Cost-effective porous-organic-polymer-based electrolyte membranes with superprotonic conductivity and low activation energy

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Preparation.

All solvents and chemicals used in the synthesis were purchased from commercial suppliers and utilized without further purification. Average molecular weight of poly(vinylidene fluoride) (PVDF) powder is ~534,000 by GPC.

Synthesis of 1 and 1S: 1 and 1S were prepared according to the reported method.¹

Synthesis of 1SXM (X = 1, 2, and 3): 1S (200 mg) was sonically dispersed in X M H₂SO₄ aqueous solution (70 mL) (X = 1, 2, and 3) for 6 h. The solid was obtained by certification, and dried under N₂ flowing and then overnight in an oven at 100 ºC.

Synthesis of 1SXP (X = 50 and 60): The mixed matrix membrane (MMM) of 1S/PVDF is labeled as 1SXP (X means the mass percentage of 1S in the membrane). The synthetic procedure of 1S60P was described as a representative. PVDF (200 mg) was fully dissolved in DMF (5 mL), and then 1S (300 mg) was sonically dispersed in the PVDF solution. After stirred at room temperature for 6 h, the viscous homogeneous suspension was prepared. The resultant mixture was carefully poured onto a circular glass plate with a diameter of 8 cm and dried at 40 ºC for 48 h. Finally, the membrane was obtained after peeled off from the plate. The other MMM (1S50P) were fabricated from the same procedure except for the mass percentage of 1S.

Synthesis of 1SXMP (X = 1, 2, and 3): The MMM of 1SX/PVDF is labeled as 1SXMP (the mass percentage of 1SX in the membrane was set at 60%). The synthetic procedure of 1SXMP is identical to that of 1SXP except for using 1SX instead of 1S.

Physical Measurements. Infrared spectra were obtained with ATR module using a Nicolet iS10 FT-IR spectrometer. Thermogravimetric analysis (TGA) was carried out in N₂ (99.999 %) atmosphere (flow rate = 30 mL / min) in the temperature range 30 – 600 ºC (heating rate = 10 ºC/min) using a Scinco TGA-N 1000. Deionized water in experiment is purified by aqua MAX™ Basic360 series. Elemental analyses for C, H, N, and S were performed at the Elemental Analysis Service Center of Sogang University. XPS were measured from Semiconductor & Display Green Manufacturing Research Center in Korea University using X-tool. Solid state ¹³C NMR experiments waere analyzed using 400 MHz Avance II+ Bruker Solid-state NMR (spinning rate: 9.5 kHz or 12 kHz, delay time(d1): 3 s, contact time: 2 ms, radio frequency: 100.4 MHz, calibration: TMS ; 0 ppm) at KBSI Seoul Western Center. EDX analysis was performed from at KBSI Seoul Center using Hitachi SU-70.
Gas Sorption Measurements. Before sorption analysis, the samples were degassed at 120 °C in vacuum for 10 hours. All gases used in measurements were highly pure (99.999 %) except for water vapor and O₂ (99.995%). H₂ and N₂ gas sorption measurement at 77 K was carried out on a Micrometrics 3 Flex instrument up to 1 atm of gas pressure. Water vapor isotherms at 298 K were performed using a Micrometrics ASAP2020 from vapor source after additionally purification using ASAP2020. O₂ isotherms at 195 K were collected by a BEL Belsorp mini II up to 1 atm of gas pressure. Filled and open symbols indicate adsorption and desorption, respectively.

Impedance Analyses. All pellets for measuring AC impedance data were prepared by homogeneously grinding the powder samples with a mortar and pestle and pressed at 2,000 ~ 4,500 kg for minutes. Whereas all membranes were intactly used. The thickness of the pellets was ranging from 0.01 to 0.05 cm and these diameter was averagely 0.5 cm. When all samples were measured, the pellet was placed in a home-made sample holder composed of Pt-based electrodes and the holder was located in a temperature and humidity controlled chamber which is ESPEC SH-222/Bench-top type. To equilibrium of temperature and humidity in the chamber, the sample was waited over 6 – 24 hours before AC measurements. And to obtain more accurate data, impedance data were collected repeatedly until the value-convergence. AC measurements were carried out using a Solartron SI 1260 Impedance/Gain-Phase Analyzer and Dielectric Interface with Pt-pressed electrodes and applied AC voltage amplitude of 100 mV and frequency range of 3 MHz – 0.1 Hz. ZView and ZPlot software were used to analyze and fit impedance plot to acquire the resistance value through designed equivalent circuit. Then, the accurate conduction values and activation energies were calculated using equations in blow.

\[ \sigma = \frac{L(cm)}{A(\pi r^2)} \times R(\Omega) \]

\[ \ln(\sigma T) = \ln(\sigma_0 T) - \frac{E_a}{K_b} \left( \frac{1}{T} \right) \]

Single PEMFC Test. MEAs were prepared by forming catalyst-coated gas diffusion layers. Electrodes were prepared by spraying the Pt/C (46.7 wt%) catalyst ink containing Nafion ionomer onto the porous carbon paper (GDL, 39BC-SGL). The catalyst loading amounts were 0.2 mg cm⁻² for anode and 0.4 mg cm⁻² for cathode. 1S3MP was placed between two catalyst coated GDL using Teflon gasket. The active area was 1 cm². The MEA was arranged between the graphite bipolar plates for single cell. The performance of prepared single cells was assessed at 50 °C and 100% RH for both anode and cathode with
gas flow rate of 200 cc min$^{-1}$, H$_2$ for anode and 600 cc min$^{-1}$ O$_2$ for cathode. The OCV hold test was conducted with same condition.
**Table S1.** Elemental analysis data about all samples.

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<tbody>
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<td>1S</td>
<td>53.43</td>
<td>3.19</td>
<td>8.35</td>
<td>0</td>
</tr>
<tr>
<td>1S1M</td>
<td>28.37</td>
<td>4.40</td>
<td>10.76</td>
<td>0</td>
</tr>
<tr>
<td>1S2M</td>
<td>19.38</td>
<td>5.00</td>
<td>14.73</td>
<td>0</td>
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<td>4.72</td>
<td>18.60</td>
<td>0</td>
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<td>1S3MP</td>
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<td>4.83</td>
<td>14.01</td>
<td>3.41</td>
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Fig. S1. IR spectra of 1S, 1S1M, 1S2M, and 1S3M.
Fig. S2. Solid-state $^{13}$C NMR spectra for 1S, 1S1M, and 1S2M. In case of 1S3M, the NMR data could not be collected due to severe noise from H$_2$SO$_4$ in 1S3M.
**Fig. S3.** SEM images for the \( \text{H}_2\text{SO}_4 \) impregnated samples. (x 5,000, x 10,000, and x 25,000)
Fig. S4. TGA data for 1S, 1S1M, 1S2M, and 1S3M. Initial weight loss indicated the evaporation of water molecules.
**Fig. S5.** N$_2$ isotherms at 77 K and pore size distributions of 1S, 1S1M, 1S2M, and 1S3M. The distributions were calculated using Tarazona NLDFT method. The horizontal and vertical axes in the distribution curves represent pore width (Å) and differential pore volume (cm$^3$ g$^{-1}$).
Fig. S6. To correct inductance error on high frequency area, an equivalent circuit was used in the impedance spectra fitting the samples.
Fig. S7. IR spectra of 1S, 1S50P, 1S60P, and PVDF.
Fig. S8. Solid-state $^{13}$C NMR spectra for 1S50P and 1S60P. Peaks observed at ~ 44 and ~ 120 ppm are assignable to carbons of -CH$_2$- and -CF$_2$-, respectively.$^2$
Fig. S9. Survey scan of XPS data for (a) 1S50P and (b) 1S60P.
Fig. S10. EDX spectra of (a) 1S50P and (b) 1S60P membranes. The peak of Cl is due to the fact that sulfonation process via chlorosulfonic acid treatment produced both –SO₃H and –SO₂Cl species. The peak of Pt is due to the fact that the samples were coated by Pt for EDX measurements to avoid a charge problem.
Fig. S11. SEM images for 1S50P with different magnifications.
Fig. S12. SEM images for 1S60P with different magnifications.
Fig. S13. TGA data for 1S50P and 1S60P. Initial weight loss indicated evaporation of solvent molecules like water and DMF.
Fig. S14. N₂ isotherms of 1S50P and 1S60P at 77 K.
Fig. S15. Nyquist plots for 1S50P at several temperatures and 90% RH condition. (30 °C – black, 40 °C – red, 50 °C – blue, 60 °C – magenta, 70 °C – navy, and 80 °C – purple)
Fig. S16. IR spectra of 1S1MP, 1S2MP, and 1S3MP.
Fig. S17. Solid-state $^{13}$C NMR spectra for 1S1MP, 1S2MP, and 1S3MP. Peaks related carbon of -CH$_2$- and -CF$_2$- were observed at ~ 44 and ~ 120 ppm, respectively.$^2$
Fig. S18. XPS data of 1S1MP, 1S2MP, and 1S3MP.
Fig. S19. EDX spectra of (a) 1S1MP, (b) 1S2MP, and (c) 1S3MP.
Fig. S20. SEM images for (a) 1S1MP, (b) 1S2MP, and (c) 1S3MP. (x 500, x 5,000, and x 25,000)
Fig. S21. TGA data for 1S1MP, 1S2MP and 1S3MP.
Fig. S22. N$_2$ isotherms of 1S1MP, 1S2MP, and 1S3MP at 77 K.
Fig. S23. Nyquist plots for 1S1MP, 1S2MP, and 1S3MP at several temperatures and 90% RH condition. (30 °C – black, 40 °C – red, 50 °C – blue, 60 °C – magenta, 70 °C – navy, and 80 °C – purple)
Fig. S24. A Nyquist plot for 1S3MP at 20 °C and 90% RH condition.
Fig. S25. Proton conductivities during heating–cooling cycle of 1S3MP at 90% RH.
Fig. S26. RH dependence of proton conductivity for 1S3MP at 25 °C.
Fig. S27. Long-term performance of 1S3MP at 80 °C and 90% RH.
Fig. S28. FT-IR spectra of as-prepared 1S3MP and 1S3MP after long-term measurements.
Fig. S29. SEM images for 1S3MP the membrane after conductivity measurements.
Fig. S30. Representation of membrane electrode assembly (MEA) cell. Test conditions were as follows. Cell temperature = 50 °C and 100 % RH, area = 1 cm² cathode/anode, catalyst loading (Pt/C 46.7 wt%) of anode = 0.2 mg cm⁻² and cathode = 0.4 mg cm⁻², flow rate of H₂ = 200 cc min⁻¹, flow rate of O₂ = 0.6 cc min⁻¹.
Table S2. List of porous organic materials-based MEA performance in order of power density.

<table>
<thead>
<tr>
<th>Compounds(form)</th>
<th>OCV (V)</th>
<th>Maximum current density (mA cm(^{-2}))</th>
<th>Maximum powder density (mW cm(^{-2}))</th>
<th>T (°C)</th>
<th>RH (%)</th>
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</thead>
<tbody>
<tr>
<td>1S3MP (film)(^{\text{this work}})</td>
<td>0.921</td>
<td>173</td>
<td>77</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>1S (pellet)(^1)</td>
<td>0.95</td>
<td>148</td>
<td>56</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>1ES (pellet)(^4)</td>
<td>0.72</td>
<td>150</td>
<td>50</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>PTSA@TpAzO COFM (film)(^5)</td>
<td>0.81</td>
<td>90</td>
<td>24</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>PA@TpBpy-MC (pellet)(^b)</td>
<td>0.86</td>
<td>29</td>
<td>7</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>MOF-801@PP-60 (film)(^7)</td>
<td>0.95</td>
<td>4.53</td>
<td>2.2</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>PA@TpBpy-ST (pellet)(^b)</td>
<td>0.66</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>0</td>
</tr>
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</table>
Fig. S31. Polarization curves of single cell with back pressure of 1.8 bar. The cell test was performed by cycling potential sweeping between 0.2–1.0 $V_{\text{RHE}}$ for 30 cycles. Test conditions were as follows. Cell temperature = 50 °C and RH = 100%, area = 1 cm$^2$ cathode/anode; catalyst loading (Pt/C 46.7 wt%) of anode = 0.2 mg cm$^{-2}$ and cathode = 0.4 mg cm$^{-2}$; flow rate of H$_2$ = 200 cc min$^{-1}$; O$_2$ = 600 cc min$^{-1}$.
Fig. S32. SEM images of 1S3MP membrane before and after OCV hold test.
Fig. S33. H₂ crossover current densities of MEAs with 1S3MP and Nafion membrane. Test conditions were as follows. Cell temperature = 27 °C and 100%, flow rate of H₂ = 200 cc min⁻¹; N₂ = 600 cc min⁻¹.
Fig. S34. Polarization curve of single cell with back pressure of 1.8 bar. The cell temperature was maintained at 27 °C. Test conditions were as follows. Cell temperature = 27 °C and RH 100%, area : 1 cm² cathode/anode; catalyst loading (Pt/C 46.7 wt%) of anode = 0.2 mg cm⁻² and cathode = 0.4 mg cm⁻²; flow rate of H₂ = 200 cc min⁻¹; O₂ = 600 cc min⁻¹.