\(^{46}\) investigated the effect of the o.d. of the tip on the size of the Taylor cone. The relationship between the o.d. of the capillary \(D_0\) and the height of the Taylor cone was plotted and indicates that the geometric shape of the Taylor cone is a strong function of the \(D_0\). The larger the capillary is, the bigger the size of the Taylor zones is. Kebarle\(^{46}\) proposed that the required ES voltage is a function of the radius of spraying capillary as well as the surface tension of the spraying liquid. Furthermore, the fabrication and evaluation of microchips with covered and sealed channels but with a coverless ES electrospray tip was presented by Svedberg et al.\(^{23}\) They concluded that the tip length influenced the test results and stated that with a 10 mM solution and 1.5-mm-long tip, myoglobin crystallized at the end of the tip causing total failure after \(\sim 15\) min of ES. With a 0.3-mm-long tip, no failure had occurred after \(110\) min (11 refills) of spraying. Long open tips can result in evaporation of the sample solution, causing the substance to dry for low flow rates.\(^{23}\)

In this study, the microchannel length was kept constant as \(12.5\) mm. Figure 6(a) shows the measured ES as a function of aspect ratio and onset voltage for various chip prototypes, and Fig. 6(b) shows the measured ES as a function of aspect ratio and size of the Taylor cone (measured in microns). The common trend observed experimentally for various replicated microchips, embossed using the laser-achined and electroformed tool, was the decrease in Taylor cone size from a wide to a narrow channel of minimum width and depth. It was found the size of the Taylor cone increases as the aspect ratio decreases. The onset voltage directly relates to the chip dimensions. The narrower the channel is, the lower the onset voltage required is for initiation of ES with minimum sample consumption and high throughput.

In this work, ES from open-channel microchip tips of relatively smaller dimensions are demonstrated in comparison to the work of Shiea and Yuan et al.\(^{58}\) The advantage of the microdevice developed in this study lies in its simplicity. The combination of hot embossing and open-channel design leads to reduced complexity and simplifies the manufacturing process. Because it is an open reservoir, no air bubbles are formed in the liquid circuit. Higher spray current and lower jet diameter indicate that the device can perform equivalent to nanospray emitters while using microscale dimensions. This allows higher sample throughput and eliminates potential clogging problems inherent in nanocapillaries.

### 3.3 Influence of Onset Voltage on ES Modes

Five ES modes were identified and recorded at relatively low voltages at open-channel hot-embossed polymer micro-fluidic tips, as shown in Fig. 7. Figure 7 shows images of top view of ES at the polymer microfluidic open-channel tips demonstrating: Drop mode \(\{1800\) V\}, \(\{3000\) V\}, \(\{3500\) V\}, \(\{1900\) V\}, \(\{2000\) V\} onset voltage \[\text{[Fig. 7(a)]}\] cusp cone/pulse mode \(\{1900\) V\}, \(\{3500\) V\} \[\text{[Fig. 7(b)]}\] Taylor cone-jet mode \(\{2000\) V\} \[\text{[Fig. 7(c)]}\], multijet mode \(\{1800\) V\}, \(\{2000\) V\}, \(\{3000\) V\} \[\text{[Fig. 7(d)]}\].
and oscillating jet mode \(\{3500 \text{ V}\}\) \([\text{Figs. } 7(d)]\), and oscillating jet mode \(\{3500 \text{ V}\}\) \([\text{Figs. } 7(e) \text{ and } 7(f)]\) at respective voltages. For open-channel ESI systems, these results are highly original and first of its kind. The results are in accordance with the theory. Leu and Teng\(^6\) used a fused silica glass-bonded microchip and reported the ES mode photographed at tip of the nozzle, namely dripping, pulsating, cone jet, and multijet mode at voltages ranging from 6.5 to 9 kV. In their case, the onset voltage was 6.5 kV. They stated that as the voltage increased, the Taylor cone shrank and when the voltage exceeded 9.0 kV, multijet mode \(\{14.5 \text{ kV}\}\) appeared. The point of interest here is that the surface energy for the liquid near the tip of an open channel should be different from the surface energy near the tip of a closed channel. Therefore, the onset voltage for these two different designs (multijet mode: 3 kV for open channel, 14.5 kV for closed channel) is different.

In this work, it was experimentally observed that, as the onset voltage increased, the ES entered the Taylor cone-jet mode and at a high voltage, multijet with small Taylor cones, and nanospray emitted from the tip of Taylor cone were recorded. With a further increase in voltage, the ES entered in oscillating mode and the cycle stopped as the flow rate decreased. However, on addition of the fluid and on application of high voltage, the cycle restarted. The next step was to evaluate the relationship between current \(I\) and the voltage potential.

### 3.3.1 Relation between current and voltage

ES was observed by the jump in the ion current. The measured ES ion current was plotted as function of time, as shown in Fig. 8(a). The stable total ion current was monitored for \(>2\) min using a multimeter attached in series to the counter electrode. Figure 8(b) shows the relation between the ion current and the applied voltage. The current increased as the voltage increased and stable cone-jet ES is observed with nearly the same ion current. The chip tip-to-counter electrode spacing was 1.2 mm, and the fluid used was methanol/water \(\{70/30\}\).

The results reported in Fig. 8 are in accordance with Kameoka\(^1\). The total ion current measured and recorded was also evaluated as a function of onset voltages at various gaps, as shown in Fig. 9. From Fig. 9, it can be concluded that for open-channel systems, the higher the chip-to-counter electrode spacing is, the higher the spray voltage and current are. If the counter electrode is placed close to the tip, the ES can be initiated at low voltages. However, the ES plume was observed to be stable only when there was sufficient flow at the channel tip.

The measured ES was also evaluated as a function of onset voltage and size of the Taylor cone as shown in Fig. 10. Figure 10(a) inset shows an image of the Taylor cone formed at the front of the tip, and Fig. 10(b) the relationship between the onset voltages versus the height of the Taylor cone. As the voltage increased, the height of the Taylor cone increased. Similar trends were reported by Lin et al.\(^26\). They developed a constant-speed-pulling method to fabricate the ESI tip by pulling mixed PMMA glue using a 30-\(\mu\)m stainless steel wire through the preformed microfluidic channel.

In this work, the ES phenomena was initiated at a voltage of 2000 V at the tip of a channel with dimension of 100 \(\mu\)m width and 100 \(\mu\)m depth, and a chip-to-counter electrode spacing of 1.2 mm. Kameoka\(^1\) concluded that the thickness of the emitter film did not influence the spraying performance and stated that the ESI activity was only de-

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**Fig. 8** (a) Measured electrospray total ion current as a function of time. The stable total ion current was monitored for \(>2\) min using a multimeter attached in series to the counter electrode and (b) measured electrospray total ion current as a function of applied potential to the reservoir.

**Fig. 9** Measured electrospray total ion current as a function of onset voltage for different gaps.
pended on the top of the two-dimensional tip. A crucial aspect for successful ESI interface is the formation and maintenance of a stable ES. ESI stability depends on a number of factors, including flow rate, and surface tension, and it is well known that a narrow or drawn capillary tip can be used to demonstrate stable ES. Furthermore, the drops formed at an electrically connected nozzle or orifice will acquire a certain amount of induced charge, which depends on the imposed electric field strength/applied voltage. Studies have also shown that the motion of charge carriers, such as ions, in a fluid can cause electro-hydrodynamic (EHD) flow or Coulomb-driven convection flow during ES formation. Information about electric charge (including free charge and induced charge) on the electroformed droplets and the electric-field intensity inside the experimental cell are also very important to study the EHD effects on the mechanism of drop formation and motion during ES. Tousis et al. studied the effect of capillary-tip configuration and voltage on pressure applied by the fluid on the grounded disk electrode, at an electrode distance of 3 cm and conical-tip capillary. The pressure increases as the distance between the electrodes is decreased, and it is approximately doubled when the distance is decreased by a factor of 2. A graph showing the effect of electrode distance and voltage on pressure applied by the fluid on the grounded disk electrode was also presented. They stated that the experimental results show that, due to EHD flow, the pressure applied on the electrically grounded disk is higher for the conical-tip electrode, the shorter distance between the electrodes, and the negative-polarity applied voltage. In this work, ES was produced at the pointed chip tip with a tip angle of 90 deg. The pointed out that ESI tip thus provides the higher local electric field needed for spraying of higher surface-tension liquids without any electric breakdown effects.

3.3.2 Voltage-current characterization in ES mode

Arscott and Troadec measured the ionization current produced during ES of a given test liquid using the current-voltage (I-V) technique. In terms of ES from a tip having a capillary-tube-based topology, the electric field at the tip was evaluated using

\[ E_{\text{tip}} = 2V_{\text{app}}/r_{\text{tip}} \ln(4d/r_{\text{tip}}), \]  

where \( V_{\text{app}} \) is the applied voltage, \( r_{\text{tip}} \) is the radius of the tip, and \( d \) is the distance from the tip to the ground plane. In addition, the onset electric field \( E_{\text{onset}} \) for ES can be estimated using the following relationship:

\[ E_{\text{onset}} = \sqrt{4\gamma \cos \theta / \epsilon_0 r_{\text{tip}}}, \]

where \( \gamma \) is the surface tension of the liquid, \( \theta \) the half-angle of the Taylor cone, and \( \epsilon_0 \) is the permittivity of free space. Thus, by combining Eqs. (3) and (4), Eq. (5) was obtained, which estimates the ES onset voltage \( V_{\text{onset}} \) at a given outer tip radius \( r_{\text{tip}} \):

\[ V_{\text{onset}} \sim \ln(4d/r_{\text{tip}}) \sqrt{(r_{\text{tip}} \gamma \cos \theta / 2\epsilon_0)}. \]

Using the above model, Arscott and Troadec predicted an onset voltage of 100 V for a device having a tip radius on the order of 150 nm. In this work, the experimental onset voltage recorded is 2000 V for a microchip having a channel width and depth of 100 \( \mu \)m. Furthermore, Arscott and Troadec stated that, first, this model predicts for devices having submicron tip radii to demonstrate very low ESI onset voltages (200 V), especially if the tip radius is on the scale of a few tens or hundreds of nanometers. Second, it was noted at low values of tip radius (e.g., 50 nm), the distance between the tip and the ground plane has little effect on the onset voltage as the electric field at the tip is governed by the tip radius. They concluded that the measured ES onset voltages for such small tip dimensions do not agree with this model because the tip-to-ground plane distance \( d \) has a greater effect in determining the value of \( V_{\text{onset}} \). In this study, it is concluded that our experimental data are in quantitative agreement with the above model. The results also indicate that the lower the chip-to-counter electrode spacing requires a lower onset potential, as shown in Fig. 5. The total ion current measured and recorded was also evaluated as a function of onset voltages at various chip tip-to-counter electrode spacing (gaps) as shown in Fig. 9, from which it can be concluded that for open-channel systems, the higher the chip-to-counter electrode spacing is, the higher the spray voltage and current are.

4 Conclusions

The aim of the research was to investigate the factors influencing the performance of ES polymer microchips in terms of repeatability, practicality, onset voltages, and functionality. Microchips used in the investigation had an open reservoir with an open microchannel attached and were fabricated by the hot-embossing technique to avoid complicated fabrication procedures. The simple design eliminated dead fluid volume normally due to external connections to the chip by using capillary forces for fluid flow along the microchannel.

The open-channel chip design combined with the hot-embossing process is different from other attempts reported in the literature. The ES performance of the emitter is evaluated with respect to its geometry, operating conditions, and ESI parameters, such as onset voltage and current. The results indicate that AR of the microfluidic chips is one of the most important design factors that affects the
ES performance. An open-channel polymer microfluidic chip with higher AR will result in lower sample consumption, a higher ES current, and requires lower onset potential. The results also indicate that the lower the chip-to-counter electrode spacing requires a lower onset potential. The correlation results are compared to the literature. The conclusions can be summarized as follows:

1. As the distance between the channel exit tip and counter electrode increases, the onset voltage also increases for open-channel ESI systems.
2. For open channels of smaller widths and depths, the narrower the channel is, the better the ES performance is at low voltages.
3. The narrower the channel is, the lower the onset voltage is required for initiation of ES with minimum sample consumption and high throughput.
4. Five ES modes, namely, drop mode, pulse mode, Taylor-cone jet mode, multijet mode, and oscillating counter electrode spacing function of time and onset voltage at various chip-to–counter electrode spacing (gap).
5. For open channel systems, the higher the chip-to-counter electrode spacing is, the higher the spray voltage and current are. As the voltage increases, the size of the Taylor cone increases.

Acknowledgments

The authors thank MiniFAB (Aust) Pty Ltd., Scoresby, Victoria, Australia, for help in hot embossing and for providing the resources during the ES experiments. Thanks are also extended to the Center for New Manufacturing (CNM), Swinburne Tafe, Victoria, Australia, for fabricating the laser-machine tool.

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