Synthesis of Highly Stable and High Water Retentive Functionalized Biopolymer-Graphene Oxide Modified Cation Exchange Membranes

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S1. Physiochemical and Electrochemical Characterization of Hybrid Membrane:

\textit{Water uptake, dimension change}

All the prepared membranes were dipped in distilled water for 24h. Wet weight and dimension of the membranes were measured. Afterwards the membranes were dried at 70°C and again the weight and dimensions were measured in dry condition. Water uptake was calculated as

\[
\phi_w = \frac{W_{\text{Wet}} - W_{\text{Dry}}}{W_{\text{Wet}}} \times 100\%
\]

where \(W_{\text{Wet}}\) and \(W_{\text{Dry}}\) are the mass of membranes in wet and dry condition.

Dimensional change is calculated taking the volume difference in dry and wet conditions and is calculated by following equation:

\[
\phi = \frac{V_{\text{Wet}} - V_{\text{Dry}}}{V_{\text{Wet}}} \times 100
\]

Where \(V_{\text{Wet}}\) and \(V_{\text{Dry}}\) are volume of NTFs in wet and dry condition.

\textit{IEC and Ionic conductivity:}
IEC refers to the number of mili equivalents of exchangeable charge in polymer. IEC of the membranes was measured by equilibrating the membranes in 1M HCl for 24 h first then in 1M NaCl for further 24h. After that membranes were titrated against 0.1M NaOH solution for exchanged H$^+$ ions. The IEC was calculated according to the equation:

$$\text{IEC} (\text{mequiv g$_{\text{dry membrane}}$}^{-1}) = \frac{C_{\text{Na}^+} V_{\text{sol}}}{W_{\text{dry}}}$$

where $C_{\text{Na}^+}$ is the concentration of Na$^+$ in the extraction solution and $W_{\text{dry}}$ is the dried membrane weight.

Ionic conductivity measurements were carried out after equilibrating the membranes in 1M NaCl. The membranes were sandwiched between two in-house made circular stainless steel electrodes (1.0cm$^2$). The proton conductivity ($\kappa_m$) was calculated from Equation:

$$\kappa_m (\Omega^{-1} \text{cm}^{-1}) = \frac{L (cm)}{R (\Omega) \times A (cm^2)}$$

where L is the distance between the electrodes used to measure the potential, R is the resistance of the membrane, and A is the surface area of the membrane.

**Methanol permeability:**

Resistance to methanol crossover of the membranes was evaluated by the measurement of the methanol permeability with a two compartment cell. The concentration of methanol in second compartment was measured as a function of the diffusion time with a refractometer. The methanol permeability ($P_M$) was obtained by the equation:

$$P_M = \frac{1}{A} \frac{C_{II(t)}}{C_{I(t)}} \frac{V_{II}}{l}$$

where $A$ is the effective membrane area, $l$ the membrane thickness, $C_{II(t)}$ the methanol concentration in second compartment at time $t$, $C_{I(t)}$ the change in the methanol concentration in first compartment at time $t$, and $V_{II}$ the volume of second compartment. For the suitability of membrane for fuel cell, we calculate the selectivity of the membrane by following equation;

$$S_P = \frac{\sigma}{P_M} \tag{6}$$
where $P_M$ is the methanol permeability (cm$^2$/s), and $\sigma$ is the membrane conductivity (S.cm$^{-1}$).

Fig. S1: FTIR spectrum of sulfonated chitosan

Fig. S2 (a): $^1$H NMR spectrum of chitosan
Fig. S2 (b): $^1$H NMR spectrum of sulfonated chitosan membrane

Fig. S2 (c): $^1$H NMR spectrum of sulfonated chitosan hybrid membrane