

IONIC MIXER ON A MICROFLUIDIC CHIP USING POLYELECTROLYTIC SALT BRIDGES

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Abstract: This paper reports an active mixing method using polyelectrolytic salt bridge-based electrode (PSBE). The PSBE is a key embedded unit in a microchip device that can mix a fluid stream using an ionic current perpendicular to the main stream. The PSBEs were fabricated by employing a photopolymerization technique with an aqueous monomer solution containing diallyldimethyl ammonium chloride (DADMAC). A pair of PSBEs was easily formed at the two lateral branches perpendicular to the main microchannel and was connected to an external AC signal source via their respective 1 M KCl solutions and Ag/AgCl electrodes. The external AC signal source generated an electric current. The electric current was converted to a chloride ionic current at the interface between 1 M KCl solution and Ag/AgCl electrode. The chloride ionic current in aqueous solution dragged water molecules in the microchannel and was found to be very useful for mixing the main stream. The performance of the PSBE mixer was verified with 50 μ M rhodamine 6G solution and 10 mM PBS, pH 7.4.

Introduction

The modern concept of micro total analysis systems (μ -TAS) dates back to the early 1990s when capillary electrophoresis (CE) was developed on a glass chip by Manz et al. [1]. As has been well-documented, chemical and biological processes on a microchip have appreciable benefits that are unattainable using macro scale process configurations. The advantages of μ -TAS are summarized to the tiny sample volume for analysis, low cost, easy automation, and high throughput by parallel processing [2]. Therefore, the applications of μ -TAS are expanding to many different areas including clinical diagnostics, single chip Polymerase Chain Reaction (PCR), DNA separation, DNA sequencing, biological and chemical analysis, cell analysis and flow cytometry.

In many applications related with μ -TAS, fluid mixing is one of critical issues because of its low Reynolds number. Mixing methods are well documented by P.-A. Auroux et al. including a three-dimensional serpentine microchannel as a passive micromixer; a passive mixer based on the Coanda effect; an ultrasonic mixer; a piezoelectrically actuated

micromixer; an electrokinetically driven mixing; a chaotic-like mixing; a mixer using turbulences; a microstirrer; and a rapid mixer with slanted wells [3]. Active mixing methods with moving mechanical parts showed high efficiency, but complicated to implement. Passive mixing methods were easy to implement, but showed low efficiency.

We developed another active mixing method using a PSBE, which requires no moving mechanical parts. The PSBE was developed by H.G. Chun et al. as an electrode for detecting moving cells and estimating their velocity in a microchannel [4]. The PSBE is easy to implement and mechanically stable.

Materials and Methods

Corning 2947 precleaned slide glasses (75 mm by 25 mm, 1 mm thick) were used as substrates. A slide glass was cleaned in piranha solution ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 3 : 1$) for 1 h before washing the slide glass with deionized (DI) water (NANOpure Diamond, Barnstead, USA) and cleaned with acetone (CMOS grade, J. T. Baker, USA), methanol (CMOS grade, J. T. Baker, USA) and DI water twice sequentially. The cleaned slide glass was dehydrated on a hot plate at 150 °C for 5 min and was cooled to room temperature. Hexamethyl disilazane (HMDS) (Clariant, Switzerland) was spin-coated (Won corporation, Korea) at 4,000 rpm for 30 s on the slide glass, on which a spin-coating of the photo resist (PR) of AZ5214-E (Clariant) was subsequently carried out at 4,000 rpm for 30 s. After soft baking the PR on a hot plate at 100 °C for 60 s, the slide glass was cooled to room temperature and aligned under a pattern mask. Exposing the slide to UV light (365 nm) with an intensity of 16 mW cm⁻² for 6.5 s (MDE-4000, Midas, Korea) was followed by developing the PR with AZ300MIF (Clariant) for 45 s. The slide glass was then washed with DI water and the PR was hard-baked on a hot plate at 105 °C for 15 min. The HMDS and PR layers were spin-coated on the other side of the slide glass and baked in the same way as described above in order to protect it from the etching solution. The slide glass was etched with 6:1 buffered oxide etch solution (J. T. Baker) for 40 min at 25 °C. The washing processes consisted of a few successive steps; rinsing with DI water and acetone, sonicating in acetone for 5 min by an ultrasonic cleaner (3510E-DTH, Branson,

USA), soaking in methanol and DI water. Another flat slide glass used to cover the etched glass was drilled at the positions for the reservoirs with a 2 mm diameter diamond drill at 18,000 rpm. The flat slide glass was then cleaned in a piranha solution for 1 h. The pair of etched and flat slide glasses was permanently attached by thermal bonding. When the two slide glasses contacted each other for bonding, DI water between the glasses keeps away from air bubbles. The glasses were heated to 600 °C in a furnace (CRF-M15, CEBER, Korea) and the temperature was maintained at 600 °C for 6 h, which was followed by slowly cooling the furnace to room temperature over 10 h. The microchannel was 50 μm wide and 30 μm deep.

Diallyldimethylammonium chloride (DADMAC) was chosen as the monomer of the polyelectrolytic polymer for the salt bridge. A 65% DADMAC aqueous solution was polymerized to yield poly-DADMAC (PDADMAC) by shedding UV light in the presence of 2% photo-initiator (2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone) and 2% cross linker (N,N'-Methylene-bisacrylamide). The high charge density makes PDADMAC hold many anions inside its structure so that the transport of the mobile anions is facile and the apparent resistance of the polymer plug decreases. The stationary charge in the PDADMAC is independent of the pH in the medium. As a result, PDADMAC possesses good properties as a salt bridge. DADMAC, the photo-initiator, and the cross-linker were purchased from Sigma-Aldrich (St. Louis, MO, USA).

The salt bridge fabrication process using the photopolymerization technique is as follows: The microchannel network of a microfluidic glass chip was filled with the DADMAC solution with a composition described above. The chip was aligned under the mask and subsequently exposed to UV light (365 nm) with an intensity of 16 mW cm⁻² for 5.0 s. Then, the DADMAC monomers were polymerized to form PDADMAC. After photopolymerization, the microchannel was washed with a 1 M KCl solution to remove the remaining DADMAC monomers. The fabricated PSBEs were exposed to the main microchannel by 100 μm wide and 30 μm height.

Figure 1 shows the configuration of the PSBE active mixer. A pair of PSBEs was formed at the two lateral branches perpendicular to the main microchannel and was connected to an external AC signal source via their respective 1 M KCl solutions and Ag/AgCl electrodes. A rectangular wave AC signal of 2 V_{pp}, 5 Hz was applied between two Ag/AgCl electrodes. The external AC signal source generated an electric current. The electric current was converted to a chloride ionic current at the interface between 1 M KCl solution and Ag/AgCl electrode. The chloride ions passed through solutions and PSBEs. The chloride ionic current in aqueous solution dragged water molecules in the microchannel and therefore could mix the main stream [Figure 2].

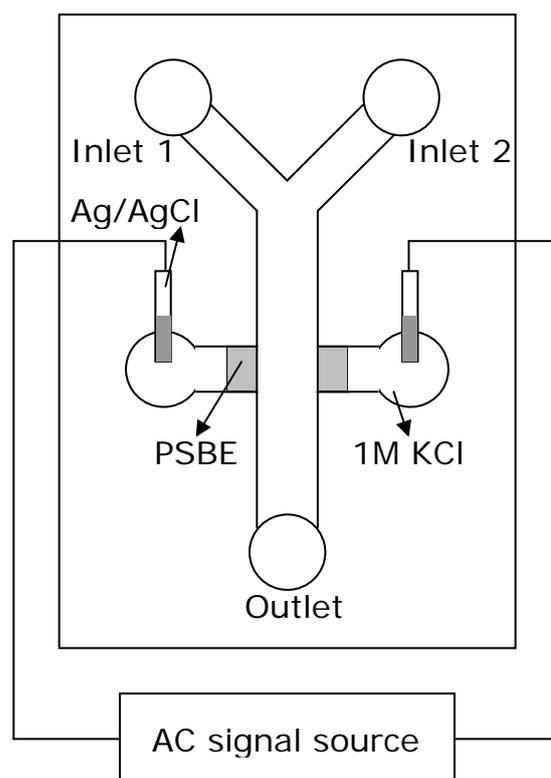


Figure 1: Fluid mixing using PSBEs. A rectangular wave AC signal of 2 V_{pp}, 5 Hz was applied between two Ag/AgCl electrodes, which were electrochemically connected to two PSBEs through 1 M KCl solution.

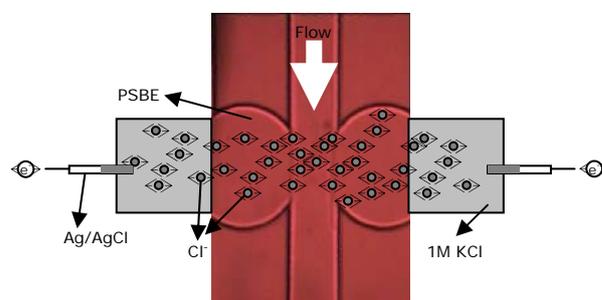


Figure 2: The mechanism of the active mixing using PSBEs. The electric current which was generated by the external AC signal source was converted to a chloride ionic current at the interface between 1 M KCl solution and Ag/AgCl electrode. The chloride ionic current in aqueous solution dragged water molecules in the microchannel and therefore could mix the main stream.

The performance of the active mixing method with PSBEs was evaluated with 50 μM rhodamine 6G solution and 10 mM PBS at pH 7.4. Each solution was injected into Inlet 1 and Inlet 2 using a syringe pump (KDS100, KD Scientific, Holliston, MA, USA), respectively.

Results

The 50 μM rhodamine 6G solution was injected to Inlet 2 and the 10 mM PBS was injected to Inlet 1 [Figure 3(a)]. Injected solutions made a laminar flow through the main channel and didn't mix each other before they reached the PSBEs [Figure 3(b)]. A rectangular wave AC signal of 2 V_{pp} , 5 Hz was applied between two Ag/AgCl electrodes. Then, the chloride ionic current flowed perpendicular the main microchannel and mixed the two solutions [Figure 3(c) and (d)]. A fluid mixing was successfully accomplished in a short length about 100 μm .

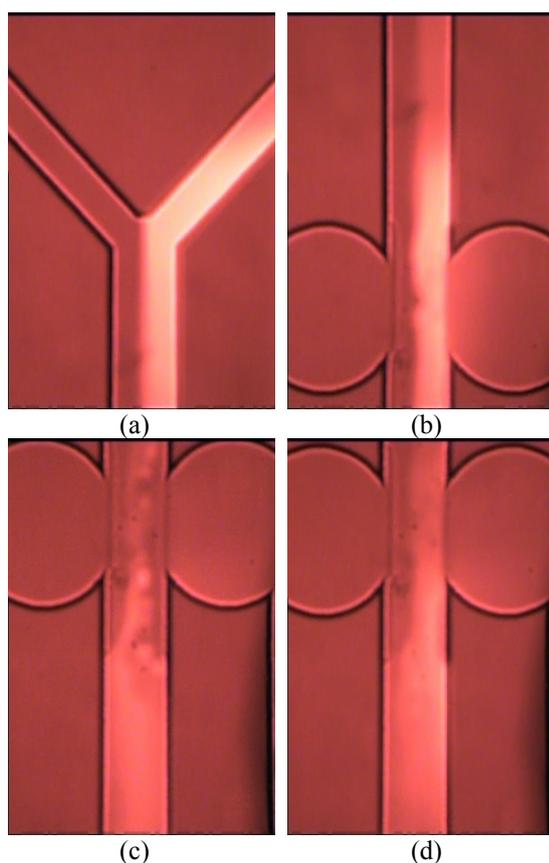


Figure 3: The performance evaluation of PSBE active mixer. The 50 μM rhodamine 6G solution was injected to right channel and the 10 mM PBS was injected to left channel (a). Injected solutions made a laminar flow through the main channel and didn't mix each other before they reached the PSBEs (b). The chloride ionic current which was caused by the external AC signal source flowed perpendicular the main microchannel and mixed the two solutions (c)-(d).

Discussion

The direction of chloride ionic current is opposite to that of protons because of their charge difference. Therefore, the direction of water molecules dragged by chloride ions is opposite to that of EOF in a glass microchannel. This phenomenon could be easily validated by applying a DC current to the Ag/AgCl

electrodes. Therefore, the mechanism of the PSBE mixer depends on the flow of chloride ions not on EOF.

To ensure that the flow in a main microchannel didn't leak out through the PSBEs and that the solution outside the PSBEs didn't leak into the main microchannel, a 100 μM rhodamine 6G solution flowed through the main microchannel [Figure 4]. It showed no leakage through the PSBEs. Therefore, the mechanism of the PSBE mixer is not caused by fluid leakage across the PSBEs.

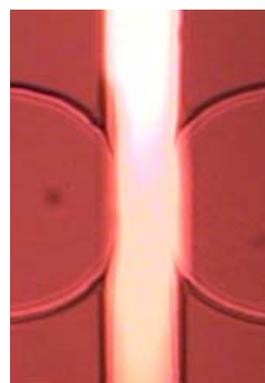


Figure 4: Sealing of the PSBEs. A 100 μM rhodamine 6G solution flowed through the main microchannel. The solution didn't leak out through the PSBEs.

The PSBEs were mechanically and chemically stable. If the microchip with PSBEs was stored in a 1 M KCl solution, the PSBEs kept their mechanical and electrical properties as in a fresh state more than several months. Also, the PSBEs kept their initial shape and there was no swelling phenomenon.

The structure of the proposed mixer using PSBEs is simple and easy to implement. And this method does not require any active mechanical part, therefore the mixing region is mechanically robust.

Conclusions

A new active mixing method using PSBE was developed and its performance was evaluated. The performance of the active mixing method with PSBEs was evaluated with 50 μM rhodamine 6G solution and 10 mM PBS at pH 7.4. It was demonstrated that the PSBE mixer is easy to implement and has good efficiency in mixing fluids. The PSBE mixer could successfully mixed two fluids in a short length about 100 μm . It is expected to be a competitive alternative to the conventional method.

References

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