ION CONCENTRATION POLARIZATION IN A SING AND OPEN MICROCHANNEL USING SURACE-PATTERNED NAFION: EXPERIMENTAL AND THEORETICAL STUDY

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ABSTRACT

We describe a novel and simple mechanism for inducing ion concentration polarization (ICP) using a surface-patterned perm-selective nanoporous film like Nafion in single, open microchannels. In this work, we not only develop a model to perform numerical simulations but also confirm the numerical simulation results with experimental results to verify the ICP phenomenon. That is, we characterize transport phenomena and distributions of ion concentration under various electric fields near the nafion film and show that single-channel based ICP (SC-ICP) is affected by nafion film thicknesses, strengths of applied electric fields, and ionic strengths of buffer solutions. We also emphasize that SC-ICP devices have several advantages over previous dual-channel ICP (DC-ICP) devices: inherently leak-tight, simple experimental setup requiring only one pair of electrodes, and low electrical resistances helping to avoid Joule heating, significant water dissociation, and membrane perm-selectivity breakdown but allowing high bulk flow. Lastly, we demonstrate that SC-ICP devices have high potential in massively parallel microchannels that require only one pair of electrodes and have higher possibilities of being easily integrated with traditional microfluidic systems for biotechnological applications.

KEYWORDS

microfluidics, ion concentration polarization, electrokinetics, pre-concentration, Nafion

INTRODUCTION

Interest is increasing in ionic and molecular transport phenomena in nanoscale channels and nanopore clusters for biomolecule concentration, filtration, and separation, and for even more intricate applications such as nanofluidic diodes, transistors, and energy convertors [1]. In particular, ion concentration polarization (ICP) induced by the biased transport between co-ions and counter-ions caused by charged channel surfaces (zeta-potentials) has widely utilized in biomolecule preconcentration. Such preconcentration increases the sample concentrations by more than million-fold and enable the ultra-sensitive detection of biomolecules [2].

In principle, most ICP devices have similar micro- and nanofluidic channel networks in which the nanofluidic channels physically connect two microfluidic channels and play a common role in selectively transporting either the cations or anions [3]. These devices are referred to as dual-channel ICP (DC-ICP) devices in this work. Most DC-ICP devices rely on complicated nanofabrication processes that connect the two microchannels with a nanofluidic channel or nanoporous material. These devices also require both microfluidic and nanofluidic channel networks in which an ionic sink channel is considered as an essential element for connection with an electric ground. Therefore, somewhat complicated electric configurations and micro-/nanofluidic networks are inevitable. To resolve the drawbacks, we present a novel and innovatively simplified ICP device that is based on a single and open microchannel with only one electrode pair with a surface-patterned nafion film, referred to as single-channel ICP (SC-ICP).

EXPERIMENT

We described the mechanism of the SC-ICP in Fig. 1. The surface-patterned nafion film in the middle of the microchannel can rapidly transport only cations from the anodic side to the cathodic side through the nanopore clusters. Since there is faster ion transport through the nafion film than bulk electrolytes, ionic neutrality is locally broken near the nafion film and the anion-rich zone (ARZ) and cation-rich zone (CRZ) are produced on the anodic and cathodic sides, respectively.



Figure 1. (A) Illustration of an open, SC-ICP device in which a nafion film is patterned at the center of the microchannel surface. (B) Top view of the device and ionic neutrality is broken in the presence of an electric field.

(C) Illustration of the ICP phenomenon by the nation film that rapidly and selectively transports cations from the anodic side to the cathodic side, resulting in the local formation of ion depletion.



Figure 2 (A) Time-course pre-concentration of negatively charged tracer molecules of 1 nM that are dissolved in the HCl buffer solution of 1 mM. (B) Concentration distribution of counter-ions (protons) along the microchannel. (C) Concentration distributions of the accumulated tracer molecules along the microchannel under various elecric fields.

In Fig. 2, we demonstrated that rapid and stable ICP can be induced in a single, open microchannel using COMSOL. To verify the simulation result, we performed experiments and characterized transport phenomena and distributions of ion concentration under various electric fields near the nafion film and found that the SC-ICP is affected by nafion film thicknesses, strengths of applied electric fields, and ionic strengths of buffer solutions (Fig. 3). Furthermore, we demonstrated that the SC-ICP is more advantageous for the massive, parallel accumulation of biomolecules (Fig. 4); up to 10^5 to 10^6 folds within 1 h, showing a good agreement with the simulation result.



Figure 3 (A) The quantified flux ratio of fluorescent intensities obtained from the cathodic side to those from the

anodic size representing passage through the IDZ of differently charged fluorescent dyes (B) Current monitoring reveals that the SC-ICP develops within 1 min and that steady states are maintained for anionic and neutral dyes, while the fluctuation of and increase in the current for cationic dyes seem to be caused by electrostatic binding/clogging of the dye molecules to/at the nanopores of the Nafion film. (C) Quantification of ion depletion areas in various electric fields (ionic strength of 5 mM was used). (D) The same quantification as in (C) at three different ionic strengths.



Figure 4. (A) shows concentration of the protein in a single and open microchannel and (C) shows a million fold accumulation of the sample. (B) and (D) demonstrate that the SC-ICP is advantageous for massive parallel expansion and integration with other microfluidic systems

We note that the SC-ICP devices have several advantages over DC-ICP devices: easy and simple fabrication processes, inherently leak-tight, simple experimental setup requiring only one electrodes pair, stable and robust ICP induced rapidly, low electrical resistances to avoid Joule heating, and significant water dissociation but allowing for higher bulk flux. Hence, the SC-ICP has high potential in massively parallel microchannels that require only one pair of electrodes and have higher possibilities of being easily integrated with traditional microfluidic systems for biotechnological applications.

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