Supplementary information

**In-situ construction of interconnected ion transfer channels in anion-exchange membranes for fuel cells application**

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*Computational calculation details:* The geometry optimizations were carried out using the density functional theory (DFT) method at the B3LYP/6-31G (d,p) level. All calculations were performed using the Gaussian 09 program. S1

*Mechanical strength:* A tensile tester (CMT6503, Shenzhen SANS Test Machine Co. Ltd, China) was used to analyse the tensile stress–strain behaviour of the fully hydrated MQ-PEEK and SQ-PEEK membranes in OH⁻ forms at room temperature. A constant crosshead speed of 5 mm/min was used for samples of 1 cm width and 3 cm length.

The ion exchange capacity (IEC): the IEC_m of membranes were determined by titration. 0.2-0.5 g of membranes in OH⁻ form was immersed in a standard hydrochloric acid solution (0.1 mol/L, 25 mL) for 48 h. The solution was then titrated with a standard solution of potassium hydroxide (0.1mol/L) with phenolphthalein as an indicator. The membrane was washed and immersed in deionized water for 24 h to remove any residual HCl, and then dried under vacuum at 45 ºC for 24 h and weighed to determine the dry mass (in Cl⁻ form). The IEC_m of the membrane is calculated with equation S1.

\[
\text{IEC}_m = \left[ n_{f(H^+)} - n_{i(H^+)} \right] / m_{\text{dry(Cl^-)}} \tag{S1}
\]

where \(n_{i(H^+)}\) is the initial amount of proton in the HCl solution, \(n_{f(H^+)}\) is the final amount of proton in the HCl solution determined by titration, and \(m_{\text{dry(Cl^-)}}\) is the mass of the dry membrane in Cl⁻ form. The IEC_m were obtained by the average of three different
measurements. The theoretical IEC were calculated from the quaternization degree (QD) of membranes.

**Fig. S1** The chemical structure (A), synthesis route (B) and $^1$HNMR spectroscopy (C) of single quaternary ammonium PEEK (using trimethylamine as quaternization agent, SQ-PEEK).

**Fig. S2** Optimized (a) monomer and (b) dimer geometries of MQ-PEEK structural units obtained from density functional theory (DFT) calculations. The hydrogen atoms are not shown for a better illustration.
**Fig. S3** SAXS profiles of SQ-PEEK 53% and MQ-PEEK 95% membranes.

**Fig. S4** SAXS profiles of MQ-PEEK 95% membrane in OH⁻ form at 25–70 ºC.

**Fig. S5** Scanning transmission electron microscope (STEM) image of MQ-PEEK 95% membrane.
**Fig. S6** Temperature-dependence of swelling degree (SD) of MQ-PEEK 53%, 85% and 95% membranes in OH− form at 30–70 ºC. The three well-segregated MQ-PEEK membranes show extremely low SD. The SD has a lower dependence on temperature as the hydrophobicity enhances with increasing temperature, indicating that MQ-PEEK membranes possess excellent dimensional stability.

**Table S1.** Comparison between the theoretical IEC\textsubscript{t} and experimental IEC\textsubscript{m} of MQ–PEEK membranes.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>IEC\textsubscript{t}</th>
<th>IEC\textsubscript{m}</th>
</tr>
</thead>
<tbody>
<tr>
<td>MQ-PEEK 53%</td>
<td>1.16</td>
<td>1.13</td>
</tr>
<tr>
<td>MQ-PEEK 85%</td>
<td>1.54</td>
<td>1.49</td>
</tr>
<tr>
<td>MQ-PEEK 95%</td>
<td>1.68</td>
<td>1.62</td>
</tr>
</tbody>
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\textsuperscript{1}The theoretical IEC calculated from the molecular weight and the quaternization degree; \textsuperscript{2}The measured IEC determined by the back titration method.
Table S2. Mechanical properties of MQ-PEEK and SQ-PEEK membranes in OH⁻ form at 25 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>53%</th>
<th>85%</th>
<th>95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQ-PEEK-OH⁻</td>
<td>9.6</td>
<td>1.1</td>
<td>N/A a)</td>
</tr>
<tr>
<td>MQ-PEEK-OH⁻</td>
<td>30.9</td>
<td>23.5</td>
<td>20.7</td>
</tr>
</tbody>
</table>

a) The tensile strength test is not available because the SQ-PEEK 95% membranes swell excessively.