Electrospray using an Ionic Liquid Counter Electrode and its Characterization by the Spray Current Measurement

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Electrospray apparatus, using ionic liquid (1-ethyl-3-methylimidazolium acetate) as a counter electrode, was developed and investigated by the spray current measurement. The current–voltage characteristics were studied using conductive ionic liquid and non-conductive silicone oil. The capturing and neutralizing of ejected droplets on the ionic liquid counter electrode were confirmed by the spray current monitoring. In addition, the electrospray apparatus was evaluated using the empirical formula of current flow characteristics. The obtained exponent value of \(n_{iq} = 0.517\) in the electrospray apparatus using the ionic liquid counter electrode was consistent with the exponent value \(n\) of \(~0.5\), which is reported by the standard electrospray set up using a metal counter electrode. The electrospray techniques using ionic liquid as a counter electrode may provide environmentally sustainable processes for the production and functionalization of nanoparticles.

Keywords: Nano/micro fabrication, Electrospray apparatus, Current-flow characteristics

1. Introduction

Electrospray phenomenon is a hydrodynamic process in which fine and monodisperse droplets can be generated by the electrical repulsion force [1, 2]. Electrospray techniques can be applied to nano/micro fabrication processes for particle production [3,4], thin-film coating [5-7], and fiber formation [8,9]. A simple configuration of an electrospray apparatus contains a nozzle and counter electrodes, a sample ejection pump, and a high voltage power supply. Thus, electrospray apparatus is an inexpensive and scalable manufacturing tool.

Ionic liquids have attracted considerable attention as promising materials for constructing environmentally sustainable processes owing to their favorable properties as green solvents such as low toxicity [10,11] and biodegradability [12]. In addition, compared to other liquid materials, including water and organic solvents, ionic liquids exhibit high conductivity, high chemical reaction rate [13], electrochemical stability [14], and thermal stability [15].

Thus, the combined use of electrospray technique and ionic liquids may provide environmentally sustainable processes for nanoparticle production and functionalization associated with chemical reaction, electrochemical reaction, and thermal processes. Although few studies have reported the use of ionic liquid in electrospraying, ionic liquids have been only applied as spraying materials (e.g., charge injection into non-conductive sample solution [16], vacuum process based on low vapor pressure property of ionic liquids [17], and electric propulsion system [18]). The research on the use of ionic liquids as a liquid counter electrode in an electrospray apparatus for the further functionalization process of nanoparticles has not been carried out.

In this study, an electrospray apparatus using an ionic liquid counter electrode was developed for the environmentally sustainable process of synthesis...
and functionalization of nanoparticles. To evaluate the capturing and neutralizing ability of ejected droplets on the liquid counter electrode, spray current was measured by changing applied voltage on the nozzle electrode. In a standard electrospray apparatus, spray current $I$ is known to be proportional to the flow rate $Q$ on the basis of the empirical formula $I \propto Q^n$ with the exponent value $n$. Thus, current flow characteristics were investigated in the electrospray apparatus using the ionic liquid counter electrode by comparing the measured values with those of a standard metal counter electrode.

2. Materials and methods

2.1. Electrospray apparatus using a liquid counter electrode

Figures 1(a) and (b) show the schematic configuration and experimental setup of an electrospray apparatus using a liquid counter electrode. A nozzle electrode with a 0.17-mm inner diameter and 0.36-mm outer diameter (Musashi Engineering Inc., Tokyo, Japan) was used. High voltage can be applied to the nozzle electrode using a power supply (HCZE-30PN0.25, Matsusada Precision Inc., Shiga, Japan). Spray current was monitored using an amperemeter (115B MILLIVOLT AMMETER, Kikusui Electronics Corp., Kanagawa, Japan). Poly (L-lactic acid) (PLLA) (Resomer L 206 S, Sigma-Aldrich Corp., USA), which is a semicrystalline polymer, 0.6% w/w in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) was ejected from the nozzle electrode using a syringe pump (MSPE-1, As One Corp., Tokyo, Japan). Ionic liquid 1-ethyl-3-methylimidazolium acetate (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) and silicone oil (KE-109E-B, Shin-Etsu Chemical Co., Ltd., Tokyo, Japan) were used as liquid counter electrode materials. Table 1 shows the material properties of the ionic liquid (1-ethyl-3-methylimidazolium acetate) and silicone oil (KE-109E-B). A relatively low specific gravity (1.00–1.10 g/cm$^3$) will improve the dispersion of polymer particles into liquids without floating at the liquid surface. Ionic liquid is conductive with a value of $2.8 \times 10^3$ μS/cm, and silicone oil is non-conductive with a value of $1.7 \times 10^{-4}$ μS/cm.

Table 1. Properties of liquid materials for counter electrodes.

| Liquid counter electrodes                                | Specific gravity (g/cm$^3$) | Conductivity (μS/cm) |
|----------------------------------------------------------|-----------------------------|----------------------|
| Ionic liquid (1-ethyl-3-methylimidazolium acetate) [19,20] | 1.10                        | $2.8 \times 10^3$   |
| Silicone oil (KE-109E-B) [21]                           | 1.00                        | $1.7 \times 10^{-4}$ |

2.2. Spray current measurement in an electrospray apparatus using liquid electrodes

To investigate the I–V characteristics of the electrospray phenomena using liquid counter electrodes, spray current was monitored using the ammeter (115B MILLIVOLT AMMETER). The applied voltage to the nozzle electrode ($V_{\text{nozzle}}$) was changed in the range of 0.0–8.3 kV. The flow rate was 3.0 μL/min. The liquid counter electrode was

![Fig. 1. (a) Schematic configuration of the nozzle electrode and liquid counter electrode in the electrospray apparatus. (b) Photograph of the experimental set up of the nozzle electrode and liquid counter electrode.]

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placed directly below the nozzle electrode, and the distance between the tip of the nozzle electrode and the surface of the counter electrode was set to 40 mm. A polystyrene container (18-mm inner diameter, 21-mm outer diameter, and 42-mm height, SANPLATEC Corp., Osaka, Japan) was filled with ionic liquid or silicone oil. A copper wire was immersed into the liquid from the bottom side of the polystyrene container; the contained was sealed, and the wire was connected to the ammeter to monitor the spray current.

2.3. Current flow characterization using the ionic liquid counter electrode

For comparison, a copper mesh electrode (60-mm diameter with 0.11-mm wire diameter, Nilaco Corp. Tokyo, Japan) was used as a standard counter electrode. A glass container (60-mm diameter) of the same size with the copper mesh electrode was filled with the ionic liquid 1-ethyl-3-methylimidazolium acetate as the liquid counter electrode. The distance between the tip of the nozzle electrode and the surface of the counter electrode was set to 20 mm. Spray current was measured with a constant flow rate of 0.0, 4.5, 7.0, and 12.0 μL/min. The applied voltage to the nozzle electrode \( V_{\text{nozzle}} \) was set to 5.0 kV.

3. Results and discussion

3.1. Spray current in the electrospray apparatus using liquid counter electrodes

Electrospraying is as electrohydrodynamic phenomenon; thus, an electrical circuit can be used [22,23], as shown in Fig. 2. During the electrospraying process, the nozzle electrode ejects charged droplets. Charged droplets can be neutralized on the surface of the counter electrode, and consequently, a current flow can be measured using an amperemeter as the spray current.

First, electrospray process using a liquid counter electrode was investigated using the ionic liquid \( (2.8 \times 10^3 \ \mu\text{S/cm}) \) and silicone oil \( (1.7 \times 10^{-4} \ \mu\text{S/cm}) \) as the counter electrode materials. Spray current was monitored using an amperemeter by varying the applied voltage to the nozzle electrode \( (V_{\text{nozzle}}) \) from 0.0 to 8.3 kV. Figure 3 shows the representative current–voltage characteristics for the ionic liquid and silicone oil as the counter electrode. When using the ionic liquid counter electrode, a clear spray current on the order of a few nA was observed above \( V_{\text{nozzle}} = 3.0 \) kV. This detection of spray current indicates that (i) electrospray was formed by overcoming the threshold voltage, and (ii) ejected charged droplets were captured and neutralized by the ionic liquid counter electrode. With a further increase above \( V_{\text{nozzle}} = 8.0 \) kV, a sharp increase in the current value on the order of few hundred nA to several μA was observed. This sharp increase in the current value can be considered as corona-type discharges at the nozzle. However, when using the silicone oil counter electrode, spray current was not detected (less than 0.3 nA). In this observation, the ejected charged droplets were not captured well on the silicone oil counter electrode owing to the charge accumulation on the surface of the silicone oil counter electrode. The charge accumulation on the surface may distort the electric field [24]; thus, charged droplets were not sufficiently captured by the silicone oil counter electrode. These results indicated that high conductivity was essential for the liquid counter electrode material to capture the ejected charged droplets by avoiding the distortion of the electric field, which arises owing to charge accumulation.

![Fig. 2. Electrical circuit of the electrospray apparatus using the liquid counter electrode.](image)

![Fig. 3. Representative I–V plots of the ionic liquid and silicone oil liquid counter electrodes during the electrospraying process.](image)
electrode was investigated by varying the flow rate. The flow rate ($Q$) was set to 0.0, 4.5, 7.0, and 12.0 $\mu$L/min. The spray current was measured with the applied voltage of 5.0 kV. For comparison, the spray current when using a copper counter electrode was also measured as the standard set up in the electrospray apparatus. Figure 4 shows the spray current ($I$) of the electrospray apparatus with ionic liquid and copper counter electrodes at each flow rate $Q$. The obtained spray current values were relatively higher than the spray current shown in Fig. 3 owing to the size difference of the counter electrodes. The value of spray current $I$ increased in both copper mesh and ionic liquid electrodes depending on the flow rate $Q$. There was no considerable difference in current flow characteristics between the ionic liquid electrode and the standard copper electrode.

![Fig. 4. Current flow characteristics of the electrospray apparatus using the ionic liquid counter electrode and the standard copper mesh electrode (circles: experiments, lines: fitted lines).](image)

For further investigation, current flow characteristics were analyzed using a theoretical equation. The relationship between the spray current $I$ and the flow rate $Q$ is described as follows,

$$I \propto \left( \frac{\gamma K Q}{\varepsilon} \right)^{\frac{1}{2}}$$

(1)

where $\gamma$ denotes the surface tension of the sample solution; $K$ denotes the conductivity; $\varepsilon$ denotes the permittivity of the sample solution [25]. Then, the experimental data of current flow characteristics was fitted with the following equation,

$$I = \alpha Q^{-niq}$$

(2)

where $\alpha$ and $niq$ are the constants. The values of $niq$ were obtained as 0.497 for the copper electrode and 0.517 for the ionic liquid electrode. The values of the constant $niq$ for both copper and ionic liquid electrodes were consistent with those previously reported for the electrospray phenomena, which showed that the spray current $I$ was proportional to the square root of the flow rate as $I \propto Q^{0.5}$ [25-28]. These results indicate that the use of ionic liquid will not distort the electrospray phenomena, and ionic liquid can be used as the counter electrode in the electrospray apparatus.

4. Conclusion

In this study, an electrospray apparatus using ionic liquid (1-ethyl-3-methylimidazolium acetate) as a counter electrode was developed for the sustainable process of synthesis and functionalization of nanoparticles in ionic liquid. To evaluate the electrospray apparatus, spray current was monitored during the electrospray process. The capturing and neutralizing of ejected droplets on the ionic liquid counter electrode were confirmed by spray current monitoring. The current flow characteristics were also evaluated. The exponent value of $niq = 0.517$ in the electrospray apparatus using the ionic liquid counter electrode was consistent with the exponent value $n$ of ~0.5 in the empirical formula $I \propto Q^n$. These results indicate that the use of the ionic liquid counter electrode will not distort the electrospray process during nanoparticle synthesis.

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References

1. A. Jaworek, J. Mater. Sci., 42 (2007) 266.
2. E. Bodnar, J. Frifoll, and J. Rosell-Llompart, J. Aerosol Sci., 125 (2018) 57.
3. J. Xie, J. Jiang, P. Davoodi, M. P. Srinivasan, and C. H. Wang, Chem. Eng. Sci., 125 (2015) 32.
4. R. T. Steipel, M. D. Gallovic, C. J. Batty, E. M. Bachelder, and K. M. Ainslie, Mater. Sci. Eng. C, 105 (2019) 110070.
5. I. B. Rietveld, K. Kobayashi, H. Yamada, and K. Matsushige, Soft Matter, 5 (2009) 593.
6. J. Xie, J. C. Tan, and C.-H. Wang, J. Pharm. Sci., 97 (2008) 3109.
7. C. Berkland, D. W. Pack, and K. K. Kim,
Biomaterials, 25 (2004) 5649.
8. C. Luo, S. D. Stoyanov, E. Stride, E. Pelan, and M. Edirisinghe, Chem. Soc. Rev., 41 (2012) 4708.
9. J. Xue, W. Tong, D. Yunqian, and Y. Xia, Chem. Rev., 119 (2019) 5298.
10. B. Jastorff, R. Störmann, J. Ranke, K. Mölter, F. Stock, B. Oberheitmann, W. Hoffmann, J. Hoffmann, M. Nüchter, and B. Ondruschka, Green Chem., 5 (2003) 136.
11. P. Wasserscheid, R. Hal, and A. Bösmann, Green Chem., 4 (2002) 400.
12. N. Gathergood, M. T. Garcia, and P. J. Scammells, Green Chem., 6 (2004) 166.
13. J. D. Holbrey and K. R. Seddon, Clean Prod. Process., 1 (1999) 223.
14. H. Matsumoto, M. Yanagida, K. Tanimoto, M. Nomura, Y. Kitagawa, and Y. Miyazaki, Chem. Lett., 29 (2000) 922.
15. M. Kosmulski, J. Gustafsson, and J. B. Rosenholm, Thermochim. Acta, 412 (2004) 47.
16. C. Larriba-Andaluz and J. Fernández de la Mora, Phys. Fluids, 22 (2010) 072002.
17. Y. Guo, S. Li, Z. Wu, K. Zhu, Y. Han, and N. Wang, Phys. Fluids, 26 (2019) 073511.
18. K. Nakagawa, T. Tsuchiya, and Y. Takao, Jpn. J. Appl. Phys., 56 (2017) 06GN18.
19. A. Nazet, S. Sokolov, T. Sonnleitner, T. Makino, M. Kanakubo, and R. Buchner, J. Chem. Eng. Data, 60 (2015) 2400.
20. Q. Zhang, S. Cai, W. Zhang, Y. Lan, and X. Zhang, J. Mol. Liq., 233 (2017) 417.
21. Data sheet of KE-109E-B (provided by Shin-Etsu Chemical Co., Ltd., Tokyo, Japan).
22. G. S. Jackson and C. G. Enke, Anal. Chem., 71 (1999) 3777.
23. K. Wang, Z. Tan, C. Ryan, K. Smith, M. Paine, and J. Stark, Sens. Actuat. B, Chem., 147 (2010) 618.
24. K. Hashimoto, H. Takehara, and T. Ichiki, Jpn. J. Appl. Phys., 58 (2019) SDDK04.
25. J. F. De La Mora and I. G. Loscertales, J. Fluid Mech., 260 (1994) 155.
26. A. M. Ganan-Calvo, Phys. Rev. Lett., 79 (1997) 217.
27. F. Higuera, J. Fluid Mech., 513 (2004) 239.
28. A. Sen, J. Darabi, D. R. Knapp, and J. Liu, J. Micromech. Microeng., 16 (2006) 620.