Supplementary Information

End-group cross-linked large-size composite membranes via lab-made continuous caster: Enhanced oxidative stability and scale-up feasibility in a 50 cm² single-cell and 220 W class 5-cell PEFC stack

Sung-Hyun Yun, a Se-Hun Oh, a Jung-Je Woo, a Ju-Young Lee, a Jin-Hyun Lee, a Jaeyoung Lee, ab Jae-Suk Lee c and Seung-Hyeon Moon*ab

a School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), 123 Cheomdan-gwagiro, Buk-gu, Gwangju 500-712, Republic of Korea
b Research Institute for Solar and Sustainable Energies, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, Republic of Korea

c School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), 123 Cheomdan-gwagiro, Buk-gu, Gwangju 500-712, Republic of Korea

[*] Corresponding author. Tel: +82-62-715-2435, Fax: +82-62-715-2434,
Email: shmoon@gist.ac.kr

Experimental: Membrane characterization

In-plane proton conductivity (k) The proton conductivity of the swollen membrane was measured using a four-probe electrochemical impedance cell.1,2 Impedance analyses were carried out using a potentiostat/galvanostat (Autolab PGSTAT 30, Eco Chemie, Netherland), operated via a galvanostatic method under a 0.1 mA AC amplitude over a frequency range of 1 MHz to 10 Hz at room temperature. The membrane resistance was determined at a zero phase angle from the Nyquist behavior. Finally, the in-plane proton conductivity k (S cm⁻¹) was calculated using

\[ k = \frac{L}{RWd} \]  

(S1)
Water uptake ($W_u$) The water uptake was calculated based on the weight of the dried ($W_{dry}$) and wet ($W_{wet}$) membranes as follows:

$$W_u(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100$$  \hspace{1cm} (S2)

Ion-exchange capacity (IEC) The IEC was measured according to the phenolphthalein endpoint detection via the titration of a NaOH aqueous solution. Before titration, the membrane in acid form was soaked in a 0.5 M NaCl aqueous solution for 12 h, and the equivalent of the protons released from the membrane in the solution was detected by titrating a 0.01 M NaOH ($C_{NaOH}$) aqueous solution in the presence of phenolphthalein. Based on the titrated NaOH volume ($V_{NaOH}$), the IEC (mequiv. g$^{-1}$) was calculated using

$$IEC = \frac{C_{NaOH}V_{NaOH}}{W_{dry}}$$  \hspace{1cm} (S3)

Swelling ratio ($S_w$) The swelling ratio of the membranes in water was calculated according to:

$$S_w = \frac{A_{wet} - A_{dry}}{A_{dry}} \times 100$$  \hspace{1cm} (S4)

where $A_{wet}$ and $A_{dry}$ are the surface area of the membrane in dried and swollen states, respectively.

Oxidative stability (Fenton’s test) Fenton’s reagent were prepared using Iron(II) sulfate hexahydrate (Sigma-Aldrich, USA) and hydrogen peroxide (Junsei Chem. Co., Japan). The concentration of Fe$^{2+}$ and hydrogen peroxide were 4 ppm Fe$^{2+}$ and 3 %, respectively. Membrane samples (1 cm $\times$ 2 cm) were prepared in proton form and soaked in 15 mL of Fenton’s solution using 20 mL glass vial. Oxidative stability of the membranes was examined by measuring the weight of dried membranes during Fenton’s oxidation at 60 °C water bath.
Scheme S1 Synthesis of the ESFx-BP copolymers.\(^3\)
Figure S1 (a) Lab-scale continuous pore-filling caster and (b) fabrication of large-size composite membrane using the lab-scale continuous caster. Moving speed of the pPTFE (1.6 cm min$^{-1}$) is controlled by the motor controller and the speed of tension release motor was the same with the speed of driving motor. Maximum width of the caster is 15 cm and the weight of the tension bar (8 g) was determined within the weight that does not shrink the dimension of pPTFE.
**Figure S2** Fabrication of large-size composite membrane using the lab-scale continuous caster. Precise distance control of the continuous casting blade facilitates the formation of a symmetric membrane structure with a uniform surface dense layer.

**Figure S3** Serpentine flow channels for (a) a 5 cm$^2$ single-cell, (b) a 50 cm$^2$ single-cell, and (c) 50 cm$^2$ five-cell stack (the width of each flow channel is 1 mm).
Figure S4 MEAs with active area of 50 cm$^2$: (a) and (b) for single-cell, (c) and (d) for five-cell stack tests.

Figure S5 Five-cell PEFC stack assembly. The stack was assembly at step-wisely increased torque from 5 kg$_f$ cm$^{-1}$ to 45 kg$_f$ cm$^{-1}$ for every 5 kg$_f$ cm$^{-1}$ to provide uniform force distribution.
**Figure S6** Materials affinities between solvents and \( p \)PTFE (*N,N*-dimethylacetamide (DMAc), \( N \)-methyl-2-pyrrolidone (NMP), and tetrahydrofuran (THF)). The \( p \)PTFE was wettable in THF whereas it was not wettable in DMAc and NMP.

**Figure S7** Fabrication of a large size composite membrane (ESF-90-BP-100/\( p \)PTFE) by using (a) original \( p \)PTFE and (b) surface modified \( p \)PTFE.
Figure S8 Large-size (50 cm²) single-cell performances for (a) Nafton® 212 and (b) ESF90-BP-pPTFE membranes at 60 °C, 70 °C, 80 °C, and 90 °C under fully humidified condition.

Figure S9 Each cell voltage recorded during polarization operation for (a) Nafton® 212 and (b) ESF90-BP-pPTFE membranes.
Table S1 Performance (power) summaries of the membranes for scale-up loss calculations\(^a\) (presented power values are obtained from their polarization curves at 80 °C under fully humidified condition).

<table>
<thead>
<tr>
<th>Tests</th>
<th>ESF90-BP-100/pPTFE</th>
<th>Naflon®212</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Power (W)</td>
<td>Power (W)</td>
</tr>
<tr>
<td></td>
<td>at 1 A cm(^{-2})</td>
<td>at max.</td>
</tr>
<tr>
<td>5 cm(^2) single cell</td>
<td>3.35</td>
<td>6.15</td>
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<tr>
<td></td>
<td>2.95</td>
<td>3.85</td>
</tr>
<tr>
<td>50 cm(^2) single-cell</td>
<td>34 (33.5)(^b)</td>
<td>45 (61.5)(^b)</td>
</tr>
<tr>
<td></td>
<td>30 (29.5)(^b)</td>
<td>39 (38.5)(^b)</td>
</tr>
<tr>
<td>50 cm(^2) five-cell stack</td>
<td>167 (170)(^c)</td>
<td>218 (225)(^c)</td>
</tr>
<tr>
<td></td>
<td>154 (150)(^c)</td>
<td>187 (195)(^c)</td>
</tr>
</tbody>
</table>

\(^a\) Scale-up losses (%) were calculated by \((\text{estimated power} - \text{experimental power})/\text{(estimated power)} \times 100.\) Negative losses (no scale-up losses) assumed to be zero.\(^b\) The values in the parenthesis are the estimated power from 5 cm\(^2\) single-cell results without losses.\(^c\) The values in the parenthesis are the estimated power from 50 cm\(^2\) single-cell results without losses.
Figure S10 Extrapolation of OCV decay rate based on the OCV change during 24 h for (a) ADT-I Nafion®212, (b) ADT-II ESF90-BP-100/pPTFE, and (c) ADT-III ESF90-BP-100/pPTFE, respectively. The ADTs were conducted at 100 °C under approximate 10% of RH (T100RH10) and flow rates of H₂ and O₂ gases were 400 cm³ min⁻¹.
Figure S11 Polarization performances of before and after ADT operation for (a) Nafion®212 and (b) ESF90-BP-100/pPTFE.
Figure S12 ESF90-BP-100/pPTFE membranes after (a) ADT-II and (c) ADT-III. The MEAs were prepared by hot-press method and well assembled before the fuel cell application. The 50 cm² electrode however, was easily separated from the membrane (ESF90-BP-100/pPTFE) after fuel cell operation whereas the MEA of Nafion®212 was not detached from the membrane. This binding problem may have affected the relatively low OCV and acceleration of the MEA degradation for the composite membrane.

References