CHEMPHYSCHEM

Supporting Information

The Influence of Divalent Anions on the Rectification Properties of Nanofluidic Diodes: Insights from Experiments and Theoretical Simulations

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Supporting information

Theory

Theoretical modeling with the continuous model based on the Poisson-Nernst-Planck equations (PNP)[1] was used to obtain important information about the geometry and surface charge of the nanochannels prior and after the modification steps. We model a BL nanochannel adjusting the base diameter with experimental data (FE-SEM).

The basic equations that describe the transport through the channels are, the Nernst-Planck equations,

$$\vec{J}_i = -D_i\left(\nabla c_i + z_i c_i \nabla \phi\right) \tag{2}$$

The Poisson Equation,

$$\nabla^2 \phi = -\frac{F^2}{\varepsilon RT}\sum_i z_i c_i \tag{3}$$

And the continuity equation,

$$\nabla \cdot \vec{J} = 0 \tag{4}$$

Where $\vec{J}_i$,Di and zi are, the ionic flux, the diffusion coefficient, the ion charge and ε is the solution permittivity inside the channel.

The surface charge density of the PET surface is between 1.5 and 1.7 |el/ nm2. With these parameters and the experimental curves we obtained the tip diameter of 20 nm.

Taking into account that the pore is very large, we can make the following assumptions[2]

1) The flow is only in the axial direction, so we can write equation (1) as

$$J_i = -D_i\left(\frac{dc_i}{dx} + z_i c_i \frac{d\phi}{dx}\right) \tag{5}$$

And the continuity equation is

$$\frac{d}{dx}\left(\pi a^2 J_i\right) = 0 \tag{6}$$

Where a is the nanopore radius and is determined by

$$a(x) = \frac{a_R - a_L \exp\left[-(d/h)^n\right] - (a_R - a_L)\exp\left[-(x/d)^n (d/h)^n\right]}{1 - \exp\left[-(d/h)^n\right]} \quad (6)$$

n>0

n and d/h are geometrical parameters that determine the pore shape

If the naopores are very large, we can use the electroneutrality condition instead the Poisson equation.

$$\sum_i z_i c_i + X_F = 0 \quad (7)$$

XF is the concentration of the fixed charges and is

$$X_F = \frac{2\sigma}{aF} \quad (8)$$

s is the superficial density charge

We assume Donnan equilibrium in the borders

$$c_i(0) = c_L \exp(-z_i \Delta\phi_L) \quad (9a)$$

$$c_i(d) = c_R \exp(z_i \Delta\phi_R) \quad (9b)$$

where

$$\Delta\phi_L = \phi(0) - \phi_L \quad (10a)$$

$$\Delta\phi_R = \phi_R - \phi(d) \quad (10b)$$

Solving these equations give us the average potential and concentration profiles

The current in any section of the nanopore is

$$I = \sum_i z_i F \pi a^2 J_i \qquad (12)$$

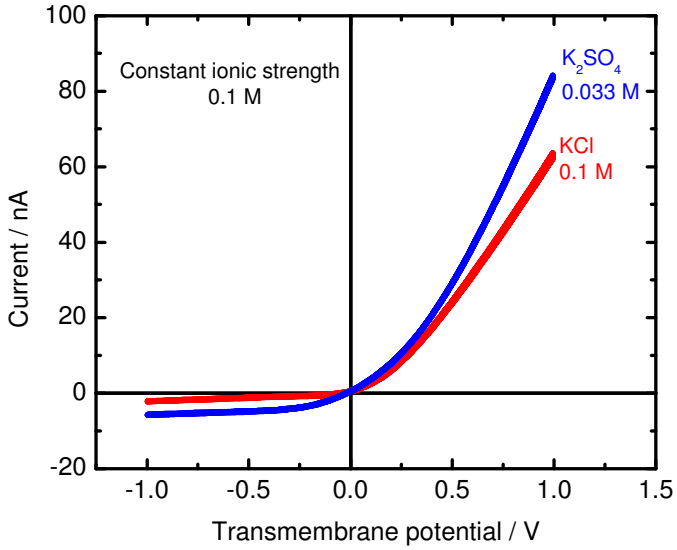

Figure S1. I-V curves at constant ionic strength of 0.1 M, of K_2SO_4 (blue) and KCl (red).

References

[1] J. Cervera, B. Schiedt, R. Neumann, S. Mafé, P. Ramírez, Ionic conduction, rectification, and selectivity in single conical nanopores, *J. Chem. Phys.*, **2006**, *124*, art. no. 104706

[2] P. Ramírez, P.Y. Apel, J. Cervera, S. Mafé, S. Pore structure and function of synthetic nanopores with fixed charges: Tip shape and rectification properties, *Nanotechnology*, **2008**, *19*, art. no. 315707.