TOWARDS HIGHLY EFFICIENT NANOPOROUS ELECTROOSMOTIC
PUMPS: EFFECTS OF CONCENTRATION POLARIZATION ZONES
SOURCED FROM THE PUMP SUBSTRATE AND ELECTRODES

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ABSTRACT

Utilizing electroosmotic (EO) pumps with nanoscale pores can allow for higher pressure capacities and pump flow rate per power compared to conventional micron-scale pores. However, operation with nanoscale pores often leads to the development of ion concentration polarization (CP), and the effects of CP on pump performance are poorly understood. We demonstrate that operation of EO pumps in the CP regime result in several effects, including the propagation of pump-sourced CP zones at mm/s velocities through millichannels, and interaction between pump and electrode-sourced CP zones. We describe the effect of these phenomena on EO pump performance.

KEYWORDS: Electroosmotic pump, Concentration polarization, Micropump

INTRODUCTION

Electroosmotic (EO) micropumps require no moving parts, and can deliver relatively high flow rates and pressures, and can be manufactured from inexpensive, readily available materials [1]. EO pump systems often consist of a porous silica substrate, or frit, in between two electrodes. The applied field exerts a Coulombic force on mobile counterions of electric double layers (EDL) that form in frit pores, and ion drag creates bulk fluid flow.

Recent work on EO pump optimizations have concluded that higher flow rate per power can often be achieved by: i) reducing frit pore size, and ii) reducing the ionic strength of the pumped electrolyte [1,2]. Each of these optimization strategies increases the ratio of surface to bulk conductivity in frit pores. Applying an electric field to a frit with significant surface conductivity results in the formation of depletion and enrichment zones respectively at the anode and cathode sides of the frit, an effect known as concentration polarization (CP) [3]. The ratio of surface to bulk conductivity is described by the Dukhin number, which for a binary electrolyte in a porous frit can be expressed as [3]:

\[ Du = \frac{z_1 \mu_1 / s}{F_c (z_1 \mu_1 + z_2 \mu_2)} l \]  

Where \( s \) is surface charge density, \( l \) represents the ratio of electrolyte volume in the porous media to pore surface area, \( c_0 \) is the pore centerline electrolyte concentration, \( \nu \) is ionic mobility, \( z \) is ionic charge, and \( F \) is Faraday’s constant. Subscript 1 denotes the counter-ion and 2 the co-ion. Optimizing EO pumps by decreasing pore size (decreasing \( l \)), or decreasing ionic strength \((c_0)\), increases Dukhin number. If \( Du \) becomes of order unity or higher, CP effects become significant [4]. In this regime, traditional models for EO pumps [1], which ignore this phenomenon, no longer hold.

In this paper, we provide new quantitative experimental characterization of CP in EO pumps under galvanostatic conditions using simultaneous visualizations, flow rate and voltage measurements. We observe a long-range propagation of enrichment and depletion fronts starting from the membrane through the connecting millimeter-scale channel (hereafter “millichannel”). Further, we show that fronts of perturbed concentration and pH are sourced by, and propagate from, the electrodes of our system. With these measurements, we elucidate key parameters affecting pump performance in the CP regime and show a scaling which collapses performance transients across all our experimental conditions.

EXPERIMENTAL

Figure 1 is a schematic of our experimental setup. We used a porous silica frit with mean pore radius of 225 nm (EoPlex, Redwood City, CA). The 1 mm thick frits were epoxied with clear UV cure epoxy (Norland, Cranbury NJ) into a clear, 5 x 5 mm square, borosilicate glass millichannel (Freidrich and Dimmock, Millville NJ). Two large diameter (3 cm) cylindrical end-channel reservoirs were filled to equal heights to insure no significant external pressure was applied to the pump system during operation. During experiments, we used 0.1 to 10 mM Na\(^+\) concentration) sodium tetraborate decahydrate buffer (Mallinckrodt, Hazelwood, MO) to set ionic strength. For simple concentration field visualizations (Fig. 2), we observed the anionic, pH insensitive tracing dye Alexa Fluor 488 (Invitrogen, Carlsbad, CA). For simultaneous pH and concentration field visualizations (Fig. 3), we simultaneously observed both the anionic Alexa Fluor 594 (Invitrogen), and pH-sensitive Fluorescein dye (JT Baker Inc. Phillipsburg NJ).

RESULTS AND DISCUSSION

Figure 2 illustrates typical results of concentration field visualizations in the millichannel around our silica frit after applying 25 μA current. These results are plotted in spatiotemporal form where the abscissa is axial position along the millichannel, and the ordinate is elapsed time. The colormap represents concentration enrichment factor, which is the concentration averaged across the cross section of the millichannel and normalized by the initial value. The axial location of the frit is between about 2 and 3 mm in all cases, and the current is applied at \( t = 10 \) s. When using 10 mM borate, no CP zones are detected, and ionic concentrations in the millichannels remain at the initial level. At 1 mM, enrich-
ment and depletion zones are observable, but remain local to the frit surfaces. At 0.1 mM, the enrichment and depletion zone interfaces propagate at constant, order mm/min velocities away from the frit surface and through the millichannel. We additionally observe propagating enrichment and depletion fronts from, respectively, the anode and cathode.

Figure 1: Schematic of the experimental setup used to perform simultaneous flow rate measurements and visualizations. The frit is epoxied into a clear, 5 x 5 mm borosilicate millichannel. An inverted epifluorescent microscope was used for visualizations, and the flow sensor measures flow rate generated by the frit.

The transition from non-propagating to propagating CP has been demonstrated for silica serial micro-nano-microchannel systems by Zangle et al. [3], and we demonstrate this transition here with porous glass in series with millichannels (Fig. 2). We note that the propagation mechanisms in these two cases are different. In the former case, propagation of the CP depletion zone in the microchannel was explained by nonlinear effects associated with a significant amount of axial transport of current through the microchannel EDL [4]. That is, one necessary condition for this mechanism is that the Dukhin number in the propagation channel should be finite. However, for the millichannel in the current experiments, achieving Du order unity would require a concentration of order nM which is physically impossible with an aqueous electrolyte (due to the ionic strength associated with water autoprotolysis). Thus Du is negligibly small in the millichannel during the observed depletion zone propagation, and propagation must be due to another mechanism.

Figure 2: Visualizations of concentration field about our silica frit. The frit is located between 2 and 3 mm, and the anode and cathode surfaces are at approximately 0 and 5.5 mm, respectively. a) Visualization using 10 mM borate as the background electrolyte shows no observable CP. b) At 1 mM, local, non-propagating enrichment and depletion zones form about the frit. c) At 0.1 mM, strong enrichment and depletion zones form and propagate away from the frit. Additionally, enrichment and depletion zones propagate away from the anode and cathode respectively.

To study whether the electrode CP zones we visualized (see Fig. 2) were sourced by water electrolysis, we performed simultaneous visualizations of both concentration field (Fig. 3a) and pH field (Fig. 3b). In these visualizations, the frit is located roughly between 3 and 4 mm, the anode surface at 0 mm, and the cathode is 3 cm out of the field of view. We used 0.1 mM borate and apply 25 µA at 10 s. In Figures 3a and b, the concentration of both dyes increases and depletes at, respectively, the cathode and anode sides of the frit; consistent with frit-sourced CP. Also, in Figure 3a, the anionic Alexa Fluor dye indicates an ion enrichment front is propagating from the anode. However, simultaneously, pH dependent Fluorescein dye shows a strong depletion propagating from the anode (Fig. 3b). The Fluorescein depletion and Alexa Fluor enrichment fronts are nearly identical in spatial extent at all times. This is strong evidence that the anode enrichment front is also a region of low pH, likely lower than pH ~3. It is therefore likely that the anode front is sourced by water electrolysis.

In Figure 4, we summarize the results of our flow rate measurements, which we used to explore the effects of CP on EO pump performance. We used 0.1 mM borate in order to insure propagating frit and electrode sourced CP (see Fig. 2). We varied applied current and the distance between the anode and the frit surface, d. In all realizations, we observed a rapid rise in flow rate, followed by an initial, locally-stable flow rate, and then a distinct transition to a significantly lower, steady flow rate (Fig. 4). Scaling the time axis with inverse current and anode distance approximately collapses the time scale at which we see the step down to the final, steady flow rate (Fig. 4 inset). We therefore hypothesize the step-down in EO pump flow rate may be due to the sudden arrival of a front of anode-sourced low pH at the frit, which can then abruptly decrease pore surface charge.
CONCLUSION
We present an experimental study leveraging simultaneous visualizations of ion concentration and pH fields, and flow rate and voltage measurements under galvanostatic conditions. We used these measurements to characterize EO pump performance in the CP regime. We show that electrode and frit-sourced CP can strongly affect pump performance, and describe how the CP propagation mechanism in millichannels requires further study.

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REFERENCES