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Electronic Supporting Information

Host-guest supramolecular chemistry in solid-state nanopores: potassium-driven modulation of ionic transport in nanofluidic diodes

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Theoretical model

The formalism based on the Poisson-Nernst-Planck equations[1] was used to model a bullet-like nanopore with a length d, a base a_b and a tip a_L. The Nernst-Planck equations are the basic equations that describe the transport through the nanopores,

$$\vec{J}_i = -D_i\left(\nabla c_i + z_i c_i \nabla\phi\right) \quad (1)$$

Along with the Poisson equation

$$\nabla^2\phi = -\frac{F^2}{\varepsilon RT}\sum_i z_i c_i \quad (2)$$

And the continuity equation

$$\nabla\cdot\vec{J} = 0 \quad (3)$$

Where $\vec{J}_i$, D_i, z_i, ε are, the ionic flux, the diffusion coefficient, the charge of the ion and the permittivity of the solution inside the nanochannel, respectively.

Assuming that the pores are long and narrow some approximations can be introduced. Firstly, we can assume that the flux has only an axial component and therefore the equation (1) and (3) can be rewritten as,

$$J_i = -D_i\left(\frac{dc_i}{dx} + z_i c_i \frac{d\phi}{dx}\right) \quad (4)$$

and

$$\frac{d}{dx}\left(\pi a^2 J_i\right) = 0 \quad (5)$$

Where a is the radius of the nanopore that is determined by the equation

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

$n>0$

Where n and d/h are geometrical parameters that controlled the shape of the nanopore.

Secondly, we can use the electroneutrality condition

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

Where X_F is the volumetric concentration of fixed charges that can be obtained from

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

Here, σ is the surface charge density. We assumed that a Donnan equilibrium sets in the entrances of the pore, therefore the ionic concentration at the base and tip of the nanopores are given by

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

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

Where $\Delta\phi_L$ and $\Delta\phi_R$ are the Donnan potentials given by

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

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

Combining equations (9) and (10), along with the electroneutrality condition (7), the ionic concentration at the base and tip of the nanopores result

$$c_i(0) = \frac{1}{2}\left(-z_i X_F(0) + \sqrt{[X_F(0)]^2 + 4c_L^2}\right) \quad (11a)$$

$$c_i(d) = \frac{1}{2}\left(-z_i X_F(d) + \sqrt{[X_F(d)]^2 + 4c_R^2}\right) \quad (11b)$$

Finally, the electric potential and ionic concentration profiles can be obtained by the numerical resolution of equations (4), (5) and (7) by the method of finite differences, along with the boundary conditions (9), (10) and (11).

The current that flows at any section of the nanopore can be obtained from

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

The geometrical parameters used to solve the PNP equations are shown in table 1, whilst the diffusion coefficients used for each ion are shown in table 2. For d, a_B and σ we have used experimental values; d/h, n and a_L were adjusted from the experimental curves.

Parameters	PNP values
a_L / nm	30
a_B / nm	410
d / µm	12
σ / |e|.nm^{-2}	1.5
d/h	8
n	1.2

Table 1. Geometrical parameters used for the theoretical simulation of the I-V curves

Ion	Coef / 10^{-5} cm.s^{-1}
Li^+	1.029
Na^+	1.334
K^+	1.957
Rb^+	2.072
Cs^+	2.056
Cl^-	2.03

Table 2. Diffusion coefficients used for each ion for the theoretical simulation of the I-V curves

Materials and methods

Poly(ethyleneterephthalate) (PET) foils (Hostaphan RN 12, Hoechst) of 12 µm were irradiated at GSI Helmholtzzentrum für Schwerionenforschung GmbH (Darmstadt, Germany) with swift heavy ions (Au+25), having an energy of ~ 2.2 GeV. For the surfactant assisted etching, the anionic surfactant Dowfax 2A1 from Dow Chemical was used. LiCl, NaCl, KCl, RbCl and CsCl were purchased from Sigma-Aldrich and used as received.

Chemical etching: PET foils irradiated with a single heavy ion were etched using a surfactant assisted technique that conferred them a highly tapered 'bullet-like' shape.[2] The etching process was conducted in a 2-compartment electrochemical cell as explained elsewhere.[3] The etching time was 6.5 minutes at a temperature of 60 °C.

Conductivity measurements: I-V characteristics were measured with a Gamry Reference 600 potentiostat, from Gamry Instruments, using a four electrode set-up. The potential was swept between 1 V and -1 V at a scan rate of 0.1 V/s and a step size of 0.01 V. The counter-electrode was always placed at the large opening base of the nanopore.

References

[1] Ramírez, P.; Apel, P. Yu; Cervera, J.; Mafé, S.; *Nanotechnology* **2008,** 19, 315707.
[2] Apel, P. Yu.; Blonskaya, I.V.; Dmitriev, S.N.; Orelovitch, O. L.;Presz, A.; Sartowska, B. A.; *Nanotechnology* **2007**,18, 305302.
[3] Pérez-Mitta, G.; Tuninetti, J.S.; Knoll, W.; Trautmann C.; Toimil-Molares, M.E.; and Azzaroni, O.; *Journal of the American chemical Society* **2015**, 137, 6011−6017.