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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 H_2SO_4 aqueous solution (70 mL) (X = 1, 2, and 3) for 6 h. The solid was obtained by certification, and dried under N_2 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 **1SXM**/PVDF is labeled as **1SXMP** (the mass percentage of **1SXM** in the membrane was set at 60%). The synthetic procedure of **1SXMP** is identical to that of **1SXP** except for using **1SXM** 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 N_2 (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^{TM} 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 ^{13}C 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 O_2 (99.995%). H_2 and N_2 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. O_2 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 homogeously 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 controllded 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 eneries were calculated using equations in blow.

$$\sigma = \frac{L(cm)}{A(\pi r^2) * R(\Omega)}$$

$$\ln(\sigma \mathrm{T}) = \ln(\sigma_o \mathrm{T}) - \frac{E_a}{K_b}\left(\frac{1}{\mathrm{T}}\right)$$

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 cm^2. The MEA was arranged between the graphite bipolar plates for single cell. The performance of prepared single cells was assessed at 50 ℃ 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 anylsis data about all samples.

Compounds	C(%) Expt.	H(%) Expt.	S(%) Expt.	N(%) Expt.
1S	53.43	3.19	8.35	0
1S1M	28.37	4.40	10.76	0
1S2M	19.38	5.00	14.73	0
1S3M	20.73	4.72	18.60	0
1S50P	44.93	4.08	7.39	1.96
1S60P	46.58	4.31	8.08	2.42
1S1MP	48.18	4.10	5.57	2.53
1S2MP	44.32	4.58	8.41	2.64
1S3MP	39.30	4.83	14.01	3.41

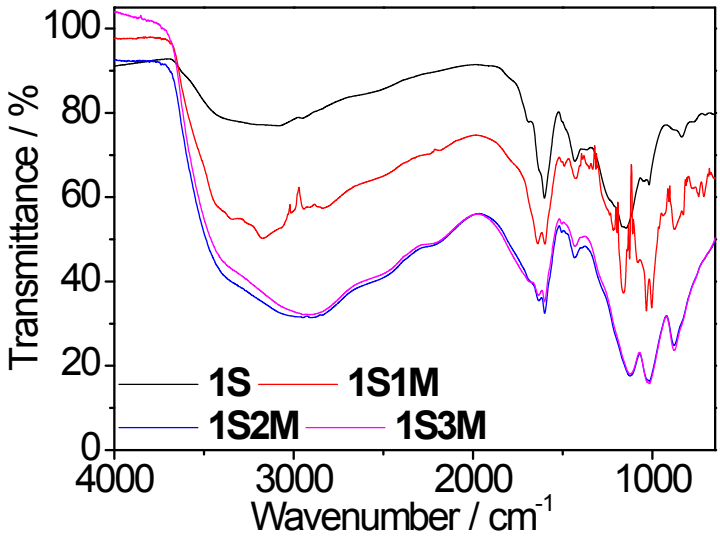


Fig. S1. IR spectra of **1S**, **1S1M**, **1S2M**, and **1S3M**.

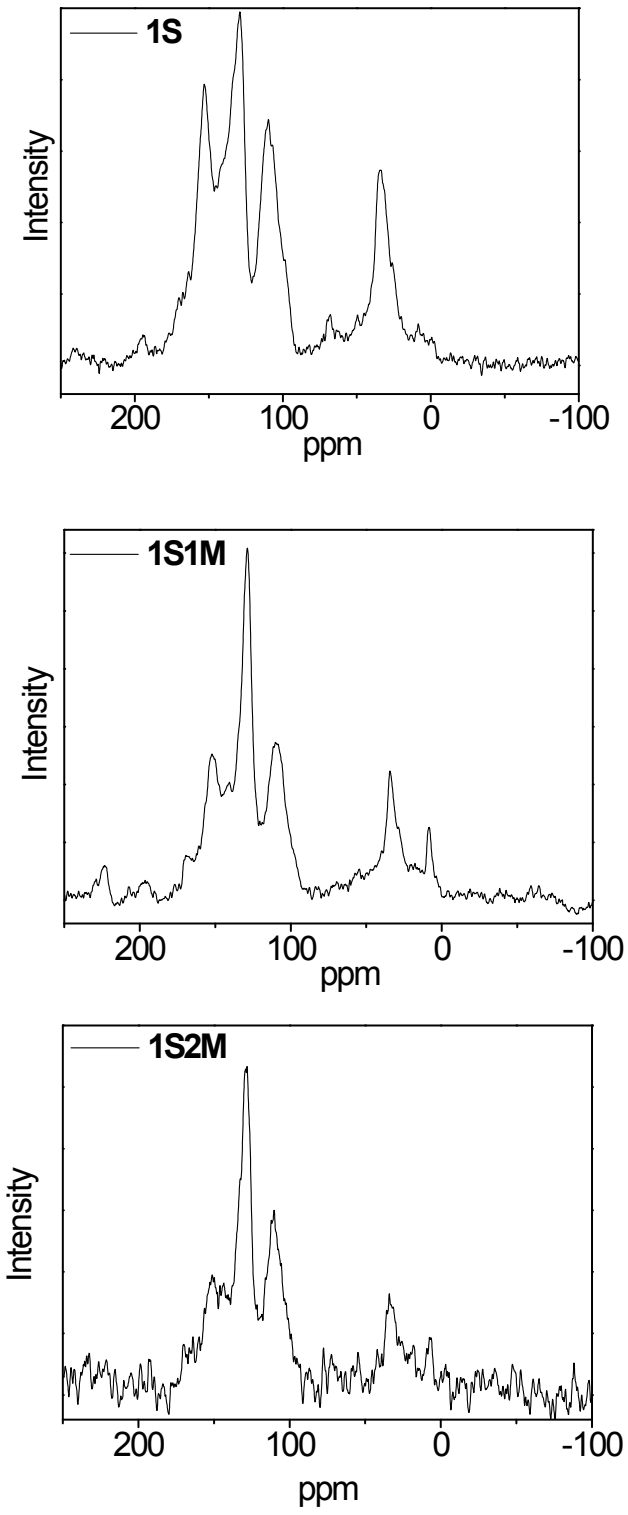
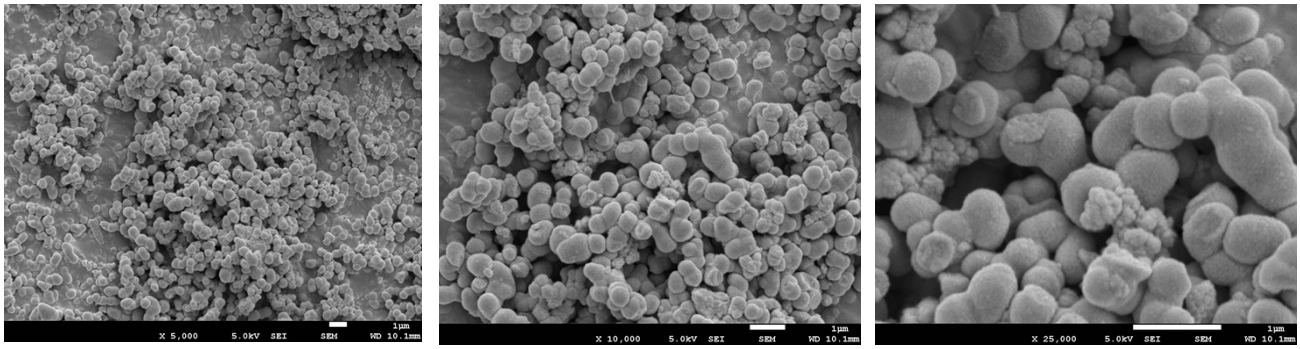
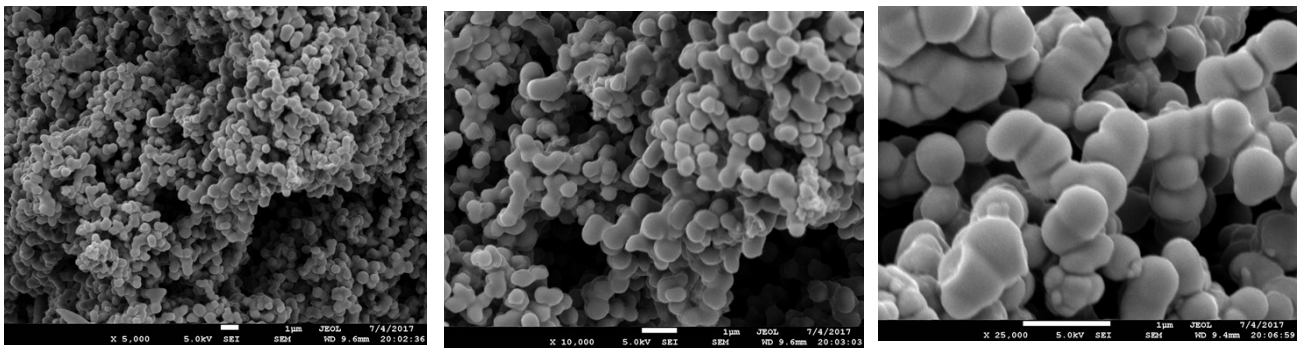


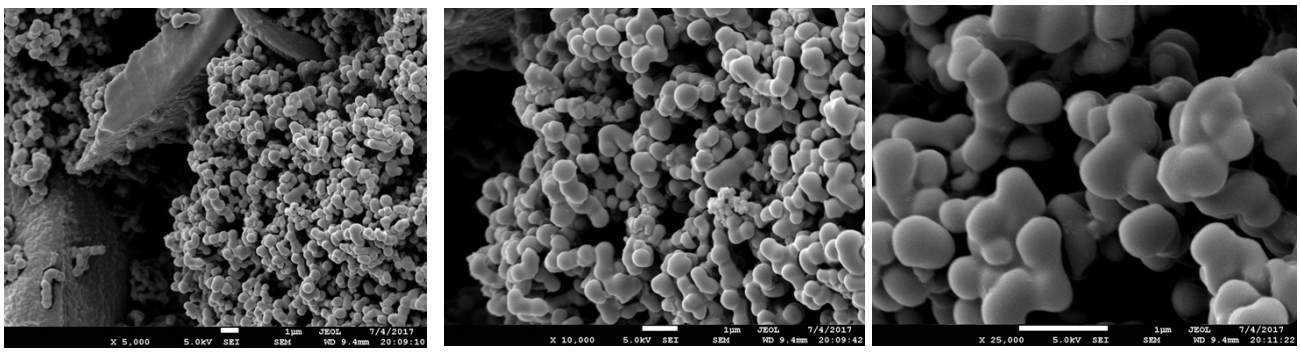
Fig. S2. Solid-state ^{13}C NMR spectra for **1**S, **1S1M**, and **1S2M**. In case of **1S3M**, the NMR data could not be collected due to severe noise from H_2SO_4 in **1S3M**.



1S1M

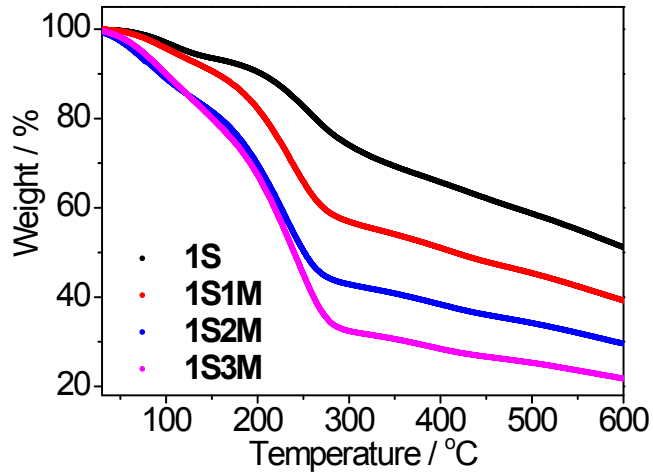


1S2M

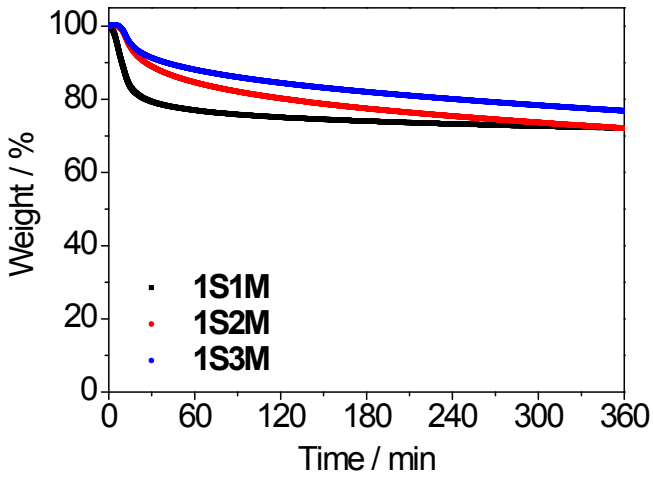


1S3M

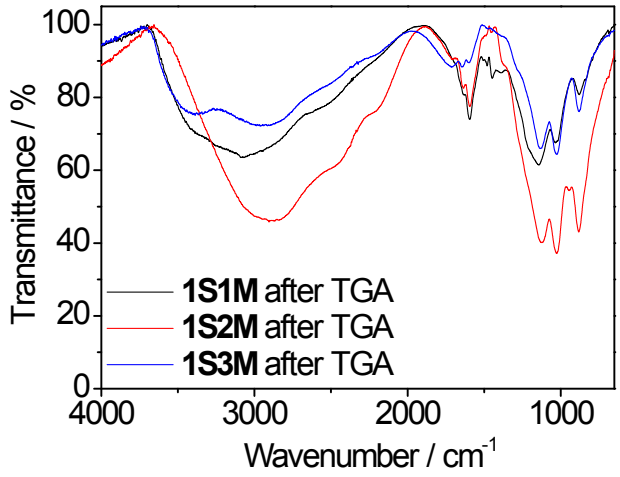
Fig. S3. SEM images for the H_2SO_4 impregenated samples. (x 5,000, x 10,000, and x 25,000)



(a)



(b)



(c)

Fig. S4. TGA data for **1S**, **1S1M**, **1S2M**, and **1S3M**. Initial weight loss indicated the evaporation of water molecules.

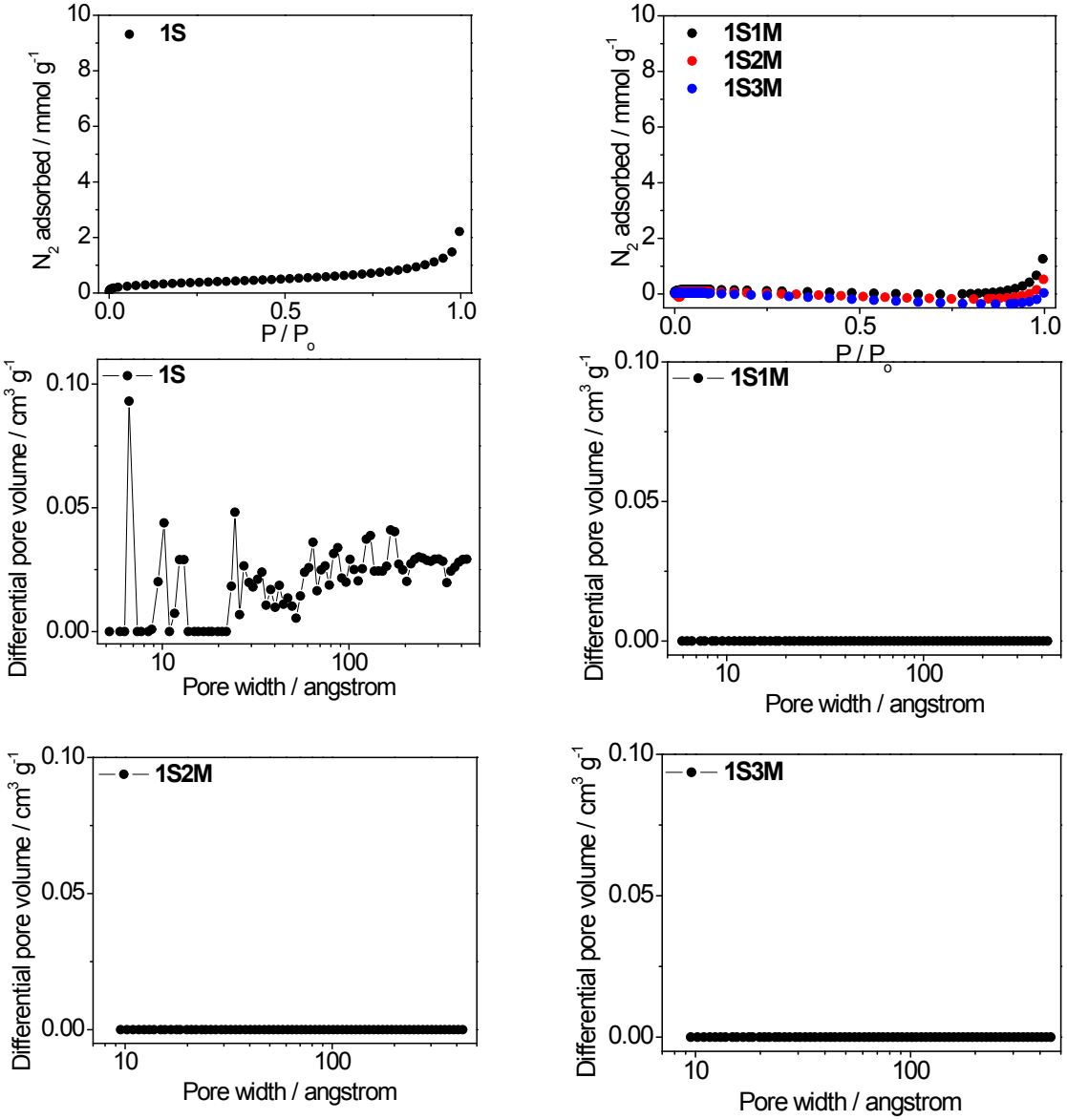


Fig. S5. N_2 isotherms at 77 K and pore size distributions of **1S**, **1S1M**, **1S2M**, and **1S3M**. The distributions were calculated using Tarazona NLDFT method. The horizontal and vertical axes in the distribution curves represent pore width (Å) and differential pore volume ($cm^3\ g^{-1}$).

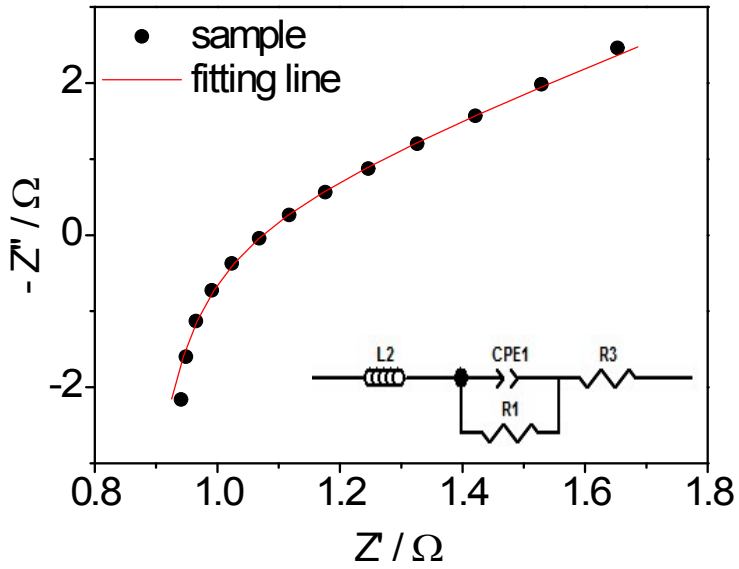


Fig. S6. To correct inductance error on high frequency area, a equivalent circuit was used in the impedance spectra fitting the samples.

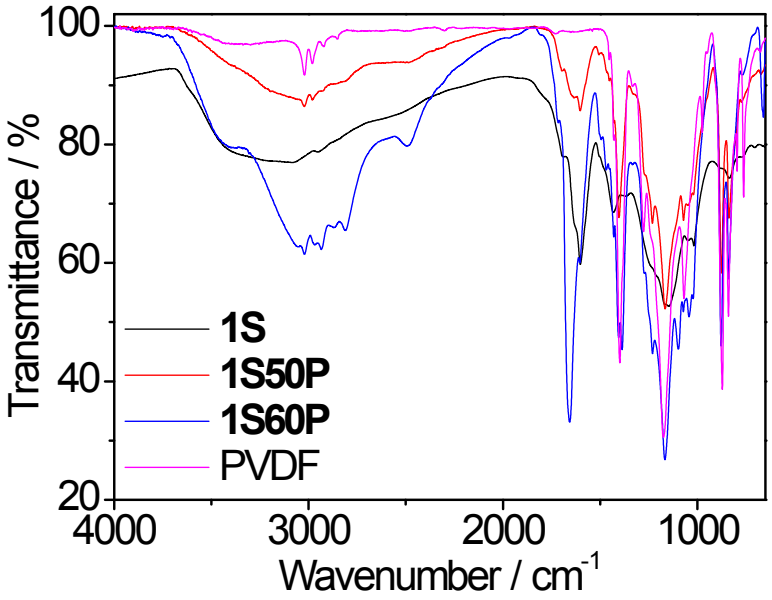


Fig. S7. IR spectra of **1S**, **1S50P**, **1S60P**, and **PVDF**.

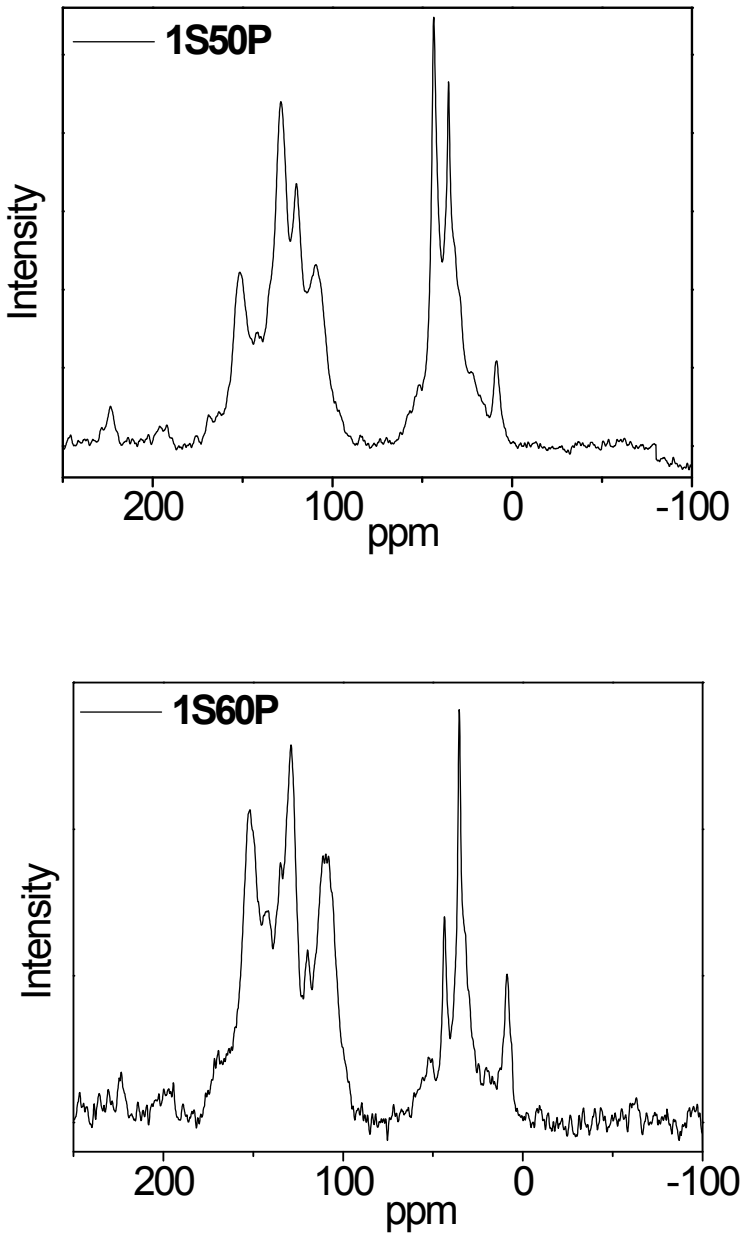


Fig. S8. Solid-state ^{13}C NMR spectra for **1S50P** and **1S60P**. Peaks observed at ~ 44 and ~ 120 ppm are assignable to carbons of $-CH_2-$ and $-CF_2-$, respectively.[2]

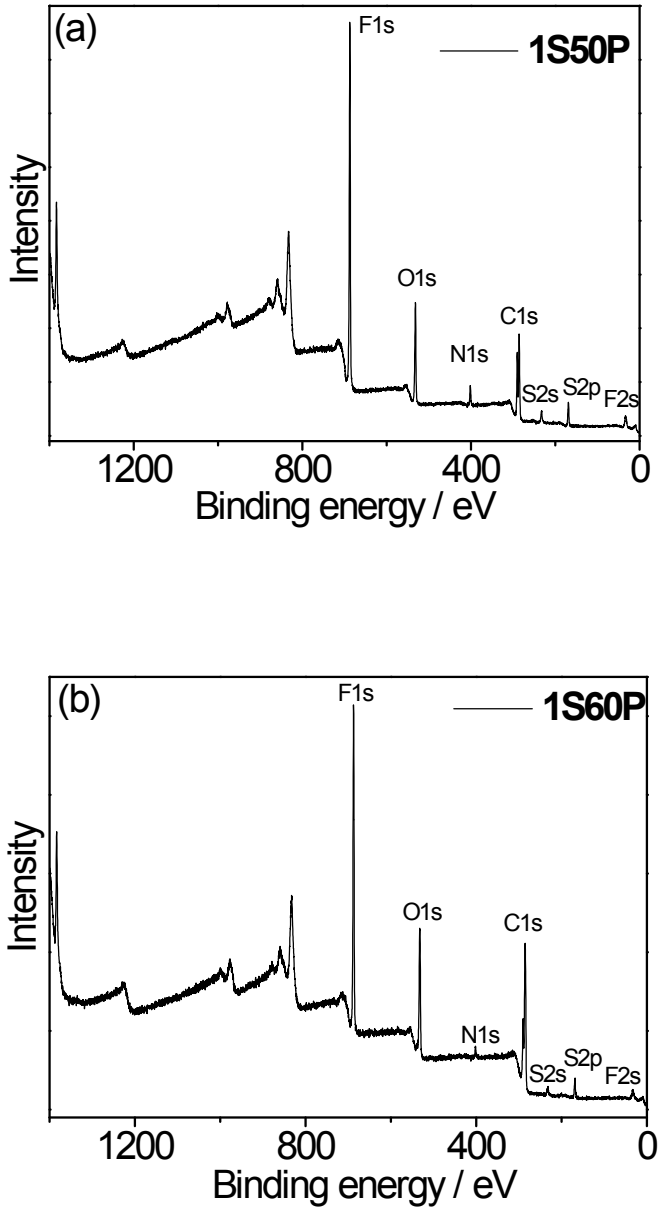
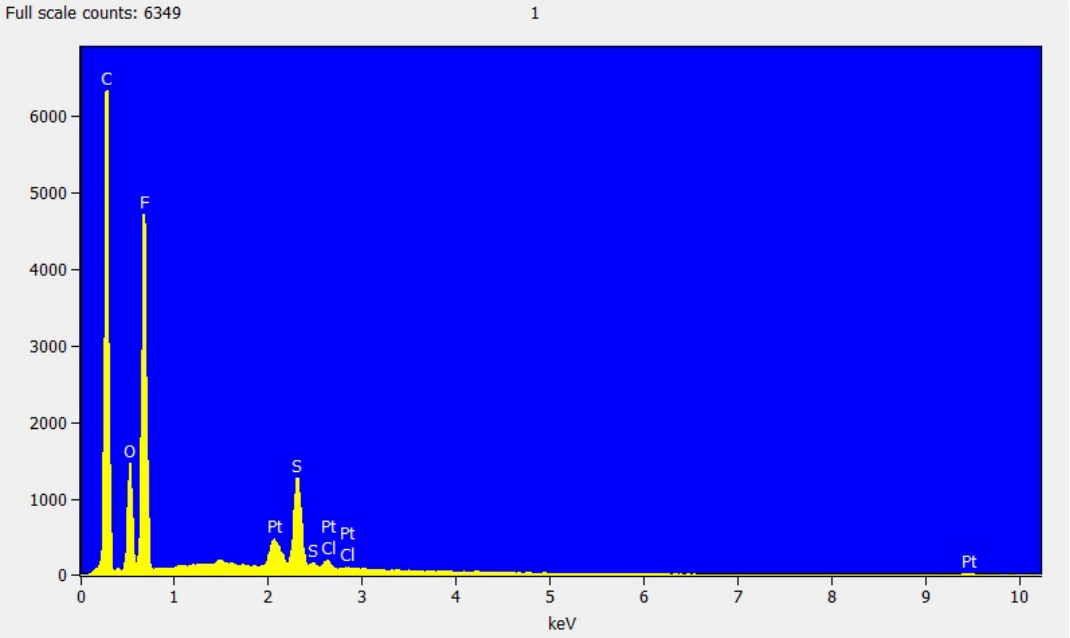
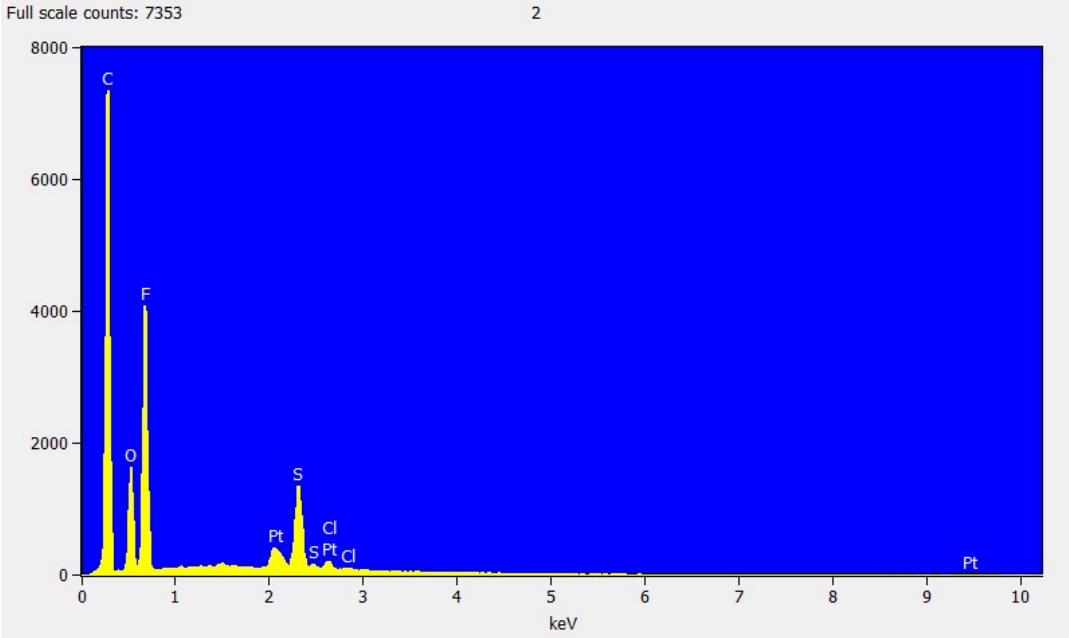


Fig. S9. Survey scan of XPS data for (a) **1S50P** and (b) **1S60P**.

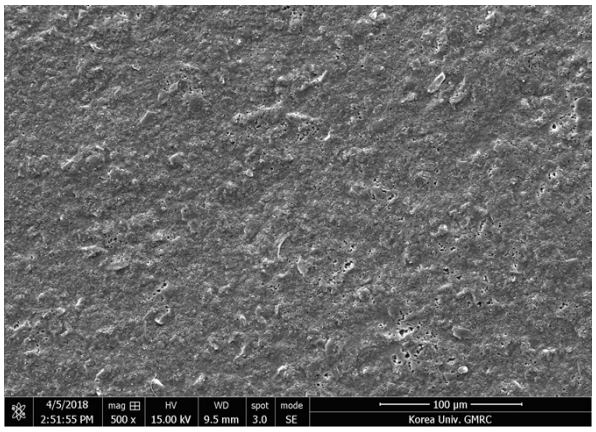


(a)

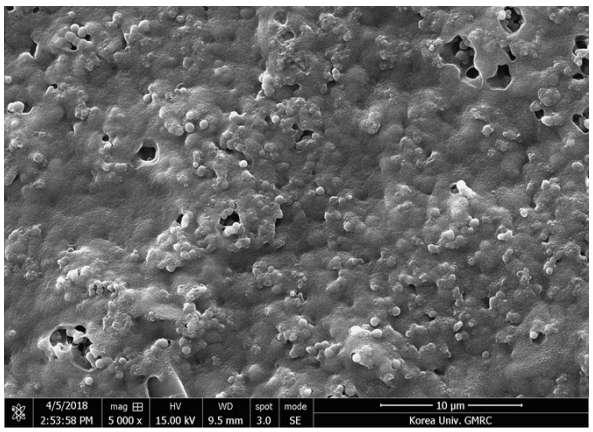


(b)

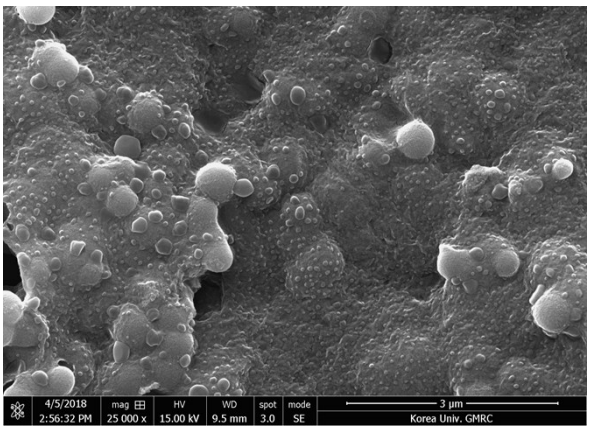
Fig. S10. EDX spectra of (a) **1S50P** and (b) **1S60P** membrames. The peak of Cl is due to the fact that sulfonation process via chlorosulfonic acid treatment produced both $–SO_3H$ and $–SO_2Cl$ species.[3] The peak of Pt is due to the fact that the samples were coated by Pt for EDX measurements to avoid a charge problem.



(a) x 500

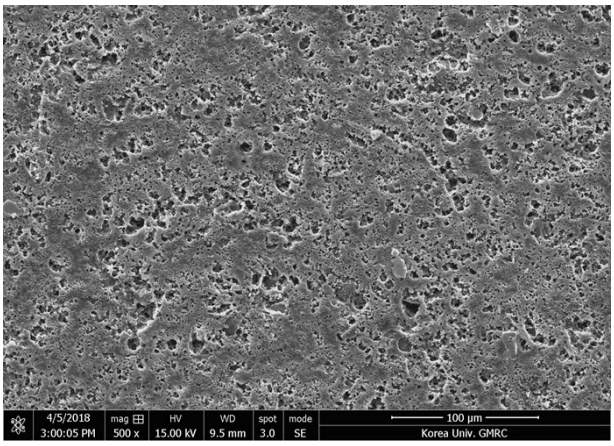


(b) x 5,000

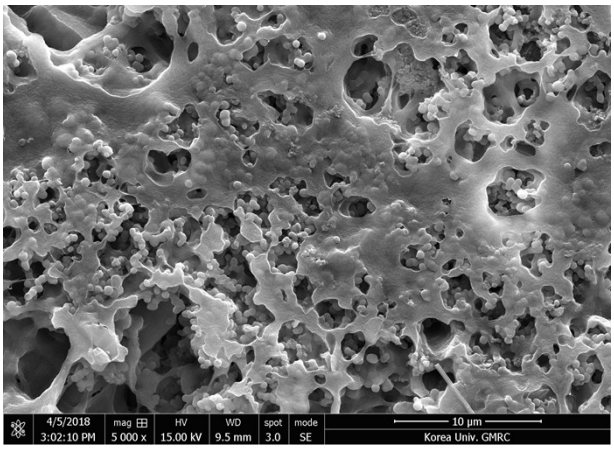


(c) x 25,000

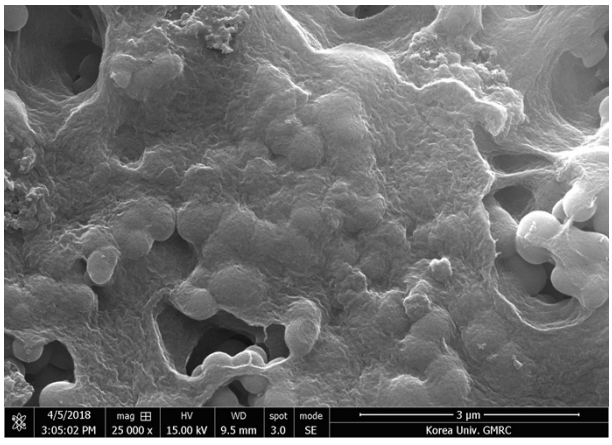
Fig. S11. SEM images for **1S50P** with different magnifications.



(a) x 500



(b) x 5,000



(c) x 25,000

Fig. S12. SEM images for **1S60P** with different magnifications.

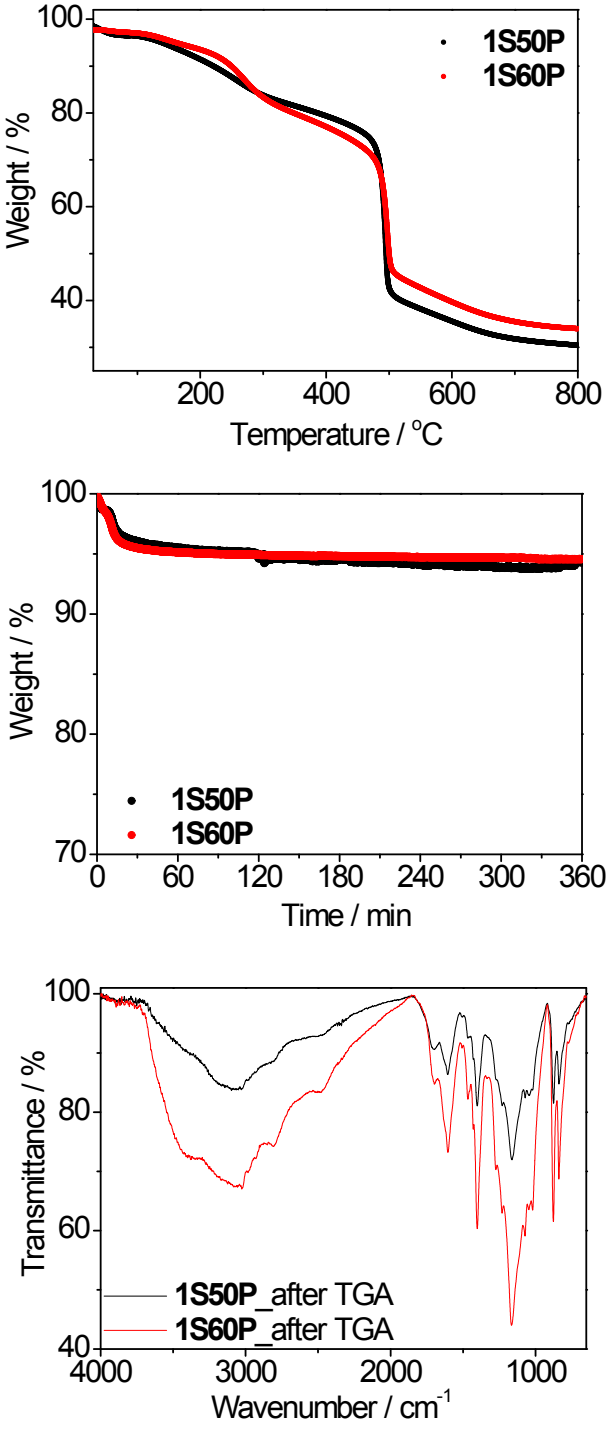


Fig. S13. TGA data for **1S50P** and **1S60P**. Initial weight loss indicated evaporation of solvent molecules like water and DMF.

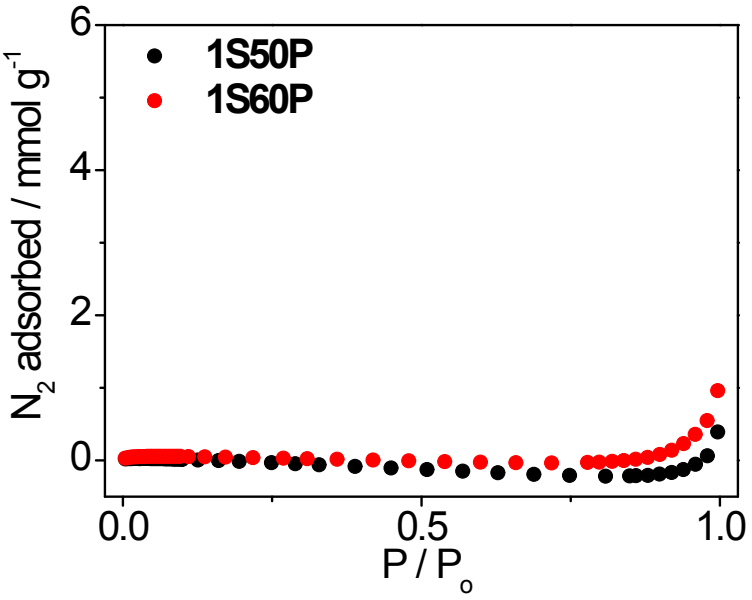


Fig. S14. N_2 isotherms of **1S50P** and **1S60P** at 77 K.

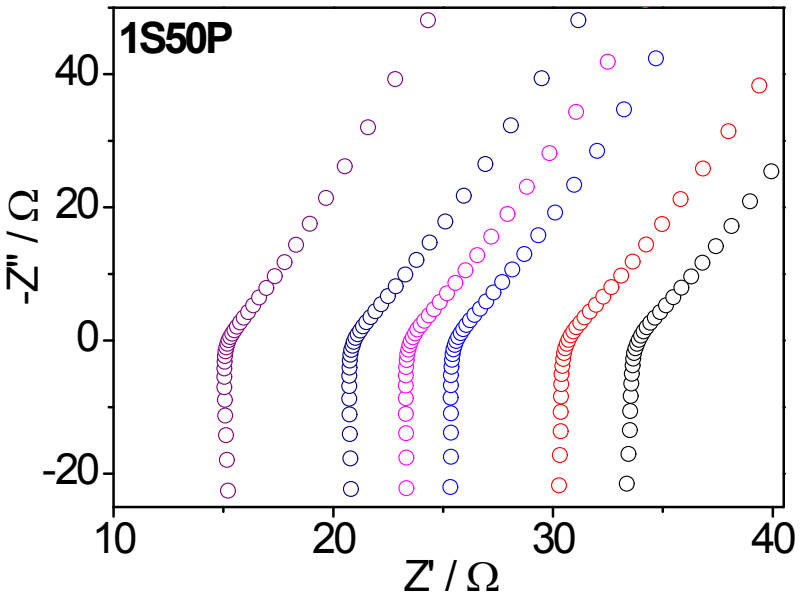


Fig. S15. Nyquist plots for **1S50P** at several temperatures and 90% RH condition. (30 °C – black, 40 °C – red, 50 °C – blue, 60 °C –magenta, 70 °C – navy, and 80 °C – purple)

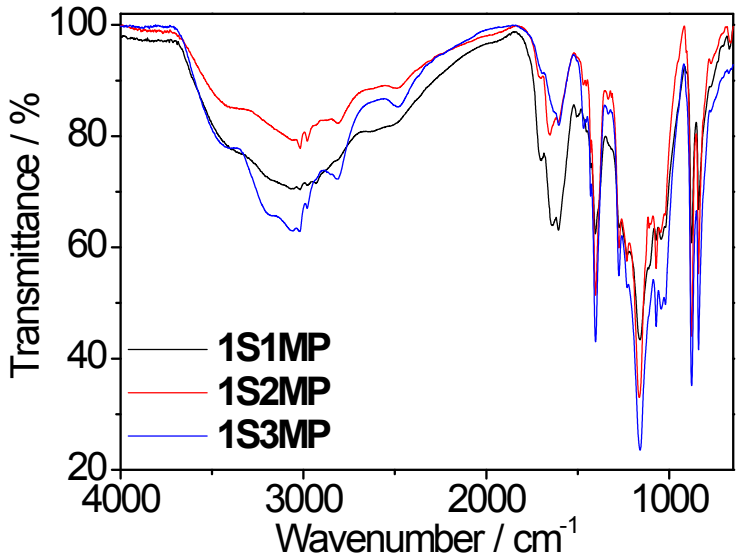


Fig. S16. IR spectra of **1S1MP**, **1S2MP**, and **1S3MP**.

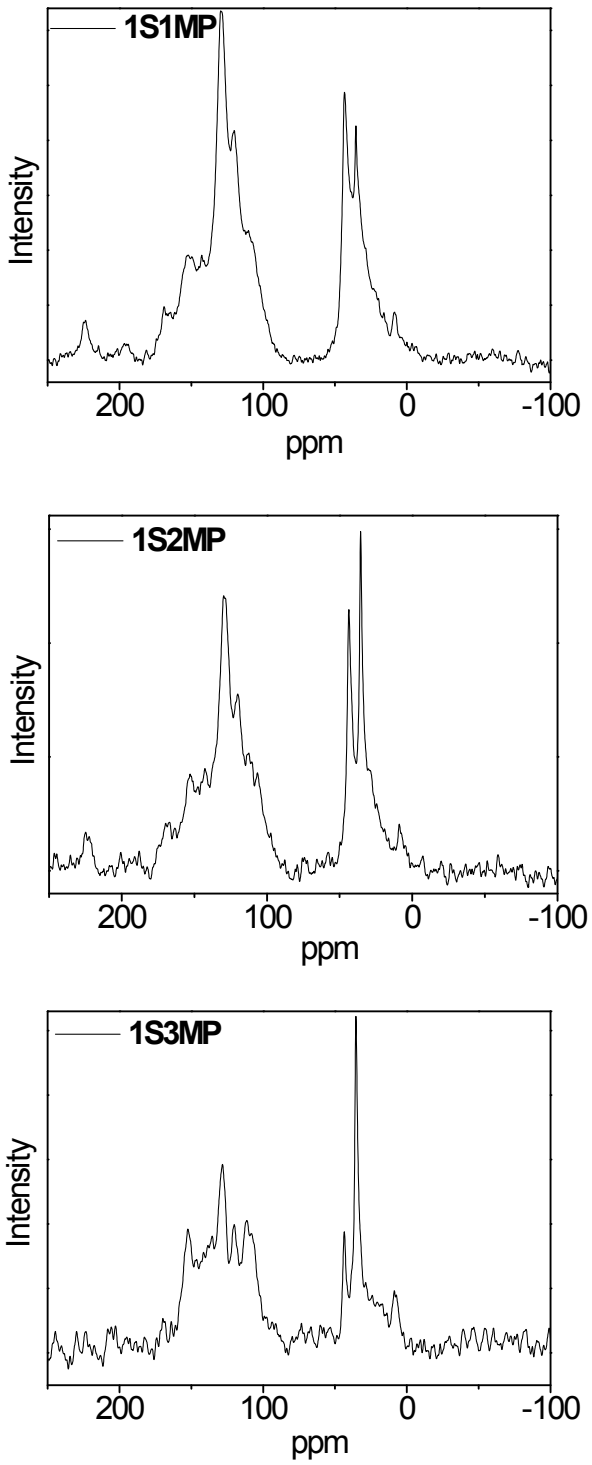


Fig. S17. Solid-state ^{13}C NMR spectra for **1S1MP**, **1S2MP**, and **1S3MP**. Peaks related carbon of -CH_2- and -CF_2- were observed at ~ 44 and ~ 120 ppm, respectively.[2]

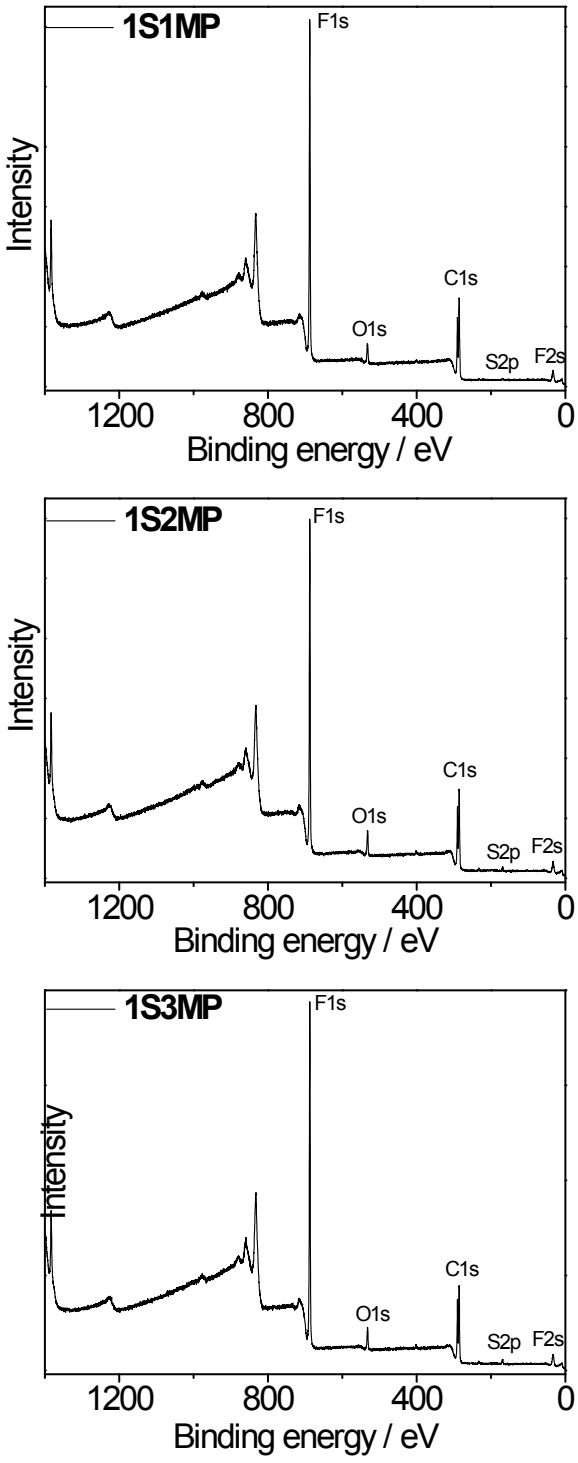
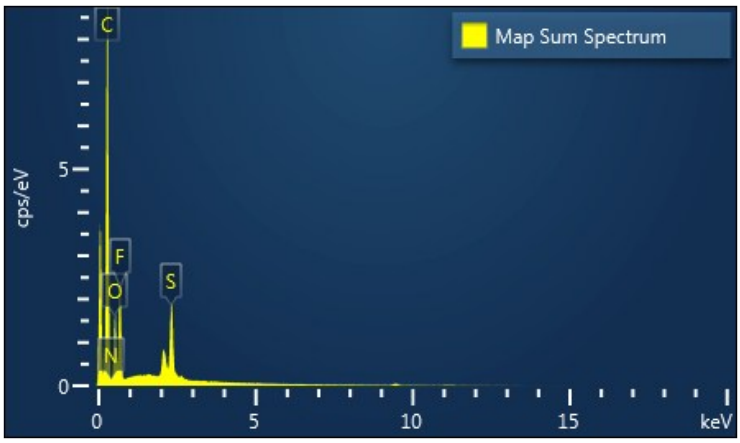
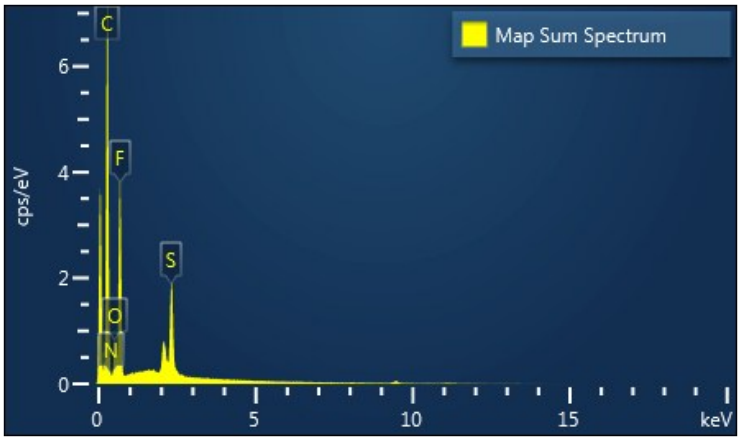


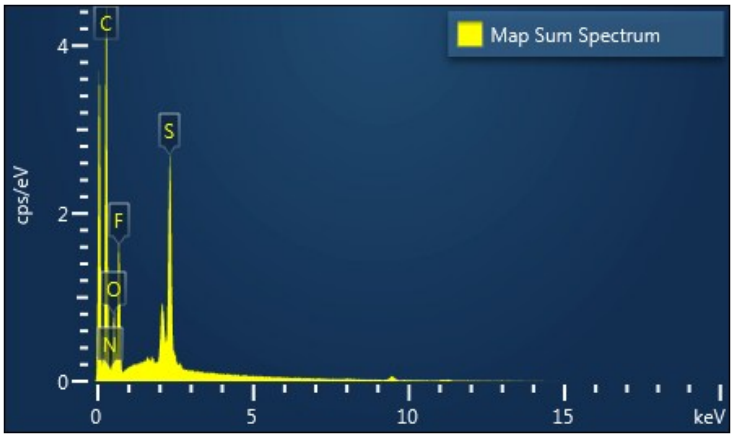
Fig. S18. XPS data of **1S1MP**, **1S2MP**, and **1S3MP**.



(a)

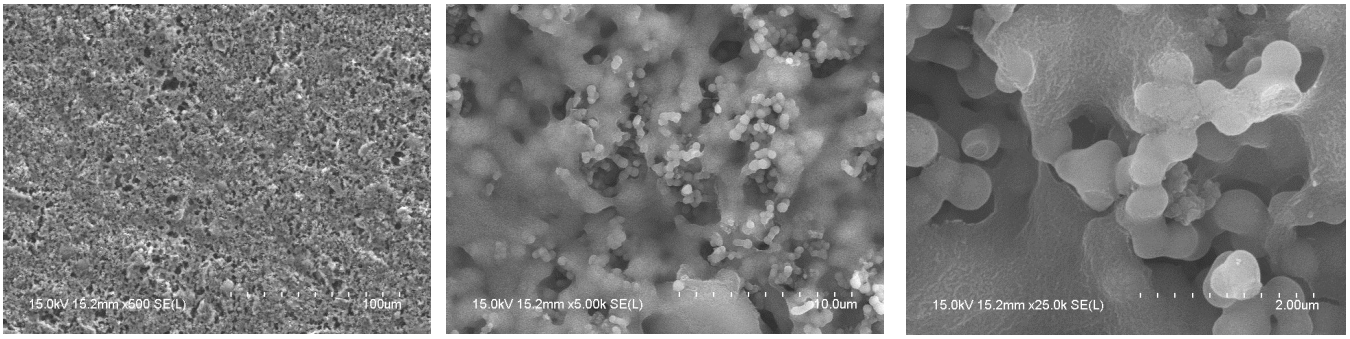


(b)

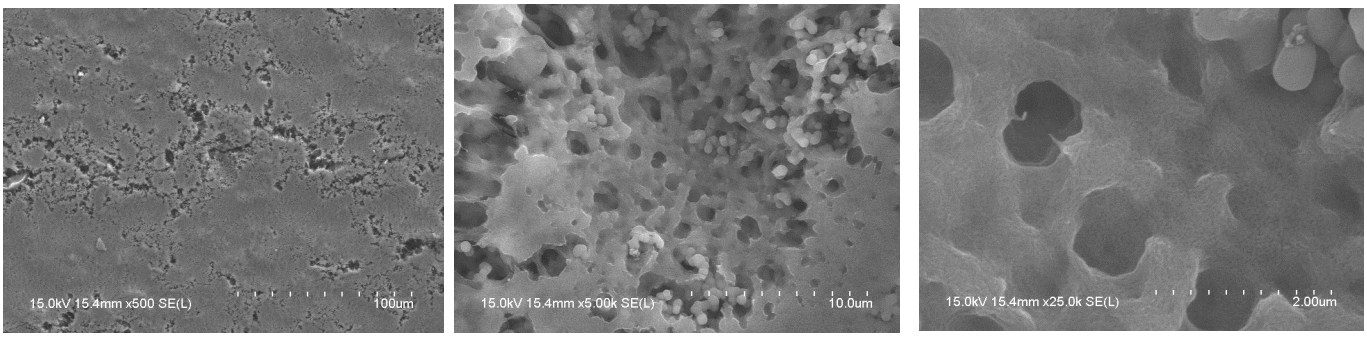


(c)

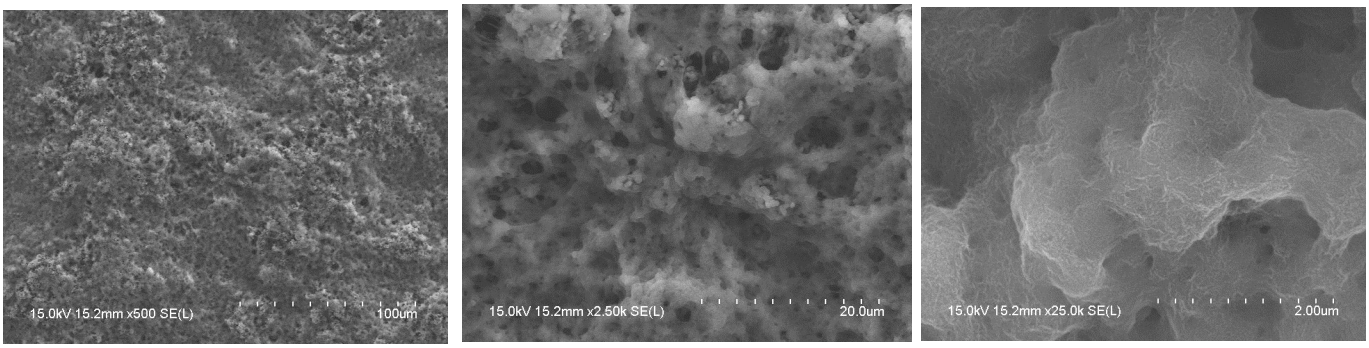
Fig. S19. EDX spectra of (a) **1S1MP**, (b) **1S2MP**, and (c) **1S3MP**.



(a)



(b)



(c)

Fig. S20. SEM images for (a) **1S1MP**, (b) **1S2MP**, and (c) **1S3MP**. (x 500, x 5,000, and x 25,000)

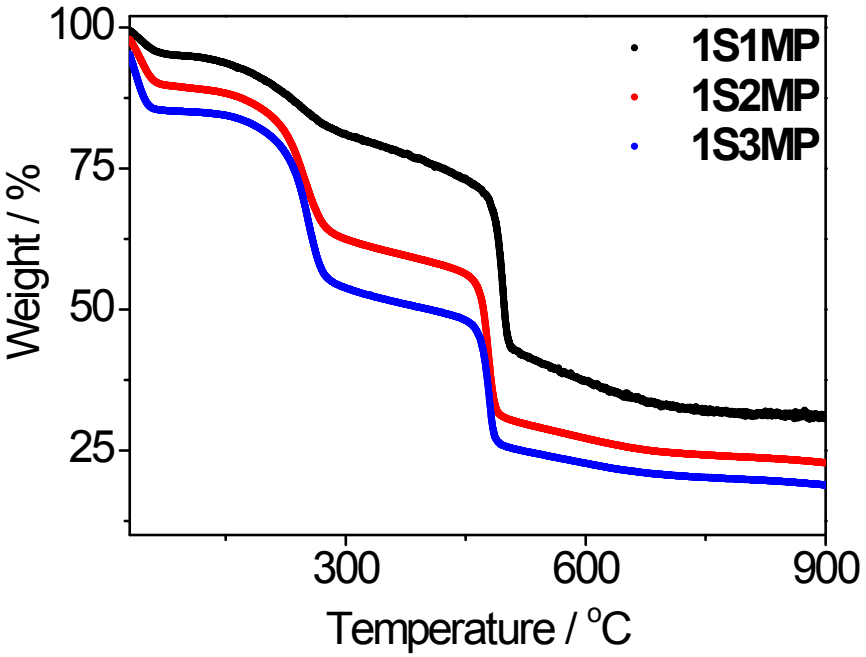


Fig. S21. TGA data for **1S1MP**, **1S2MP** and **1S3MP**.

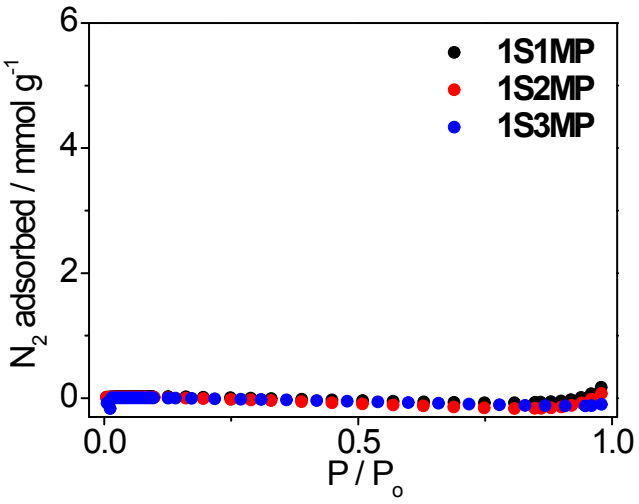


Fig. S22. N_2 isotherms of **1S1MP**, **1S2MP**, and **1S3MP** at 77 K.

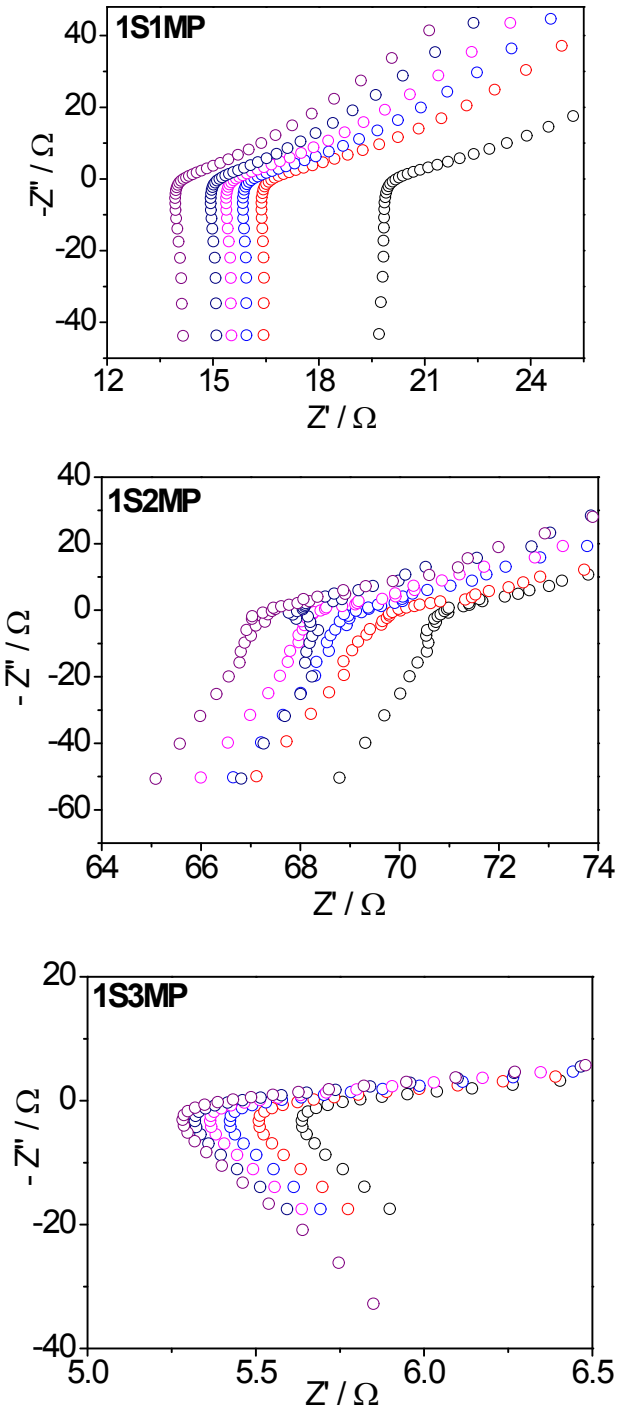


Fig. S23. Nyquist plots for **1S1MP**, **1S2MP**, and **1S3MP** at several temperatures and 90% RH condition. (30 °C – black, 40 °C – red, 50 °C – blue, 60 °C –magenta, 70 °C – navy, and 80 °C – purple)

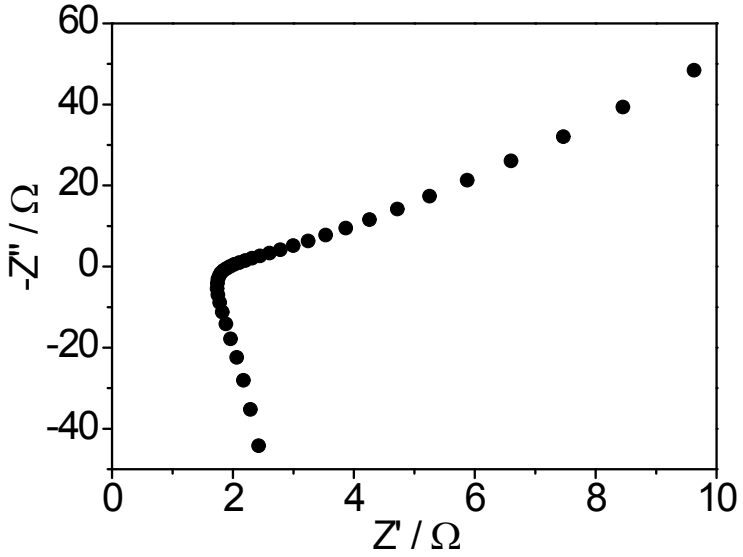


Fig. S24. A Nyquist plot for **1S3MP** at 20 °C and 90% RH condition.

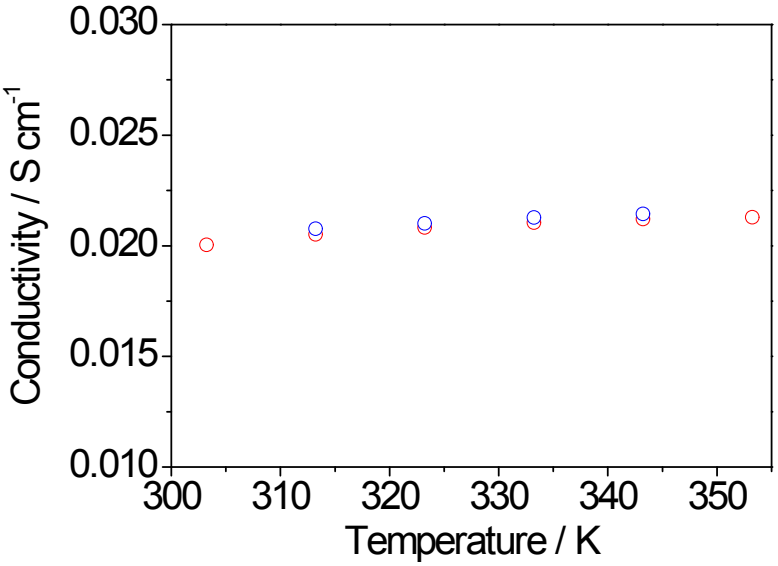


Fig. S25. Proton conductivities during heating–cooling cycle of **1S3MP** at 90% RH.

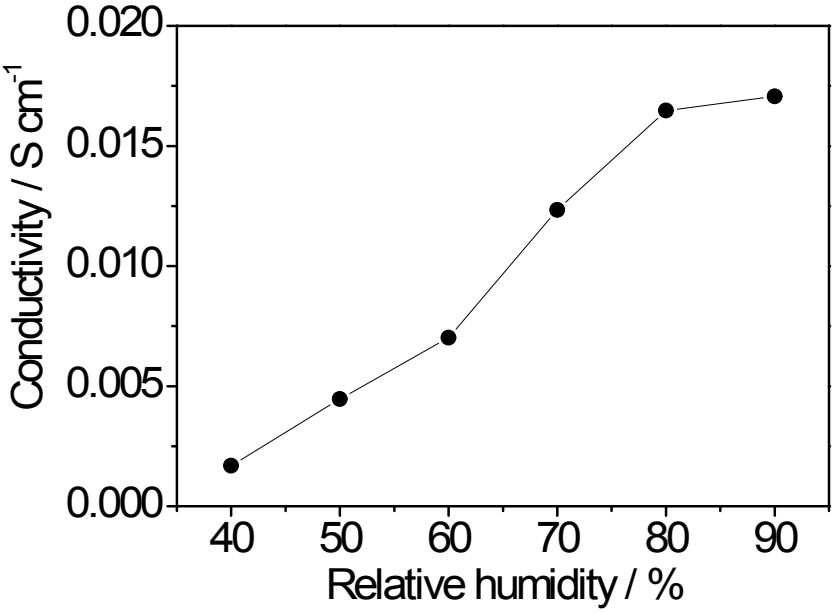


Fig. S26. RH dependence of proton conductivity for **1S3MP** at 25 °C.

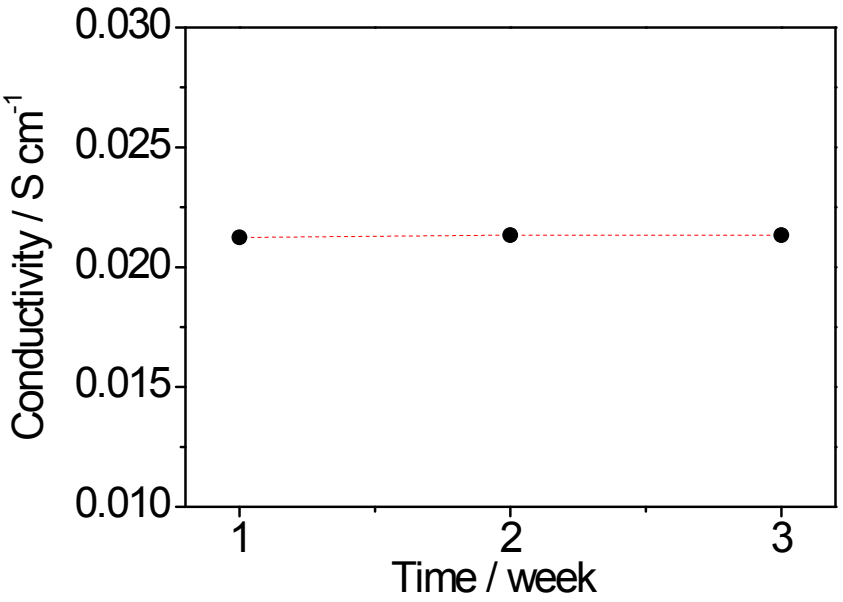


Fig. S27. Long-term performance of **1S3MP** at 80 °C and 90% RH.

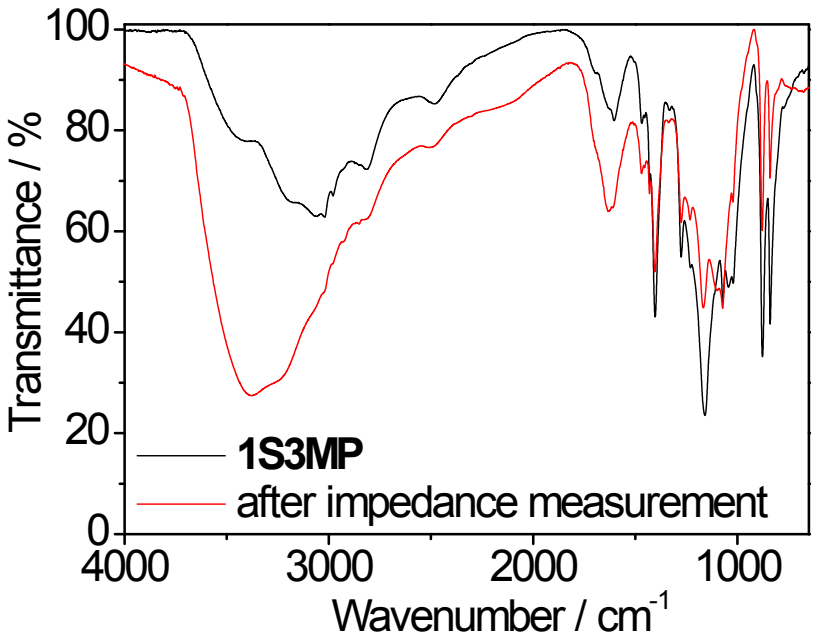
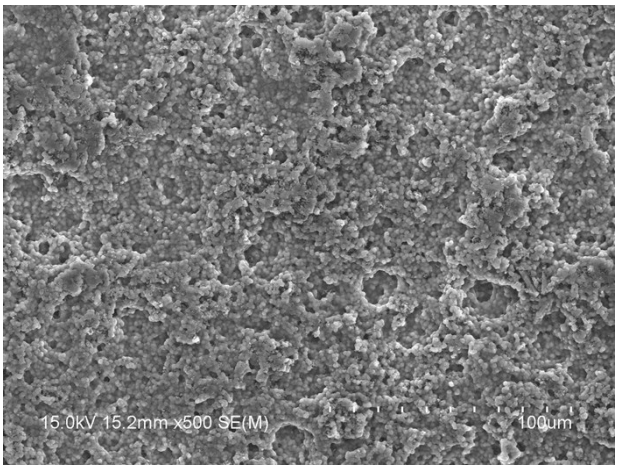
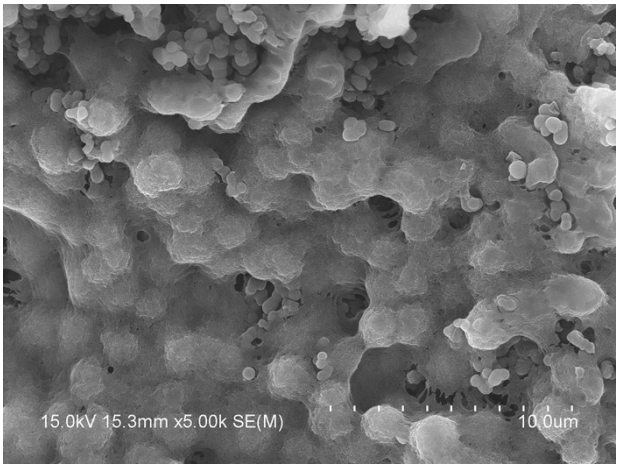


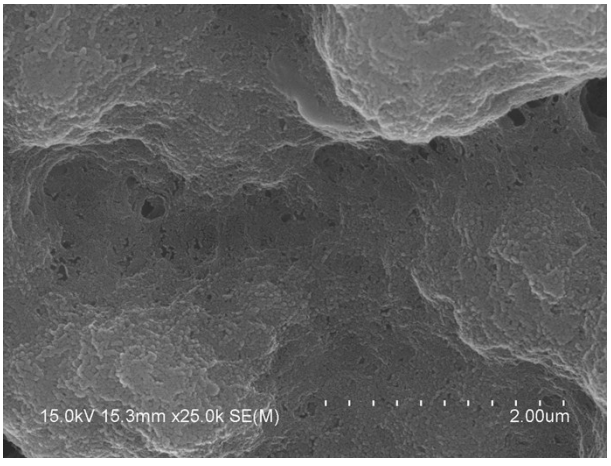
Fig. S28. FT-IR spectra of as-prepared **1S3MP** and **1S3MP** after long-term meausurements.



(a) x 500



(b) x 5,000



(c) x 25,000

Fig. S29. SEM images for **1S3MP** the membrane after conductivity measurements.

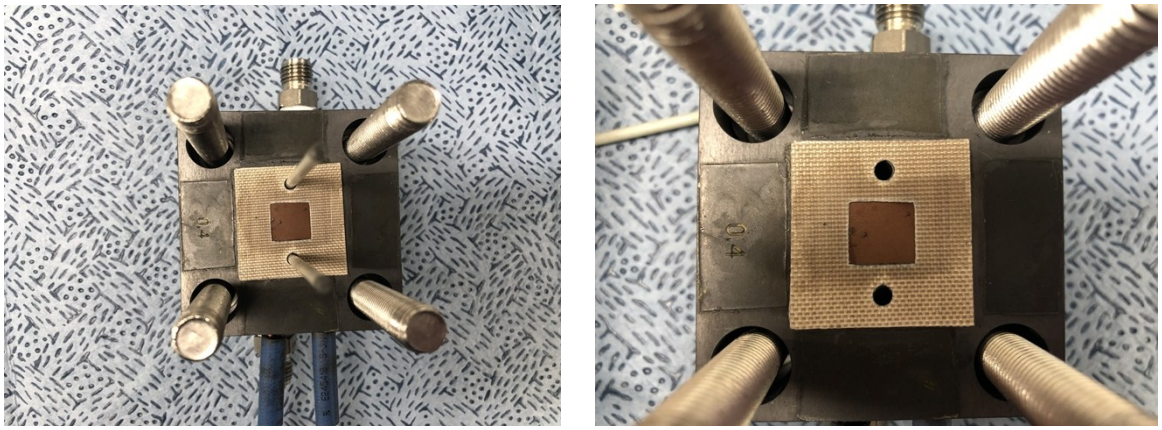


Fig. S30. Representation of membrane electrode assembly (MEA) cell. Test conditions were as follows. Cell temperature = 50 ^{o}C and 100 % RH, area = 1 cm^2 cathode/anode, catalyst loading (Pt/C 46.7 wt%) of anode = 0.2 mg cm^{-2} and cathode = 0.4 mg cm^{-2}, flow rate of H_2 = 200 cc min^{-1}, flow rate of O_2 = 0.6 cc min^{-1}.

Table S2. List of porous organic materials-based MEA performenace in order of power density.

Compounds(form)	OCV (V)	Maximum current density (mA cm^{-2})	Maximum powder density (mW cm^{-2})	T (^oC)	RH (%)
1S3MP (film) this work	0.921	173	77	50	100
1S (pellet)[1]	0.95	148	56	80	100
1ES (pellet)[4]	0.72	150	50	80	100
PTSA@TpAzo COFM (film)[5]	0.81	90	24	60	100
PA@TpBpy-MC (pellet)[6]	0.86	29	7	50	0
MOF-801@PP-60 (film)[7]	0.95	4.53	2.2	30	100
PA@TpBpy-ST (pellet)[6]	0.66	-	-	50	0

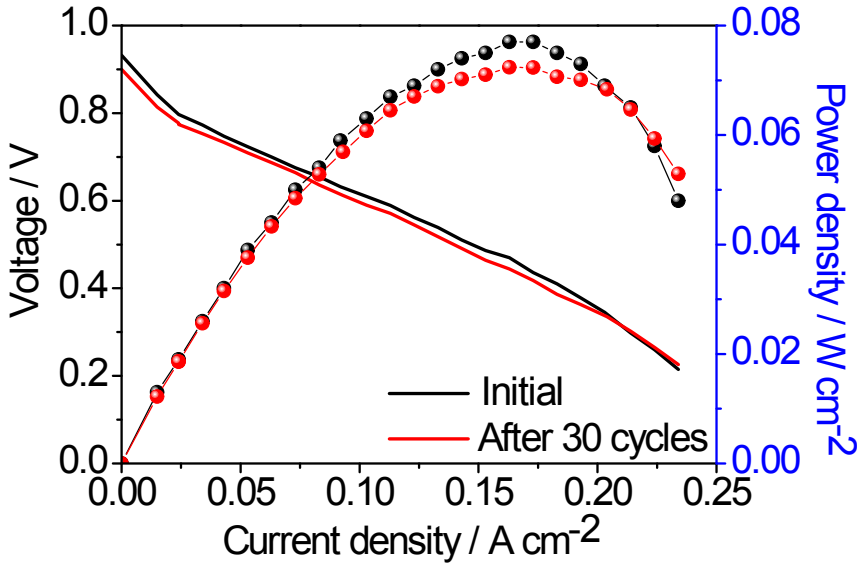


Fig. S31. Polarization curves of single cell with back pressure of 1.8 bar. The cell test was performed by cycling potential sweeping between 0.2–1.0 V_{RHE} for 30 cycles. Test conditions were as follows. Cell temperature = 50 ℃ and RH = 100% , area = 1 cm^2 cathode/anode; catalyst loading (Pt/C 46.7 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}.

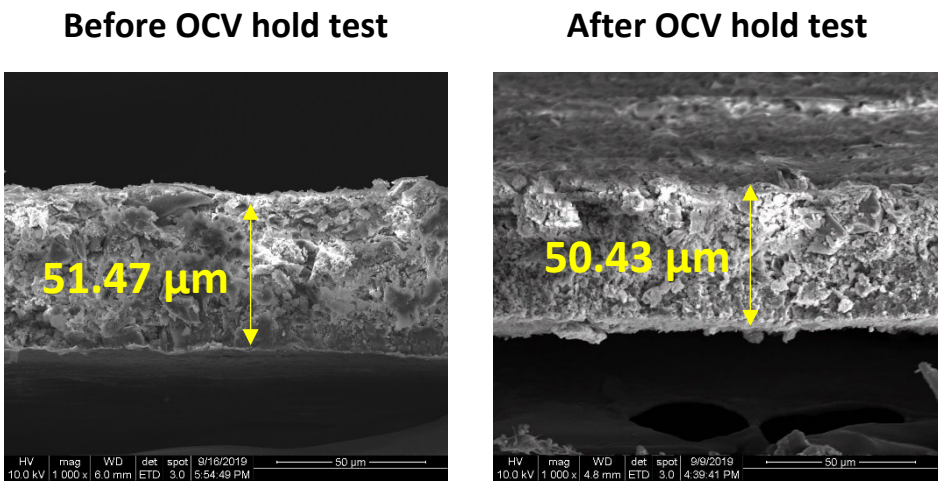


Fig. S32. SEM images of **1S3MP** membrane before and after OCV hold test.

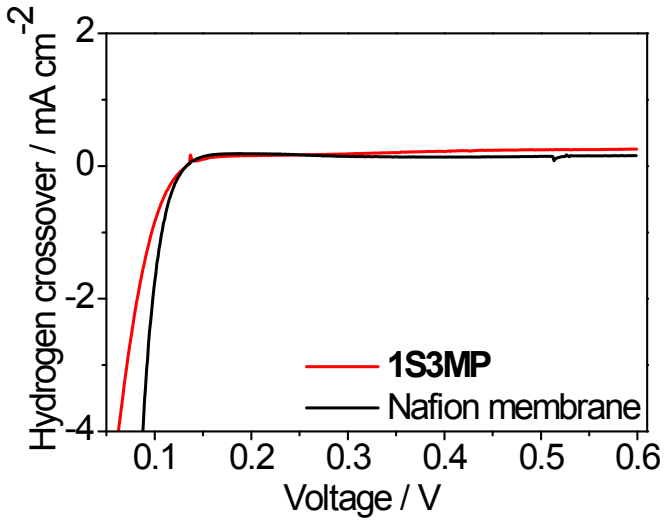


Fig. S33. H_2 crossover current densities of MEAs with **1S3MP** and Nafion membrane. Test conditions were as follows. Cell temperature = 27 ℃ and 100% , flow rate of H_2 = 200 cc min^{-1}; N_2 = 600 cc min^{-1}.

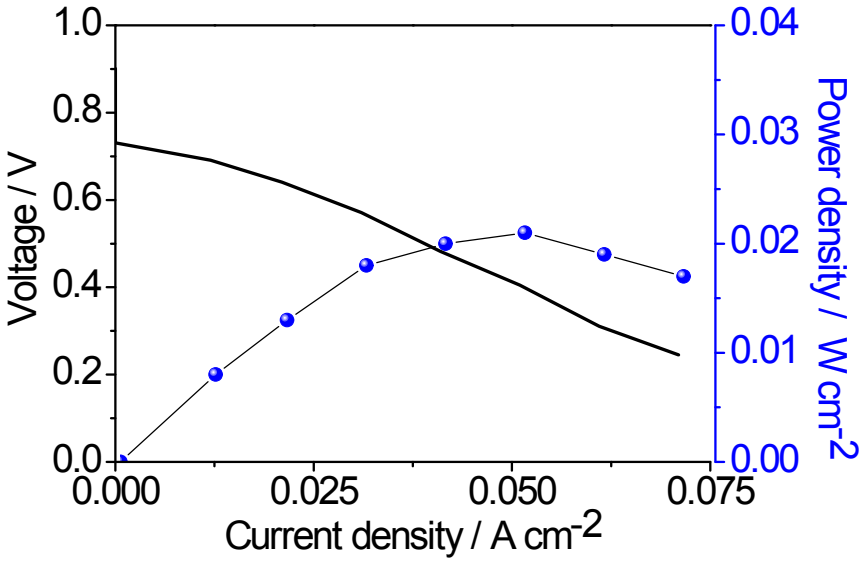


Fig. S34. Polarization curve of single cell with back pressure of 1.8 bar. The cell temperature was maintained at 27 °C. Test conditions were as follows. Cell temperature = 27 ℃ and RH 100% , area : 1 cm^2 cathode/anode; catalyst loading (Pt/C 46.7 wt%) of anode = 0.2 mg cm^{-2} and cathode = 0.4 mg cm^{-2}; flow rate of H_2 = 200 cc min^{-1}; O_2 = 600 cc min^{-1}.

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