

Ion Current Rectification and Rectification Inversion in Conical Nanopores: A Perm-selective View

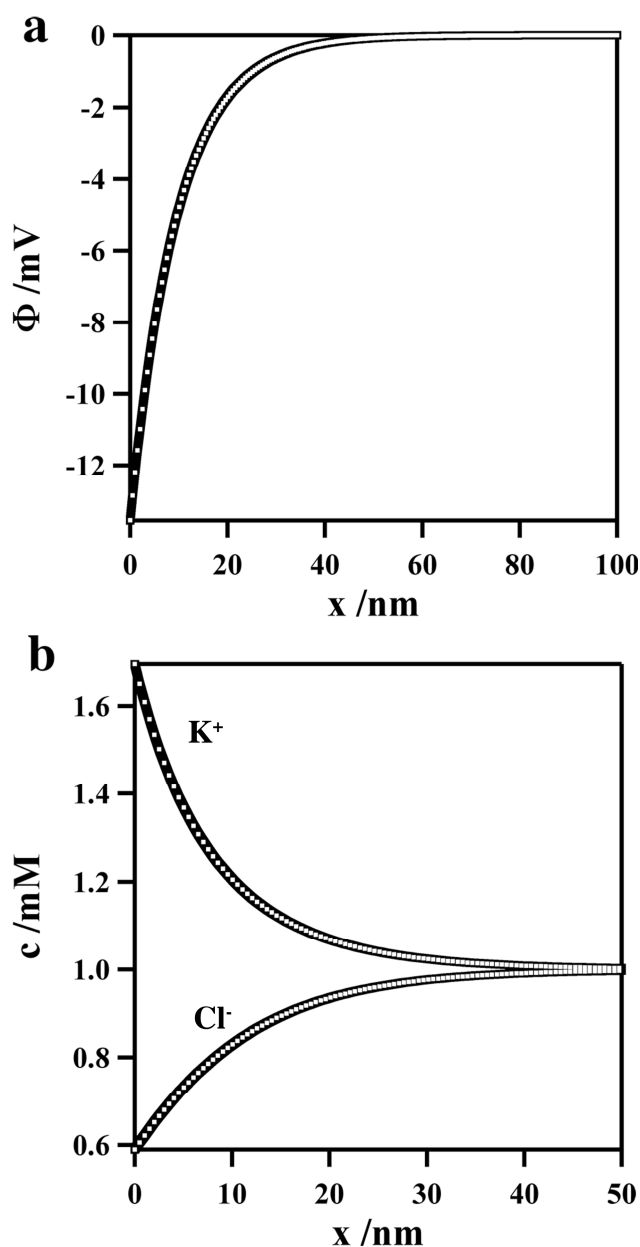
Electronic Supplementary Information

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10 **Fig.S-1** Comparison between theoretical values (solid lines) and experimental results (dots) for a) electric potential and b) ion concentration distributions near the charged wall. Theoretical curves are calculated within the frameworks of Gouy – Chapman theory.

Validation procedure details

15 The calibration procedure was carried out in a 2D geometry ($0.2 \mu\text{m} \times 0.5 \mu\text{m}$) perpendicular to a charged plane (surface charge density $\sigma = -1 \text{ mC} \cdot \text{m}^2$). The values of electric potential for 1 mM, 10 mM and 100 mM KCl solutions are -13.55 mV, -4.33 mV and -1.37 mV respectively, while
20 theoretical values, predicted by Gouy – Chapman theory are -13.55 mV, -4.33 mV and -1.37 mV. The distributions of potential and ion concentrations near the charged wall for 1 mM KCl are given on Fig. S-1. Concentrations of K^+ and Cl^- near the wall were calculated (1.695 mM and 0.590 mM
25 respectively) and these values are in good agreement with the Gouy – Chapman theory. Theoretical values calculated within the framework of the Gouy – Chapman theory are 1.695 mM and 0.590 mM, very close as the model share the same physical assumptions, *i.e.* point charges in a dielectric
30 continuum considering only the electrostatic interactions, but proving the validity of the present numerical approach.

The results were also compared to the FEM simulations made by White *et al.* The ion current rectification in the pore of 10 μm length and half-cone angle of 12° , filled with 1 mM KCl
35 solution was simulated. In this case the rectification ratio $r(E)$ is 1.39, while White *et al.*²⁴ report 1.38. The tiny difference in the obtained result is probably caused by slightly different constants taken.

Maps of electroneutrality for electrolyte solutions of different concentrations

40 As shown on Fig. S-2, electroneutrality condition is broken only close to the charged walls and also in a very small region near the pore opening, where the Gouy-Chapman layer interactions are the strongest. Of course, the size of this zone
45 depends on the electrolyte concentration and increases at low ionic strength. In diluted electrolytes the size of a zone where the electroneutrality is not sustained and where cations are concentrated is enlarged.

Conductivity distributions within the pore at very low (*i.e.* <0.03 mM) electrolyte concentrations.

50 The plot of relative ionic conductivity along central axis of the pore is shown on Fig. S-3. The conductivity values are strongly affected not only at the tip, but even deeper inside the pore. Most likely, this would cause the increase of

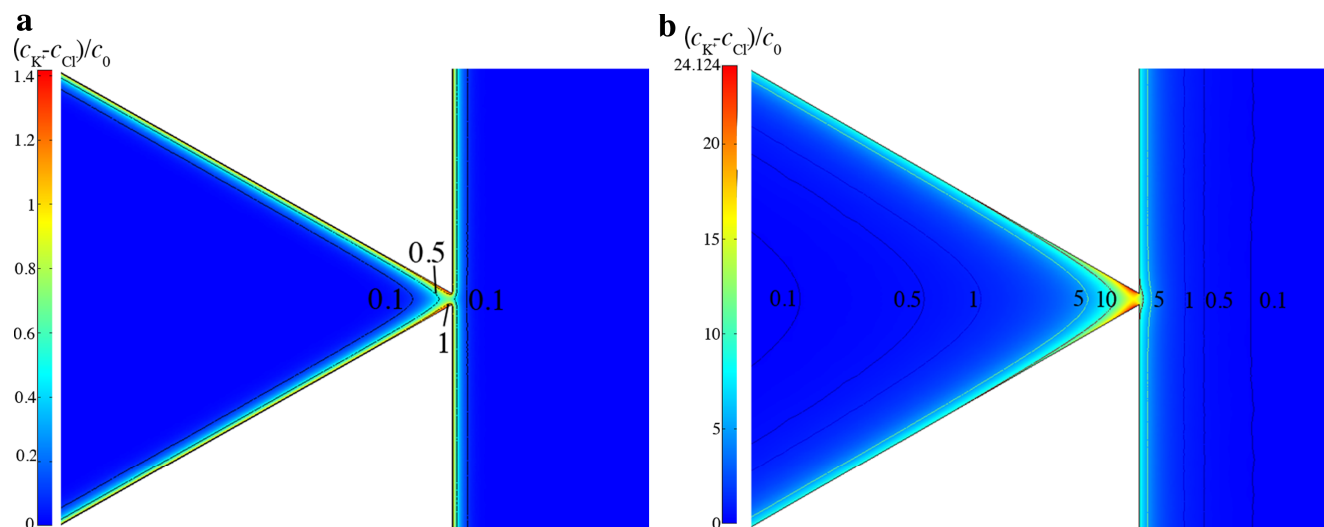


Fig.S-2 Maps of $(c_{K^+}-c_{Cl^-})/c_0$ illustrating electroneutrality condition near the tip of 30.87° charged pore filled with a) 1 mM and b) 0.04 mM KCl solution. The graph illustrates the tip region in between $z=-600$ nm and $z=200$ nm. The numbers denote the isovalues at surfaces, specified as solid lines on the graph.

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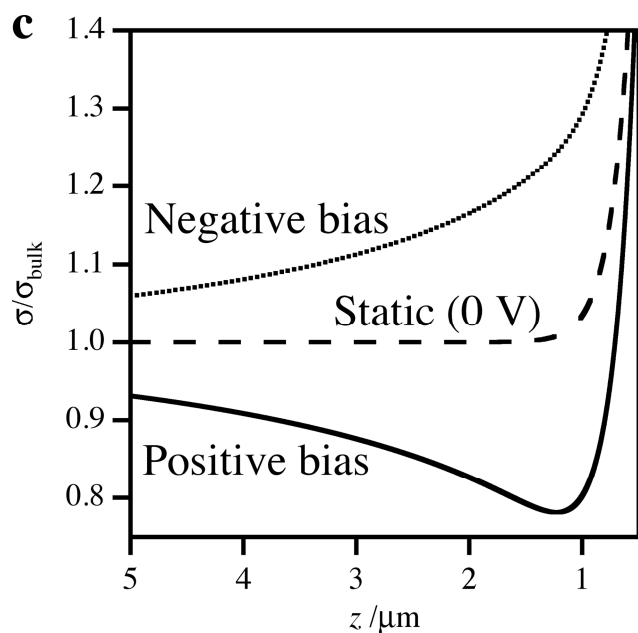


Fig.S-3 Relative ionic conductivity distributions in 0.03 mM KCl solution along z axis of the charged nanopore in case when positive (solid line) and negative (dotted line) bias applied. Dashed line denote the conductivity in the static case (*i.e.* $\Delta\phi=0$ V).

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rectification factor in very diluted electrolytes.

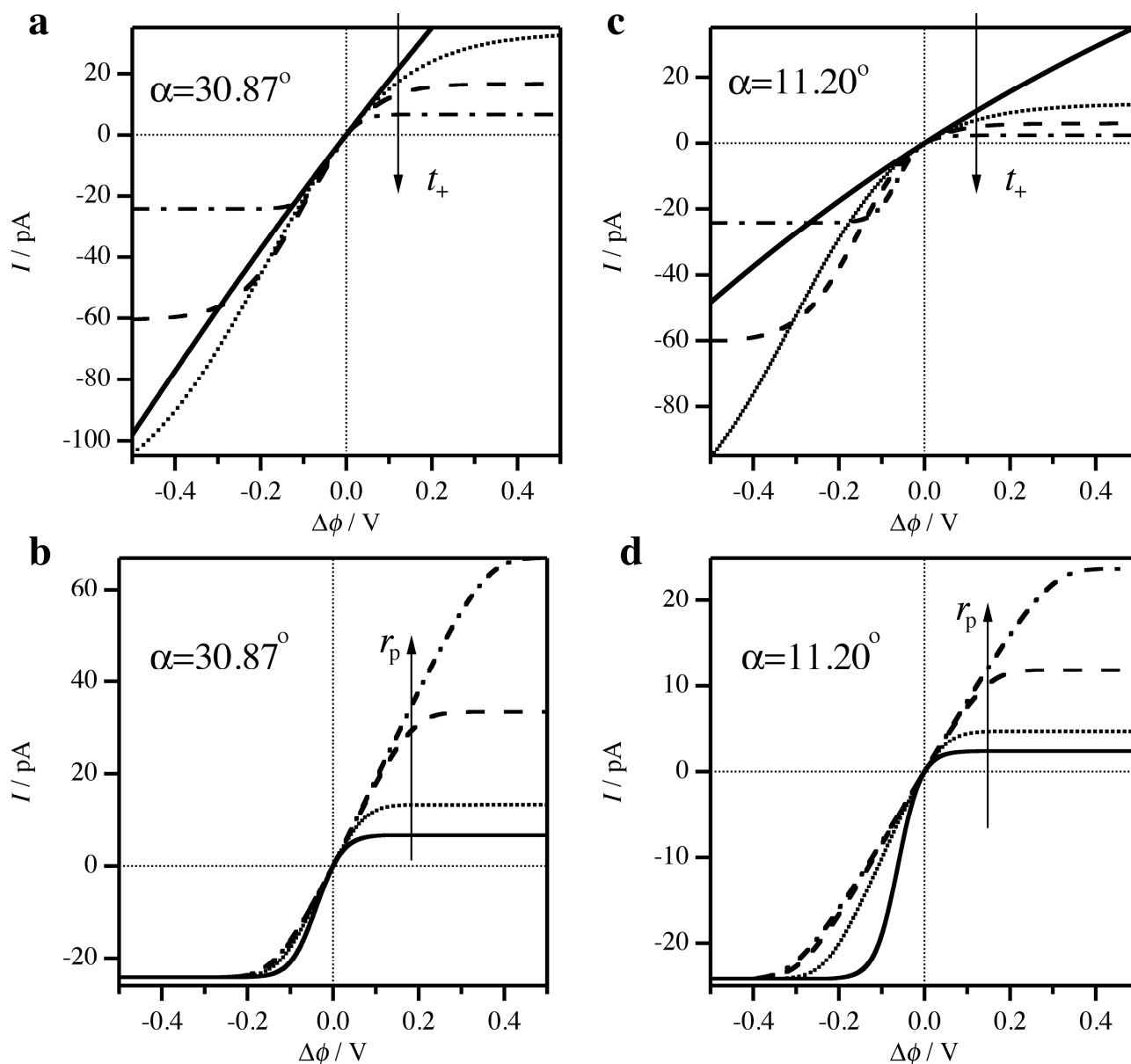


Fig.S-4 Current-voltage characteristics of the pores of different geometry according to the model of a perm-selective pore (eq. 24). The influence of pore perm-selectivity (t_{\pm} equal to 0.51, 0.6, 0.7 and 0.9 for solid, dotted, dashed and dash-dotted lines, respectively) and size of a perm-selective plug (r_p is 1, 2, 5 and 10 $r_{\text{tip}} \cdot \sin \alpha$ for solid, dotted, dashed and dash-dotted lines, respectively) is shown for the pores with half-cone angle value of 30.87° for a), b) and 11.20° for c), d).

Current-voltage characteristics of uncharged pores with a perm-selective region at the tip

Fig. S-4 illustrates the current-voltage curves for the pores possessing perm-selective properties at the tip. The influence of the perm-selectivity of this region, the size of a perm-selective plug and the half-cone angle is demonstrated. The increase of a perm-selectivity leads to the increase of rectification ratio, however, the change of the perm-selective plug leads to the linear current-voltage characteristic in case of the pores with small half-cone angle and to the inversion of rectification for the pores having large semi-angles.