Flow characterization of electroconvective micromixer with a nanoporous polymer membrane *in-situ* fabricated using a laser polymerization technique

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Electroconvection is known to cause strong convective mixing in a microchannel near a nanoporous membrane or a nanochannel in contact with an electrolyte solution due to the external electric field. This study addresses micromixer behavior subject to electroconvection occurring near a nanoporous membrane *in-situ* fabricated by a laser polymerization technique on a microfluidic chip. We found that the micromixer behavior can be categorized into three regimes. Briefly, the weak electroconvection regime is characterized by weak mixing performance at a low applied voltage and KCl concentration, whereas the strong electroconvection regime has a high mixing performance when the applied voltage and KCl concentration are moderately high. Finally, the incomplete electroconvection regime has an incomplete electric double-layer overlap in the nanopores of the membrane when the electrolyte concentration is very high. The mixing index reached 0.92 in the strong electroconvection regime. The detailed fabrication methods for the micromixer and characterization results are discussed in this paper. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4922082>]

INTRODUCTION

Mixing in a microfluidic system is well known to be very slow because it is dominated by the process of molecular diffusion at low Reynolds numbers (Re). As a result, various types of micromixers have been developed to enhance mixing in microfluidic systems.¹ They are categorized as passive mixers or active mixers, in general, depending on their operational mechanism. A passive mixer utilizes either the microstructure of the mixing channel to disturb the laminar flow or multiple laminate flows to reduce the mixing distance for molecular diffusion. Such a mixer requires no external power except the flow driving power. Passive mixers are further categorized as parallel/serial lamination,² injection,³ chaotic advection,⁴ and droplet⁵ mixers. On the other hand, active mixers increase the mixing efficiency by using external power in the form of pressure, temperature, an electric field, or acoustic waves. Due to the applied external power, the mixing channel in such a mixer is much shorter than those of passive mixers. Among the various external power sources, an electric field is often used because electrodes are readily integrated on a micromixer chip. In addition, the diversity of microfluidic characteristics responding to the electric field makes it popular means for mixing. For example, electrokinetic instability,^{6,7} dielectrophoretic force,^{8,9} electrohydrodynamic disturbance,¹⁰ electroosmotic force,¹¹ and electroconvection^{12,13} have been reported as mixing mechanisms for active mixers.

Electroconvection involves non-equilibrium electrokinetic phenomena occurring near nanochannels or nanopores with a net surface charge and is known to cause strong convective

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mixing. If the nanopores or nanochannels are filled with an electrolyte, the counterions, having opposite charge to the surface charge, form an electric double layer (EDL) on the surface of the nanopores or nanochannel.¹⁴ If EDLs are overlapped in nanopores or nanochannels, charge screening effect occurs in the nanopores or nanochannels. Consequently, coions in the electrolyte are inhibited to pass through the nanochannels or nanopores.¹⁵ For example, if a nanochannel with a negative surface charge is subject to EDL overlap, only cations can pass through the nanochannel, as shown in Fig. 1(a). When a DC voltage is applied across the nanochannel in a microchannel, the anions on the anode side move away from the nanochannel toward the anode, and the cations freely move to the cathode. However, the anions moving toward the anode from the cathode side are blocked near the entrance of the nanochannel due to the EDL overlap with a net negative charge, resulting in agglomeration near the entrance of the nanochannel. As a result, the ions are concentrated near the nanochannel on the cathode side (ion enrichment zone) and are depleted on the anode side of the nanochannel (ion depletion zone). This phenomenon is referred to as ion concentration polarization (ICP).¹⁵ When the ion concentration in the ion depletion zone nears zero, the current remains constant (limiting current) even if the applied voltage is increased (Fig. 1(b)). When the voltage is increased further, the local electric field becomes significantly higher due to the extremely low local conductivity in the ion depletion zone. This causes a locally amplified, non-equilibrium electrokinetic flow and, consequently, strong convective mixing disturbing the ion depletion zone. This process is referred to as electroconvection and generates an overlimiting current proportional to the applied voltage.¹⁶

Three non-equilibrium electrokinetic micromixers utilizing electroconvection have been reported in the literature. One is a micromixer with an array of nanochannels bridging two microchannels,¹² in which electroconvective mixing occurs near the inlets of the nanochannels.

FIG. 1. Schematics of (a) ion concentration polarization and (b) current density variation with respect to the voltage across the nanochannel.

The mixing index was reported to reach 0.84 with a 0.5 mM KCl solution. However, the index decreased to 0.51 due to weak EDL overlap when the concentration of the KCl solution was increased to 50 mM. Another micromixer consists of a commercial Nafion film sandwiched between two polymethylmethacrylate (PMMA) substrates with a microchannel pattern.¹³ De-ionized water with and without a dye was used as a mixing solution, and a mixing index as high as 0.87 was reported with an applied voltage of 0.9 kV. The last one used electric breakdown to create nanojunction at the bonded layer of two PDMS substrate,¹⁷ and showed 90% mixing of two fluid streams.

Although the three micromixers exhibited superior mixing performance, the first mixer requires an expensive nanochannel fabrication process such as two-step reactive ion etching, and the second mixer has difficulties in integrating other microfluidic functionalities due to the 3-dimensional sandwiched substrate structure. The last mixer has a nanojunction between microchannels, but the shape and size seem hardly controllable. Thus, it will be beneficial to develop a 2-dimensional (2-D) micromixer using non-equilibrium electrokinetic mixing phenomena that can be fabricated by a facile and inexpensive method. At the same time, it is desirable for the micromixer to maintain the EDL overlap or the capability of ICP at a high salt concentration, because ICP technology has great potential in the desalination of sea water.¹⁸

This paper investigates the flow characteristics and mixing performance of a 2-D non-equilibrium electrokinetic micromixer with a nanoporous polymer membrane, which can be readily *in-situ* fabricated on a microfluidic chip using a laser polymerization technique. The mixing performances are thoroughly investigated with varying the applied voltage and concentration of mixing solution.

EXPERIMENTAL SECTION

A schematic of an electroconvection micromixer with a nanoporous membrane is shown in Fig. 2. The micromixer is composed of a U-shape microchannel with a height and width of 10 μm and 100 μm , respectively, with two inlets and one outlet. There is a by-pass junction connecting the upstream and downstream flows of the microchannel, containing a nanoporous membrane *in-situ* fabricated using a laser polymerization technique.

The preparation of the micromixer consists of chip fabrication using a standard wet-etching process followed by anodic bonding and *in-situ* fabrication of a nanoporous polymer membrane. The micromixer is made of borosilicate. An amorphous 500-nm-thick poly-silicon layer was deposited by low pressure chemical vapor deposition (LPCVD, SJF-1000P2, SUNGJIN SEMITECH) on a borosilicate glass wafer (BOROFLOAT[®] 33, SCHOTT). A positive photoresist (AZ4620, AZ Electronic Materials) was spin-coated (YS-100MD, YOOIL Eng.) on the wafer, exposed to UV light (MA6-II, SUSS Microtec) through a film mask with a microchannel

FIG. 2. Schematic of the electroconvective micromixer chip with a nanoporous polymer membrane *in-situ* fabricated using laser polymerization.

pattern and developed (AZ300 MIF, AZ Electronic Materials). Then, the amorphous polysilicon was etched by reactive ion etching (Vision RIE, Advanced Vacuum) followed by wet-etching of the glass substrate using a buffered oxide etchant with a 6:1 volume ratio of 40% ammonium fluoride (NH₄F, JUNSEI) in water to 49% hydrofluoric acid in water (48%–51% HF, J.T. Baker). The etched glass substrate was anodic-bonded to a cover glass plate (BOROFLOAT[®] 33, SCHOTT) with its holes aligned with the inlets and outlet after removing the photoresist. Finally, it was thoroughly rinsed with acetone, isopropanol, and deionized (DI) water in order.

A nanoporous polymer membrane was *in-situ* fabricated on a micromixer chip. The fabrication process of the membrane is the same as that employed by Song *et al.*¹⁹ In the present study, the membrane with a low molecular weight cut-off (MWCO) was used, for which the pore size was reported to be smaller than that of FITC-insulin (5700 Da). Briefly, the U-shape microchannel was coated with a 2:2:1 (vol) mixture of deionized water, glacial acetic acid (DAEJUNG), and 3-trimethoxysilylpropyl acrylate (Sigma-Aldrich) so that the channel surface could be covalently bonded with the nanoporous membrane. Then, we utilized the laser polymerization technique depicted in Fig. 3(a) to fabricate the nanoporous polymer membrane using a phase separation method.^{19,20} A monomer solution was prepared using 2-(N-3-sulfopropyl-N, N-dimethylammonium)ethyl methacrylate (SPE, RASCHIG) as a monomer, N,N'-methylenebisacrylamide (BIS, Sigma-Aldrich) as a crosslinker, 2,2' azobis(2-methylpropanimidamide)-dihydrochloride (v50, Sigma-Aldrich) as a photoinitiator, and a solvent mixture of DI water and 2-methoxyethanol (Sigma-Aldrich). The laser beam with a wavelength of 355 nm (FTSS355-Q048, CryLaS) was shaped to a laser sheet using a slit and lenses. Then, the by-pass junction of the microchannel filled with the monomer solution was exposed to the laser sheet. After about 1 min, a nanoporous membrane with a width of 40 μm was formed, as shown in Fig. 2(b).

To evaluate the mixing performance of the mixer, potassium chloride solutions (Wako) with concentrations in the range of 1–100 mM were used as the working fluid. Also, a 0.05 mg/ml Rhodamine B (JUNSEI) fluorescent dye, an electrically neutral dye in a buffer solution with pH 6.8–7.0, was added to the inlet solution to distinguish the flows from each inlet. An electroosmotic flow was generated by applying a DC voltage (PS350, Stanford Research System) across the microchannel using platinum wires (Goodfellow Cambridge Ltd.) placed in the reservoirs, as shown in Fig. 2. Note that the pressure driven flow was suppressed by carefully maintaining the menisci in the reservoirs during the experiments. The mixing caused by electroconvection was observed and recorded on an inverted fluorescence microscope (IX71, Olympus) with a 20 $\times$ objective and a CCD camera (DP71, Olympus).

FIG. 3. (a) Schematic of the *in-situ* fabrication of a polymer membrane on a micromixer chip using a laser polymerization technique, and (b) a microscope image of a nanoporous polymer membrane about 40 μm in thickness.

FIG. 4. Consecutive fluorescence images after the onset of a voltage of 400 V applied to the micromixer. The concentration of KCl solution is 50 mM.

RESULTS AND DISCUSSION

To confirm the EDL overlaps in the nanopores of the *in-situ* fabricated nanoporous membrane and mixing by electroconvection, we applied an electric field to the microchannel filled with a 50 mM KCl solution. Figure 4 shows consecutive flow images after the onset of a voltage of 400 V. There was no flow until the electric field was applied so that the entire channel initially appeared to emit the red fluorescence of Rhodamine B, which was transported by molecular diffusion. Applying the electric field allowed us to vividly distinguish the two inlet flows with and without Rhodamine B due to creation of an electroosmotic flow (EOF) about 760 ms after the onset. The images clearly show that the two flow streams are almost instantly mixed near the membrane. This implies that the mixing is caused by electroconvection and that an EDL overlap occurs in the nanopores of the polymer membrane. In addition, zeta potential measurements for the polymer in a form of particles (Nano ZS, Malvern Instrument Ltd) yield about -16.8 and -12.7 mV in a 10 mM and 50 mM KCl solution, respectively. This indicates that the polymer has a non-zero net surface charge even if the monomer is zwitterionic. We think that the surface charge was caused by unknown sources during the polymerization since the surface charge of many polymers is affected by fabrication technique.²¹

The next phase of the study was to quantify the contribution of electroconvection on the mixing performance compared to the molecular diffusion of Rhodamine B. We compared the mixing performance with and without electroconvection, as shown in Fig. 5. The channel on the left-hand side is identical to that on the right-hand side except for the absence of the by-

FIG. 5. Comparison of mixing with and without electroconvection in a 50 mM KCl solution. The applied voltage ranged from 50 to 400 V. The left-hand side of each fluorescence image pair shows mixing by molecular diffusion in a microchannel without a by-pass, while the right-hand side shows electroconvective mixing in a micromixer with a nanoporous membrane.

pass junction and, consequently, the nanoporous membrane, such that the mixing is generated by only molecular diffusion. Because the EOF is slow at a low voltage of 50 V, the two inlet flows of the EOF-only case appear to be well mixed by molecular diffusion. However, at a voltage of 400 V, the two inlet flows of the EOF-only case remain separated downstream because the fast EOF does not allow sufficient time for molecular diffusion. On the other hand, the right-side images show the mixing caused by electroconvection occurring near the nanoporous membrane in addition to molecular diffusion. Regardless of the applied voltage, mixing appears to occur instantly near the membrane. Although we show only three comparisons for simplicity in Figure 5, we repeated the experiments for 8 different voltages ranging from 50 V through 400 V. These results indicate that the main cause of mixing at high voltages is electroconvection. In addition, it was found that the electroconvection becomes stronger with the increase in voltage because the inlet flows are mixed equally well despite the increased EOF velocity at higher voltages.

After confirming the effects of the electric field strength on mixing, we investigated the effects of the KCl solution concentration on mixing performance. The concentration of KCl solution was varied from 1 through 50 mM, and the resulting mixing performances were compared, including the case with no by-pass junction. Figure 6(a) shows fluorescence images for the cases subjected to a voltage of 400 V. In the no-bypass channel filled with a 10 mM KCl solution, the two inlet flows are clearly distinguished over the entire image. For the micro-mixers with a nanoporous membrane, mixing appears to be very weak with 1 mM KCl solution but improved with a concentration of 5 mM. Finally, almost perfect mixing was observed at KCl concentrations of 10 and 50 mM. The fluorescence intensity profiles measured 100 μm downstream of the membrane are shown in Fig. 6(b). The intensity was normalized by the

FIG. 6. Effects of KCl solution concentration on electroconvective mixing at an applied voltage of 400 V. (a) Fluorescence images and (b) normalized fluorescence intensity profiles measured 100 μm downstream of the membrane along the blue line in the image.

average intensity across the channel. In accordance with the fluorescence images, these profiles indicate that the mixing is gradually enhanced with increasing concentration of KCl solution.

In order to quantify the mixing performance enhancement, following the qualitative investigation, we utilized the mixing index suggested by Kim *et al.*,¹²

$$\text{mixing index} = \frac{\int |I(x) - I_{diff}(x)| dx}{\int |I_{100\%}(x) - I_{diff}(x)| dx}, \quad (1)$$

where $I(x)$ is the local fluorescence intensity 100 μm downstream of the nanoporous membrane, $I_{diff}(x)$ is the fluorescence intensity at the same location of the channel without the by-pass junction under the same experimental conditions, and $I_{100\%}(x)$ is the fluorescence intensity of perfect mixing at the same location. This definition excludes the contribution of molecular diffusion to mixing. Figure 7(a) plots the mixing index variations with respect to the applied voltages for various KCl solution concentrations. For a KCl solution of 1 mM, the mixing index due to electroconvective mixing is low, regardless of the applied voltage. However, the mixing index increases with the increase in voltage for KCl solution concentrations higher than 1 mM. For example, the mixing index was about 0.92 for the case of 50 mM and 200 V. The only exception was at a concentration of 100 mM, where the mixing index decreases with the increase in voltage beyond 100 V. This is attributed to the weakening of electroconvection resulting from a thin EDL and consequent incomplete EDL overlap caused by the too high concentration of KCl solution. As a result, the repulsive force on the coions of the nanopore surface decreases so that the KCl solution appears to pass through the membrane at a high voltage (400 V), as shown in Fig. 7(b).

Based on the dependence of the mixing performance on the concentration of the mixing solution and applied voltage, we suggest three regimes of electroconvective mixing: weak, strong, and incomplete, as shown in Fig. 8. Weak mixing occurs when either the applied voltage or concentration of the mixing solution is low. Consequently, EDLs are overlapped, but electroconvection mixing is weak. We define the weak electroconvection regime as the area with a mixing index less than 0.70. All cases with a KCl solution concentration below 10 mM are included in this regime. On the other hand, the strong mixing regime involves both moderately high concentration and voltage. A complete EDL overlap still exists, and strong electroconvection causes strong, instant mixing near the membrane. Thus, we define the strong electroconvection regime as the area where the mixing index is greater than 0.70. As depicted in Fig. 8, KCl solutions with concentrations of 10–20 mM approach this regime as the voltage increases, whereas the

FIG. 7. (a) Mixing index variation with respect to the applied voltage for various KCl solution concentrations. The mixing index accounts for the effects of electroconvection only. Each mixing index is an average value of the mixing indices obtained from three independent experiments. In addition, the mixing index in each experiment was calculated by averaging the fluorescence intensity profiles from 10 consecutive images taken in 1 s. The error bars indicate the standard deviations of the repeated experiments. (b) A fluorescence image obtained with a KCl concentration of 100 mM and an applied voltage of 400 V. The black streak through the membrane probably indicates incomplete EDL overlap in the nanopores.

FIG. 8. Three regimes of electroconvection: weak, strong, and incomplete.

KCl solutions with concentrations of 20–100 mM belong to this regime regardless of the applied voltage. Finally, incomplete electroconvection mixing occurs at a KCl high concentration that produces incomplete EDL overlap, allowing coions to pass through the membrane in aid of the high applied voltage, as shown in Fig. 7(b). Thus, both ICP and electroconvection seem to be incomplete or weak. The area with a mixing index lower than 0.70, a concentration greater than 100 mM, and a voltage greater than 300 V is defined as the incomplete electroconvection regime for the given system. It is expected that the incomplete electroconvection regime would extend to the lower voltage range due to thinner EDLs when the KCl concentration increases beyond 100 mM, as in the case of sea water.

The mixing behavior relying on the applied voltage and the KCl solution is in accordance with the previous results in literature. The effects of the applied voltage on mixing performance can be explained with the analysis of electrohydrodynamic chaos in an electrokinetic system containing an ion-selective surface.²² According to the analysis, if electroconvective mixing is chaotic, as in the present studies, the chaotic flow velocity increases with the increase in the applied voltage. On the other hand, the effects of KCl concentration on the mixing performance in the weak and strong electroconvection regime are due to the fact that the higher concentration of the KCl solution leads to greater concentration gradient near the membrane. This is because the magnitude of a local concentration gradient near the membrane depends on the difference between the concentrations of the ion depletion zone created by EDL overlap and the incoming flow solution. The greater concentration gradient is expected to lead to more unstable electrokinetic response. However, an excessively high concentration leads to the incomplete electroconvection regime because the EDL overlap in the nanopores is probably incomplete. Note that the EDL thickness is inversely proportional to the square root of the concentration, as expressed in Eq. (2),¹⁴

$$\text{EDL thickness} = \sqrt{\frac{\varepsilon RT}{2F^2 I_c}}, \quad (2)$$

where ε is the absolute permittivity of the medium, R is the gas constant, T is the absolute temperature, F is Faraday's constant, and I_c is the ionic strength of the electrolyte. Consequently, the EDLs may not overlap or may loosely overlap at a high electrolyte concentration, resulting in weak mixing. This argument is reasonable in that the EDL thicknesses for 1 and 100 mM KCl solutions are about 9.7 and 0.97 nm, respectively, and that the membrane pores were known to allow the transport of Rhodamine 560 but block FITC-insulin (5700 Da).¹⁹

FIG. 9. (a) The optical images of membrane positions. With (left) and without (right) the confinement. (b) Mixing index comparison for the two membrane positions.

The position of the membrane in the by-pass junction should be discussed to insist the electroconvective mixing. It was reported that a confinement geometry in a microchannel, like the half space divided by the membrane in the by-pass junction region, might create a chaotic mixing due to electroosmotic flows^{23,24} instead of electroconvection. To confirm the occurrence of convective mixing, therefore, we fabricated the membrane as close as possible to the inlet side of the U-shape microchannel as shown in Fig. 9(a). The mixing index comparison (Fig. 9(b)) between the two membrane positions, i.e., with and without the confinement, reveals that the confinement has little influence on the mixing. This strongly implies that the mixing is caused by electroconvection.

CONCLUSIONS

A 2-D electroconvective micromixer with a nanoporous polymer membrane *in-situ* fabricated using a laser polymerization technique was developed, and its mixing performance and electroconvection characteristics were thoroughly examined. The mixing by electroconvection was confirmed near the nanoporous membrane when a KCl solution flowed into the micromixer by EOF. We demonstrated that the electroconvective mixing is affected strongly by the concentration of KCl solution and the applied voltage. As a result, we suggest that electroconvection mixing can be categorized in three regimes for the given system. First, weak electroconvection mixing occurs when either the applied voltage or concentration of KCl solution is low. Consequently, EDLs are overlapped, but mixing is weak. Next, a strong electroconvection regime exists where both the concentration and voltage are moderately high. Complete EDL overlap still exists, and mixing is strong. The mixing index in this regime was as high as 0.92. Finally, incomplete electroconvection occurs at a very high KCl concentration. The EDL overlap seems incomplete due to thinning of EDL at the high concentration, resulting in weak electroconvective mixing. The main advantage of this micromixer lies in the simple fabrication technique for the membrane and its 2-D structure that enables facile integration with other microfluidic functional components.

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