Supporting information

Surface Charge Density Determination of Single Conical Nanopores Based on
Normalized Ion Current Rectification

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Experimental details.

Table SI-1. Simulated current at different cutline positions under ± 0.4 V bias potential
(outside vs. inside) in 50 mM KCl solution. The surface charge density is at **-170** mC/m^2.

mC/m^2.

Details of simulation:

Figure SI-1. A typical adaptive free triangular mesh used in numerical simulation.

Figure SI-2. Normalized conductivity curves of A: 161-nm-radius; B: 123-nm-radius
nanopore in KCl solutions at different concentration.

Figure SI-3. Electric conductivity at $+ 0.4$ V (red) and $– 0.4$ V (black) along the
centerline of a 26-nm-radius nanopore in 50 mM KCl with SCD at -170 mC/m^2.

Figure SI-4. The effects of nanopore radius and half cone angle on simulated current

Figure SI-5. Concentration profiles of K$^+$ (red) and Cl$^-$ (green) at **A:** $+ 0.4$ V; and **B:** -0.4
V along centerline.

Figure SI-6. Comparison of the computed and measured current from a 26 nm nanopore
in 1 M KCl solution.

Table SI-1 Simulated current at different cutline positions under ±0.4 V bias potential (outside vs. inside) in 50 mM KCl solution. The surface charge density is at **-170** mC/m^2. The Cl$^-$ current is consistent at each cutline: +0.4 V, i_{Cl^-} = 3.149±0.001 nA; -0.4 V, i_{Cl^-} = -1.055±0.001 nA. The data were retained after Q test at 90% confidence level.

Cutline (nm)	+0.4 V		-0.4 V	
	Current by K$^+$ (nA)	Total Current (nA)	Current by K$^+$ (nA)	Total Current (nA)
-1	5.07	8.22	-2.91	-3.96
-2	5.04	8.19	-2.94	-3.99
-5	5.10	8.25	-2.87	-3.93
-8	5.07	8.22	-2.90	-3.96
-10	5.07	8.22	-2.91	-3.97
-20	5.06	8.21	-2.92	-3.97
-30	5.09	8.24	-2.89	-3.94
-40	5.06	8.21	-2.92	-3.97
-50	5.08	8.23	-2.90	-3.95
-60	5.11	8.26	-2.87	-3.92
-70	5.04	8.19	-2.94	-3.99
-80	5.12	8.27	-2.86	-3.92
-90	5.05	8.19	-2.93	-3.99
-100	5.05	8.20	-2.93	--3.98
-120	5.13	8.28	-2.85	-3.90
-150	5.11	8.26	-2.87	-3.92
-180	5.04	8.19	-2.94	-3.99
-200	5.07	8.21	-2.91	-3.97
Average	5.1±0.1	8.2±0.1	-2.9±0.1	-4.0±0.1
Standard Deviation	0.1	0.1	0.1	0.1
RE	5.1	8.2	-2.9	-4.0

Details of simulation:

COMSOL Multiphysics Package (Version 4.0a) was used. The modules of Electrostatics and Transport of Diluted Species were employed to solve Poisson equation and Nernst-Planck equation.

The nanopore geometry and mesh elements are shown in Figure SI-1 with 1.3 maximum element growth rate, 0.3 curvature resolution and 1993912 degree freedom. In consideration of the symmetry along the centerline Z direction, half of the cross-section is used in the computation. Boundary 1 represents the center line. The nanopore orifice is at z = 0. To provide sufficient materials for the transport studies with reasonable computation expenses, and to maintain bulk concentration near electrodes for steady state response, the Z dimension extends to 10 microns inside the pore and 2 microns outside. The bias potential is applied between Boundary 3 (working electrode, out of pore) and Boundary 2 (reference electrode, inside pore). Boundary 5 represents negatively charged interior glass surface that are expected to affect the ion transport. To minimize the computation expenses without affecting the charge distribution near the mass transfer limiting region, negative charges are placed on the exterior surface represented by boundary 4, which is 20 times of the pore radius. Boundary 6 and 7 define the bulk dimension. As Boundary 6 and 7 are away from the mass transport limiting region, they are not charged to save the computation expenses.

Ion diffusion coefficient calculation:

It is known that the diffusion coefficient varies in different concentration. Instead of using the value at infinite dilution, effective diffusion coefficient of K^+ and Cl^- in each concentration is calculated shown below, with the details discussed in "Electrochemical Systems", Third Ed. (Ch 11 & 12).

$$\frac{1}{\kappa} = \frac{-RT}{c_0 z_+ z_- F^2}\left(\frac{c_0 t_-}{c_+ D_-}\right)$$

$$\frac{1}{\kappa} = \frac{-RT}{c_T z_+ z_- F^2}\left(\frac{1}{D_\pm} + \frac{c_0 t_-^0}{c_+ D_{0-}}\right)$$

in which $D_\pm$ is related to drag or friction coefficient and addresses ion-ion interaction. Based on the solution conductivity and ion transference number from literature, the conductivity and diffusion coefficient of cation and anion are calculated respectively.

$$\kappa_i = \kappa * t_i$$

$$D_i = \frac{\kappa_i RT}{|z_i| F^2 c_i}$$

The conductivity of species (ion) i equals to its transference number multiply solution conductivity. Since the conductivity already includes the correction of ion-ion interaction, the calculated ion diffusion coefficient in each concentration offers better fitting of experimental results by simulation. Note *the diffusion coefficient at infinite dilution* could not be correlated to the solution conductivity following the above definition (reference data in Table 1). The comparison of 1M KCl results can be found in Fig. SI-6.
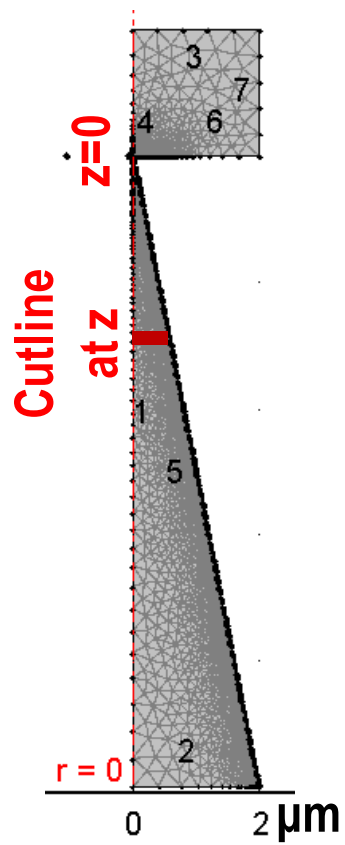
Figure SI-1 A typical adaptive free triangular mesh used in numerical simulation.
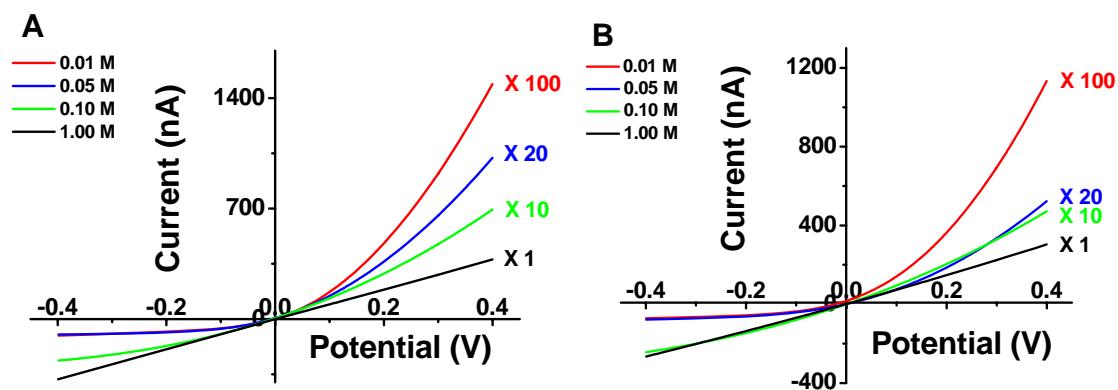
Figure SI-2. Normalized conductivity curves of A: 161-nm-radius B: 123-nm-radius nanopore in KCl solutions at different concentration: red 0.01 M, blue 0.05 M, green 0.10 M, black 1.00 M. The current is normalized by the factors listed next to each curve based on the concentration. The nanopore surface was modified with 3-aminopropyldimethyl-ethoxysilane, which is found to offer more reproducible measurements as previously described [ref. 21].
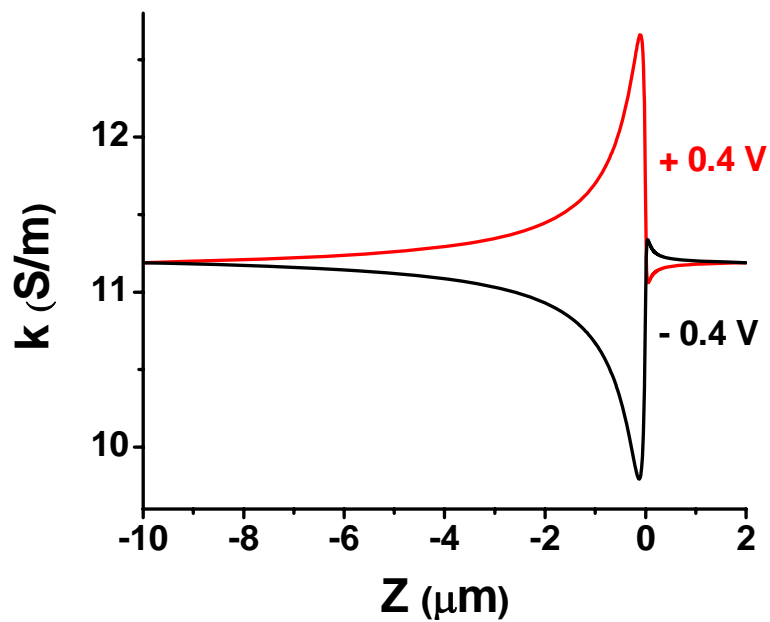
Figure SI-3 Electric conductivity at + 0.4 V (red) and – 0.4 V (black) along the centerline of a 26-nm-radius nanopore in 50 mM KCl with surface charge density at -170 mC/m^2.
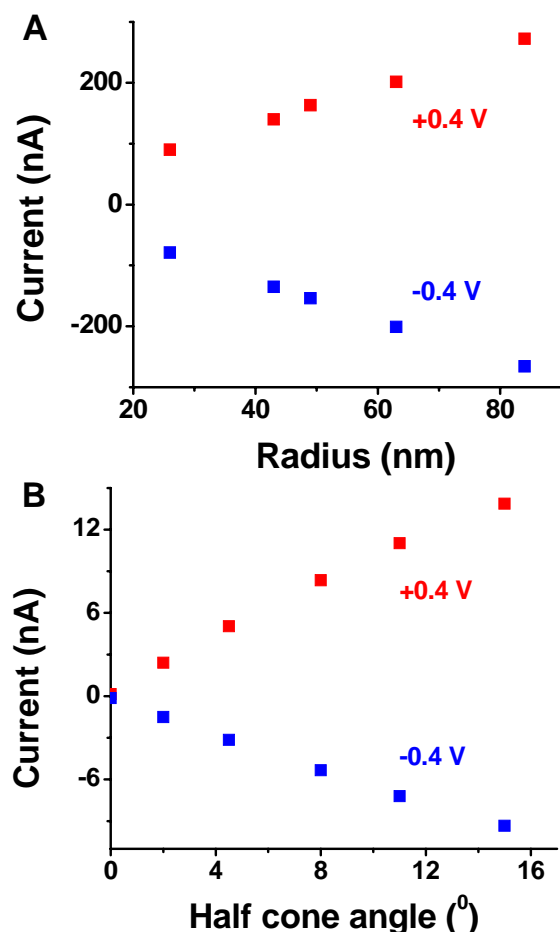
Figure SI-4. The effects of nanopore radius and half cone angle on simulated current at + 0.4 V (red square) and -0.4 V (blue square). The half-cone angle is 11.2^0 in Panel A at 1 M KCl solution. The radius is 26 nm in Panel B at 0.1 M KCl solution.
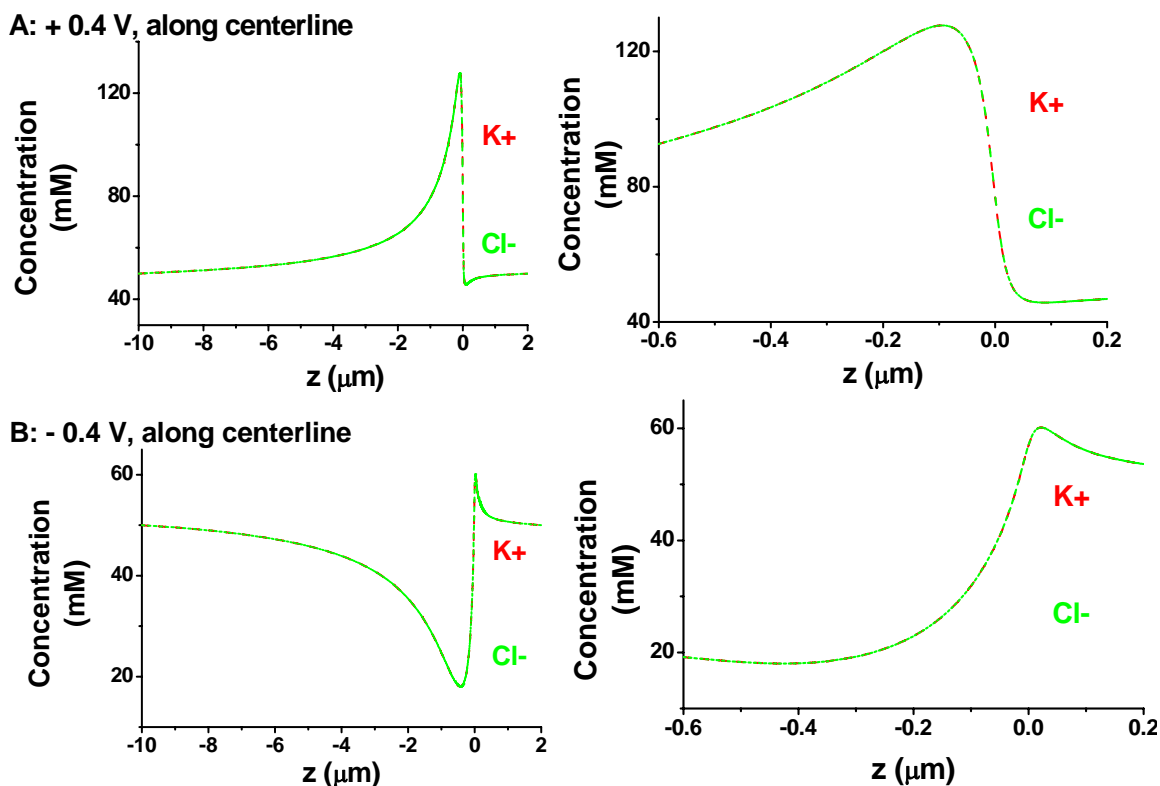
Figure SI-5. Concentration profiles of K^+ (red) and Cl^- (green) at **A:** + 0.4 V; and **B:** -0.4 V along centerline. Negative values on x axis represents the depth inside the pore, with pore orifice at zero. The radius of the nanopore is set at 26-nm with surface charge density defined at -170 mC/m^2 (value based on Figure 6). The bulk concenstrion of KCl is 50 mM. The maximum and minimum concentration of each ion (overlapped) along Z direction can be seen in the enlarged panel shown on the right.
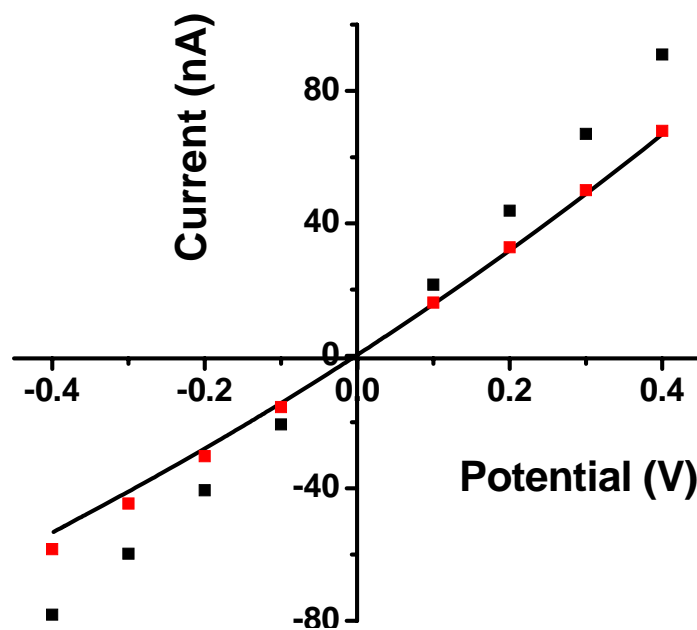
Figure SI-6. Comparison of the computed and measured current from a 26 nm nanopore in 1 M KCl solution. Black symbols represent data calculated with diffusion coefficient at infinite diluted KCl solution. The red symbols represent the data from the effective diffusion coefficient listed in Table 1. Black line is the measured current-voltage curve in 1 M KCl solution.