Supplementary Materials

Tuning transport properties of nanofluidic devices with local charge inversion

Yan He[1], Dirk Gillespie[2], Dezső Boda[3], Ivan Vlassiouk[1], Robert S. Eisenberg[2],
Zuzanna S. Siwy[1]
[1]Department of Physics and Astronomy, University of California, Irvine, Irvine, CA
[2]Department of Molecular Biophysics and Physiology,
Rush University Medical Center, Chicago, IL
[3]Department of Physical Chemistry, University of Pannonia, Veszprém, Hungary

1. Preparation of single conical nanopores in polyethyelene terephtahalate films.

Single-pore membranes used in the experiments were prepared by the track-etching technique, described before [1,2]. Briefly, stacks of six 12 μm thick polyethylene terephthalate (PET) (Hostaphan RN 12, Hoechst) films were irradiated under normal incidence with single energetic ions of Au. The Au ions were accelerated to the total kinetic energy of 2.2 GeV (UNILAC, GSI Darmstadt, Germany). For single-ion irradiation, a metal mask with 0.1 mm aperture was placed in front of each stack. A strongly defocused beam was blocked promptly as soon as one ion passed through the foils and was detected by a particle detector placed behind the foils. Chemical etching of the single-ion irradiated foils resulted in single-pore membranes. To obtain a conically-shaped nanopore, an irradiated polymer film was mounted between two chambers of a conductivity cell, and etched from one side in 9 M NaOH. The other side of the membrane was in contact with an acidic stopping solution [1]. 1 V was applied across the membrane and the etching process was monitored by measuring the etching current. At the beginning of the etching process the current was zero. Breakthrough of the pore was observed as a current increase. The etching was stopped at ~50–100 pA. The diameter of the large pore opening, D, was estimated on the basis of the bulk etch rate, which for PET with 9 M NaOH, and at room temperature, is 2.13 nm/min [1]. The diameter of the small opening, d, is related to the resistance R of a conical nanopore filled with electrolyte of specific conductivity, κ, via

$$R = \frac{4L}{\pi \kappa D d} \tag{S1}$$

where L is the length of the pore (thickness of the membrane). In 1 M KCl, and in the voltage range between −100 mV and +100 mV, current-voltage curves of conical nanopores are linear and thus allow for the determination of the values of R and d.
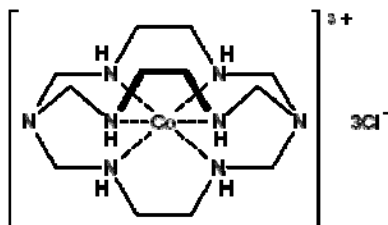
Schematic 1. Chemical structure of cobalt sepulchrate trichloride, http://www.sigmaaldrich.com/

Table S1. Total junction potentials created across the membrane when two chambers of the conductivity cell were filled with different solutions (Fig. 10 of the manuscript). The junction potentials were calculated using the Henderson equation [3,4]. In the calculations, we used bulk values of diffusion coefficients of K^+, Cl^-, and Ca^{2+} [5]. Diffusion coefficient of CoSep was assumed to be four times smaller than the bulk diffusion coefficient of K^+. The data were recorded with reference electrodes filled with 3 M NaCl (MF-2052, BASi).

Salt and its concentration on one side of the membrane	Salt and its concentration on the second side of the membrane	Absolute value of the total junction potential
10 mM CoSepCl$_3$	10 mM KCl	5.57 mV
1.0 M CaCl$_2$	10 mM CaCl$_2$	27.27 mV

Table S2. Total junction potentials (calculated as described in [3,4]) created across the membrane when one chamber was filled with a given concentration of KCl, CaCl$_2$ or CoSep, while the other side of the membrane was in contact with 10^{-6} M (or 10^{-5} M for CoSep) solution of a given salt (Figs. 5-8 of the manuscript). In the calculations, we used bulk values of diffusion coefficients of K^+, Cl^-, and Ca^{2+}. Diffusion coefficient of CoSep was assumed to be four times smaller than the diffusion coefficient of K^+. These data were recorded with reference electrodes filled with 1 M KCl (CH Instruments, CHI111P).

Salt	Concentration on one side of the membrane	Concentration on the second side of the membrane	Absolute value of the total junction potential
KCl	1.0 M	10^{-6} M	6.19 mV
KCl	0.1 M	10^{-6} M	4.58 mV
KCl	0.02 M	10^{-6} M	3.28 mV
CaCl$_2$	1.0 M	10^{-6} M	20.96 mV
CaCl$_2$	0.1 M	10^{-6} M	9.51 mV
CaCl$_2$	0.02 M	10^{-6} M	3.95 mV
CoSepCl$_3$	1 mM	10^{-5} M	2.23 mV
CoSepCl$_3$	0.01 M	10^{-5} M	4.15 mV

2. Poisson-Nernst-Planck modeling of ion currents in asymmetric electrolyte conditions.
In order to underscore our interpretation of ionic selectivity based on experimental data with asymmetric electrolyte conditions, we performed Poisson-Nernst-Planck (PNP) modeling of ion current through a single conical nanopore. The calculations were performed for KCl, for which PNP with ions treated as point charges is sufficient to correctly model ion currents [6,7,8].
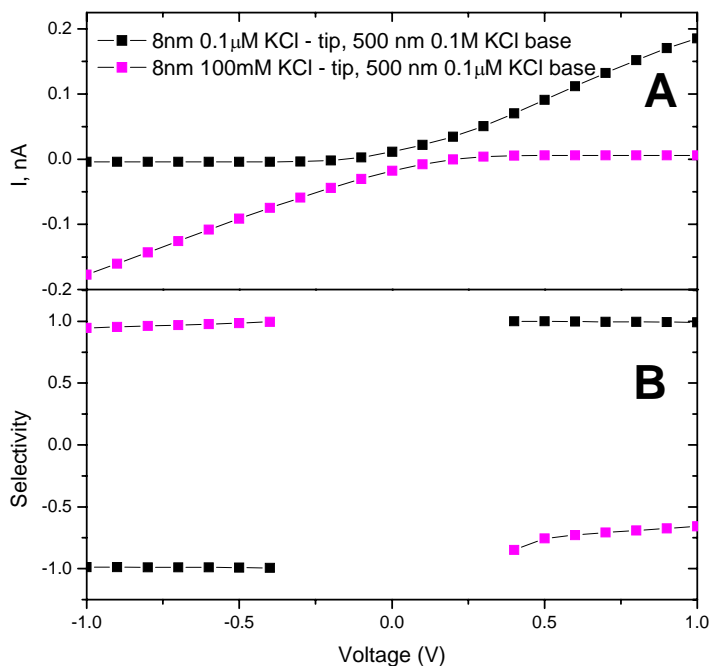

Figure S1. Poisson-Nernst-Planck (PNP) modeling of ion current through a single conical nanopore with opening diameters of 8 nm and 500 nm, respectively. The surface charge density used in the calculations was -0.5 e/nm^2. The pore was in contact with 0.1 µM and 0.1 M KCl, as indicated in the legend. The calculations were done using Comsol Multiphysics 3.4 package. Details of calculations can be found elsewhere [6].
A. Calculated current-voltage curves have the same rectification direction as the experimental data (compare the calculated curves with experimental data in Figure 6 of the main manuscript).
B. Nanopore ionic selectivity vs. voltage. Ionic selectivity is defined as in previous publications [6,7] $S = \dfrac{I_+ - I_-}{I_+ + I_-}$, where I_+ is the current carried by potassium ions, and I_- is the current carried by chloride ions. For $S = 1$ a nanopore is perfectly K$^+$ selective and $S = -1$ indicates a perfectly Cl$^-$ selective pore. This figure is consistent with the pore selectivity interpretation presented in the main text (see for example Figure 6). The selectivity values are shown for voltages higher than 0.3 V. The numerically predicted values of ion currents between -0.3 and 0 V for the black curve, and between 0 and $+0.3$ V for the magenta curve are too low to allow for a reliable estimation of ionic selectivity.
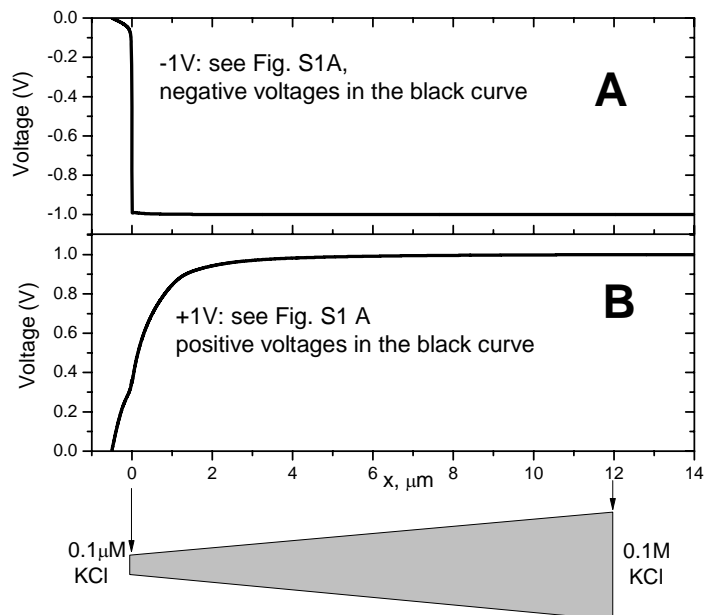
Figure S2. Example of calculated voltage profiles along a nanopore axis *x*. The calculations were performed for a conical nanopore with opening diameters of 8 nm and 500 nm, respectively, and the surface charge of –0.5 e/nm². The pore was in contact with 0.1 μM KCl at the tip side, and with 0.1 M KCl at the base side.

A. Voltage profile for –1V applied across the membrane. At the voltage polarity for which the currents are lower (e.g., negative voltages for the black curve in Fig. S1 A, and negative voltages for the black curve in Fig. 6A), the depleted and uneven concentrations of K^+ and Cl^- at the pore entrance in the left reservoir (depletion zone) and access resistance result in a sharp voltage drop at this nanopore entrance. This effect is similar to the concentration polarization effects discussed earlier for symmetric electrolyte conditions [7]. Similar voltage profiles were also found for asymmetric electrolyte concentration conditions for a slit nanochannel [8].

B. Voltage profile for +1V applied across the membrane. At the voltage polarity for which the currents are higher (e.g., positive voltages for the black curve in Fig. S1 A), the voltage drop occurs primarily across the whole pore.

Note that an inverse situation (i.e., when low KCl concentration is placed at the base of the nanopore) results in an inverse behavior of the voltage drop (not shown). That is, the sharp voltage drop is observed for positive voltages at the base entrance, while the voltage drop across the whole pore length occurs at negative voltages.

References

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