Supplementary Material (ESI) for Energy & Environmental Science

Supplementary Information for

Towards Understanding the Nanofluidic Reverse Electrodialysis System: Well Matched Charge Selectivity and Ionic Composition

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1. Electrode calibration

In the presence of concentration gradient, potential difference ($V_{electrode}$) generates between the two Ag/AgCl electrodes due to the redox reactions on the electrode|electrolyte interface.[1] As shown in Fig. S1, the actual potential applied across the nanopore ($V_{nanopore}$) is describe as:

$$V_{nanopore} = V_{app} - V_{electrode}$$

Where V_{app} is the voltage output from the Keithley 6487 picoammeter/voltage source.

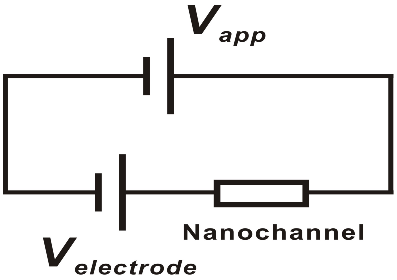

Fig. S1 Equivalent circuit for single-nanopore device in the presence of concentration gradient.

Using Ag/AgCl or calomel reference electrodes with saturated KCl bridges may provide a way to eliminate the offset electrode potentials. However, when measuring the zero-volt current (i_0) and the reversal potential (V_{rev}), the scanning *I-V* cycles were required. A long testing time of at least 750 seconds (~ 3 cycles for each *I-V* measurements) is needed. The inevitable leakage of high concentrated KCl solution to the electrolyte cell would affect the results. Therefore, the Ag/AgCl electrodes were selected for the *I-V* measurements and the electrode calibration was performed in separate experiments with a calomel reference electrode. Thus, the zero-volt current and the reversal potential contributed by the nanopore can be extracted from the $I-V$ curves by compensating the potential drop difference on the two electrode-electrolyte interfaces.

When contacting with the electrolyte solutions of different concentrations, the electrode potential drops at the two electrode-electrolyte interfaces are not the same.[1] The electrode potential of each Ag/AgCl electrodes was calibrated with respect to the saturated calomel reference electrode. The two electrodes were connected with a standard resistance of $1G\Omega$, which is far higher than the inherent resistance of the electrodes and the electrolyte solution. No external voltage was applied across the two electrodes, thus, the total current recorded by the picoammeter was driven by the potential difference generated on the two electrode-electrolyte interfaces. The electrode potential of each Ag/AgCl electrode with respect to the calomel reference electrode was obtained by multiplying the recorded current by the standard resistance. The potential calibration was conducted with the KCl, NaCl, and LiCl solutions at varied concentrations of 1 mM, 10 mM, 30 mM, 100 mM, 300 mM, and 1000 mM and buffered to pH 3.4, or 5.6, which is the same set with that used in the current recording through nanopores in the main text. The calibration was performed at room temperature of about 293 K.

The potential differences between two Ag/AgCl electrodes, in the presence of concentration gradient are shown in Fig. S2. Under symmetric concentrations, the electrode potential differences between the two Ag/AgCl electrodes were less than ±2 mV. Under asymmetric concentrations (1 mM|1 mM, 1 mM|10 mM, 1 mM|30 mM, 1 mM|100 mM, 1 mM|300 mM, 1 mM|1000 mM, at pH 5.6 and 10 mM|10 mM, 10 mM|100 mM, 10 mM|300 mM, 10 mM|1000 mM, at pH 3.4), the electrode potential differences between the two Ag/AgCl electrodes were generally agree with the Nernst relation.[1] We use these data to calibrate the potential output from the voltage source.

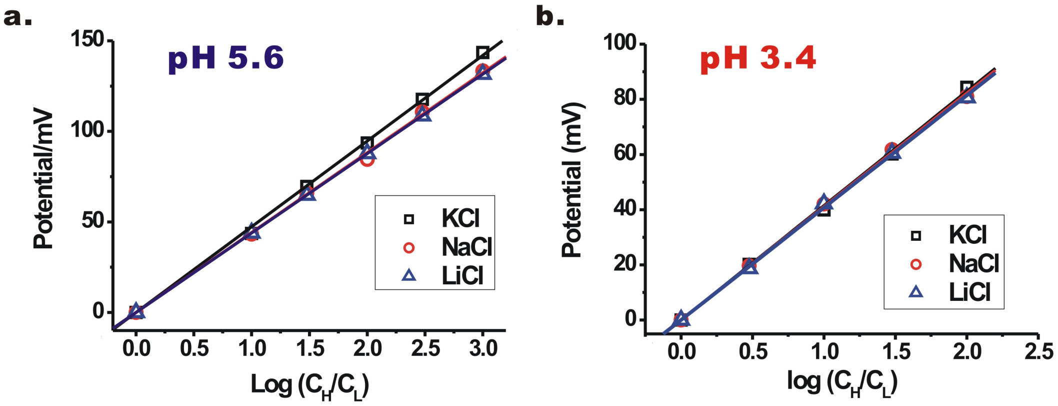

Fig. S2 The electrode potential difference under asymmetric electrolyte concentrations at pH 5.6 (a) and 3.4 (b). Four kinds of electrolyte are used in these experiments, that is, KCl (square), NaCl (circle), and LiCl (triangle). The data points showed in panel (a) in stand for 1 mM|1 mM, 1 mM|10 mM, 1 mM|30 mM, 1 mM|100 mM, 1 mM|300 mM, 1 mM|1000 mM and in panel (b) stand for 10 mM|10 mM, 10 mM|30 mM, 10 mM|100 mM, 10 mM|300 mM, 10 mM|1000 mM.

2. Model calculation

We calculate the net diffusion current, reversal potential, and the resulting electrical power as a function of I_+ and I_-. The model nanochannel is illustrated in Fig. S3. The calculated region is cylindrical in shape and 500 nm in length. The length and radius of the reservoirs are both set to 500 nm. The only fitting parameter in our model is the surface charge density (σ), which is consistence with the experimental condition ranging from 0.1 to 100 mC/m^2.[2-3] The polarity of the surface charge is either negative to simulate cation-selective nanopores or positive to simulate anion-selective nanopores. The concentration gradient applied on the calculation model is 1000-fold, by placing 1 mM electrolyte solution on one side of the nanochannel and 1000 mM on the other side.

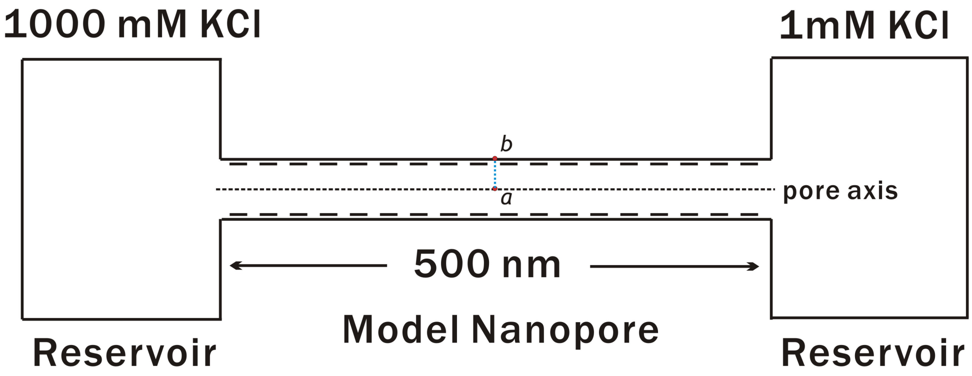

Fig. S3 The calculate nanopore model (not in scale).

The Poisson-Nernst-Plack (PNP) equations are used to describe the ion transport down their concentration gradient inside nanochannels:

$$\nabla^2 \Phi = -\frac{e}{\varepsilon}(c_+ - c_-)$$

$$\vec{j}_i = -D_i\left(\nabla c_i + \frac{z_i e c_i}{k_B T}\nabla \Phi\right),$$

$i = + / -$, for cations and anions respectively, and the continuity equation:

$$\nabla \cdot \vec{j}_i = 0$$

where Φ, c_i, j_i, D_i, and T are the local electrical potential, the concentration of species i, the ion flux, the diffusion coefficient, and the temperature. e, ε_0, ε_r, and k_B is the electron charge, the permittivity of vacuum, the dielectric constant of the electrolyte solution, and the Boltzmann constant as their usual meaning. The diffusion coefficients for simple monovalent ions in this calculation are used the as their bulk value, as listed in Table 1 in the maintext.[4] The boundary conditions for potential Φ are given by the Gauss law:

$$-\vec{n}\cdot\nabla\Phi = \frac{\sigma_s}{\varepsilon_0\,\varepsilon_r}$$

When it was applied to the charged pore walls, $\sigma_s = \sigma$, and to the reservoir walls $\sigma_s = 0$. The ion flux $\vec{j}_i$ also has the zero normal components at boundaries, for

$$\vec{n}\cdot\vec{j}_i = 0$$

The total diffusion current can be calculated by integrating the ion flux density in the cross section of the nanochannel, as shown in Fig. S3, from point a, at the pore axis, to point b, at the pore wall, in the middle of the entire length of the nanochannel:

$$I_i = 2\pi e\int r\ j_i\ dr\ ,\ i=+/-.$$

3. Estimation of the surface charge density

The surface charge density is the most important parameter for ion transport in nanopore, which is very difficult to characterize experimentally. To address this challenge, we use a combined experimental and theoretical approach to elucidate and quantify the electrostatic changes taking place inside the nanopore in the presence of different monovalent inorganic salts. The experimental *I-V* curves measured in KCl, NaCl, and LiCl electrolytes have been theoretically fitted with a continuum model based on the Poisson and Nernst-Planck equations, which have been described in the manuscript. The validity and reliability of this method can be found in our previous publications[3, 5] and also the recent work by Azzaroni, et al., (***J. Am. Chem. Soc.*** 2010, 132, 8338).[6] The dimensions of the model nanopore are estimated from the experimental results: the model nanopore is cone-shaped and 12 μm long with the large opening (the base side) of 1.2 μm and the small opening (the tip side) of 40 nm in diameter. The only fitting parameter in the model calculation is the surface charge density (σ). As shown in **Fig S4 and S5**, the theoretical results fit the experimental data very well. For cation-selective nanopores, the best fitting results are obtained with σ = -0.05 C/m^2 for all the three kinds of electrolyte. This result is consistent with previous works published by other groups (e.g. Siwy et al., ***Appl. Phys. A***, 2003, 76, 781; Cervera et al., ***J. Chem. Phys.*** 2006, 124, 104706).[2,7] For anion-selective nanopores, similar results have been found that the surface charge density is about +0.03 C/m^2 for all the three kinds of electrolyte. Based on the calculation results, we can know that the surface charge density for cation-selective nanopores are nearly one time higher than that in anion-selective nanopores owing to the limited efficiency of the chemical modification. The difference in ionic composition between the three kinds of monovalent simple salt would not remarkably influence the surface charge density in either types of nanopore.

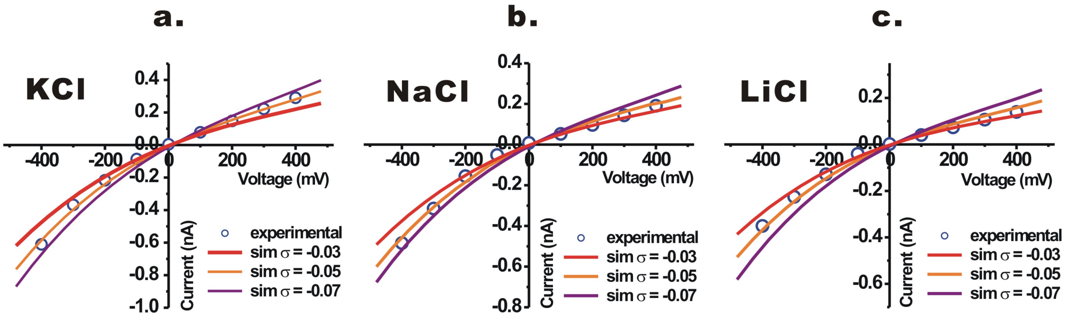

Fig. S4 In the case of cation-selective nanopores, the experimental *I-V* curves are numerically fitted with theoretical results to calculate the surface charge density in the presence of 1 mM KCl (a), NaCl (b), and LiCl (c). The dimensions of the model nanopore are estimated from the experimental results: the model nanopore is cone-shaped and 12 μm long with the large opening (the base side) of 1.2 μm and the small opening (the tip side) of 40 nm in diameter. The only fitting parameter in the model calculation is the surface charge density (σ). Experimental results are shown in blue circles. In model calculation, σ = -0.03 (red), -0.05 (orange), -0.07 (purple) C/m^2, respectively.

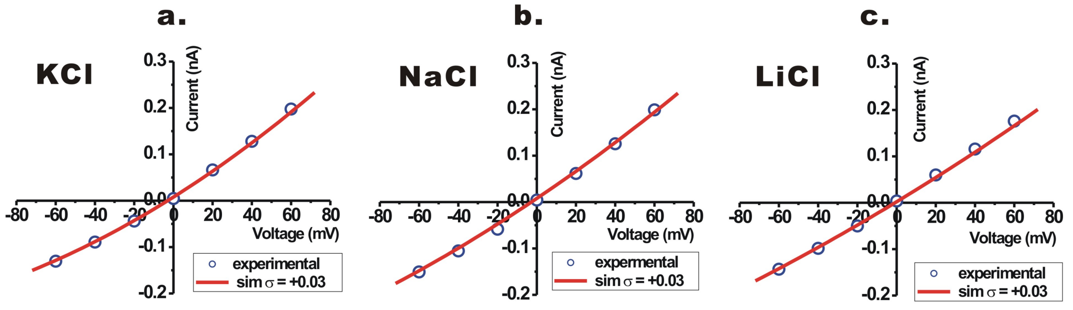

Fig. S5 In the case of anion-selective nanopores, the experimental *I-V* curves are numerically fitted with theoretical results to calculate the surface charge density in the presence of 10 mM KCl (a), NaCl (b), and LiCl (c). The geometry of the model nanopore is identical with that shown in Fig. S4. Experimental results are shown in blue circles. In model calculation, $\sigma = +0.03\ \mathrm{C/m^2}$ (red curves).

References:

1. A.J.Bard and L.R.Faulkner, ***Electrochemical methods Fundamental and Applications***, New York : John Wiley, 2001.
2. J. Cervera, B. Schiedt, R. Neumann, S. Mafe and P. Ramı´rez, ***J. Chem. Phys.***, 2006, 124, 9.
3. Q. Liu, Y. Wang, W. Guo, H. Ji, J. Xue and Q. Ouyang, ***Phys. Rev. E***, 2007, 75, 051201.
4. Y. W. Tang, K.-Y. Chan and I. Szalai, ***J.Phys. Chem. B***, 2004, 108, 18204.
5. X. Wang, J. Xue, L. Wang, W. Guo, W. Zhang, Y. Wang, H. Ji and Q. Ouyang, ***J. Phys. D***, 2007, 40, 7077.
6. M. Ali, B. Yameen, J. Cervera, P. Ramı´rez, R. Neumann, W. Ensinger, W. Knoll, and O. Azzaroni, ***J. Am. Chem. Soc.*** 2010, 132, 8338.
7. Z. Siwy, D. Dobrev, R. Neumann, C. Trautmann and K. Voss, ***Appl. Phys. A***, 2003, 76, 781.