

# Electrolyte Concentration Dependence of Ion Transport through Nanochannels

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## ABSTRACT

The magnitude of current through a conical nanochannel filled with an electrolyte solution depends on the polarity of the applied bias, indicating an asymmetric diode-like current-voltage (I-V) curve. This kind of phenomenon refers to current rectification and it indicates that there is a preferential direction for ion flow in the asymmetrical nanochannels. In this study, the rectification phenomenon through an asymmetrical nanochannel simultaneously subjected to an electric field and electrolyte concentration gradient is numerically investigated. A mathematical model consisting of the PNP equations has been developed. The obtained simulation results are in great agreement with the literature. In this research, the effect of the imposed electrolyte concentration gradient on the current rectification has been studied for the first time.

## ABOUT THE AUTHORS

**Murat Bakirci** is a doctoral student in the Department of Modeling Simulation and Visualization Engineering at Old Dominion University. His research interests include a variety of dynamical system simulations, especially computational fluid dynamics, micro/nanofluidic systems, high performance computing, and unmanned systems.

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## INTRODUCTION

Within the last decade, nanochannels have drawn continuous attention from researchers in different disciplines. In fact the efforts in the field of nanochannels have seen significant growth mostly because of scientific and technological advancement as well as progression of nanofabrication technology. Nanochannels have found many applications in various research branches such as development of biosensors and bioelectronic devices (Siwy & Fulinski, 2002), separation (Stein & Kruithof & Dekker, 2004), extra small volume chemical delivery (Pivonka & Smith, 2005), maturation of scanning probe microscopy (Vlassioug & Siwy, 2007), and DNA sequencing (Woermann, 2003). Studies on the ion transport in channels with nano-scale sized have shown some fascinating characteristics due to the presence of electric double layers (EDL) (Qian & Joo, 2008). Indeed asymmetric nanochannels possessing overabundance surface charge and the diameter of the small opening comparable to the electrical double layer thickness of electrolyte show non-linear, diode-like current-voltage (I-V) responses (Lin & Lin & Hsu & Tseng, 2016). This kind of phenomenon refers to ionic current rectification (ICR) (Wang & Nandigana & Jo & Aluru & Timperman, 2015). In other words, the magnitude of current through the nanochannel at negative potentials is greater or less than the current at positive potentials. ICR can be quantified by the ratio of the two countercurrents generated by potential gradients equal in magnitude with opposite senses. These (I - V) responses show that there is a preferential direction for ionic flow. Several researchers have analyzed the mechanism of current rectification and proposed various theoretical models (Siwy, 2006) to explain the origin of ICR. In spite of all the proposed different mechanisms, transport of ions in asymmetrical nanochannels has not yet found a generally agreed explanation. The Poisson – Nernst – Planck (PNP) equations have widely been used to simulate the ICR behavior in nanochannels. Compared recent experimental and numerical studies showed that the continuum model properly describes the ion transport and ICR in nanochannels with diameters higher than 0.1 Debye length (Yan & Wang & Xue & Chang, 2013).

## MATHEMATICAL MODEL

A sketch of the computational domain for the conically shaped nanochannel is shown in Figure 1. As stated in the figure, the axial length of the pore, the radius of the tip and the base are respectively,  $L$ ,  $R_t$ , and  $R_b$ . The identical upper and lower fluid wells filled with various KCL solutions to generate various concentration gradients. In order to provide the bulk ionic concentration as a constant value the dimensions of the fluid cells are selected wide enough. The wall of the nanochannel has a uniform surface charge density and this provide to compose an electric double layer (EDL) near this charged wall. As one can assume that an applied potential between fluid wells (AB and GH) induces an ionic current through the nanochannel. In accordance with the asymmetric geometry of the domain, a cylindrical coordinate system has been fixed at the center of the nanochannel. In the domain, segment AH represents the axis of the symmetry. Segments AB, BC, CD, EF, FG, and GH are the boundaries of the fluid wells and DE is the wall of the nanochannel.

Since the Reynolds number of the electrokinetic flow is on the scale of  $10^{-6}$ , we can simply neglect the inertial terms in the Navier – Stokes equations. As a result an incompressible flow of an electrolyte solution is depicted as

$$\nabla \cdot \mathbf{u} = 0 \quad (1)$$

$$-\nabla p + \mu \nabla^2 \mathbf{u} - F(z_1 c_1 + z_2 c_2) \nabla \varphi = 0 \quad (2)$$

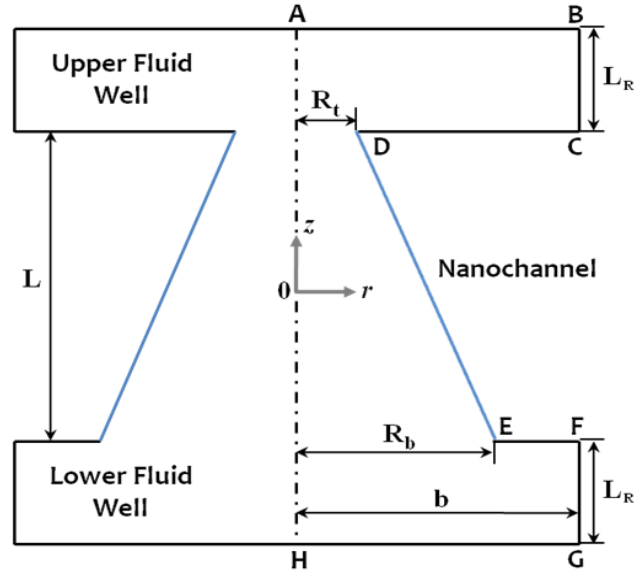


Figure 1. Computational domain

In these equations  $\mathbf{u}$  denotes the fluid velocity,  $p$  is the pressure,  $\varphi$  is the electric potential in the electrolyte solution,  $c_1$  and  $c_2$  are the molar concentrations of the positive ( $K^+$ ) and negative ions ( $Cl^-$ ),  $z_1$  and  $z_2$  are the valences of the positive and negative ions respectively, and  $F$  is the Faraday constant. The interactions between applied potential and net charge in the electrolyte are taken into account by the last term of the Equation 2. In addition to these, suitable boundary conditions are properly fixed to the boundaries of the domain. Nonslip boundary conditions are set on the CD, DE, and EF segments. As mentioned before the top and bottom boundaries of the fluid wells are far away from the nanochannel therefore a normal flow with zero pressure is used for AB and GH. Since BC and FG boundaries are far away from the pore openings, slip boundary conditions are used for these segments.

A complete description of the ionic mass transport of a charged nanochannel starts with the flux equations for each aqueous species. The convection, diffusion, and migration mechanisms provide the equation for the flux density of each ionic species as stated below.

$$\mathbf{N}_i = \mathbf{u}c_i - D_i \nabla c_i - z_i \frac{D_i}{RT} F c_i \nabla \varphi, \quad i = 1 \text{ and } 2 \quad (3)$$

where  $D_i$  is the diffusion coefficient of the  $i$ th ionic species,  $T$  is the absolute temperature of the electrolyte solution, and  $R$  is the universal gas constant. When steady state condition is assumed, Nernst – Planck equation governs the concentrations of each species as follows.

$$\nabla \cdot \mathbf{N}_i = 0, \quad i = 1 \text{ and } 2 \quad (4)$$

On the other hand the Poisson equation governs the electric potential in the electrolyte solution

$$-\varepsilon \nabla^2 \varphi = \sum_i z_i c_i \quad (5)$$

Since the segment CD, and EF of the fluid wells and the wall of the nanochannel (DE) are solid surfaces, we assume that these surfaces are impervious to ions and consequently the normal ionic flux must be zero as stated below.

$$\mathbf{n} \cdot \mathbf{N}_i = 0, \quad i = 1 \text{ and } 2 \quad (6)$$

Here,  $\mathbf{n}$  is the local unit normal vector of the above segments. Same boundary conditions are set for the BC, and FG walls of the fluid wells which is a direct consequence of being in the bulk electrolyte wells. Similarly, zero normal ionic flux is used along AH due to the axisymmetric condition.

As assumed the top boundary of the upper well and the bottom boundary of the lower fluid well are significantly far away from the nanochannel, therefore the ionic concentrations are considered same as the bulk concentration of the electrolyte solution.

$$c_i \left( r, - \left( L_R + \frac{L}{2} \right) \right) = C_{U0}, \quad i = 1 \text{ and } 2 \quad (7a)$$

$$c_i \left( r, - \left( L_R + \frac{L}{2} \right) \right) = C_{L0}, \quad i = 1 \text{ and } 2 \quad (7b)$$

In order to perform an electric potential through the nanochannel, an external potential is applied along the AB edge of the upper fluid well and zero potential is applied along the GH edge of the lower fluid well respectively.

$$V = \varphi \quad (8)$$

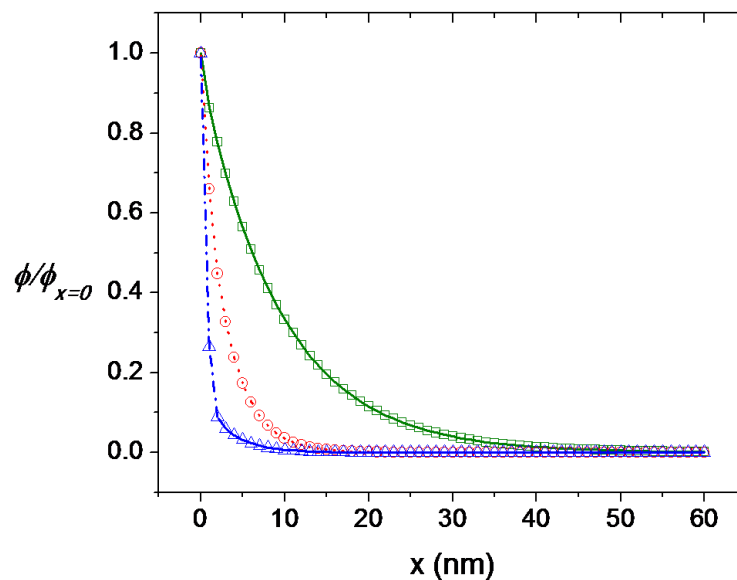
$$V = 0 \quad (9)$$

The boundaries CD, and EF of the fluid wells are assumed to be uncharged and because of the long distance from the nanochannel, no charge condition is set for the side boundaries BC, and FG of the fluid wells as shown below.

$$\mathbf{n} \cdot \nabla \varphi = 0 \quad (10)$$

### Model Validation

In order to test the numerical model, results of a benchmark problem involving electrical double layer structures for which analytical solution exists is presented. The numerical result and the analytical solution are compared.



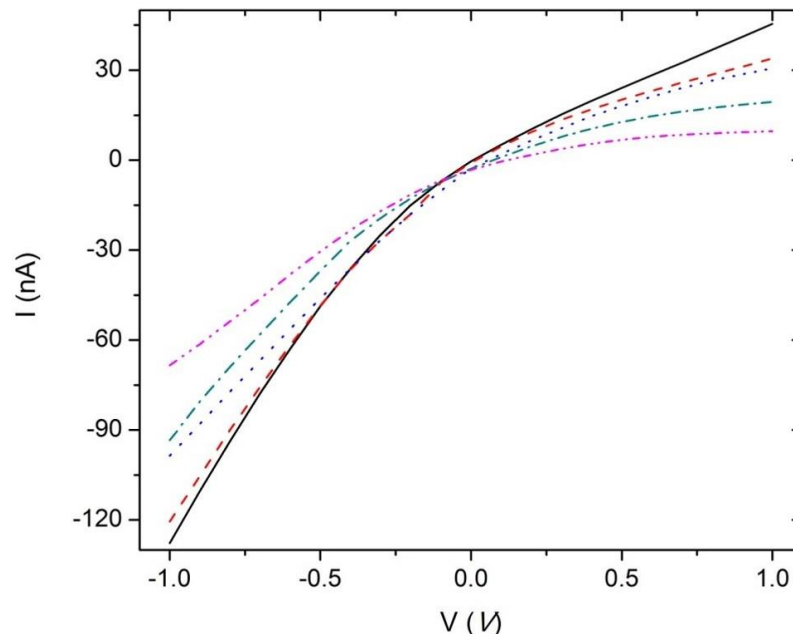
**Figure 2. Comparison between the analytical solutions (lines) and numerical results (symbols) of the electric potential near a planar charged surface ( $\sigma = -1mC/m^2$ ) in 1 mM (solid line and squares), 10 mM (dashed line and circles), and 100 mM (dash-dotted line and triangles) KCl solution. The electric potential,  $\varphi(x)$ , is normalized by its value at  $x = 0$ .**

A diffuse double layer adjacent to a flat surface is selected as the benchmark problem. The concentration field and the electric field were simulated in a rectangular ( $500\text{nm} \times 200\text{nm}$ ) computational domain with a surface charge density  $\sigma = -1\text{mC}/\text{m}^2$  ( $-6.24 \times 10^{-3} \text{ e}/\text{nm}^2$ ) on the left. At equilibrium (i.e., no current flow,  $N_i = 0$ ,  $\mathbf{u} = 0$ ) the potential distribution normal to a charged wall can be compared with the analytical expression developed in the framework of the Gouy – Chapman theory (Siwy, 2006). As shown in Figure 2, the agreement between numerical simulation and the analytical solution is excellent

## RESULTS

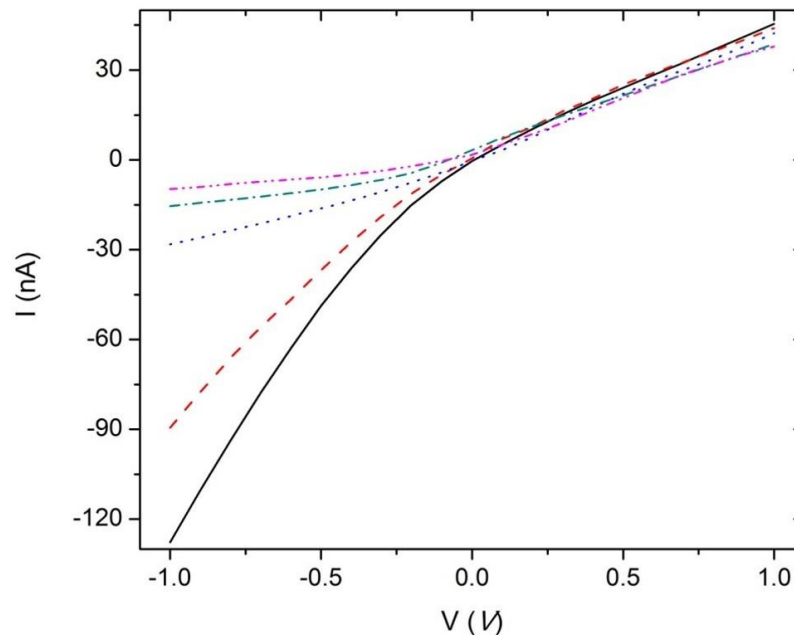
The system of coupled PNP-NS equations (equations 2, 3, 5) must be simultaneously solved for the given geometry using appropriate boundary conditions. Given the complexity of asymmetric domain, an analytical solution of this system of equations will not be possible. The nonlinear system of equations was solved numerically with the finite-element package Comsol which is better fitted for irregular geometries. The computational domain was discretized into quadratic triangular elements with various sizes. Because of the forming an EDL near the charged nanochannel wall, finer mesh was used near the pore wall in order to obtain better quality for simulations. Convergence and grid independence of the obtained solutions was examined by many strict mesh refinement tests. For the simulations, the computational domain was assumed to be in an aqueous KCl solution with room temperature.

Figure 3 shows the current – voltage (I-V) characteristics of a single asymmetrical nanochannel for various electrolyte concentration gradients. The case which both upper and lower fluid wells were fixed with  $100 \text{ mM}$  KCl is called as the *reference case*. In the reference case, the current rectification can be seen clearly. The magnitude of the current for  $-1 \text{ V}$  is approximately three times of that for  $+1 \text{ V}$ . As seen in the figure, the electrolyte concentration gradient also affects the current – voltage (I - V) curves. In the model, the positive ionic current is defined as a current directed from the large opening (base) toward the small opening (tip) when a positive voltage ( $V = \varphi_{base} - \varphi_{tip} > 0$ ) is applied. As can be seen in Figure 3, the magnitude of a negative ionic current under a negative voltage is higher than the corresponding ionic current for a positive applied voltage, which is consistent with the existing experimental and numerical studies.



**Figure 3. I-V responses of the asymmetrical nanochannel. The upper fluid well was fixed by  $100\text{mM}$  KCl while the concentrations of the lower fluid well were variably changed. The solid line, dashed line, dotted line, dash-dot line, and dash-dot-dot line represents  $100, 50, 10, 5, 1\text{mM}$  concentration values of the lower fluid well.**

In the second set of simulations, the lower fluid well was fixed at 100 mM KCl while the concentrations of the upper fluid well were varied. The results are presented in Figure 4. When the concentration in the upper fluid well is above a critical value, the magnitude of the negative current is higher than that when the polarity of the voltage is reversed. However, when the concentration in the upper fluid well is below the critical value, the direction of the ICR is reversed, and the magnitude of the current for a positive voltage is higher than that for a negative voltage with same magnitude. Therefore, one might control the degree and direction of ICR by adjusting the salt concentrations in the two fluid wells.



**Figure 4. I-V responses of the asymmetrical nanochannel. The lower fluid well was fixed by 100mM KCl while the concentrations of the upper fluid well were variably changed. The solid line, dashed line, dotted line, dash-dot line, and dash-dot-dot line represents 100, 50, 10, 5, 1mM concentration values of the upper fluid well.**

## CONCLUSIONS

Ionic current rectification in asymmetrical nanochannels subjected to axial electric field and concentration gradient was numerically investigated. The verified continuum model, composed of the coupled Poisson-Nernst-Planck equations and Navier-Stokes equations, is implemented to study the ionic current rectification (ICR). Some interesting characteristics of asymmetric nanochannels such as ion selectivity and ICR have been observed. It has been showed that the superimposed KCl concentration gradient affects the resulting ionic current flowing through the nanochannel. We believe that, the ICR originates from the surface charge of the nanochannel, which generates an asymmetric distribution of ions along the nanochannel, rendering the asymmetrical nanochannel similar to a nanofluidic diode. It may be concluded that ionic transport through chemically modified nanochannels could be tuned effectively by manipulating the surface charge of the channel. In other words, the ion transport properties could be used to measure changes in the surface charge of the nanochannel.

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