SUPPORTING INFORMATION

Electroosmotic Flow Rectification in Pyramidal-Pore Mica Membranes

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Materials. Muscovite mica ($\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$) membranes, $\sim 10.4\ \mu\text{m}$ thick and 3 cm in diameter, were obtained from Spruce Pine Co. (Spruce Pine, NC). The linear accelerator at GSI (Darmstadt, Germany) was used to ion track the mica; Pb^{2+} ions of $\sim 8.6\ \text{MeV}$ kinetic energy were used. Samples with 10^5 tracks per cm^2 , were prepared. Hydrofluoric acid ($\sim 50\ \%$) was obtained from Acros Organics USA (Morris Plains, NJ). Phenol was obtained from Sigma-Aldrich (St. Louis, MO). All other chemicals were reagent grade and used as received. Purified water, obtained by passing house-distilled water through a Barnstead, E-pure water purification system, was used to prepare all solutions.

Asymmetric nanopore fabrication. An asymmetric chemical etching method was developed to fabricate pyramidally shaped nanopores in the ion-tracked muscovite mica membranes. A $\sim 1\ \text{cm}$ diameter hole was cut into a $\sim 4 \times 4\ \text{cm}$ piece of parafilm (Alcan Inc. Neenah, WI), and the mica membrane was sandwiched between two such films. The sandwiched membrane was placed between the two halves of the etching cell¹ described previously.

To check that there were no leaks in the parafilm seals, the half cells were filled with 1 M KCl that was 100 mM in phosphate buffer, $\text{pH} = 7.0$. A Ag/AgCl reference electrode was placed into each half-cell solution, and a Keithley 6487 picoammeter/voltage source (Keithley Instruments, Inc., Cleveland, OH) was used to apply 1 V across the membrane and measure the

resulting trans-membrane current. If there were no leaks a negligible current (<10 pA) was obtained. This is because the ionic conductivity of the unetched damage track is negligibly small.

After the leak check, the half-cells were emptied, rinsed, and ~ 3 mL of 10 M NaOH solution was pipetted into one of the cells. The membrane was exposed to this solution for 5 minutes, a Pt wire electrode was inserted into each half cell, and ~ 3 mL of 10 M HF was then added to the other half cell. The Keithley was used to apply a trans-membrane voltage of 10 V (with the anode in the HF solution) and measure the resulting ionic current through the membrane during etching.

After 10 minutes the etch was terminated by placing 1 M NaOH on both sides of the membrane and applying 10 V for 5 minutes, to ensure complete neutralization of the HF in the pores. The membrane was then rinsed with water, and water was placed in both half cells for 30 minutes to wash the NaOH from the pores. We call this procedure a 10-minute etch cycle. Asymmetric shape pores were obtained with the large-diameter (base) opening facing the HF solution and the small-diameter (tip) opening facing the NaOH solution.

Nanopore openings in mica membranes etched for different time (cycles) was studied using FESEM. Figure S1 demonstrate that the length of major axis l_{maj} of both tip and base openings increase with longer etch time.

Symmetric nanopore fabrication. A symmetric chemical etching method was used to prepare straight shape nanopores in the ion-tracked muscovite mica membranes. A 3 mL 5 M HF was placed on both sides of the membrane to etch mica from both directions at the same time.

After 2.5 minutes, the etch was terminated in the same way as the etching of asymmetric nanopores. The nanopores etched under this condition have almost equal size openings on both sides of the membrane.²

Chemical vapor deposition of carbon in nanopores. The replicas of nanopores were composed of graphitic carbon, deposited within the pores by a CVD method.² The etched mica membrane was placed vertically into a quartz tube (diameter = 4.5 cm, length = 48 cm) with the nanopore base openings facing the gas flow. The quartz tube was then inserted into a high-temperature tube furnace (Thermolyne 21100, Aldrich) and heated to 670 °C under argon flow. When the temperature stabilized, the argon gas was replaced with a 30% ethylene/helium mixture at a flow rate of 20.0 sccm (standard cubic cm per min). After 5.5 hours, the flow was changed back to argon, the furnace heater was turned off, and the tube was allowed to cool to room temperature. The asymmetrically shaped carbon replicas deposited in the pores were then exposed by the dissolution of the mica template. This was accomplished by first using a methanol-wetted cotton swab to remove the carbon surface film covering the tip side of the mica membrane. The base side was then attached to a piece of double-side copper tape, which was attached to the bottom of a small (3 cm) plastic Petri dish.

Several drops of 50 % HF solution were pipetted onto the center portion of the tip-side surface. The Petri dish was then covered with parafilm and allowed to sit for 8 hours to dissolve the portion of the mica that was covered with the HF solution. The parafilm was then removed and the HF solution was allowed to evaporate to dryness. Several drops of deionized water were then applied to the same spot on the surface, and this was allowed to evaporate. The sample

residue was then mounted on a SEM stem and sputtered with Au/Pd by using a cold sputter instrument (Desk II, Denton Vacuum).

Current voltage curve measurements. To measure the conductance of the system and determine the ion current rectification ratio, current voltage curves of pyramidal nanopores and straight nanopores mica membrane were measured. Briefly, the mica membranes containing nanopores were mounted between the two half cells, and an electrolyte solution of 10 mM phosphate buffer at pH 7.0 was placed on either side of the membrane. A Ag/AgCl electrode was placed into each half-cell solution, and a current-voltage curve was obtained by scanning the potential from -10.0 V to +10.0 V at a scan rate of 10 V min^{-1} .

Phenol transport measurements

The mica membranes containing asymmetric or symmetric nanopores (pore density $\sim 10^5$ per cm^2) at different size were used for the phenol transport experiment. The mica membrane was mounted between the two half cells and a 0.785 cm^2 portion of the mica membrane was exposed to the electrolyte solution.

The rate of EOF was investigated by measuring the flux of a probe molecule (phenol) across the membrane and into the permeate half-cell. The feed half-cell contained $\sim 3 \text{ mL}$ of a solution that was 10 mM in phenol and 10 mM in phosphate buffer, at $\text{pH} = 7.0$. The permeate half-cell initially contained only the buffer. A Pt wire electrode was placed into each half cell. The Pt wire in the feed solution was the working electrode (anode) and the Pt wire in the permeate solution was used as reference and counter electrode (cathode).

A Solartron SI 1287 electrochemical interface (Farnborough, UK) was used to apply a constant current of 100 μ A flowing through the multipore mica membrane. After every 20 minutes, the applied current was terminated and both the permeate solution and feed solution were pipetted out of the half cells. An Agilent 8453 UV-visible spectrometry system (Waldbronn, Germany) was used to measure the UV absorbance of phenol in the permeate solution. The concentration of phenol in permeate solution was calculated from the calibration curve measured at wavelength 270 nm. We call this procedure a 20-minute transport cycle.

After the UV-visible spectrum measurement, the permeate solution was placed back into the original half cell for the next 20-minute transport cycle. To avoid the phenol oxidized species affecting on transport and UV-visible spectrum, a fresh feed solution with the same concentration of phenol was placed into the cell on the feed side. This 20-minute transport cycle was repeated for 6 times and the total time we applied current was 120 minutes. The UV-visible spectrum of permeate solution was measured after each 20-minute transport cycle.

Then the permeate and the feed solutions were switched to measure the phenol transport from both sides of the nanopore membrane.

The diffusion of phenol across the asymmetric nanopore membrane without applying voltage was also measured at the same 20-minute time interval. But for the straight nanopores membrane, the diffusion flux was too small, and the concentration of phenol could not be measured accurately after the 20-minute transport cycle. Therefore, a 2-hour transport cycle was performed for the symmetric nanopores. The cycle was repeated three times, giving the total transport time of 6 hours.

The diffusion coefficient of phenol ($D = 8.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$)³ was used to calculate v_{eof} .

Figure S1. Length of major axis (l_{maj}) for base (■) and tip (●) openings of pyramidal nanopores in mica membrane at different etch time.

Experimentally measured EOF and diffusive fluxes

Table S1. Rate of phenol transport in the presence or the applied current (N_i) and rate of diffusive transport (N_{diff}) for the membranes studied here.

Tip l_{maj} (nm)	Base l_{maj} (nm)	Rate of transport (nmol/min)			Enhancement Factor, E	
		N_i		N_{diff}		
		Base-to-Tip	Tip-to-Base		Base-to-Tip	Tip-to-Base
17	122	7.69	0.76	0.18	43	4.2
35	244	10.12	2.13	0.52	20	4.1
52	366	12.46	7.56	1.98	6.30	3.82
70	488	12.04	8.69	3.123	3.86	2.78
11	11	2.13	2.12	0.0152	140	139

See Equation 2 of the correspondence.

v_{eof} increase with decreasing pore size.

The electroosmotic velocity, v_{eof} , is given by the Helmholtz-Smoluchowski equation, which can be found in Probstein's classic text (our reference 1)

$$v_{eof} = -\varepsilon\zeta E(x)/\eta \quad (1)$$

where ε and η are the permittivity and viscosity of the solution, respectively, ζ is the zeta potential of the pore wall and $E(x)$ is the electric field strength in the pore. What we see is that v_{eof} increases linearly with electric field strength.

This explains why v_{eof} is larger for smaller diameter pores. This is because a smaller pore has a higher resistance than a larger pore. And since we are doing our experiments at constant current, this means that the electric field strength will be larger in the smaller pore. As a result, v_{eof} is larger for the smaller pore. This can be shown mathematically as follows.

The voltage drop across the pore, ΔE , is related to the pore resistance, R_p , and the applied current, I_{app} , via Ohm's law

$$\Delta E = I_{app} R_p \quad (2)$$

The field strength, $E(x)$, is just this ΔE divided by a characteristic length scale for the pore, l_p . So Equation 2 can be re-written as

$$\Delta E/l_p = I_{app} R_p / l_p \quad (3)$$

Substituting Equation 3 into Equation 1 gives

$$v_{eof} = -\varepsilon\zeta I_{app} R_p / \eta l_p \quad (4)$$

which shows that v_{eof} increases with increasing pore resistance.

References

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2. Xu, F.; Wharton, J. E.; Martin, C. R. *Small* **2007**, 3, 1718-1722.
3. *CRC Handbook of Chemistry and Physics*, 86th ed.; Lide, D. R., Ed.; Taylor & Francis: Boca Raton, FL, 2005.