**Supplementary Information**

# Reinforcement effect in tandemly sulfonated, partially fluorinated polyphenylene PEMs for fuel cells

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**Experimental section**

**1. Preparation of reinforced membranes**

The polymer (BSP-TP-f-4.1) was dissolved in dimethyl acetamide (15-20 wt) and then, uniformly spread onto a flat glass plate (preirradiated with plasma light) with a bar coater (slit width = 71.2 μm) to form a coating layer. Over this layer, a porous PE substrate (preirradiated with plasma light for 1 min on both sides to improve the compatibility with the solvent) was placed and impregnated. Additional polymer solution was placed on the top and spread with the bar coater (slit width = 177.8 μm). Then, a silicone sheet (2 mm thick, polydimethylsiloxane, ASONE Corporation) was placed on the coating layer to prevent the entry of air bubbles (no additional pressure was applied other than the original weight of the silicone sheet). After being dried at room temperature for 48 h, the silicone sheet was removed and the reinforced membrane was peeled off from the glass plate and immersed in 1 M hydrochloric acid and pure water, respectively, and dried to afford the target PE-reinforced membrane.

**2. Preparation of catalyst coated membrane (CCM)**

The catalyst ink was prepared by mixing Pt/CB (carbon black) (TEC10E50E, Tanaka Kikinzoku Kogyo K. K.), ethanol, pure water, and Nafion dispersion (IEC = 0.95-1.03 meq $g^{-1}$, D-521, DuPont) for 30 min by a ball mill. The mass ratio of Nafion ionomer to the carbon black was set to be 0.7. The obtained ink was evenly sprayed on both sides of the membrane with a square geometric area of 4.41 $cm^2$ using a pulse swirl spray machine. The CCM was dried at 60 ºC overnight and then, hot-pressed at 140 ºC at 1.0 MPa for 3 min. For the polarization test, the Pt loading amount in the catalyst layer was adjusted to be 0.50 ± 0.02 mg $cm^{-2}$ on both the cathode and the anode for the comparison with our previous work. For the *in-situ* durability test, the Pt loading was 0.1 ± 0.02 (cathode) and 0.2 ±

0.02 mg cm$^{-2}$ (anode), respectively, according to the United States Department of Energy (US DOE) protocol.[1]

## 3. Measurements

**NMR spectra**. $^1$H and $^{19}$F NMR spectra were measured by a JEOL JNM-ECA ECX500 using deuterated dimethyl sulfoxide (DMSO-$d_6$) containing 1 vol% tetramethylsilane as internal reference.

**Molecular weight**. Molecular weight of the polymers was estimated by gel permeation chromatography (GPC) with a UV detector (Jasco 805 UV) and a Shodex K-805L column. DMF containing 0.01 M LiBr was used as the eluent. Measurement was conducted at 50 ºC, and molecular weight was calibrated with standard polystyrene samples.

**Ion exchange capacity (IEC)**. IEC of the membranes was measured by acid-base titration at r.t. A piece of dry membrane (ca. 20 mg) was immersed in 50 mL of 2 M NaCl aqueous solution for at least 24 h to ensure complete ion exchange reaction. The released HCl by the ion exchange reaction was titrated with standard 0.01 M NaOH aqueous solution. The volume of NaOH solution in titration was used to calculate the amount of released HCl and then, the IEC of the membranes was deduced.

**Morphology**. The cross-sectional SEM images of the reinforced membrane was observed by scanning electron microscopy (SEM, Hitachi SU3500) with an accelerating voltage of 5kV.

**Tensile test**. Membrane sample was cut into a dumbbell shape (DIN-53503-S3, 35 mm × 6 mm (total) and 12 mm × 2 mm (test area)). The stress versus strain curve was obtained at a stretching rate of 10 mm min$^{-1}$ at 80 ºC and 60% RH with a Shimadzu AGS-J 500N universal testing instrument attached with a Toshin Kogyo Bethel-3A temperature/humidity controllable chamber.

**Dynamic mechanical analysis (DMA)**. Membrane sample was cut into a strip (0.5 cm × 3 cm) and DMA was conducted with an ITK DVA-225 dynamic viscoelastic analyzer at 80 ºC from 0 to 90%

RH. The storage modulus (E'), loss modulus (E''), and tan $\sigma$ (= E''/E') of the membrane were recorded as a function of the humidity.

**Water uptake and proton conductivity**. Water uptake and ion-conducting resistance (in-plane) (R) of the membranes were measured at 80 ºC with a solid electrolyte analyzer system (MSBAD-V-FC, Bel Japan Co.) in a temperature/humidity-controllable chamber. The humidity was changed from 20 to 95% RH. The R value was measured using a four-probe conductivity cell equipped with an AC impedance analyzer (Solartron 1255B and 1287, Solartron Inc.). After equilibrating under a given humidity, weight of absorbed water in the membrane was automatically measured by a magnetic suspension balance, and meanwhile, the R value was also recorded as impedance plots in the frequency range from 1 to $10^5$ Hz. The proton conductivity ($\sigma$) was measured in the in-plane direction of membrane, and calculated from the following equation: $\sigma$ = L/(A × R), where L and A are the distance between the two reference electrodes and the cross-sectional area, respectively.

**Figures and tables**
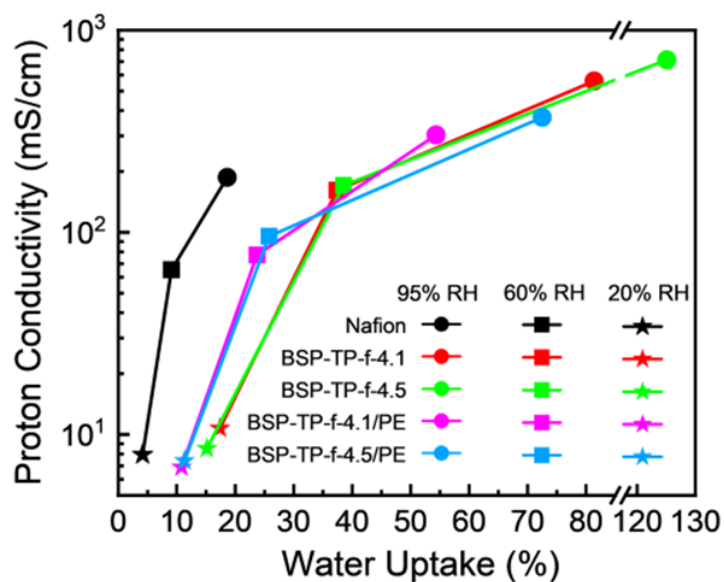


**Fig. S1** Proton conductivity as a function of water uptake at 80 °C, 20% RH, 60% RH, and 95% RH.

**Table S1** Proton conductivity as a function of water uptake at 80 °C, low (20%RH) and high (95% RH) humidity.

| Sample | Low humidity (20%RH) | | High humidity (95%RH) | |
|---|---|---|---|---|
| | Proton conductivity (mS cm⁻¹) | Water uptake (%) | Proton conductivity (mS cm⁻¹) | Water uptake (%) |
| BSP-TP-f-4.1 | 10.7 | 17.4 | 560.8 | 81.4 |
| BSP-TP-f-4.5 | 8.5 | 15.1 | 714.0 | 125.1 |
| BSP-TP-f-4.1/PE | 6.9 | 10.8 | 303.2 | 54.3 |
| BSP-TP-f-4.5/PE | 7.4 | 11.3 | 389.2 | 72.5 |
| Nafion | 7.9 | 4.2 | 187.2 | 18.6 |
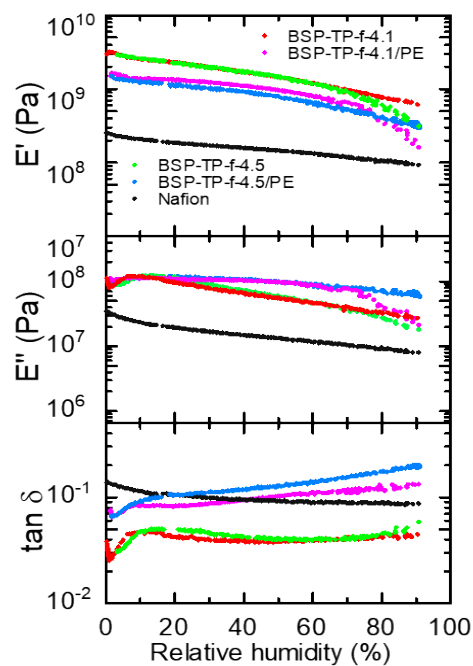
**Fig. S2** Humidity dependence of viscoelastic properties of parent and reinforced BSP-TP-f, Nafion and PE membranes at 80 °C.

**Table S2** Swelling ratio of parent and reinforced membranes

| Membrane | Swelling ratio (%)[a] | |
|---|---|---|
| | In-plane | Through-plane |
| BSP-TP-f-4.1 | 27 | 25 |
| BSP-TP-f-4.1/PE | 9 | 13 |
| BSP-TP-f-4.5 | 40 | 51 |
| BSP-TP-f-4.5/PE | 12 | 17 |

[a]Calculated from $(S_{wet} - S_{dry})/S_{dry}$, where $S_{wet}$ was area under wet condition and $S_{dry}$ was area under dry condition at r.t.

**Table S3** Tensile properties of parent and reinforced BSP-TP-f, Nafion and PE membranes at 80 °C and 60% RH.

| Sample | Young's modulus (GPa) | Yield stress (MPa) | Maximum stress (MPa) | Maximum strain (%) |
|---|---|---|---|---|
| BSP-TP-f-4.1 | 0.61 | 25.9 | 39.6 | 90 |
| BSP-TP-f-4.5 | 0.48 | 21.9 | 28.5 | 63 |
| BSP-TP-f-4.1/PE | 0.36 | 12.6 | 28.4 | 453 |
| BSP-TP-f-4.5/PE | 0.27 | 8.7 | 23.6 | 284 |
| Nafion | 0.04 | 3.0 | 10.8 | 335 |
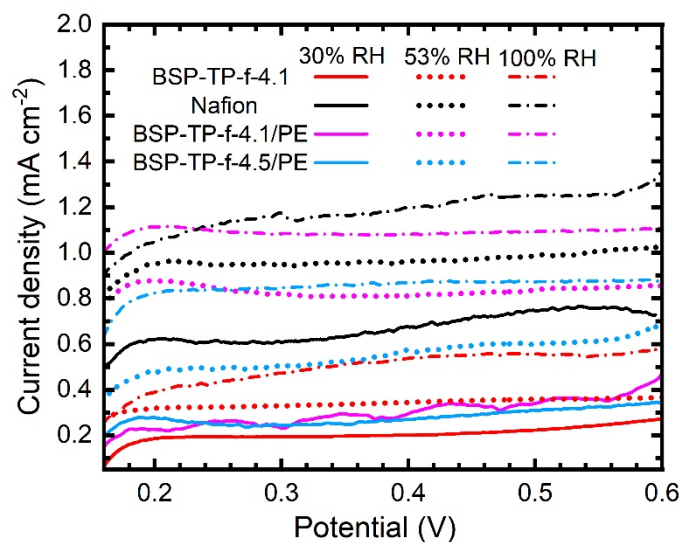


**Fig. S3** Linear sweep voltammograms (LSVs) of fuel cells at 80 °C, 100% RH, 53% and 30% RH.
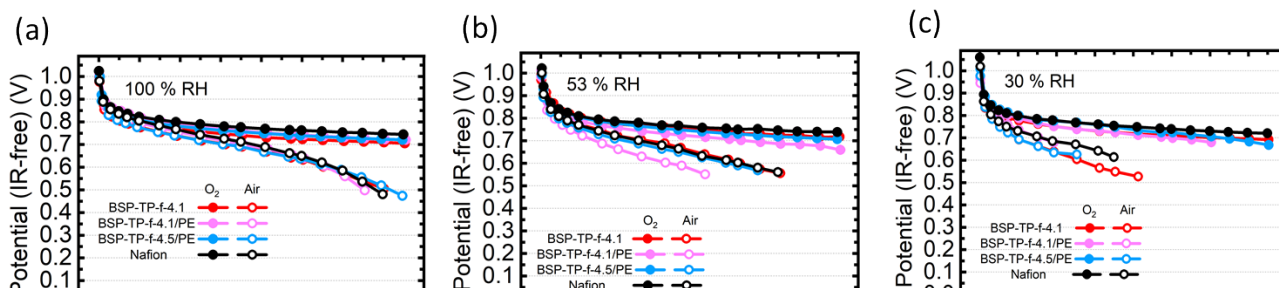
**Fig. S4** *IR*-free polarization curves for BSP-TP-f-4.1, BSP-TP-f-4.1/PE, BSP-TP-f-4.5/PE and Nafion fuel cells at 80 °C, (a) 100% RH and (b) 30% RH.

**Table S4** Mass activity of tested cells at 0.85 V with $O_2$ as the oxidant.

| Membrane | Mass activity at 0.85V (A $g_{Pt}^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| | 100% RH | | 53% RH | | 30% RH | |
| | $O_2$ | Air | $O_2$ | Air | $O_2$ | Air |
| Nafion | 179.8 | 136.3 | 126.7 | 82.4 | 95.5 | 58.2 |
| BSP-TP-f-4.1 | 112.5 | 82.7 | 77.7 | 72.7 | 72.2 | 37.9 |
| BSP-TP-f-4.1/PE | 136.6 | 113.6 | 103.4 | 66.2 | 99.9 | 52.4 |
| BSP-TP-f-4.5/PE | 138.2 | 118.4 | 132.5 | 99.7 | 122.3 | 59.7 |
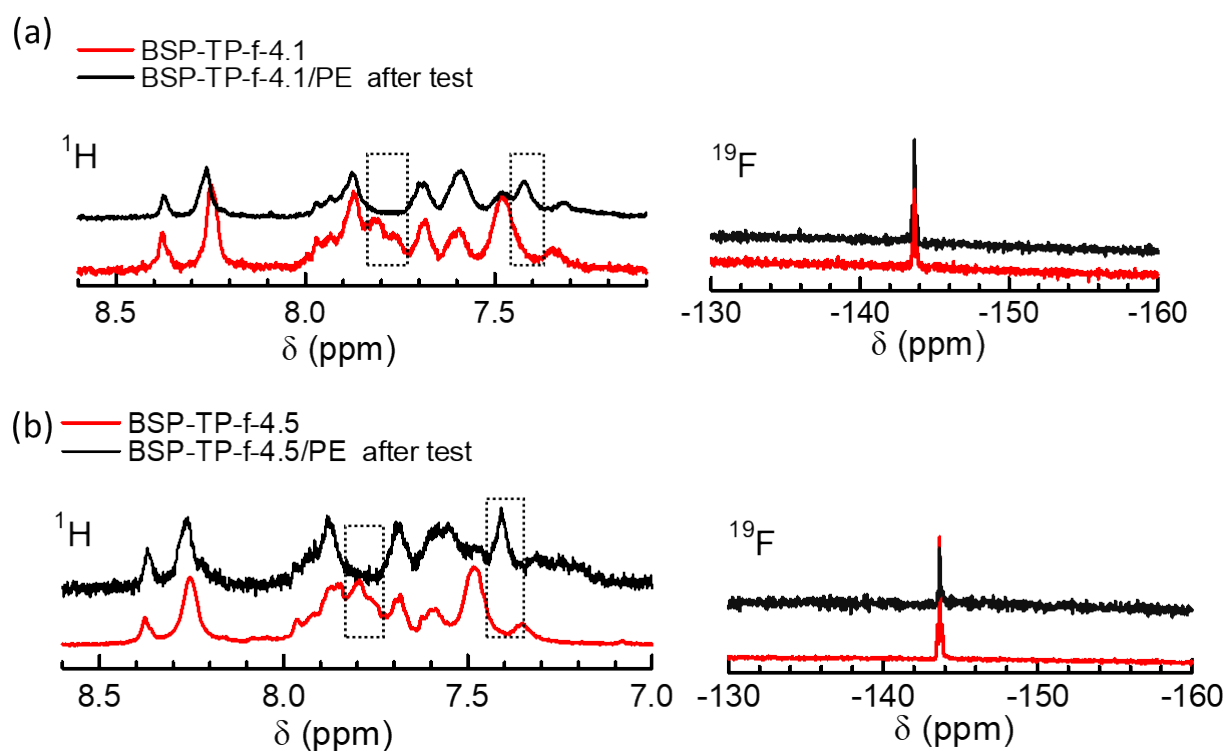
**Fig. S5** $^1H$ and $^{19}F$ NMR spectrum of (a) BSP-TP-f-4.1 and (b) BSP-TP-f-4.5 ionomers in DMSO-$d_6$ at 80 °C before and after the accelerated durability test (the black curves represent the recovered ionomers from the reinforced membrane after the test, and the dotted boxes mark the differences before and after the test).

**Table S5** Molecular weight and IEC values of BSP-TP-f-4.1 and BSP-TP-f-4.5 after the accelerated durability test.

| Sample | Molecular weight (kDa) | | | Residual molecular weight[a] (%) | | $IEC_{Target}$ (meq g$^{-1}$) | $IEC_{Titrated}$ (meq g$^{-1}$) | $IEC_{NMR}$[b] (meq g$^{-1}$) | Residual IEC[c] (%) |
|---|---|---|---|---|---|---|---|---|---|
| | $M$w | $M$n | $M$w/$M$n | $M$w | $M$n | | | | |
| BSP-TP-f-4.1 | 533.0 | 148.6 | 3.6 | 96 | 81 | 4.10 | 3.45 | 4.09 | 88 |
| BSP-TP-f-4.1/PE after test | 354.9 | 80.5 | 4.4 | 67 | 54 | - | - | 2.78 | 68 |
| BSP-TP-f-4.5 | 242.4 | 86.6 | 2.8 | - | - | 4.50 | 4.75 | 4.35 | - |
| BSP-TP-f-4.5/PE after test | 180.3 | 47.8 | 3.8 | 74 | 55 | - | - | 3.17 | 73 |

[a]Calculated from the value before and after the accelerated durability test.

[b]Calculated from the integrated area of the relevant peaks on the $^1$H NMR spectra.

[c]Calculated from the $IEC_{NMR}$ value before and after the accelerated durability test.

**Reference**

1. U.S. Department of Energy，Fuel Cell Technical Team Roadmap, https://www.energy.gov/sites/default/files/2017/11/f46/FCTT_Roadmap_Nov_2017_FINAL.pdf, (accessed February, 2023).