

Ion Transport through Perforated Graphene

Supporting Information

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A. Picture of membrane and the experimental setup:

A1. Picture of the membrane before and after etching:

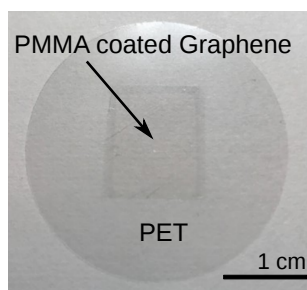


Figure S1. PMMA coated graphene membrane transferred on to 13 μm PET support.

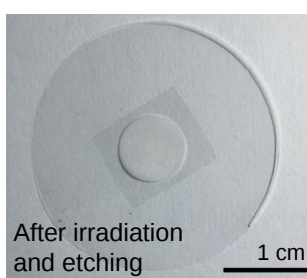


Figure S2. Graphene membrane after irradiation, etching and PMMA removal.

A2. Picture of the holders:

Graphene is placed between the holders and sealed with O rings as shown in Figure S3.

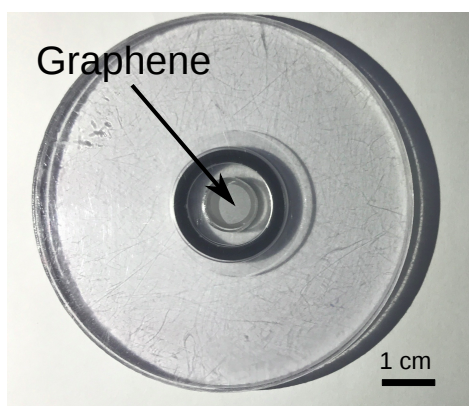


Figure S3: Holders that graphene is placed between.

A3. Picture of measurement setup.

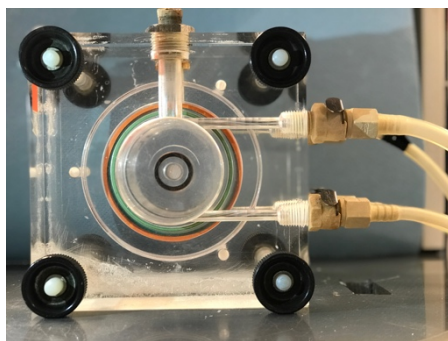


Figure S4. Front view of the experimental setup. Graphene is placed between the reservoirs using the holders.

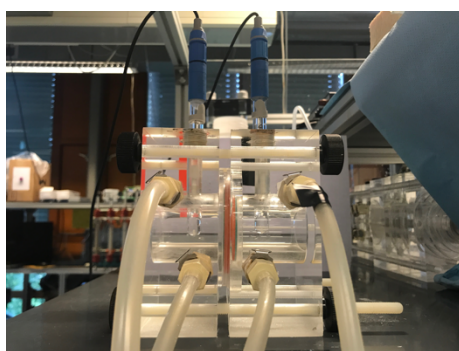


Figure S5. Side view of the setup. Two inlets and outlets are used to circulate water inside the reservoirs. Electrodes are placed on both sides of the membrane at an equal distance.

B) Experimental result for PET membranes without any graphene on top:

We have measured the potential of a PET membrane irradiated with the same fluence and etched in the same condition as that of the graphene membrane mentioned in the paper. The result is shown in Figure S6. We have done our measurement with three different salts (KCl, LiCl, K_2SO_4), we have used for the experiment with the composite Graphene/PET membrane. We have observed that for KCl the membrane potential is around zero which implies that the PET membrane is not selective for K^+ ions. The positive value of membrane potential for K_2SO_4 is due the diffusion potential generated for fast moving K^+ ions than SO_4^{2-} ions and the negative value of membrane potential for LiCl is due to diffusion potential generated due to the fast-moving Cl^- ions than the Li^+ ions. The potential remains steady with time. This result confirms that the selectivity we have observed in our membrane is appearing only do to the graphene membrane and PET pores have no influence on ion transport through the graphene nanopores.

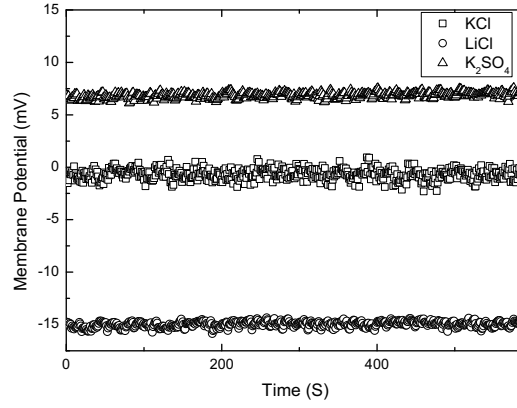


Figure S6. Membrane potential for PET is measured with respect to time for KCl, LiCl and K_2SO_4 .

C) TMS equation for 1:2 salt:

The dimensionless membrane potential for is expressed as¹

$$\Delta\bar{\psi}_{TMS} = \frac{1}{z_2} \ln \frac{k_2^P}{k_2^f} + \frac{\bar{u}_+ - \bar{u}_-}{z_2\bar{u}_- - z_1\bar{u}_+} \ln\left(\frac{T_r k_2^P + t_1 \zeta_f}{k_2^f + t_1 \zeta_f}\right)$$

Where,

$$\Delta\bar{\psi} = \frac{F\Delta\psi}{RT}, \quad t_1 = \frac{|z_1|\bar{u}_+}{|z_1|\bar{u}_+ + |z_2|\bar{u}_-}, \quad \zeta_f = \frac{\bar{c}_R}{|z_1|v_1 c_f}, \quad T_r = \frac{c_p}{c_f}$$

z_i is the electrochemical valence, \bar{u}_+ is the diffusion coefficient of cations and \bar{u}_- is the diffusion coefficient of anions and k_i is the partition coefficient of ion i . T_r is the transmission, which denotes the ability of solute to pass through the membrane. v_i is the stoichiometric coefficient of electrolyte, 1 represents counter ions.

$\zeta_{f(p)}$ is the ratio of the volume charge density to equivalent salt concentration in the feed side or in the permeate side of membrane. F is the Faraday constant, R is the gas constant and T is the temperature.

$\Delta\psi$ is the membrane potential

$\Delta\bar{\psi}$ is the dimensionless form of the membrane potential.

\bar{c}_R is the constant volume charge density of charged membrane (mole/l of pore volume).

c_f is the high concentration and c_p is the low concentration.

For, 1:2 asymmetric salt, the partition coefficient of co-ions can be expressed as,

$$k_2^{p(f)} = [\Gamma_{1:2,p(f)}^-]^{-2},$$

$$\Gamma_{1:2,p(f)}^- = \left[\frac{\Lambda(1, 1, \zeta_{p(f)})^{1/3}}{6} - \frac{2\zeta_{p(f)}}{\Lambda(1, 1, \zeta_{p(f)})^{1/3}} \right]^{-1}$$

where,

$$\Lambda(1, 1, \zeta_{p(f)}) = 108 + 12\sqrt{3}\sqrt{(27 + 4\zeta_{p(f)}^3)}$$

D) TEM image of graphene pore:

The TEM image in Figure S7 shows a hole of ~ 9 nm diameter. This confirms our estimated pore size, at least as order of magnitude.

We found this pore at the location where a PET pore is located. Graphene pore is expected to be found at that location.

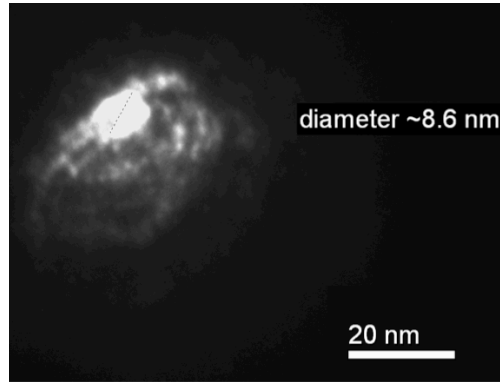


Figure S7: TEM image of graphene nanopore.

References:

(1) Shang, W. J.; Wang, X. L.; Yu, Y. X. Theoretical Calculation on the Membrane Potential of Charged Porous Membranes in 1-1, 1-2, 2-1 and 2-2 Electrolyte Solutions. *J. Membr. Sci.* **2006**, 285, 362–375.