Electronic Supplementary Information

A general strategy to simulate osmotic energy conversion in multi-pore nanofluidic systems

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1. Characterization of the nanopores.

The geometry of the track-etched nanopores was characterized by scanning electron microscope (SEM) observation on the surface and cross section of the PET films (fig. S1a and S1b). The mean pore diameter increases linearly with the etching time (fig. S1c). The mean diameter of the cylindrical nanopores used in following tests was about 22 nm. A scheme of the electrochemical cell used for the measurement of diffusion current and membrane potential is shown in fig. S2.[1]

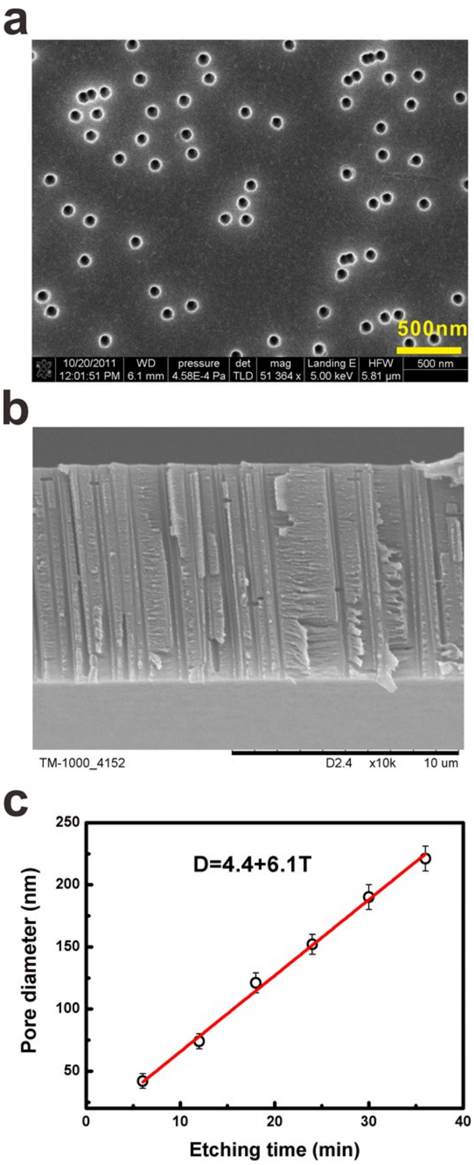

Fig. S1 Characterization of the nanopores. (a, b) SEM observations on the surface (a) and cross-section (b) of the track-etched PET films. The etching time was 12 minutes. (c) The mean pore size with respect to the etching time.

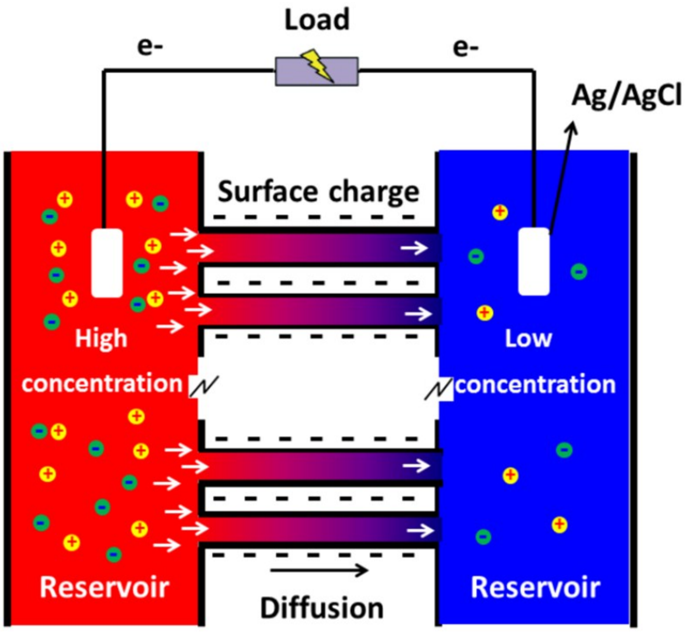

Fig. S2 Schematic illustration of the electrochemical cell. The membrane samples were mounted in between the two halves of the electrolyte reservoirs. Each half-cells were filled with potassium chloride solutions. Ag/AgCl electrodes were used to apply the transmembrane potential and measure the resulting current.

2. Details of simulation method.

2.1. Governing equations

Ion transport through the nanopore is governed by the Poisson and Nernst-Planck (PNP) equations in equilibrium state.[2-4] They were expressed as:

$$\vec{j}_i = -D_i\,(\nabla c_i + \frac{z_i e c_i}{k_B T}\nabla\Phi) \tag{S1}$$

$$\nabla^2\Phi = -\frac{e}{\varepsilon}(c_+ - c_-) \tag{S2}$$

Where i was the ion specie, $\vec{j}_i$ was the local ionic flux, D_i was the diffusion coefficient, c_i was the local ion concentration, z_i was the valence, and Φ was the local electrical potential. k_B, T, e, ε represented for the Boltzmann constant, the temperature, the electron charge, and the dielectric constant of the electrolyte solution, respectively.

2.2. Computational domain and boundary conditions

The continuity equation of the incompressible steady-state solution should satisfy:[5]

$$\nabla\cdot\vec{j}_i = 0 \tag{S3}$$

The boundary condition for potential Φ was given by the Gauss law:

$$-\vec{n}\cdot\nabla\Phi = \frac{\sigma_s}{\varepsilon_0\,\varepsilon_r} \tag{S4}$$

The local ion flux $\vec{j}_i$ should have zero normal components at boundaries:

$$\vec{n}\cdot\vec{j}_i = 0 \tag{S5}$$

The total diffusion current was calculated by integrating the ionic flux density in the cross section of the nanopore:

$$I_i = 2\pi e\int r\, j_i\, dr\text{ , } i\text{=+/-.} \tag{S6}$$

Where r was the radius of the nanopore.

3. Model Parameters.

Two reservoirs were connected by an array of cylindrical nanopores containing the central pore and its nearest neighbors (Figs. 2-4). The parameters for the reservoir size were a_0 = 5 μm, b = 2 μm, and a_1 = 0.3 μm (3×10^8 pores/cm^2). The channel length (L) was 1 μm, the pore diameter (D) was 10 nm, and the surface charged density (σ) was -0.06 C/m^2. The concentration difference applied in the model was 100|1 mM. By changing the inter-pore distance, one can simulate the multi-porous system with different pore density (Table S1).

Table S1. The relationship between the pore density and the inter-pore distance in multi-porous system.

a_1 (nm)	Pores density (pores/cm^2)
5000	1×10^6
1600	1×10^7
500	1×10^8
225	5×10^8
160	1×10^9

4. Effective concentration difference.

The decline in diffusion current through the central pore results from the degradation in the effective concentration difference (ECD). Due to ion concentration polarization,[6] the local ion concentration difference across the nanopore is lower than that in the bulk solution. We calculated the ECD near the central pore in the 2-D planar model under different nearest-neighbor approximation. With increased orders of nearest-neighbor approximation, the ECD near the central pore gradually decreases (fig. S3), resulting in lower diffusion current shown in Fig. 2b.

This trend

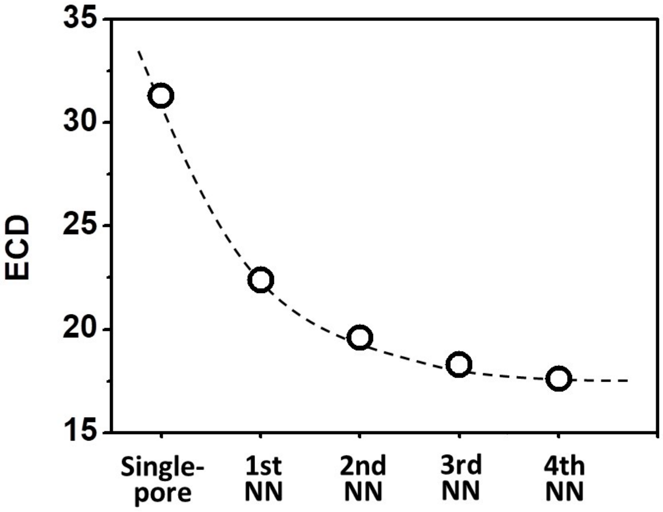

Fig. S3 Effective ion concentration difference across the central pore gradually decreases with the increasing orders of the nearest-neighbor approximation.

5. Local ion concentration near pore orifices.

Under the 4th nearest-neighbor approximation, the ECD and the local ion concentrations near the pore orifices were calculated (fig. S4). Similar with that found in the diffusion current (Fig. 3c), the ECD across the inner pores are less influenced by the boundary conditions, but are more sensitive to the presence of neighboring nanopores (fig. S4a). From the calculated local ion concentrations near the pore orifices, one can see that the ion concentration polarization is more severe across the inner pores due to the influence of adjacent pores (fig. S4b and S4c).

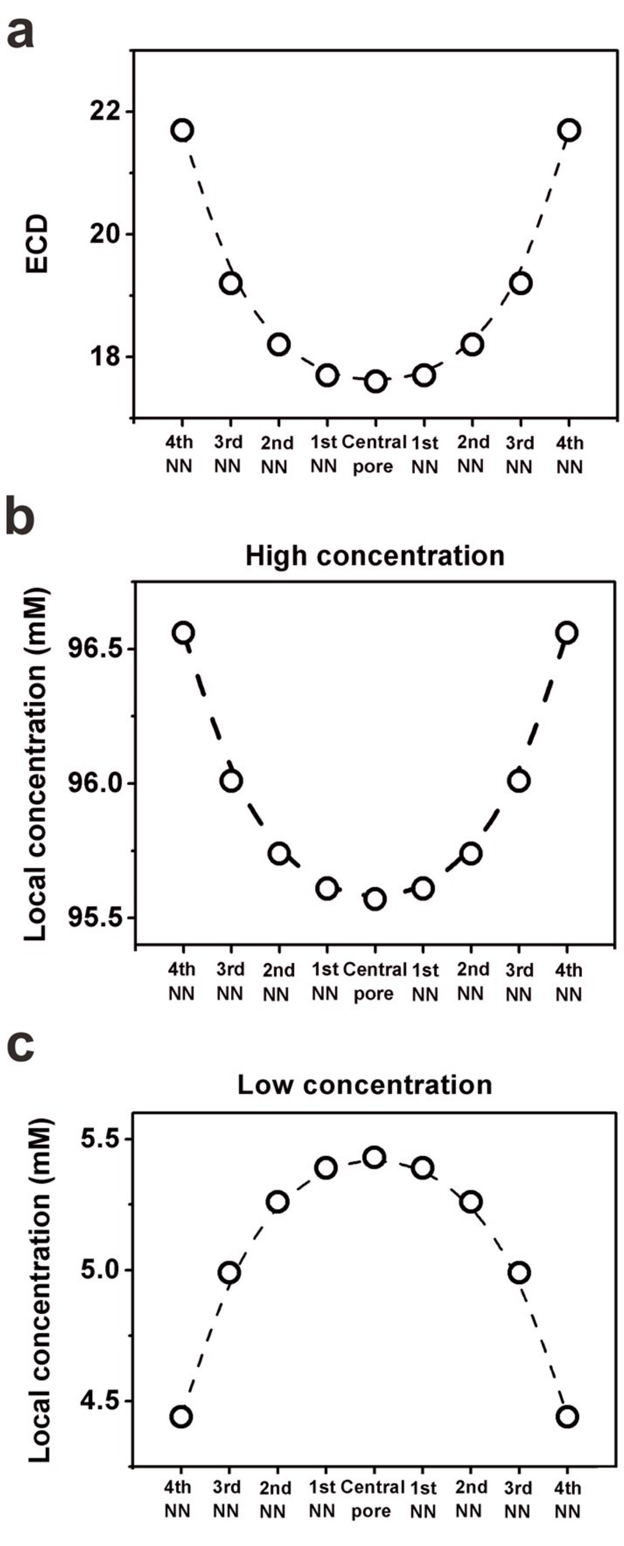

Fig. S4 Effective ion concentration difference (a) and local ion concentration at high- and low-concentration side (b and c). The simulations were conducted under the 4th nearest-neighbor approximation. The bulk concentration difference is 100|1 mM.

6. References

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