

## Supporting information

# Estimation of electrical parameters inside nanofiltration membrane in varying electrolyte solutions by dielectric spectroscopy analysis

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## 1. Calculation formulas and computational procedures

The cell system can be represented by a series combination of a membrane (capacitance  $C_m$  and conductance  $G_m$ ) and a solution ( $C_w$  and  $G_w$ ), as illustrated in Fig. 1a, which can be measured in terms of the equivalent capacitance  $C(f)$  and equivalent conductance  $G(f)$  in parallel at each frequency, as shown in Fig. 1b.

Complex capacitance  $C^*$  of the whole system is represented by

$$1/C^* = 1/C_m^* + 1/C_w^* \quad (\text{S.1})$$

where  $C_m^*$  and  $C_w^*$  are the complex capacitance of membrane and solution respectively, defined as

$$C^* = C + G/2\pi jf \quad (\text{S.2})$$

where  $f$  is measuring frequency and  $j(=\sqrt{-1})$ .

Substituting Eq. (2) for Eq. (1) and rearranging Eq. (1),  $C$  and  $G$  observed experimentally are expressed by phase parameters ( $C_m$ ,  $G_m$ ,  $C_w$  and  $G_w$ ) as

$$C = \frac{(C_m G_w^2 + C_w G_m^2) + \omega^2 C_m C_w (C_m + C_w)}{(G_m + G_w)^2 + \omega^2 (C_m + C_w)^2} \quad (\text{S.3})$$

$$G = \frac{G_m G_w (G_m + G_w) + \omega^2 (C_m^2 G_w + C_w^2 G_m)}{(G_m + G_w)^2 + \omega^2 (C_m + C_w)^2} \quad (\text{S.4})$$

where  $\omega = 2\pi f$ , angular frequency of the applied ac voltage. According to Eqs. (S.3) and (S.4), the relations between the phase parameters and the dielectric parameters (the limiting values of  $C$  and  $G$  at high (subscript  $h$ ) and low (subscript  $l$ ) frequencies) are given by following equations:

$$C_h = \frac{C_m C_w}{C_m + C_w} \quad (\text{S.5})$$

$$C_l = \frac{C_m G_w^2 + C_w G_m^2}{(G_m + G_w)^2} \quad (\text{S.6})$$

$$G_h = \frac{C_m^2 G_w + C_w^2 G_m}{(C_m + C_w)^2} \quad (\text{S.7})$$

$$G_l = \frac{G_m G_w}{G_m + G_w} \quad (\text{S.8})$$

Solving Eqs. (5) to (8) gives the expressions for calculating phase parameters,

$$\omega_0 = \frac{G_h - G_l}{C_l - C_h} = 2\pi f_0 \quad (\text{S.9})$$

$$B = \omega_0 + \frac{G_h}{C_h} \quad (\text{S.10})$$

$$D = \sqrt{B^2 - 4 \frac{G_l \omega_0}{C_h}} \quad (\text{S.11})$$

$$a = \frac{B - D}{2} \quad (\text{S.12})$$

$$b = B - a \quad (\text{S.13})$$

$$C_m = C_h \frac{D}{\omega_0 - a}, \quad \varepsilon_m = C_m \frac{t}{S \varepsilon_0} \quad (\text{S.14})$$

$$C_w = C_h \frac{D}{b - \omega_0}, \quad \varepsilon_w = C_w \frac{L}{S\varepsilon_0} \quad (\text{S.15})$$

$$G_m = aC_m, \quad \kappa_m = G_m \frac{t}{S} \quad (\text{S.16})$$

$$G_w = aC_w, \quad \kappa_w = G_w \frac{L}{S} \quad (\text{S.17})$$

where  $B, D, a$  and  $b$  are introduced parameters for convenience of calculation. By use of the formulas (S.9) to (S.17), the phase parameters  $C_m, G_m, C_w$  and  $G_w$  (or  $\varepsilon_m, \kappa_m, \varepsilon_w$  and  $\kappa_w$ ) can be calculated in turn from the dielectric parameters.

## 2. Concentration dependence of pH of different electrolyte solutions

Table S1 and Fig. S1 show the concentration dependence of pH of different electrolyte solutions. It is clear that different salts and different concentrations of identical salts show great differences in pH values. More importantly, by comparing the concentration dependence of pH of different electrolyte solutions (Fig. 1S) with that of surface charge density (Fig. 12(a), 13(a) and 14(a)), we can deduce that the differences in pH may also affect the protonation of the carboxylate groups located the pore walls, giving rise to different surface charge density.

Table S1 The pH of stock solutions of all salts at all concentrations

$c(\text{mol/m}^3)$	NaCl	KCl	MgCl <sub>2</sub>	CuCl <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>	MgSO <sub>4</sub>	CuSO <sub>4</sub>
<b>0.05</b>	6.7	6.5	5.9	5.4	6.5	6.2	5.9	5.4
<b>0.1</b>	6.5	5.9	5.8	5.4	6.0	5.9	5.8	5.3
<b>0.2</b>	6.3	5.7	5.8	5.3	5.8	5.7	5.7	5.3
<b>0.4</b>	6.0	5.6	5.8	5.2	5.7	5.7	5.6	5.2

<b>0.7</b>	5.9	5.6	5.8	5.2	5.7	5.6	5.6	5.2
<b>1.0</b>	5.8	5.6	5.8	5.1	5.7	5.6	5.6	5.1
<b>2.0</b>	5.7	5.6	5.7	5.0	5.6	5.6	5.5	5.0
<b>4.0</b>	5.7	5.6	5.7	4.9	5.6	5.6	5.5	4.9
<b>7.0</b>	5.7	5.6	5.7	4.9	5.6	5.6	5.5	4.8

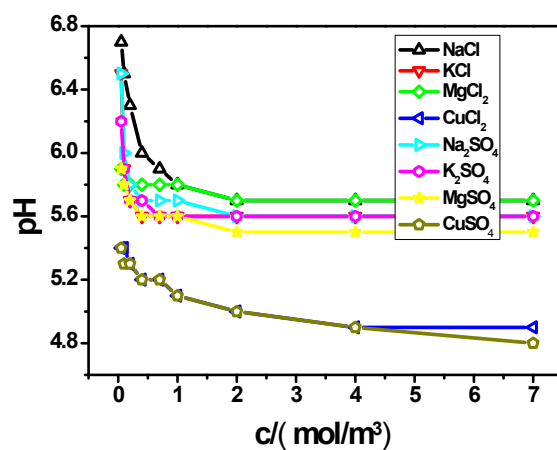


Fig. S1 Concentration dependence of pH of different electrolyte solutions