

# Deposition and Structuring of Ag/AgCl Electrodes into a closed Polymeric Microfluidic System for Electroosmotic Pumping

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This work presents the fabrication and characterization of an electroosmotic (eo) pump with a low actuation voltage integrated into a polymeric microfluidic chip. A general encountered problem with the design of eo pumps is the coupling of the electrical current into the ionic solution, which is commonly done with electrodes made out of platinum (Pt). However, using Pt electrodes inherently implies that the electrochemical transfer of electrons from the electrode into the solution initiates electrolysis of the liquid into gas. Electrodes like silver/silverchloride (Ag/AgCl) have the outstanding advantage that during pumping the electrochemical reaction transforms Ag into AgCl and vice versa, rather than electrolyzing the liquid. Furthermore, Ag/AgCl electrodes are the most common and well understood electrodes for biological and chemical measurements [1]. Suzuki et al. [2] already integrated Ag/AgCl electrodes in order to improve electrochemical measurements in microfluidic systems.

For studying integration of these Ag/AgCl electrodes into a microfluidic system, a six step microfabrication process was developed as shown in Fig.1. The capillaries of the microfluidic system were fabricated, based on polymer vacuum casting in a sequence of SU8-PDMS-NOA63 (Fig.1a-d), as suggested by Dupont et al. [3]. The idea was to take advantage of the high resist thickness and photolithographic structuring of SU8. To avoid bonding between SU8 and NOA63, an intermediate step of casting the shape in PDMS was necessary. NOA63 chosen for the final structure due to its hydrophilic properties [3]. The NOA63 trenches were capped with a glass slide. A scanning electron microscopy image of the NOA63 eo pump's cross section is shown in Fig. 2 a) where its dimension were measured to be  $65\ \mu\text{m} \times 55\ \mu\text{m}$ . The Ag/AgCl electrodes were deposited and structured inside the capillaries with an electroless deposition process, as previously published [4] except that here a flow deposition was used instead of multiple depositions to sufficiently increase the electrode thickness for a longer actuation time of the pump (Fig.1e, f). This had the additional advantage that the electroless solution concentration could be kept constant throughout the capillary, once the supply of reactants by a high flow rate exceeds the loss of reactants during the electroless reaction. The Ag layer was structured by limiting filling the electroless plating solution to certain parts of the capillary by means of microfluidic stop-valves. Retaining of the liquid and a subsequent electroless Ag/AgCl electrode deposition is shown in Fig. 2 b, c). The actuation of the stopvalve was designed such that by reducing the liquid-air surface tension  $\gamma_{la}$ , hence decreasing the contact angle  $\theta$  of the solution on the capillary sidewall, the valve switched from a retaining negative capillary pressure  $p$  to a liquid transmitting positive pressure  $p$ . This stopvalve was analytically modeled in three dimensions. In Fig. 3 the capillary pressure  $p$  is shown as a function of the liquid meniscus position defined by the opening angle  $\kappa$  for three different contact angles  $\theta$ .

Besides for electrochemical sensing as published in [4], the Ag/AgCl electrodes were used for eo pumping. The eo pump was investigated by observing the motion of fluorescently labeled microspheres in a solution of 10 mMol KCl at a pH 10. This motion was the sum of two electrohydrodynamic effects, the electroosmotic pumping of the liquid and the electrophoretic movement of the spheres itself. Fig. 4 shows the measured and averaged velocity  $v$  of the microspheres as a function of the voltage drop  $U_{eh}$  across the eo pump. From this graph, the eo pump rate was determined to be  $0.12\ \text{nl s}^{-1}\ \text{V}^{-1}$

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