

Transport Phenomena in Nanofluidic Channels

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Abstract

When the Debye length is on the order of or larger than the height of a nanofluidic channel containing surface charge, a unipolar solution of counterions is generated within the channel and the coions are electrostatically repelled to maintain electrical neutrality. By locally modifying the surface charge density through a gate electrode, the ion concentration can be depleted under the gate and the ionic current can be significantly suppressed. It is proposed that this could form the basis of a unipolar ionic field-effect transistor. A pressure-gradient driven flow under such conditions can be used for ion separation, which forms the basis for electro-chemo-mechanical energy conversion. The current-potential ($I-\phi$) characteristics of such a battery were calculated using continuum dynamics. When the Debye length of a solution is about half of the channel height, the efficiency is maximized.

Keywords: nanofluidics, electrokinetic phenomena, electrical double layer, Debye length, unipolar solution

1 INTRODUCTION

Ion transport in nanoscale channels has recently received increasing attention. Much of that has resulted from experiments that report modulation of ion transport through the protein ion channel, α -hemolysin, due to passage of single biomolecules of DNA or proteins [1]. This has prompted research towards fabricating synthetic nanopores out of inorganic materials and studying biomolecular transport through them [2]. Recently, the synthesis of arrays of silica nanotubes with internal diameters in the range of 5-100 nm and with lengths 1-20 μm was reported [3]. These tubes could potentially allow new devices to control the transport of ions and biomolecules.

When the tube diameter is smaller than the Debye length, which characterizes the size of the electrical double layer, a unipolar solution of counterions is created within the nanotube and the coions are electrostatically repelled. We proposed two different types of devices to use this unipolar nature of solution, i.e. 'nanofluidic transistor' [4] and 'nanofluidic battery' [5]. When the electric potential bias is applied at two ends of a nanotube, ionic current is generated. By locally modifying the surface charge density through a gate electrode, the concentration of counterions can be depleted under the gate and the ionic current can be significantly suppressed. This could form the basis of a unipolar ionic field-effect transistor. By applying the pressure bias instead of electric potential bias, a streaming current and a potential are produced. This could form the basis of an electro-chemo-mechanical battery.

In this study, transport phenomena in nanofluidic channels were investigated and the performance characteristics of these devices were evaluated.

2 GOVERNING EQUATIONS

In the analysis of microchannel flow, the Poisson-Boltzmann equation is often assumed for the potential of an electrical double layer [6]. This is valid when the electrical double layers of two adjacent walls do not overlap. For overlapping double layers, the Poisson-Nernst-Planck (PNP) equations and the Navier-Stokes (NS) equations are used to calculate the ionic current in nanofluidic channels. The governing equations are as follows:

$$\nabla^2 \phi = -\frac{1}{\varepsilon_0 \varepsilon} \sum_a z_a e n_a, \quad (1)$$

$$\nabla \cdot (n_a \mathbf{u} + \mathbf{J}_a) = 0, \quad (2)$$

$$\nabla \cdot \mathbf{u} = 0, \quad (3)$$

$$\mathbf{u} \cdot \nabla \mathbf{u} = \frac{1}{\rho} \left\{ -\nabla p + \mu \nabla^2 \mathbf{u} - \left(\sum_a z_a e n_a \right) \nabla \phi \right\}. \quad (4)$$

The electrostatic potential ϕ is calculated with the Poisson equation (eq 1), where ε_0 is the permittivity of vacuum, ε is the dielectric constant of medium, n_a is the concentration of ions of species a , and $z_a e$ is their charge. The Nernst-Planck equation for ion species a can be written as eq 2, where \mathbf{J}_a is the particle flux due to concentration gradient and electric potential gradient, which is given by

$$\mathbf{J}_a = -D_a \left(\nabla n_a + \frac{z_a e n_a}{kT} \nabla \phi \right), \quad (5)$$

where D_a is the diffusivity of ion species a . The equation of continuity and the modified Navier-Stokes equations including electrokinetic effects can be written as eqs 3 and 4, respectively, where ρ is the fluid density and μ is the viscosity. The boundary conditions at channel walls are as follows.

$$\nabla_{\perp} \phi = -\frac{\sigma}{\epsilon_0 \epsilon}, \quad (6)$$

$$\mathbf{J}_{a\perp} = 0, \quad (7)$$

$$\nabla_{\perp} p = \mu \nabla_{\perp}^2 \mathbf{u} - \left(\sum_a z_a e n_a \right) \nabla_{\perp} \phi, \quad (8)$$

$$\mathbf{u} = \mathbf{0}, \quad (9)$$

where \perp denotes the wall-normal component. The boundary condition for the Poisson equation is given by eq 6, where σ is the surface charge density. Here we assume that inside the Stern layer, the ions are rigidly held and do not contribute to the ionic current. The wall is regarded as the interface between the Stern layer and the diffuse layer, and the surface charge density here is that of the wall plus that of ions within the Stern layer [4]. Equations 1-4 are solved simultaneously using a finite difference algorithm, yielding the electric potential, ionic concentration, pressure and velocity in the system. If these are known, the current density of the ion species a is obtained by the following equation:

$$\mathbf{i}_a = \mathbf{i}_{a, \text{adv}} + \mathbf{i}_{a, \text{dif}} = z_a e (n_a \mathbf{u} + \mathbf{J}_a). \quad (10)$$

Figure 1 shows the 2D domain for the calculation, where the total length of the channel L_x is 5 μm and the height, L_y , is 30 nm, the reservoirs of 1 $\mu\text{m} \times 1 \mu\text{m}$ are located at two ends of a channel. For a nanofluidic transistor, because the fluid flow does not occur, only the PNP equations were solved. A gate electrode is located at the center of the channel and the length L_{gx} is 2 μm . The surface charge densities inside the channel, $\sigma = -10^{-3}$ and -2×10^{-3} C/m², whereas the surface charge density at the gate, σ_g is different from that of other parts due to the presence of the gate electrode. The electric potentials and the concentrations at the boundaries are given by constant values. For a nanofluidic battery, the surface charge density inside the channel ranged from 0 to -5×10^{-3} C/m². There are two calculation modes: the calculations of

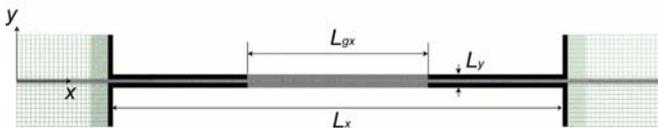


Figure 1. Computational grid (316 \times 45) inside a silica nanotube with height of 30 nm, length of 5 μm with 1 $\mu\text{m} \times 1 \mu\text{m}$ reservoirs on either side. The gate is centered along the length of the nanotube with a length, $L_{gx}=2 \mu\text{m}$.

(i) the electromotive force, that is, the potential at zero current; and (ii) the current-potential characteristics, that is, the current at fixed potential biases. At the end of reservoirs, the boundary conditions are given as follows:

$$\nabla \phi = 0 \text{ or } \phi = \phi_0, n_{K^+} = n_{Cl^-} = n_0, p = p_0, \nabla \mathbf{u} = \mathbf{0}. \quad (11)$$

In this study, KCl aqueous solutions were used. The dielectric constant of KCl aqueous solution, ϵ , is 80, the diffusivities of K^+ and Cl^- , D_{K^+} and D_{Cl^-} , are 1.96×10^{-9} and 2.03×10^{-9} m²/s, respectively [8]. The density and viscosity of the solution are assumed to be 10^3 kg/m³ and 10^{-3} Pa·s, respectively. Temperature is 300 K and the bulk concentration of KCl aqueous solution varies from 10^{-5} to 10^{-2} M.

3 CALCULATION RESULTS

3.1 Nanofluidic Transistor

Consider the concentration of KCl aqueous solution to be 10^{-4} M and the surface charge density is -10^{-3} C/m². The electric potential at the left reservoir is 0 V. Figure 2 shows the electric potential profiles at $y=0$ and the concentration profiles averaged over the y direction, along the x direction for five different potential biases. Inside the channel the difference in concentration between K^+ and Cl^- is determined by the surface charge density. From the requirement of overall electroneutrality, the following equation is satisfied.

$$\Delta n = -\frac{2\sigma}{eL_y}, \quad (12)$$

where Δn is the average concentration difference between K^+ and Cl^- in the y direction. When the surface charge

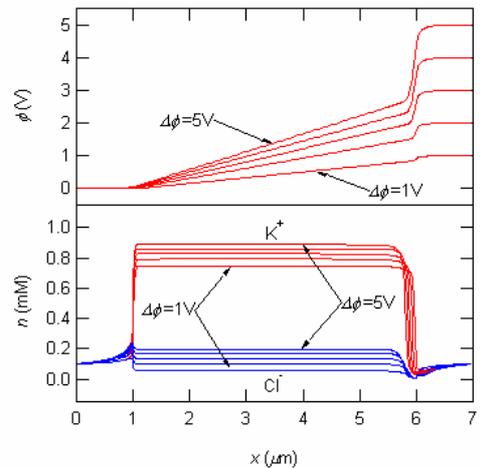


Figure 2. For surface charge density, $\sigma = -10^{-3}$ C/m² on the tube surface, electric potential profiles along the axis of the channel (top) and concentration profiles (bottom) in the x direction for five different potential biases. The bulk concentration of KCl aqueous solution is 10^{-4} M.

densities is -10^{-3} C/m^2 and the height of the channel is 30 nm, the difference $\Delta n = 4.17 \times 10^{23} \text{ m}^{-3}$, which corresponds to 0.69 mM. The average concentration difference shown in Figure 2 (bottom) agrees well with this value. If the bulk concentration is less than Δn , there exists a large potential barrier for the Cl^- ions to enter the channel, and the channel becomes essentially a unipolar solution of K^+ ions that neutralize the negative surface charge. As the potential bias increases, the potential jump at $x=6 \mu\text{m}$ increases because the overall K^+ ion transport is restricted by that in the reservoir.

Figure 3a shows the effect of gate electrode on the ionic currents of K^+ and Cl^- . The bulk KCl concentration is 10^{-4} M and the potential bias is 5 V. For both cases $\sigma = -10^{-3}$ and

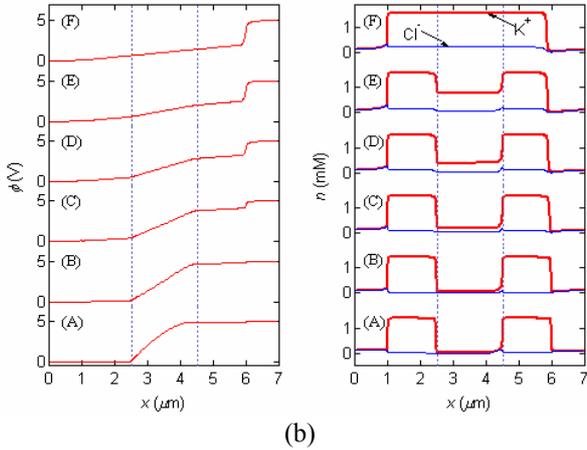
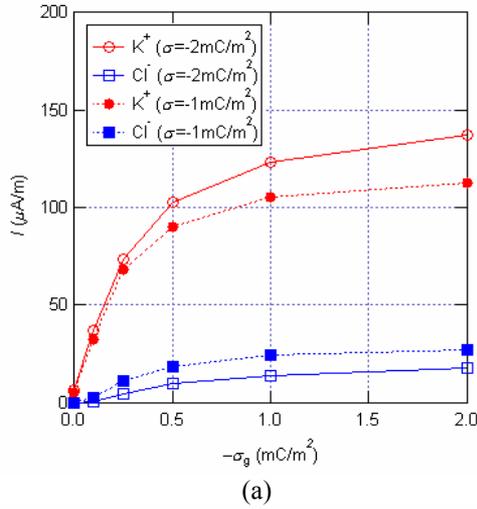


Figure 3. The effect of surface charge density at the gate, σ_g , on ionic current: (a) I - σ_g characteristics; (b) electric potential profiles at the center of the channel (left) and ionic density profiles (right) in the channel direction for six different surface charge densities (C/m^2) at the gate, (A) 0, (B) -10^{-4} , (C) -2.5×10^{-4} , (D) -5×10^{-4} , (E) -10^{-3} and (F) -2×10^{-3} . The charge densities on the channel surface except for the gate region are -2×10^{-3} and -10^{-3} C/m^2 (dashed lines in I - σ_g characteristics) The bulk concentration of KCl aqueous solution is 10^{-4} M and the potential bias is 5V.

$-2 \times 10^{-3} \text{ C/m}^2$, as the surface charge density at the gate, $\sigma_g \rightarrow 0$, the ionic current is blocked almost completely. However, when $\sigma_g \sim \sigma$, the magnitude of the ionic current is almost the same to the value at σ , suggesting that the effect of σ_g on the ionic current is nonlinear. The ionic current of Cl^- decreases monotonically with decreasing the surface charge density at the gate. As σ on the remaining surface increases from -10^{-3} to $-2 \times 10^{-3} \text{ C/m}^2$, the unipolar nature of charge transport appears more clearly. Figure 3b shows the electric potential profiles at the center of the channel and ionic density profiles in the channel direction for six different surface charge densities at the gate. As $\sigma_g \rightarrow 0$, the K^+ ions are depleted from under the gate such that the concentration drops to that of Cl^- . As a result most of the potential drop occurs at the gate. Since J_{K^+} is constant along the channel, its value anywhere along the channel is determined by the depleted concentration under the gate.

3.2 Nanofluidic Battery

Figure 4 shows the electromotive force, that is, the electric potential at zero current, as a function of the surface charge density of the channel for four different bulk concentrations of KCl aqueous solutions, 10^{-5} , 10^{-4} , 10^{-3} , and 10^{-2} M . The surface charge density ranges from 0 to $-5 \times 10^{-3} \text{ C/m}^2$. The pressure bias is 0.5 MPa. When the surface charge density is small and the average concentration difference between K^+ and Cl^- inside the channel, Δn , is not much larger than the bulk concentration n_0 , the coions of Cl^- as well as the counterion of K^+ enter the channel. Hence, the solution inside the channel is not unipolar. As a result the electromotive force is small. When Δn is much larger than n_0 , only K^+ ions are located inside the channel independent of the bulk concentration but they are accumulated near the channel walls. The K^+ ions near the walls do not contribute to the current density due to advection, $i_{\text{K}^+, \text{adv}}$, because the velocity near the wall is small. But the current density due to diffusion, $i_{\text{K}^+, \text{diff}}$, increases independent of its concentration profile. As a result the electromotive force decreases with increasing the surface charge density. For the bulk concentrations, $n_0 = 10^{-5}$ and 10^{-4} M , there is an optimum surface charge density at which the maximum electromotive force can be generated.

Figure 5 shows the current-potential (I - $\Delta\phi$) characteristics of the channels with the surface charge density of -10^{-3} and $-5 \times 10^{-3} \text{ C/m}^2$. The bulk concentrations are assumed to be 10^{-5} , 10^{-4} , 10^{-3} , and 10^{-2} M and the pressure bias is assumed to be 0.5 MPa. Except of the I - $\Delta\phi$ characteristics of $n_0 = 10^{-5} \text{ M}$ at $\sigma = -10^{-3} \text{ C/m}^2$, and $n_0 = 10^{-5}$ and 10^{-4} M at $\sigma = -5 \times 10^{-3} \text{ C/m}^2$, the curves are almost linear with negative gradient. This negative gradient expresses ohmic drop. When the average concentration difference between K^+ and Cl^- inside the channel, Δn , is much larger than the bulk concentration, n_0 , the overall ion transport is restricted by that in the reservoir and the potentials drop rapidly in the high current density region.

The efficiency is one of the most important performance indicators for energy conversion systems. The input power, the output power and the efficiency can be expressed as follows:

$$P_{in} = \Delta p \int_{-L_y/2}^{L_y/2} u(y) dy, \quad (13)$$

$$P_{out} = \Delta \phi I, \quad (14)$$

$$\eta = \frac{P_{out}}{P_{in}}. \quad (15)$$

Assuming the Poiseuille flow, the input power is calculated to be $112.5 \mu\text{W}/\text{m}$ at $L_x=5 \mu\text{m}$, $L_y=30 \text{ nm}$ and $\Delta p=0.5 \text{ MPa}$. But the volumetric flow rate slightly decreases with increasing the potential and decreasing the current. Here, the volumetric flow rate is assumed to be proportional to the potential and current for simplicity. If the $I-\Delta\phi$

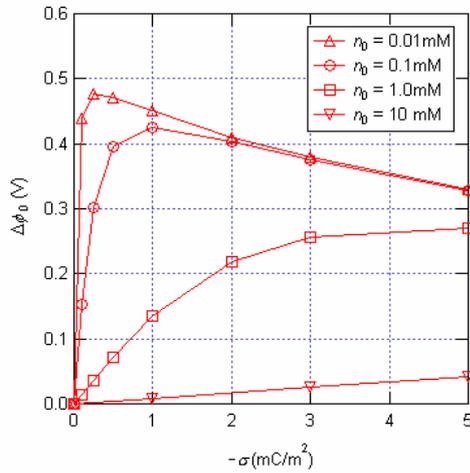


Figure 4. Electromotive force vs. surface charge density curves. The bulk concentrations of KCl aqueous solutions are 10^{-5} , 10^{-4} , 10^{-3} and 10^{-2} M. The pressure bias is 0.5 MPa.

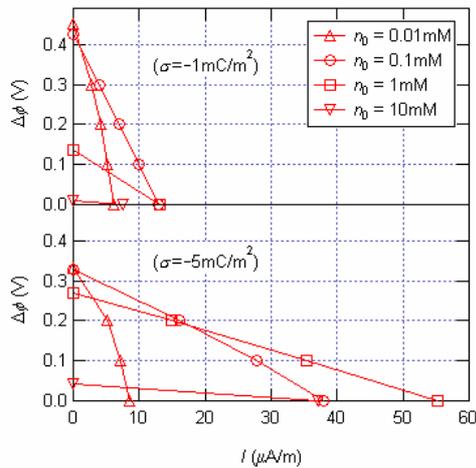


Figure 5. Current-potential curves for two different surface charge densities, $\sigma=-10^{-3} \text{ C}/\text{m}^2$ (top) and $\sigma=-5 \times 10^{-3} \text{ C}/\text{m}^2$ (bottom) on the channel surface. The bulk concentrations of KCl aqueous solutions are assumed to be 10^{-5} , 10^{-4} , 10^{-3} , and 10^{-2} M. The pressure bias is 0.5 MPa.

characteristics are assumed to be linear, for the surface charge density, $\sigma=-10^{-3} \text{ C}/\text{m}^2$, the maximum output power is $1.36 \mu\text{W}/\text{m}$ and the maximum efficiency is 1.26 % at $n_0=10^{-4} \text{ M}$ (at $I=6.40 \mu\text{A}/\text{m}$ and $\Delta\phi=0.215 \text{ V}$). For the surface charge density, $\sigma=-5 \times 10^{-3} \text{ C}/\text{m}^2$, the maximum output power is $3.73 \mu\text{W}/\text{m}$ and the maximum efficiency is 3.56 % at $n_0=10^{-3} \text{ M}$ (at $I=26.7 \mu\text{A}/\text{m}$ and $\Delta\phi=0.139 \text{ V}$). When the electrical double layers are overlap near the center of the channel and the Debye length of a solution is about half of the channel height, the efficiency is maximized.

4 CONCLUSIONS

The Poisson-Nernst-Planck equations and the Navier-Stokes equations were employed to calculate ionic distribution and transport in a nanofluidic channel, $5 \mu\text{m}$ long and 30 nm high. The surface charge density ranged from 0 to $-5 \times 10^{-3} \text{ C}/\text{m}^2$, the bulk concentration of KCl aqueous solution ranged from 10^{-5} to 10^{-2} M . The following conclusions can be drawn from this study.

1. When the channel size is smaller than the Debye length and the channel surface is charged, the channel becomes a unipolar solution of counterions at a concentration that neutralizes the surface charge. The coions are essentially repelled from the channel.
2. By controlling the surface charge density in a region along the length of the channel, the ion current can be modulated, similar to modulation of charge transport in a field effect transistor due to a gate bias.
3. By applying the pressure bias instead of electric potential bias, a streaming current and a potential are produced. This could form the basis of nanofluidic battery. When the Debye length of a solution is about half of the channel height, the efficiency is maximized.

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