

## **Supporting Information**

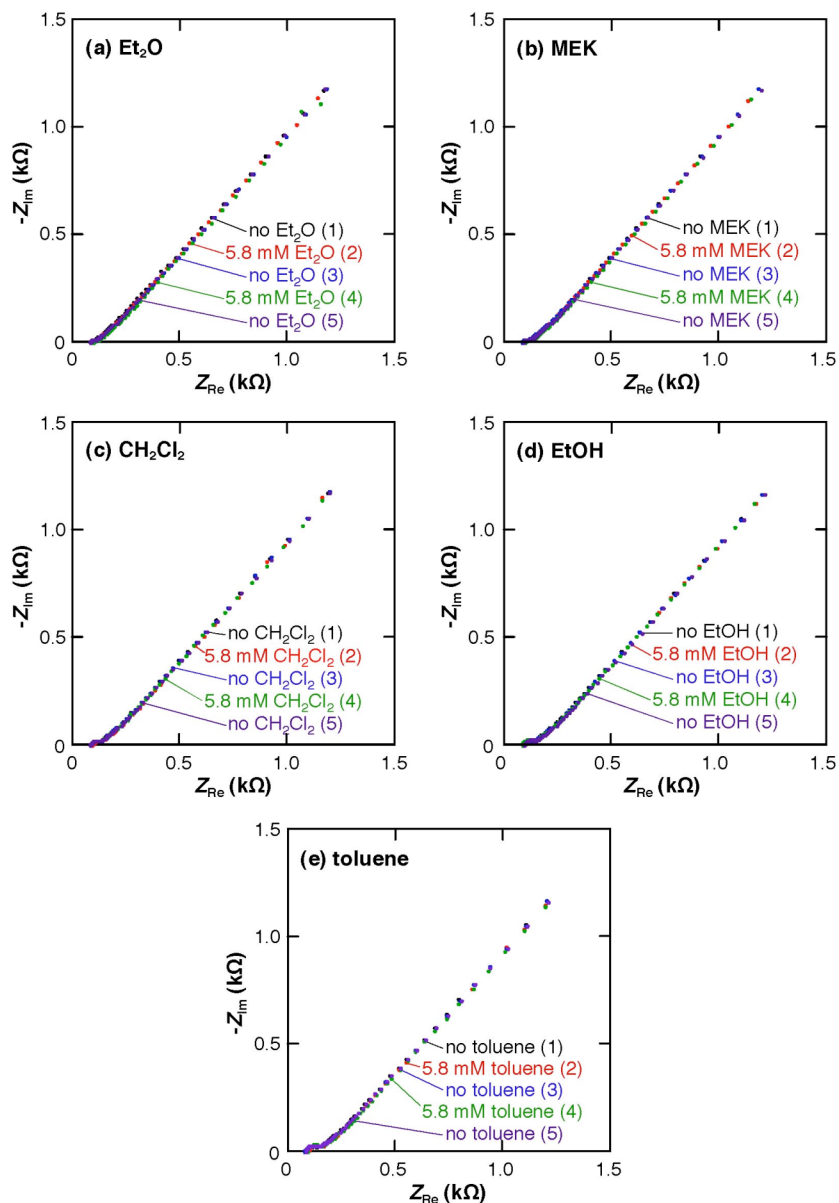
### **Electrochemical Impedance Spectroscopy Studies of Organic-Solvent-Induced Permeability Changes in Nanoporous Films Derived from a Cylinder-Forming Diblock Copolymer**

D. M. Neluni T. Perera, Bipin Pandey and Takashi Ito\*

Department of Chemistry, Kansas State University, 213 CBC Building, Manhattan, Kansas  
66506-0401, USA

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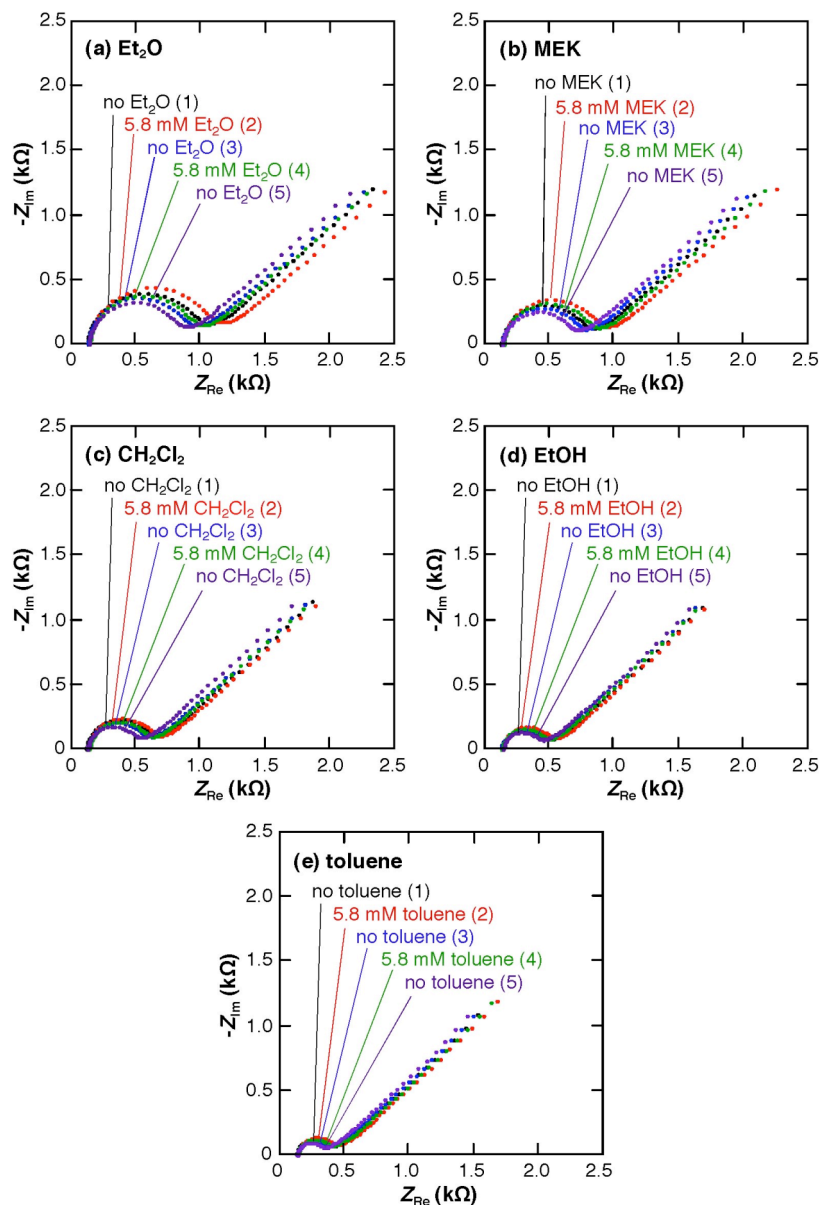
# 1. EIS data on a bare gold electrode in the presence and absence of 5.8 mM solvents.



**Figure S1.** EIS data obtained on a bare gold electrode in aqueous solutions with and without 5.8 mM organic solvents. The aqueous solutions contained 3.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6$ , 3.1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  and 0.1 M  $\text{KH}_2\text{PO}_4$ - $\text{K}_2\text{HPO}_4$  buffer (pH 7).

$R_{\text{sol}} = 110 \pm 20 \text{ } (\Omega)$ ;  $R_{\text{ct}} = 70 \pm 30 \text{ } (\Omega)$ , which are similar to those obtained on electrodes coated with PS-*b*-PMMA-derived nanoporous films.

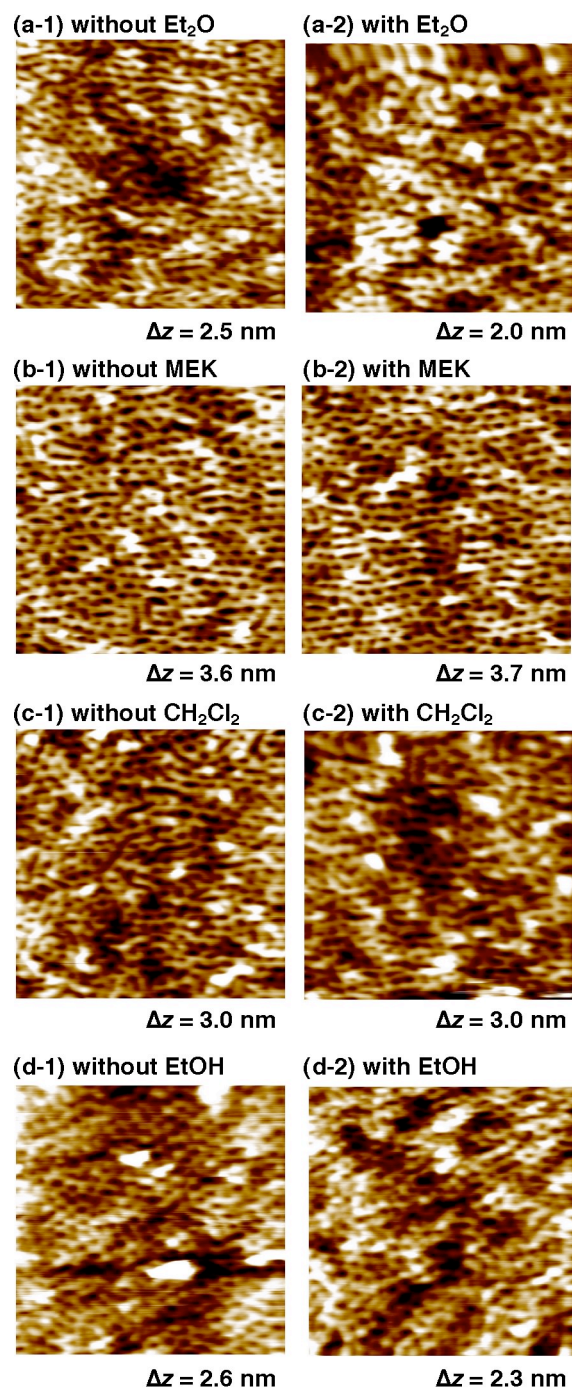
## 2. EIS data on a gold electrode modified with a PS homopolymer layer in the presence and absence of 5.8 mM solvents.



**Figure S2.** EIS data obtained on a gold electrode modified with a PS homopolymer layer in aqueous solutions with and without 5.8 mM organic solvents. The aqueous solutions contained 3.0 mM K<sub>3</sub>Fe(CN)<sub>6</sub>, 3.1 mM K<sub>4</sub>Fe(CN)<sub>6</sub> and 0.1 M KH<sub>2</sub>PO<sub>4</sub>-K<sub>2</sub>HPO<sub>4</sub> buffer (pH 7).

The largest EIS responses were observed in the first set of measurements regardless of organic solvents. In this specific set of measurements, Et<sub>2</sub>O was first measured, exhibiting larger EIS responses. For PS-coated electrodes,  $R_{sol} = 110 \pm 20$  ( $\Omega$ ), but  $R_{ct} \sim 2 \times 10^4$   $\Omega$ , which is significantly larger than the  $R_{ct}$  of electrodes coated with PS-*b*-PMMA-derived nanoporous films.

**3. Effects of 5.8 mM solvents on the AFM images ( $1 \times 1 \mu\text{m}^2$ ) of PS-*b*-PMMA-derived nanoporous films.**



**Figure S3.** AFM images ( $1 \times 1 \mu\text{m}^2$ ) of PS-*b*-PMMA-derived nanoporous films in aqueous buffer solutions (0.1 M phosphate, pH 7) in the absence (right) and presence (left) of 5.8 mM organic solvent. The two images were measured successively.

#### 4. Calculation of the nanopore shrinkage ( $\Delta x$ ).

Under the assumptions that the pore diameter, spacing and length in a nanoporous film were uniform, the following unit cell with tubular structure was considered:  $r$ : inner diameter (= pore diameter, 15 nm),  $s$ : outer diameter (= half of pore spacing, 27 nm); and  $l$ : pore length (= film thickness, 30 nm). The volume of the unit tube,  $V$ , is given as follows:

$$V = \pi(s^2 - r^2)l \quad (\text{S1})$$

From the assumption (3) in the main text, the volume of the swollen unit tube is expressed by:

$$V' = \pi(s^2 - (r - \Delta x)^2)(l + \Delta x) \quad (\text{S2})$$

The ratio of these two volumes ( $V'/V$ ) offers the increase in volume due to the swelling.

From Eq (2) in the main text, the pore resistance of a swollen polymer is described by:

$$R_{pore}^{solv} = \rho \frac{l + \Delta x}{N\pi(r - \Delta x)^2} \quad (\text{S3})$$

From Eqs (2) and (S3),

$$\frac{R_{pore}^{solv}}{R_{pore}^0} = \frac{\frac{l + \Delta x}{(r - \Delta x)^2}}{\frac{l}{r^2}} = \left(1 + \frac{\Delta x}{l}\right) \bigg/ \left(1 - \frac{\Delta x}{r}\right)^2 \quad (\text{S4})$$

$R_{pore}^{solv}/R_{pore}^0 \sim 1.5$  for aqueous solutions saturated with toluene and  $\text{CH}_2\text{Cl}_2$  (**Table 1**) gives

$\Delta x = 2.3$  nm. From Eqs (S1) and (S2), the volume change was calculated to be 21.2%.