Supplementary Information

Cation Exchange Membrane with Low Frictional Coefficient and High Limiting Current Density for Energy Efficient Water Desalination

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Section S1

Frictional interpretation

Based on Kedem and Katchalsky approach, membrane conductivity ($\kappa^m$) is related with tortuosity factor ($\theta$) by following equation:

$$\theta = \frac{\kappa^m f^0_{1w} \Delta x}{F^2 X} \quad (1)$$

The effective pathway of solute within membrane with thickness ($\Delta x$), i.e., the true path length defined by $\delta = \Delta x / \theta$. $f^0_{1w}$ is the frictional coefficient between counter-ion and water in free solution.

The solute permeability coefficient ($\omega$) of a membrane can be described as:

$$\omega = \frac{C_s \varphi_w^2 \theta}{X \Delta x f^0_{2w}} \quad (2)$$

Where $f^0_{2w}$ the frictional coefficient between co-ion and water is in free solution, $C_s$ is the average salt concentration in both compartments, and $\varphi_w$ is the volume fraction of water in the membrane phase.

Frictional coefficients are defined as $f^0_{1w} = RT/D_i$, where $D_i$ is the diffusion coefficient of single ion, i, in the free solution. The ionic diffusion coefficient $D_i$ at a given electrolyte concentration may be obtained by the ionic conductance data. For example, at 0.01 M NaCl solution, the ionic diffusion coefficient for Na$^+$ and Cl$^-$ were found to be $D_{Na^+} = 1.347 \times 10^{-5}$ cm$^2$ s$^{-1}$ and $D_{Cl^-} = 2.005 \times 10^{-5}$ cm$^2$ s$^{-1}$, respectively. In the same electrolyte concentration the frictional
coefficient values are: \( f_{1w}^0 = 2.038 \times 10^{15} \text{ dyn s mol}^{-1} \text{ cm}^{-1} \) and \( f_{2w}^0 = 1.338 \times 10^{15} \text{ dyn s mol}^{-1} \text{ cm}^{-1} \).

**Section S2**

**Instrumental analysis**

FT-IR spectra of PGO and APSGO were recorded by KBr technique in the range of 4000–400 cm\(^{-1}\). \(^1\)H NMR spectra was used to estimate the degree of sulphonation of PEEK and obtained by an NMR spectrometer (Bruker 500MHz) in a solvent. Scanning electron microscopy (SEM) images for SPEEK pristine and SPEEK/PGO-8 dried membranes were recorded using a LEO Instruments (Kowloon, Hong Kong) micro- scope after the gold sputter coatings on desired membrane samples. The thermal degradation and stabilities of different composite membranes were investigated using a thermo gravimetric analyser (TGA, Mettler Toledo TGA/SDTA851 with Star\(^\circ\) software) under N\(_2\) atmosphere with 10 °C/min heating rate between 40-600 °C. Burst strength tester machine provided by Test Techno Consultant, Vadodara, Gujarat, India (Model 807 DMP), was used for the investigation of pressure (Kg cm\(^{-2}\)) required to rupture the membrane.

**Section S3**

**Water uptake, ion-exchange capacity, and swelling ratio measurements**

Detailed procedures for measuring water uptake, ion-exchange capacity and swelling ratio have been included in in section S2 of Supporting Information. To estimate the water uptake (WU) and swelling ratio (SR), membrane samples were soaked in the deionized water for 24 h at room temperature. After removal of surface water by adsorbent paper, length and weight of wet membrane sample were measured. Afterwards, membrane samples were dried in vacuum oven at 90-100 °C for 24 h and further length and weight of dried membrane sample were measured. The WU (%) and SR (%) were estimated using following equations.

\[
WU(\%) = \frac{W_w - W_d}{W_d} \times 100 \quad (3)
\]

Where \( W_w \) and \( W_d \) are the weights of wet and dried membranes, respectively.

\[
SR(\%) = \frac{L_w - L_d}{L_d} \times 100 \quad (4)
\]

Where \( L_w \) and \( L_d \) are the length of the wet and dry membrane, respectively.
The ion exchange capacity (IEC) was measured by acid-base titration method. Membrane samples were equilibrated in 50 mL 1.0 M NaCl solution for 24 h to exchange the H$^{+}$ by Na$^{+}$. Afterwards, the solution was back titrated with NaOH (0.10 M) using phenolphthalein indicator. The IEC was estimated according to the following equation:

$$IEC (mmol \ g^{-1}) = \frac{C_{NaOH} \times V_{NaOH}}{W_d} \quad (5)$$

$C_{NaOH}$ and $V_{NaOH}$ are concentration and volume of NaOH solution consumed.

**Section S4**

**Chronopotentiometric studies**

The chronopotentiometric studies responses for the membranes in equilibrium with 0.01 M NaCl solution were recorded in a two-compartment perspex cell separated by membrane (25.0 cm$^2$). A constant current was applied across the membrane using two dimensionally stable titanium electrodes coated with precious metal oxide, with the help of potentiostat/galvanostat (Auto Lab, Model PGSTAT 30 (EcoChemie, B.V. Utrecht, The Netherlands)). Electrolyte solutions were continuously recirculated in two compartments with the help of peristaltic pumps. Variation in potential with time under static conditions was recorded. In all these studies, the direction of the current was set in such a way that the counter-ion should move vertically upward from the outer to the inner compartment with minimal perturbations caused by natural convection. Two saturated calomel electrodes were used for the measurement of the potential difference across the ion-exchange membrane under static conditions. The solutions of both the compartments were vigorously recirculated between two successive experiments to ensure the return of equilibrium conditions in two solution-membrane interfacial zones.

**Detailed analysis of chronopotentiograms**

If an ion-exchange membrane separates two identical monovalent electrolytic solution of concentration $C$, then according to Fick’s second law of linear diffusion, at the membrane–solution interfacial zone, the variation in counter-ion ($i$) concentration ($C_i$) with time ($t$), may be given as follows:

$$\frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial x^2} \quad (6)$$

where $D$ is the diffusion coefficient of the electrolyte. Passage of constant electric current $I$ (mA cm$^{-2}$) across the membrane cause migration of counter-ion from one of membrane–solution interfacial zone towards the membrane surface, while away from the membrane.
surface in the other zone. Under concentration polarization, the incoming flux through the ion-exchange membrane \( (J_m) \) and outgoing flux from membrane surface \( (J_s) \) eventually becomes equal as counter-ion concentration is constant within the membrane phase \( (J_m = J_s) \).

Considering contribution of electro-osmotic transport of H\(_2\)O along with \( I \) to change the potential is negligible, concentration and electric current are related as:

\[
\frac{\partial c_i}{\partial x} = \frac{I}{z_i F D_i} (t_i^m - t_i) \quad (7)
\]

\( t_i^m \) and \( t_i \) are counter-ion transport number in the membrane and solution phase, respectively.

At the transition time \( (\tau) \) (concentration polarization), \( C_i \to 0 \) at the membrane surface \( (x = 0) \). Thus, under boundary conditions \( (C_i = 0 \text{ at } x = 0 \text{ and } t = \tau) \), following equation express the relationship between \( \tau^{1/2} \) and membrane permselectivity \( (P_s) \).

\[
\tau^{1/2} = \frac{z_i F \alpha \text{D}_i}{2(1-t_i)P_s} C_i \quad (8)
\]

Eq. 8 indicates inversely relation between \( \tau^{1/2} \) and \( P_s \) of the IEM.

**Section S5**

**Estimation of rate of desalting \((J)\), energy consumption \((E)\) and current efficiency \((CE)\).**

The ED process performance was evaluated in terms of rate of salt (NaCl) removal \((J)\), current efficiency \((CE)\) and energy consumption \((W, \text{kWh/kg of NaCl removed})\). Considering negligible mass flow through membranes, \((J)\) may be obtained by following equation:

\[
J = \frac{V_a C_t - C_0}{A} \frac{\Delta t}{\Delta t} \quad (9)
\]

where \( C_0 \) and \( C_t \) are the initial and final concentration of NaCl in CC \((\text{mol}^{-3})\), \( \Delta t \) the time \( (s) \) allowed for ED, \( V_a \) is the total volume of CC feed \((0.50 \times 10^{-3} \text{m}^2)\), and \( A \) is the effective membrane area \((8.0 \times 10^{-3} \text{m}^2)\).

Energy consumption \((E, \text{kWh/kg of salt removed})\) was estimated by following eqn:

\[
E(\text{kWh/kg}) = \int_0^t \frac{V I \, dt}{m} \quad (10)
\]

where \( V \) is the applied voltage, \( I \) the current, \( t \) the time allowed for ED process, and \( m \) is the weight of salt removed. Current efficiency \((CE)\) was estimated by:
\[ CE(\%) = \frac{m \cdot n \cdot F}{M \cdot Q} \times 100 \]  

(11)

where \( F \) is the Faraday constant, \( M \) the molecular weight of salt, \( n \) the stoichiometric number (\( n = 1 \) in this case), and \( Q \) is the electric quantity passed (Coulombs; A s).

**Table S1**

Physicochemical and electrochemical properties of AEM (ASV, supplied by Selemion, Japan).

| Properties                              | ASV membrane  |
|----------------------------------------|---------------|
| Characteristic                         | Anion-exchange membrane |
| Thickness (µm)                         | 130           |
| Brust strength (MPa)                   | 0.40          |
| Ion-exchange capacity (mequiv./g)      | 1.13          |
| Transport number for Cl \(^{a}\)      | 0.97          |
| Resistance (\( \Omega \) cm\(^2\))\(^{b}\) | 3.2           |

\(^a\)measured in equilibration with 0.055 M NaCl solution.

\(^b\)measured in equilibration with 0.5 M NaCl solution.
Figure S1. TGA curves for pristine SPEEK and different SPEEK/PGO membranes.
Figure S2. Schematic diagram of the two-compartment membrane cell used for chronopotentiometry and i-V curves.