Electronic Supporting Information

"Proton-regulated rectified ionic transport through solid-state conical nanopores modified with phosphate-bearing polymer brushes".

Materials and methods

4,4'-Azobis(4-cyanopentanoic acid), purum \geq 98.0%, (Fluka), *N*,*N*'-dicyclohexylcarbodiimide (DCC), puriss., \geq 99.0% (GC) (Fluka), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride 98%, (Fluka), pentafluorophenol (PFP) +99%, methacryloyl ethylene phosphate (Aldrich) and *N*-hydroxysuccinimide 98% (Aldrich), were obtained from Sigma-Aldrich, Schnelldorf, Germany. Dry *N*,*N*-dimethyl formamide (DMF) was obtained from Acros organics, Geel, Belgium. ethylenediamine 99+ % was obtained from, Merck, Germany).

Conical nanopore fabrication

In order to obtain conical pores, the heavy ion-irradiated polyethylene terephthalate (PET) membrane was etched from one side only in a conductivity cell in which it served as a dividing wall between the two compartments.¹ An etching solution sodium hypochlorite (13% active chlorine content) was filled on one side at 50 °C, while a stopping solution potassium iodide (1 M KI) was placed on the other side of the membrane, so that as soon as the track etched through completely, the etchant in the pore tip was neutralized, thus keeping the diameter small. This was helped further by applying a potential of -1 V on the side containing the etchant with the other grounded, so that once the pore opened, the active ClO⁻ ions were swept back from the pore tip. Shortly after breakthrough the pores were washed with stopping solution, followed by deionised water. The etched membrane was immersed in deionized water in order to remove the residual salts. After etching, the diameter of the large opening (*D*) of the pore was determined by scanning electron microscopy (SEM) using a PET sample containing 10^7 pores/cm^2 , which was etched simultaneously with the single pore under the same conditions. The diameter of the small opening (*d*) was estimated from its conductivity using the following equation.

$$d = \frac{4L}{\pi \kappa D} \frac{I}{V}$$

Functionalization with ethylenediamine

The above described etching results in surface with carboxyl groups. For the activation of the carboxyl groups, it was derivatised into pentafluorophenyl esters. An ethanolic solution containing 0.1 M EDC and 0.2 M PFP was placed on both sides of the track-etched polymer membrane. The reaction was carried out for 1h at room temperature. After washing with ethanol several times, the

solution was replaced with 0.1 M ethylendiamine (EDA) on both sides of the membrane and left overnight. The following day the chemically modified membrane was washed three times with ethanol followed by distilled water.

Anchoring 4,4'-Azobis(4-cyanopentanoic acid) moieties on the surface of single conical nanoporecontaining PET membranes.

0.5g (1.78 mmole) of 4,4'-Azobis(4-cyanopentanoic acid) and 0.92g (4.5 mmole) of DCC were added to a single neck Schlenk flask and closed with a rubber septum.² The reactants were degassed under vacuum for 15 minutes followed by back filling with $N_2(g)$. 40 mL of dry DMF was added to the flask through the septum with the help of a syringe and the reactants were allowed to dissolve. After complete dissolution 0.13 mL of dry pyridine was added. PET membrane with a single conical nanopore was sealed in a Schlenk tube and degassed (4 × high vacuum pump/N₂ refill cycles). The above prepared reaction mixture was syringed into this Schlenk flask and left overnight under $N_2(g)$ at room temperature. The following day the PET membrane was taken out of the reaction mixture and placed in beaker containing DMF. The beaker was gently shaken over a period of 2 h. The membrane was then washed twice with DMF followed by washing with water and ethanol (twice each). The initiator functionalized membrane was stored under nitrogen below 4 °C till further use.

Poly(methacryloyl ethylene phosphate) brush growth onto initiator-functionalized single conical nanopore-containing PET membranes.

In a 50 mL Schlenk flask, 5.5 g of the methacryloyl ethylene phosphate was dissolved in 200 mL of THF. The solution was degassed by $N_2(g)$ bubbling for 1 h. The initiator functionalized single conical nanopore containing PET membrane was sealed in a Schlenk tube and degassed (4 × high vacuum pump/N₂ refill cycles). The monomer solution was syringed into this Schlenk flask adding enough to wholly immerse the membrane. The flask was immersed in an oil bath preheated to 65 °C. The polymerization was carried out at 65 °C for 1 h. The PET membrane was then removed from the polymerization solution and rinsed with THF. The poly(methacryloyl ethylene phosphate) brush-modified membrane was stored in water till further use.

Theoretical estimation of the average monomer charge as a function of pH.

The average charge per monomer unit as a function of pH was obtained from the derivation of the fractional composition equations for a diprotic chemical system:³

$$MEPH_2 \stackrel{K_1}{\longleftrightarrow} H^+ + MEPH^-$$
$$MEPH^- \stackrel{K_2}{\longleftrightarrow} H^+ + MEP^{2-}$$

In the case of MEP equilibrium, pK_1 and pK_2 correspond to 4.5 and 7.7, respectively.⁴

$$K_{1} = \frac{[\mathrm{H}^{+}][\mathrm{MEPH}^{-}]}{[\mathrm{MEPH}_{2}]} \implies [\mathrm{MEPH}^{-}] = [\mathrm{MEPH}_{2}]\frac{K_{1}}{[\mathrm{H}^{+}]}$$
$$K_{2} = \frac{[\mathrm{H}^{+}][\mathrm{MEP}^{2-}]}{[\mathrm{MEPH}^{-}]} \implies [\mathrm{MEP}^{2-}] = [\mathrm{MEPH}^{-}]\frac{K_{2}}{[\mathrm{H}^{+}]} = [\mathrm{MEPH}_{2}]\frac{K_{1}K_{2}}{[\mathrm{H}^{+}]^{2}}$$

The mass balance for the "nominal" amount of MEP monomer is

$$[MEP] = [MEPH_2] + [MEPH^-] + [MEP^{2-}]$$

This balance describes the distribution of the original MEP monomer into different chemical species interrelated through acid-base equilibria.

$$[MEP] = [MEPH_2] + [MEPH_2] \frac{K_1}{[H^+]} + [MEPH_2] \frac{K_1K_2}{[H^+]^2}$$

or

$$[MEP] = [MEPH_2] \left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2} \right)$$

For a diprotic system, like MEP, we can designate the fraction in the form MEPH₂ as α_{MEPH_2} , the fraction in the form MEPH⁻ as α_{MEPH_2} and the fraction in the form MEP²⁻ as α_{MEP_2} . Then, we can write

$$\alpha_{\text{MEPH}_{2}} = \frac{[\text{MEPH}_{2}]}{[\text{MEP}]} = \frac{[\text{H}^{+}]^{2}}{[\text{H}^{+}]^{2} + K_{1}[\text{H}^{+}] + K_{1}K_{2}}$$
$$\alpha_{\text{MEPH}^{-}} = \frac{[\text{MEPH}^{-}]}{[\text{MEP}]} = \frac{K_{1}[\text{H}^{+}]}{[\text{H}^{+}]^{2} + K_{1}[\text{H}^{+}] + K_{1}K_{2}}$$
$$\alpha_{\text{MEP}^{2-}} = \frac{[\text{MEP}^{2-}]}{[\text{MEP}]} = \frac{K_{1}K_{2}}{[\text{H}^{+}]^{2} + K_{1}[\text{H}^{+}] + K_{1}K_{2}}$$

These equations provide a quantitative description of distribution of MEP-related species as a function of pH (Figure 2a in the manuscript). In a similar fashion, the pH dependence of the average charge of each MEP monomer unit (q) (Figure 2b in the manuscript) can be estimated as follows,

$$q = 0 \times \alpha_{\text{MEPH}_2} + 1 \times \alpha_{\text{MEPH}^-} + 2 \times \alpha_{\text{MEP}^{-2}}$$

or

$$q = \frac{K_1[\mathrm{H}^+] + 2K_1K_2}{[\mathrm{H}^+]^2 + K_1[\mathrm{H}^+] + K_1K_2}$$

References

- ¹ (a) Z. Siwy, D. Dobrev, R. Neumann, C. Trautmann, K. Voss, *Appl. Phys. A* 2003, **76**, 781. (b) P.Y. Apel, Y.E. Korchev, Z. Siwy, R. Spohr, M. Yoshida M, *Nucl. Instrum. Methods Phys. Res., Sect. B* 2001, **184**, 337.
- ² W. Huang, G. Skanth, G.L. Baker, M.L. Bruening *Langmuir* 2001, **17**, 1731.
- ³ D.C. Harris, "*Quantitative Chemical Analysis*" 6th ed. (W.H. Freeman and Company, New York, 2002) p. 216.
- ⁴ J. Zhang, J. Kirkham, C. Robinson, M.L. Wallwork, D.A. Smith, A. Marsh, M. Wong, *Anal. Chem.* 2000, **72**, 1973.