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Deposition and structuring of Ag/AgCl electrodes inside a closed polymeric microfluidic system for electroosmotic pumping

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ABSTRACT

The design, fabrication and analysis of a low voltage electroosmotic (eo) pump with integrated Ag/AgCl electrodes are shown. The fabrication was based on casting the hydrophilic polymer NOA63, capping the NOA63 trenches with a glass-slide and subsequently depositing Ag/AgCl electrodes by a flow of electroless solution and structuring the electrodes by microfluidic stopvalves. The herewith obtained eo pump embedded into the microfluidic system had a capillary cross-section of 65 μm × 55 μm and its flow rate was determined to be 0.12 nl s^{-1} V^{-1} U_{eh} within the range of applied voltages U_{eh} from −1.5 up to 1.5 V.

1. Introduction

In microfluidics, electroosmotic (eo) pumps take advantage of an electric field induced movement of the Debeye layer of free charges in a liquid parallel to a charged surface [1,2]. Since these pumps do not require any mechanically moving parts to propel the liquid, they have a high potential for miniaturization and high density integration [1,2]. Generally encountered problem with designing and miniaturizing eo pumps is the coupling of the electrical current into the ionic solution. For this purpose, platinum (Pt) electrodes are commonly used. The electrochemical reaction at the Pt electrodes initiates electrolysis of the liquid into gas. Several methods to avoid mixing of the electrolyzed gases with the functional fluidic system have been reported. Brask et al. [3] used a hybrid approach for the current coupling by assembling an ion exchange membrane between the electrodes and the eo pump. In another approach we suggested to use a gas–liquid-separator to part the electrolyzed gas from the liquid [1,2]. However, electrodes like silver/silver chloride (Ag/AgCl) have the outstanding advantage that during pumping the electrochemical reaction transforms Ag into AgCl and vice versa, hence avoiding the inherent gas bubbles of electrolysis. In addition, Ag/AgCl electrodes are the most common and well understood electrodes for biological and chemical measurements [4]. Here, we present the fabrication of an eo pump with integrated Ag/AgCl electrodes a polymeric, fluidic system. The suggested process provides a quick and cheap alternative to standard bulk silicon micromachining. Following the approach from Dupont et al. [4,5], the capillaries of the microfluidic system were fabricated out of the hydrophilic polymer NOA63. Afterwards, the Ag/AgCl electrodes were deposited and structured in a similar way to the previously reported electroless process [6]. This allowed the fabrication and the subsequent analysis of an eo pump embedded in a polymeric microfluidic system.

2. Design and process flow

The layout of this design was chosen to obtain a better understanding of the fabrication of the polymeric microfluidic system, the electroless AgCl electrode deposition and structuring, as well as, the performance of the Ag/AgCl electrodes for eo pumping. For the layout, a symmetric microfluidic system was chosen with the eo pump in its center, see Fig. 1a. Large reservoirs provided fluidic and electrical connection to the microfluidic system. These four reservoirs were designed into two pairs, where each pair is linked by one capillary representing one electrode. These two electrode capillaries are connected with each other in their center by the eo pump.

The process presented here was intended for a cheap, quick and easy fabrication using a polymer based microfluidic chip fabrication. As suggested by Dupont et al. [4,5], a hydrophilic microfluidic system, made out of NOA63,[1] can be fabricated following the sequence: (a) photolithographical structuring of a SU8[2] layer, (b) SU8-polydimethylsiloxane (PDMS)[3] casting and (c) PDMS-NOA63 casting. The idea behind it was to take advantage of the high resist thickness of up to 75 μm and of the photolithographic structuring of SU8. SU8 process, for high aspect ratio and vertical sidewalls, established in our cleanroom by Miessner et al. [7]. An intermediate

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[1] Norland, NOA63.
[2] Microchem, SU8 2025.
[3] Dow Corning, Sylgard 184 PDMS.

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casting step in PDMS was necessary, to avoid bonding between SU8 and NOA63. The microfluidic system was completed by capping the NOA63 trenches with a microscope glass-slide. This glass-slide allowed an observation of the movement of fluorescently labeled microspheres within the eo pump. In a purely NOA63 microfluidic system, this would have been impossible since NOA63 exhibits high fluorescent auto-emission at the wavelength of fluorescein [4,5]. To facilitate the fluidic and electrical connections, Cord End terminals were glued to the fluidic connections of the NOA63 cast.

The Ag/AgCl electrodes were, afterwards, electrolessly deposited and structured into the closed capillaries of the microfluidic system. According to Polk et al. [8], one of the major challenges when integrating Ag/AgCl electrodes into microfluidic systems is their poor stability due to dissolution of an only a few nanometer thick AgCl layer. Additionally during eo pump actuation, the Ag/AgCl electrode was continuously further transformed from Ag into AgCl and vice versa. Hence, for a stable electrode and a long actuation time, thick Ag/AgCl electrodes were required. In order to fabricate them inside the NOA63/glass capillaries, an Ag deposition and a subsequent transformation into AgCl, both using electroless solutions, were chosen. To sufficiently increase the electrode thickness, the electrodes were fabricated in a flow configuration [9], instead of previously reported multiple depositions [6]. This had the additional advantage that the concentration of the electroless solution could be kept constant throughout the capillary, as long as the supply of reactants exceeded its loss due to the deposition reaction.

The Ag electrodes were fabricated from a Tollen's solution, similar to the one previously described [6]. The solution consisted of 0.1 mol l^{-1} silver nitrate, 1 mol l^{-1} ammonium hydroxide, 0.1 mol l^{-1} glucose and 0.55 mol l^{-1} sodium hydroxide. In contrast to our previous report, neither sodium citrate was used, since the reaction speed was decreased by setting the reaction temperature to about 20 °C, nor a silanization was required, since at these cross-sections the adhesion of Ag to the surface was sufficient to create a stable electrode. For the flow deposition, the solution was freshly prepared and stored in a reservoir at 3 °C to suppress the reaction. From there, the solution was pumped within about 15 s through silicone tubing to the chip. Each electrode was fabricated separately, hence the solution enters the microfluidic system through one fluidic connection and exits through the corresponding second microfluidic connection. The temperature and, hence, the deposition rate was expected to be constant throughout the chip, since the solution was flushed comparatively fast through the chip within 1 s. Microfluidic stopvlaves were used at the entrance of the eo pump for structuring the Ag electrodes, see Fig. 1b. The valves prevented the filling of the eo pump with electroless solution. The deposition was stopped by flushing with deionized water. More details on the functionality and the design of the microfluidic stopvalves are given in Ref. [10].

Finally, the Ag electrodes were partially transformed into AgCl by pumping a 0.3 mmol l^{-1} sodium hypochloride solution through the capillary for 15 s. The reaction was again stopped by flushing with deionized water. This transformation process was based on the oxidation of the Ag layer by the hypochloride and an immediate precipitation of AgCl due to the presence of Cl^- ions.

3. Results and discussion

3.1. Fabrication

Both casts, the PDMS master and the NOA63 trench, were demolded by gently pulling off the structured SU8 layer or the PDMS master, respectively. In both cases the master remained unaffected and could be reused several times. A summary of the measured

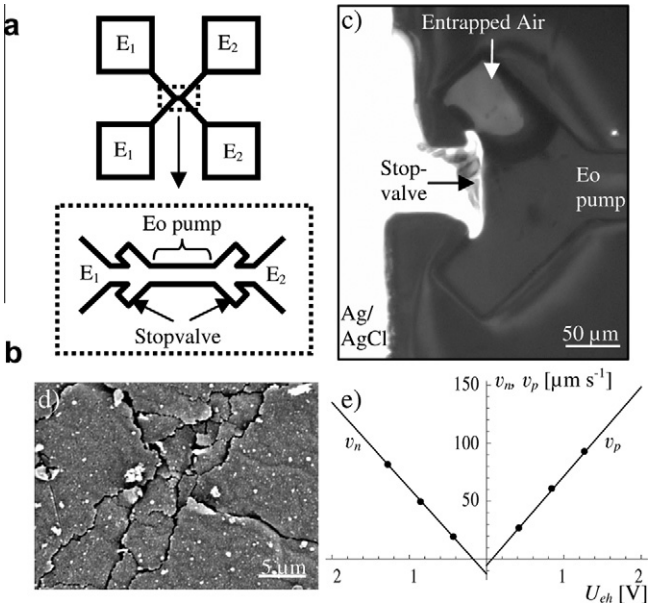

Fig. 1. (a) Layout of the fluidic system with an embedded eo pump. (b) Detail of (a) showing the eo pump and the electrodes (E_1 & E_2). The electrodes were structured by microfluidic stopvalves. (c) Optical microscope image of a successful Ag electrode deposition & structuring with a microfluidic stopvalve. During the subsequent filling with water an airbubble was entrapped in a pocket of the stopvalve. (d) Scanning electron image of a crack formation during the electroless transformation from Ag into AgCl. (e) Average velocity v_m of the microspheres as a function of the electrohydrodynamic voltage U_{eh} drop over the eo pump.

NOA63 cast dimensions were: (a) an electrode capillary: length from microfluidic connection to eo pump 3.5 mm, cross-section 395 µm × 65 µm and (b) an eo pump: length l_p = 600 µm, cross-section w_p = 65 µm × h_p = 55 µm.

From optical observations, it was concluded, that the Ag layer homogeneously deposited inside the capillary, except at the contact points to the Cord End terminals. The measured conductance between the Cord End terminals was 0.25 s. At the contact points to the Cord End terminals, the reaction was decreased and the gap between the contact and the electrode closed only slowly during the deposition. This locally slower growth was explained by the high sensitivity of the Ag deposition on contamination. The thinner contact reduced the overall conductance as measured between the two Cord Ends. This made an estimation of the Ag layer thickness not very reliable. A successful Ag electrode deposition and structuring can be seen in Fig. 1c. The Ag layer can be seen as the highly reflective and bright surface on the left side of the optical microscope image.

The transformation of the Ag into the AgCl electrode was challenging since the electrode tended to delaminate or crack, as e.g. shown in Fig. 1d. The growth of AgCl resulted in compressive stress in the electrode due to the lower molar density of AgCl (38 mmol cm^{-3}) than Ag (97 mmol cm^{-3}) based on values taken from Atkins et al. [11], General Chemistry, and Cain et al. [12] . In the progress of many deposition and AgCl transformation experiments, it turned out that a mechanically stable Ag/AgCl electrode could be fabricated by limiting the transformation to 20% of the initial Ag layer thickness.

The experiments performed with the electrode lasted in the range of 5 min at currents of 1 µA. During this time no significant electrode deterioration was observed. However, applying an excessive voltage of 10 V and above caused the dissolution of white flakes, probably patches of AgCl, and the onset of undesired hydrolysis.

3.2. Flow measurement

The eo flow was determined by measuring the velocity of fluorescently labeled monodisperse carboxylated microspheres[4] of radius 0.7 μm dispersed in a test-solution of 10 mmol l^{-1} potassium chloride (KCl) and 2 mmol l^{-1} tris(hydroxymethyl)aminomethane, at a pH of 10 adjusted with NaOH. The solution was freshly prepared before each experiment and its specific conductivity was measured to be $\sigma_s = 0.197$ Sm^{-1}. For the electrokinetic flow measurements, the chip with the eo pump was mounted with the glass-slide towards an inverted fluorescent microscope[5] and voltages in the range up to 5 V were applied at the Cord End terminals.

The average velocity v of the microspheres was measured as a function of the voltage drop over the eo pump $U_{eh,}$ shown in Fig. 1e. The average velocity of six microspheres was taken, at different positions within the capillary cross-section. The microsphere's velocity v was split into two parts for better illustration, v_n and v_p for negative and positive applied voltage U_{eh} drops over the eo pump, respectively. The linear fit of the microsphere velocity was determined to be $v_n = 74\ \mu m\ s^{-1}\ V^{-1}\ |U_{eh}| - 12.8\ \mu m\ s^{-1}$ and $v_p = 77\ \mu m\ s^{-1}\ V^{-1}\ U_{eh} - 5.4\ \mu m\ s^{-1}$. From this result, it was speculated that the difference in the offset of the velocities $v_{hy,p} = -7.4\ \mu m\ s^{-1}$ at $U_{eh} = 0$ V was caused by a remaining hydrostatic pressure difference. The hydrostatic pressure induced flow was calculated to be $Q_{hy} = 26\ pl\ s^{-1}$, which equaled an average height difference of the solution level in the two electrode reservoirs of 6.1 μm. The slope of the microsphere velocities v_n and v_p was not significantly different, which was a good indicator of a similar transformation into AgCl for both electrodes. Using the average offset at $U_{eh} = 0$ V and the average microsphere velocity v_m, lead to an offset in the voltage drop over the eo pump U_{eh} of 0.12 V. This slight offset was expected to be caused by the electrochemical reaction at the electrode.

The average electrokinetic contribution of the microsphere's velocity v_m was calculated to be $v_m = 75\ \mu m\ s^{-1}V^{-1}\ U_{eh}$. The velocity v_m of the carboxylated microspheres was the result of two electrohydrodynamic effects: the voltage drop U_{eh} over the eo pump induced an eo flow of the test solution in the capillary and an electrophoretic (ep) movement of the microspheres itself. In order to extract and estimate the contribution of the eo flow, the eo mobility μ_{eo} needed to be determined, the latter correlates to the zeta-potential ζ of the charged capillary surface. In the presented case, the capillary consisted of a glass capped NOA63 trench. The zeta-potential ζ_{gl} of the glass-slide was expected to be in the same range, as reported by Scales et al. [13], for a 10 mmol KCl solution on a fused silica glass capillary, at pH 10, $\zeta_{gl} = -74$ mV. However, the usage of NOA63 for microfluidic devices is a recent development and not many experimental results on the eo mobility μ_{eo} are available in literature. It is known that NOA63 is based on polyurethane [14] . We approximate, therefore, the zeta-potential ζ_{NOA63} for the NOA63 surface with that of a polyurethane surface. This represents only a rough estimate, since the NOA63 surface charge σ_{ch} might be strongly influenced by any eventual functional sidegroups as well as by the degree of polymerization. Voigt et al. [15], investigated the zeta-potential ζ of a polyurethane surface[6] for pH values up to 9 at a NaCl concentration of 1 mmol l^{-1}. In their experiments, it can be seen that the zeta-potential ζ remained relatively constant, around −50 mV from pH 6 to −55 mV at pH 9. Hence, we assumed that the zeta-potential ζ_{NOA63} at pH 10 could be approximated by a value of −55 mV. For a low concentration c of counter ions, the zeta-potential ζ, depending on this concentration c, can be approximated by $\zeta \sim -\log c$ [16] . This resulted in an estimated zeta-potential of the NOA63 surface exposed to the test solution of $\zeta_{NOA63} = -36$ mV. The average zeta-potential ζ_{cs} for the capillary surface was determined by the weighted fraction of the cross-sectional perimeter to $\zeta_{cs} = [\zeta_{gl}w + \zeta_{NOA63}(2d + w)]/(2d + 2w) = -48$ mV. The eo mobility μ_{eo} was determined to:

$$\mu_{eo} = \frac{\varepsilon\varepsilon_0\zeta_{cs}}{\eta} = -3.3 \times 10^{-8}\ m^2\ V^{-1}\ s^{-1}, \quad (1)$$

where $\varepsilon\varepsilon_0$ and η denote the dielectric constant of water ($\varepsilon = 78$) and the viscosity of water ($\eta = 1$ mPa s), respectively. According to Morf et al. [17], the eo induced flow in the microfluidic system can be described by:

$$Q_{eo} = U_{eh}\mu_{eo}\frac{R_{hy,p}}{R_{hy,e} + R_{hy,p}}\frac{wh}{l}, \quad (2)$$

where $R_{hy,e}$ and $R_{hy,p}$ denote the hydraulic resistance of the electrode and of the eo pump, respectively. With the eo mobility μ_{eo} and the capillary's hydraulic resistances, the average eo velocity contribution to the microsphere velocity v_{eo} can be calculated. The average eo velocity v_{eo} contribution was calculated with Eq. (2), to:

$$|\,v_{eo}| = \frac{|Q_{eo}|}{wh} = 39\ \mu m\ s^{-1}V^{-1}|U_{eh}|. \quad (3)$$

Behrens et al. [18], measured the ep mobility μ_{ep} of carboxylated latex microspheres[7] to be $\mu_{ep} = 6.5 \times 10^{-8}\ m^2V^{-1}s^{-1}$ for a solution of 10 mmol l KCl at pH 1. An ep experiment for a rough estimation, performed with the microspheres used in this research, indicated a similar ep mobility μ_{ep}. Hence, the ep velocity v_{ep} contribution to the microsphere velocity was calculated to be:

$$|\,v_{ep}| = \frac{|\mu_{ep}U_{eh}|}{l} = 108\ \mu m\ s^{-1}V^{-1}|U_{eh}| \quad (4)$$

The contribution of the eo velocity and ep velocity need to be combined to obtain the actual velocity of the microspheres, with respect to a stationary capillary. Both surfaces, the surface of the chip and the surface of the microspheres, were negatively charged. This resulted in an opposing effect of electroosmosis and electrophoresis. The resulting velocity v_{mm} of the microspheres was calculated to:

$$v_{mm} = (v_{ep} - v_{eo})U_{eh} = 69\ \mu m\ s^{-1}\ V^{-1}\ U_{eh}.$$

The direction of the velocity v_{mm} was defined in the same direction as the voltage drop over the eo pump U_{eh}. This estimated microsphere velocity was in good agreement with the measured average microsphere velocity of $v_m = 75\ \mu m\ s^{-1}\ V^{-1}\ U_{eh}$. From that, the eo pump rate Q_{eo} was calculated from the measured average slope of the microsphere velocity v_m, as shown in Fig. 1e and corrected for an estimated ep velocity v_{ep} of 108 μm s^{-1} V^{-1}. The eo pump rate Q_{eo} as a function of the voltage drop over the eo pump U_{eh} was calculated to be $Q_{eo} = 0.12\ nl\ s^{-1}\ V^{-1}\ U_{eh}$.

4. Summary and conclusions

A quick, easy and cheap fabrication of an eo pump with integrated Ag/AgCl electrodes was shown based on casting the hydrophilic polymer NOA63 and capping the trenches (hydraulic dimension in the range of 55 μm) with a glass-slide and a subsequent Ag/AgCl electrode deposition by flow of electroless solution and microfluidic structuring by stopvalves. The final eo pump was modeled and characterized by measuring the velocity of fluores-

[4] Polyscience, Flouresbrite YG Carboxylated Microspheres, diameter 1.5 μm.
[5] Zeiss, Axiovert S40 with a mounted camera AxioCam Mrm and a metal halide lamp HXP 120.
[6] VEB, SYSpur.
[7] Interfacial Dynamics Cooperation, radius of 155 nm

cent carboxylated microspheres inside the eo pump. From that, the eo flow rate of the low voltage pump was determined to be $Q_{eo} = 0.12\ \text{nl}\ \text{s}^{-1}\ \text{V}^{-1}\ U_{eh}$.

The integration of Ag/AgCl electrodes into the microfluidic system reduced the footprint of the eo pump, since hydrolysis is suppressed at this specific kind of electrodes and elements for liquid gas separation were not required. Furthermore, the integration reduced the length of the eo pump, hence, commonly applied voltages in the range of kV were reduced down to a few Volts. The presented eo pump design, fabrication and analysis represents a promising strategy towards a high density integration of micropumps into a microfluidic system.

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