Supplementary Information

Well-designed polyphenylene PEMs with high proton conductivity and chemical and mechanical durability for fuel cells

Fanghua Liu,[a] and Kenji Miyatake*[,b,c,d]

[a]*Graduate School of Medical, Industrial and Agricultural Science, University of Yamanashi, Kofu, Yamanashi 400-8510, Japan.*

[b]*Clean Energy Research Center, University of Yamanashi, Kofu, Yamanashi 400-8510, Japan.*

[c]*Fuel Cell Nanomaterials Center, University of Yamanashi, Kofu, Yamanashi 400-8510, Japan.*

[d]*Department of Applied Chemistry, and Research Institute for Science and Engineering, Waseda University, Tokyo 169-8555, Japan.*

*Corresponding Author

E-mail: miyatake@yamanashi.ac.jp; Tel +81 552208707; Fax +81 552208707 (K. Miyatake)

Measurements

Spectroscopy

^{1}H and ^{19}F NMR spectra were obtained with a JEOL JNM-ECA/ECX500 spectrometer, where DMSO-d_6 and tetramethylsilane (TMS) were used as solvent and internal reference, respectively. Fourier transform infrared (FT-IR) spectra of the membranes were measured on NICOLET 6700 FT-IR. Gel permeation chromatography (GPC, detector: Jasco 805 UV, column: Shodex KF-805L) was used for the molecular weight measurement of the polymers, in which the eluent was N, N-dimethylformamide (DMF) containing 0.01 M lithium bromide and calibration was conducted using standard polystyrene samples.

Morphology

For transmission electron microscopic (TEM) images, the membrane sample was stained in 0.5 M $Pb(OAc)_2$ aqueous solution and rinsed thoroughly with water. The stained membrane sample was embedded in resin, sectioned to 50 nm thickness with Leica microtome Ultracut UCT, and placed on a copper grid. TEM images were taken with a Hitachi H-9500 at an accelerating voltage 200 kV. Small-angle X-ray scattering (SAXS) patterns were obtained with a Rigaku NANO-Viewer diffractometer under controlled temperature and humidity conditions. The surface and cross-section scanning electron microscope (SEM) images of CCMs after combined chemical and mechanical durability were carried out by SU3500 (Hitachi) with an accelerating voltage of 5 kV.

Titrated IEC

The ion exchange capacity (IEC) of the membrane was measured by acid/base titration. A piece of dry membrane in H^+ forms was soaked in 2 M sodium chloride aqueous solution for 24 h. HCl released by the ion exchange reaction was titrated with a standard 0.01 M NaOH aqueous

solution using a Kyoto electronics AT-710 Kyoto electronic potentiometric titrator. The IEC was obtained averaging three measurements.

Water uptake and proton conductivity

Water absorption (uptake) and proton conductivity of the membranes were measured simultaneously using a Bel Japan MSBAD-V-FC solid electrolyte analyzer system containing a temperature and humidity controllable chamber. The dry weight of a sample was obtained after drying at 80 ℃ for 3 h and the wet weight was obtained by exposing to the set temperature and humidity for more than 2 h. The proton conductivity was measured using a Solartron 1255B and SI1287 impedance analyzers. The proton conductivity (mS cm^{-1}) was calculated as follow: $\sigma = l/(A \times R)$, where R is the ion conducting resistance, A and l are the conducting area and the electrode distance, respectively.

Mechanical properties

The tensile properties of the membranes were measured with a Shimadzu AGS-J 500N universal test machine under controlled temperature and humidity conditions. The dumbbell shaped sample (DIN-53504-S3, 35 × 6 mm (total) and 12 × 2 mm (test area)) was stabilized for more than 2 h at 80 ℃ and 60% relative humidity (RH) prior to the measurement. An ITK DVA-225 dynamic viscoelastic analyzer was used for dynamic mechanical analyses (DMA) of the membranes. Storage modulus (E', Pa), loss modulus (E", Pa), and tan δ (= E"/E') were measured under controlled temperature and humidity conditions.

Thermal stability

Thermogravimetric analyses of the SPP-TFP membranes were carried out with a Rigaku TG-DTA8122 thermogravimetric analyzer at 20 ℃ min^{-1} of the heating rate under nitrogen atmosphere.

Oxidative stability

Oxidative stability of the membranes was evaluated using Fenton's reagent (3% H_2O_2 aq containing 2 ppm Fe^{2+} ($FeSO_4 \cdot 7H_2O$). A piece of membrane sample was soaked in Fenton's reagent 80 ℃ for 1 h. The recovered sample was rinsed with water thoroughly prior to the post-test analyses.

Preparation of catalyst coated membrane (CCM)

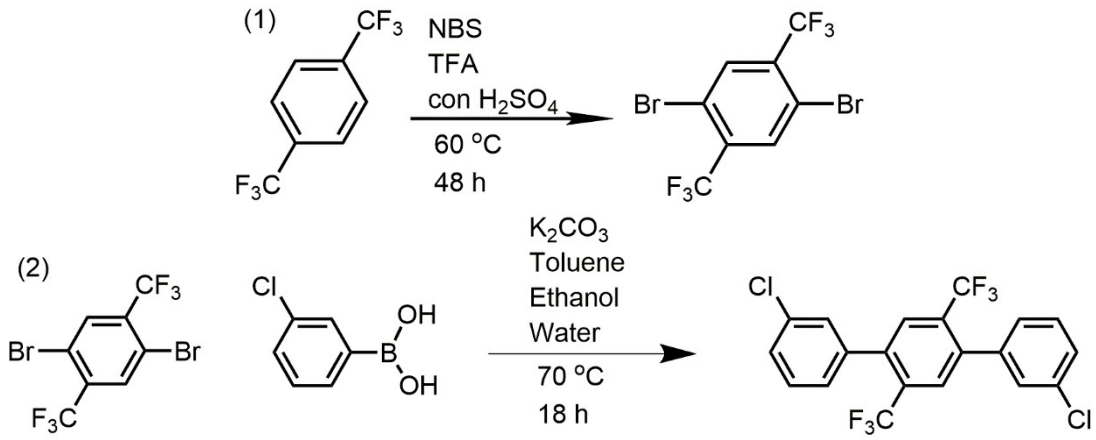
Commercial Pt/C catalyst (Tanaka Kikinzoku Kogyo, TEC10E50E), 5wt% Nafion dispersion (DuPont, D521, IEC = 0.95-1.03 mmol g^{-1}), deionized water, and ethanol were used to prepare the catalyst ink. The mass ratio of Nafion to the carbon support (N/C) was adjusted to 0.70. Catalyst coated membrane (CCM) was prepared by spraying the catalyst paste on both sides of the membrane by pulse swirl spray technique. The CCM was dried at 60 ℃ overnight and hot-pressed at 140 ℃ and 1.0 MPa for 3 min. The geometric area and the Pt loading amount in the catalyst layer were 4.41 cm^2 and 0.50 ± 0.02 mg cm^{-2}, respectively. The CCM was sandwiched by two gas diffusion layers (SGL Group, 29BC GDL) and mounted into a cell.

Evaluation of fuel cell performance and durability

Linear sweep voltammetry (LSV) was measured to evaluate the permeability of hydrogen gas from the anode to the cathode through the ionomer membranes. LSV measurement was carried out at 30 or 100% RH and 80 ℃. Prior to the LSV measurements, H_2 (0.1 L min^{-1}) and N_2 (0.1 L min^{-1}) were supplied to the anode and the cathode, respectively. The polarization curves were measured at 80 ℃, 100% and 30% RH, supplying hydrogen to anode and oxygen to cathode, respectively. The durability test at a constant current density (0.15 A cm^{-2}) was carried out at 90 ℃ and 30% RH for 300 h, supplying hydrogen (0.11 L min^{-1}) to anode and air (0.1 L min^{-1}) to cathode, respectively.

Combined chemical (OCV hold) and mechanical (relative humidity cycling, RHC) durability test

The test was carried out according to this literature[1] and the US-DOE (the U.S. Department of Energy) protocol. The preparation of CCM was the same as aforementioned method except that the Pt loading amount in the catalyst layer was 0.2 ± 0.03 and 0.1 ± 0.04 mg cm^{-2} for the anode and the cathode, respectively. The durability test was carried out at 90 °C feeding H_2 (0.06 L min^{-1}) and air (0.06 min^{-1}) to the anode and cathode, respectively. Simultaneously, humidity was switched frequently between wet (duration: 15 s) and dry (duration: 2 s) states.



Scheme S1. Synthesis of (1) 2,5-dibromo-3,6-bis(trifluoromethyl)benzene (BFB) and (2) 3,3”-dichloro-2’,5’-bis(trifluoromethyl)-1,1’:4’,1”-terphenyl (TFP).

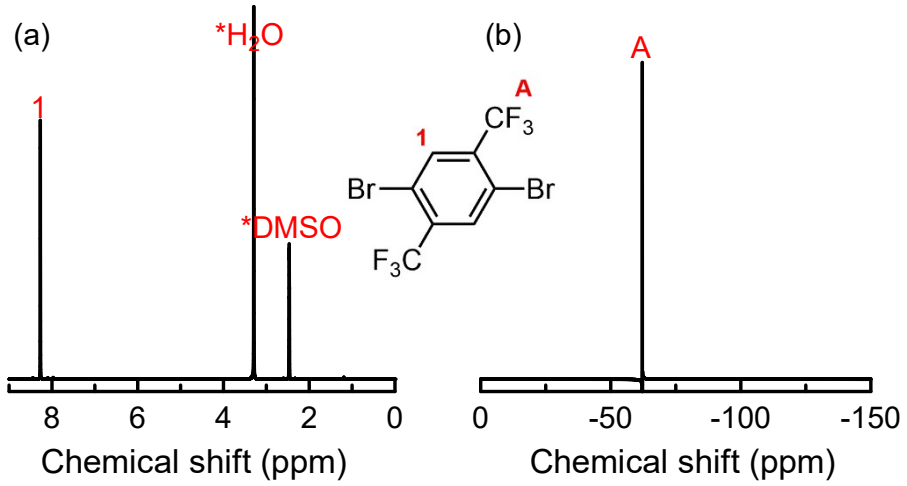


Fig. S1 (a) ^{1}H and (b) ^{19}F NMR spectra of BFB in DMSO-d_6 at r.t.

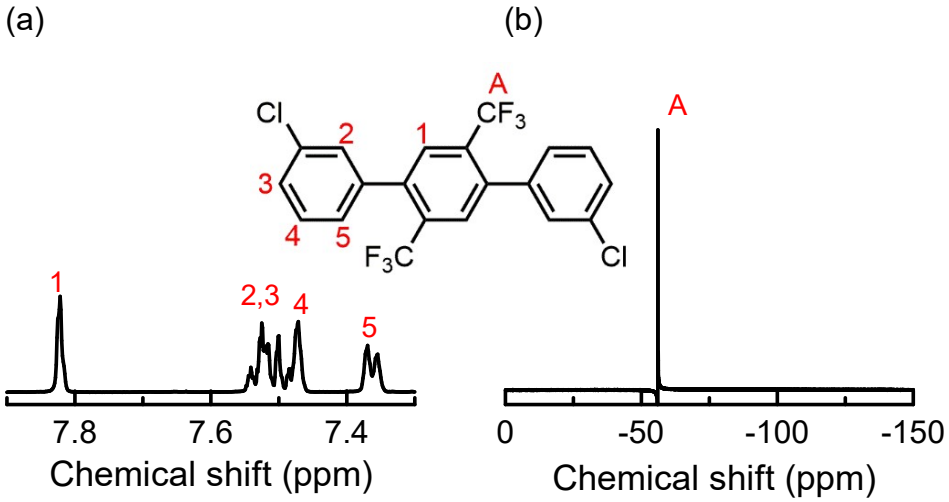


Fig. S2 (a) ^{1}H and (b) ^{19}F NMR spectra of TFP monomer in DMSO-d_6 at 80 °C.

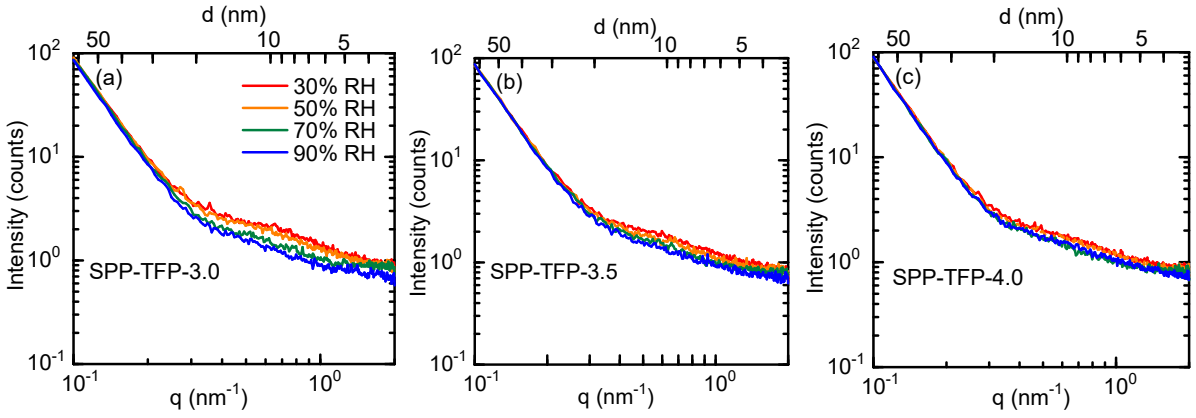


Fig. S3 SAXS profiles of (a) SPP-TFP-3.0, (b) SPP-TFP-3.5 and (c) SPP-TFP-4.0 membranes as a function of the scattering vector (q) at 30-90% RH and 80 °C.

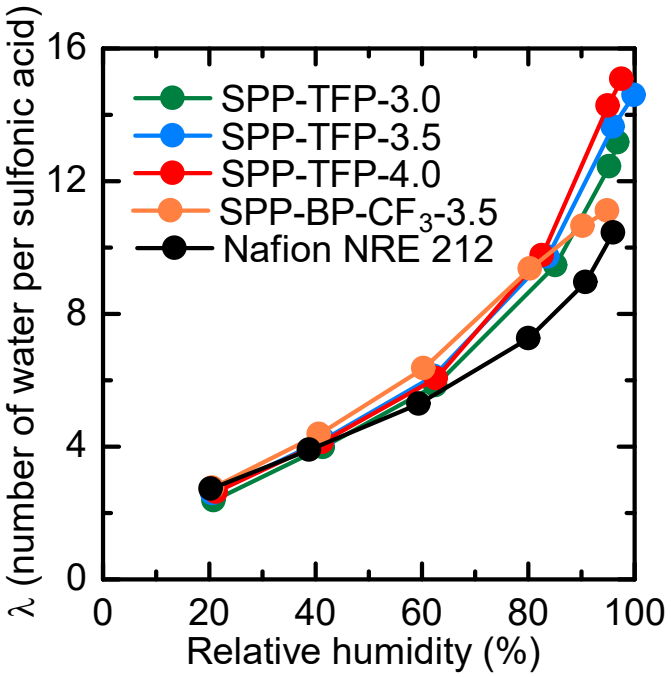


Fig. S4 Relative humidity dependence of the number of absorbed water molecules per sulfonic acid group (λ) of SPP-TFP, SPP-BP-CF_3-3.5 and Nafion NRE 212 membranes at 80 °C.

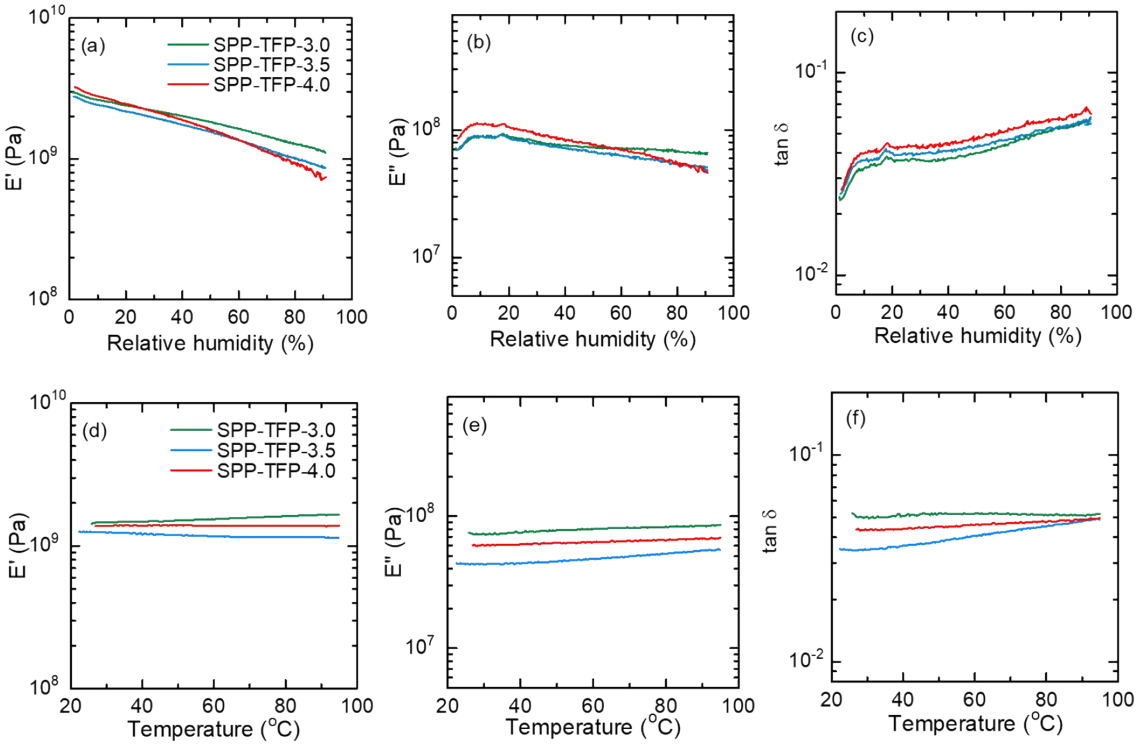


Fig. S5 E', E'' and tan δ curves of SPP-TFP membranes as a function of relative humidity (a-c) at 80 °C and as a function of temperature (d-f) at 60% RH.

Table S1. Tensile properties of SPP-TFP and SPP-BP-CF_3-3.5 at 80 ℃ and 60% RH.

Membrane	Titrated IEC (mmol g^{-1})	Yield stress (MPa)	Maximum strain (%)	Young's modulus (GPa)
SPP-TFP-3.0	2.58± 0.06	33.0 ± 2.0	84 ± 2	0.92 ± 0.07
SPP-TFP-3.5	2.99± 0.04	33.6 ± 0.8	155 ± 5	0.62 ± 0.05
SPP-TFP-4.0	3.40± 0.08	28.1 ± 1.2	141 ± 8	0.54 ± 0.12
SPP-BP-CF_3-3.5	2.70± 0.05	38.5 ± 1.4	5.2 ± 0.8	1.40 ± 0.12
Nafion NRE 211	0.97± 0.06	3.4 ± 0.2	391.1 ± 20	0.05 ± 0.01

Table S2. Physical properties of SPP-TFP-3.0, -3.5 and -4.0 after Fenton's test.

Membrane	Remaining weight (%)	Titrated IEC (mmol g^{-1})		Molecular weight (kDa)						Remaining M_w (%)
				Before			After			
		Before	After	M_n	M_w	PDI	M_n	M_w	PDI	
SPP-TFP-3.0	97	2.6	2.3	51.2	196.1	3.8	38.9	153.0	3.9	78
SPP-TFP-3.5	97	3.0	2.9	123.4	527.4	4.3	61.9	339.3	5.5	64
SPP-TFP-4.0	95	3.4	3.4	104	556.1	5.3	74.9	347.6	4.6	63
Nafion NRE211	98	0.97	0.97	--	--	--	--	--	--	--

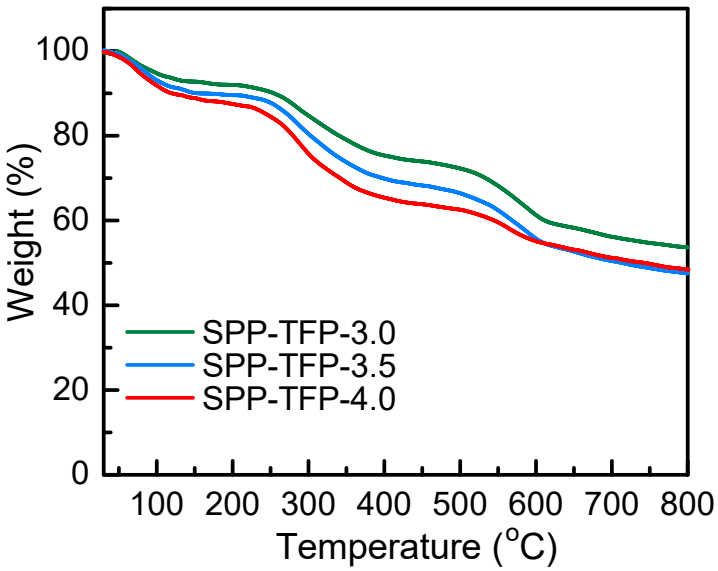


Fig. S6 TGA curves of SPP-TFP membranes under N_2 atmosphere.

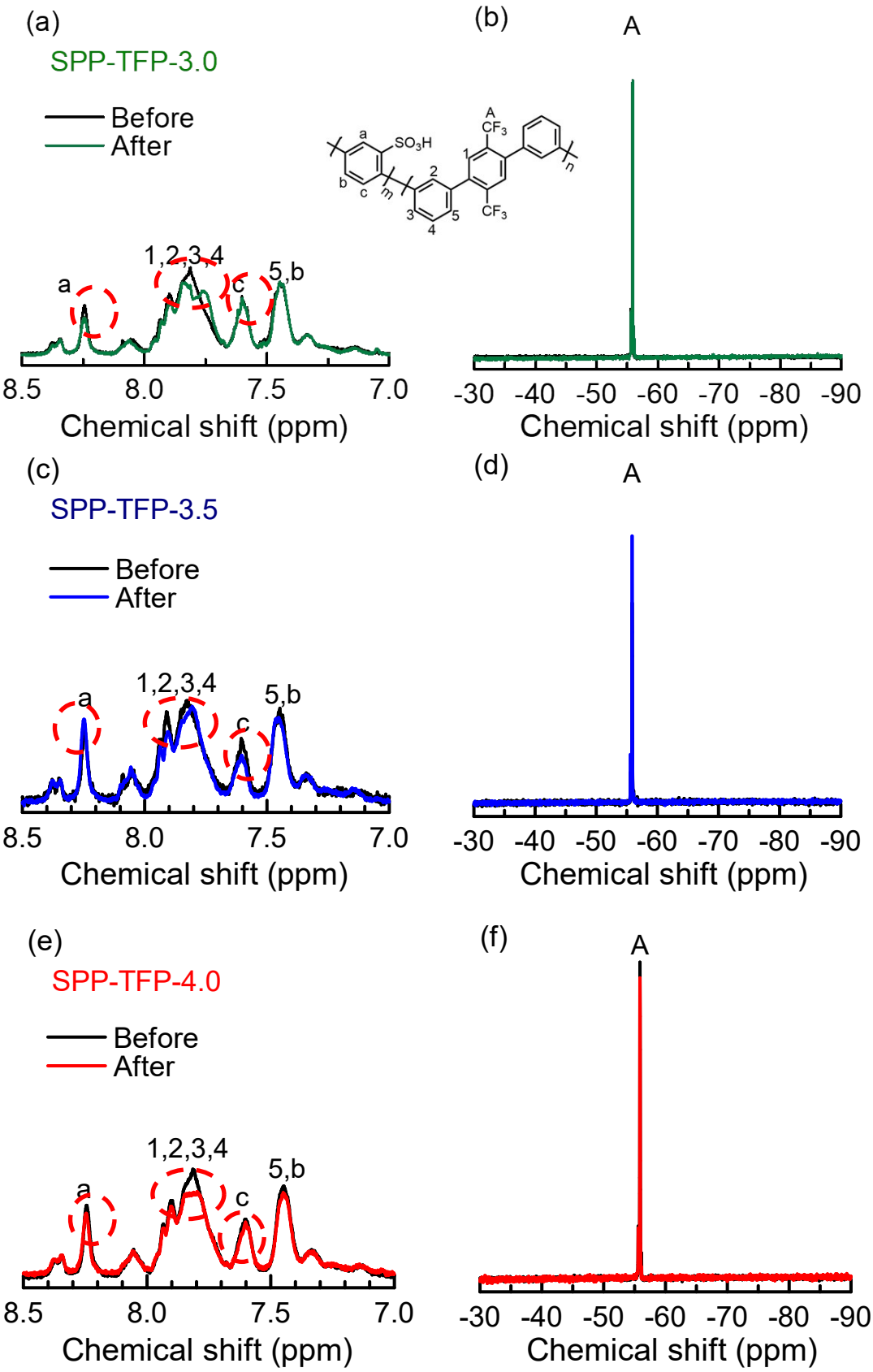


Fig. S7 ^{1}H (left) and ^{19}F (right) NMR spectra of (a) and (b) for SPP-TFP-3.0, (c) and (d) for SPP-TFP-3.5 and (e) and (f) for SPP-TFP-4.0 before and after the Fenton's test.

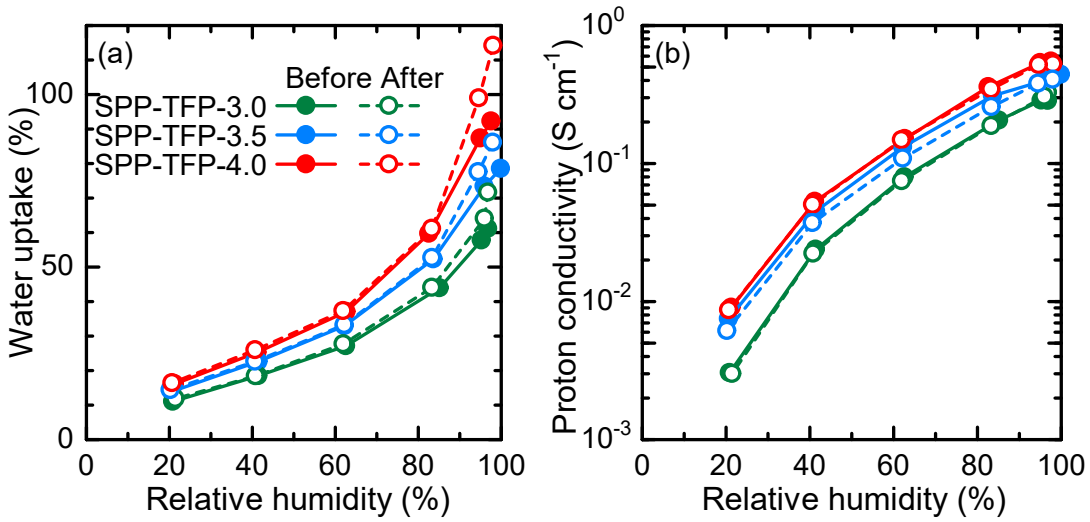


Fig. S8 (a) Water uptake and (b) proton conductivity of SPP-TFP membranes as a function of relative humidity at 80 ℃ before and after the Fenton's test.

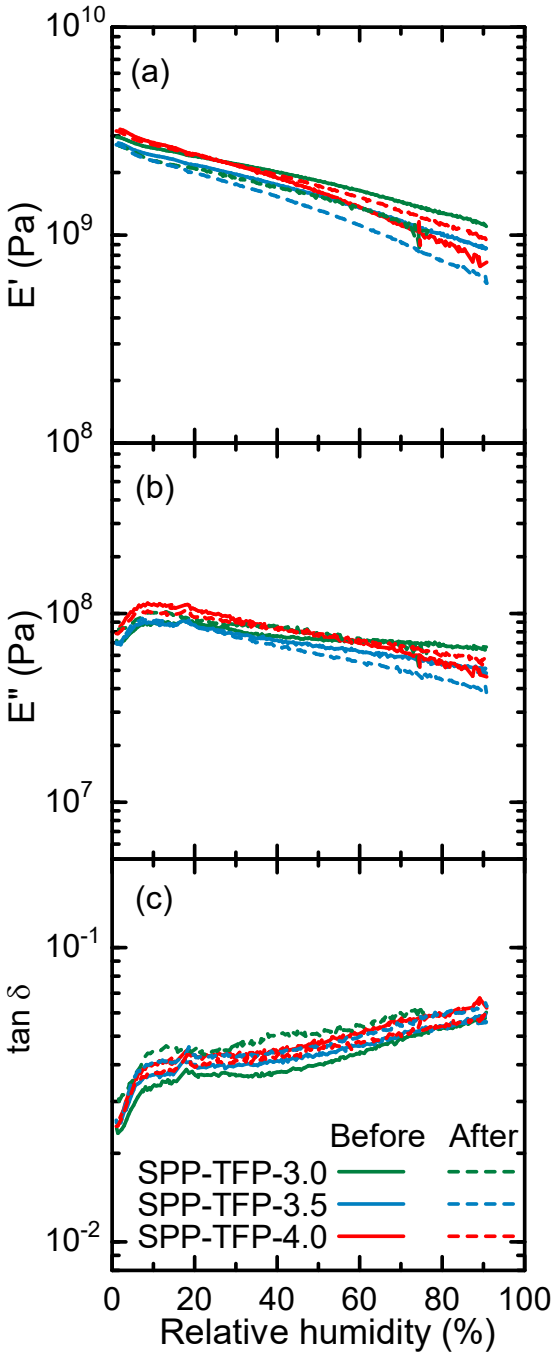


Fig. S9 Dynamic mechanical properties of SPP-TFP membranes at 80 ℃ before and after the Fenton's test.

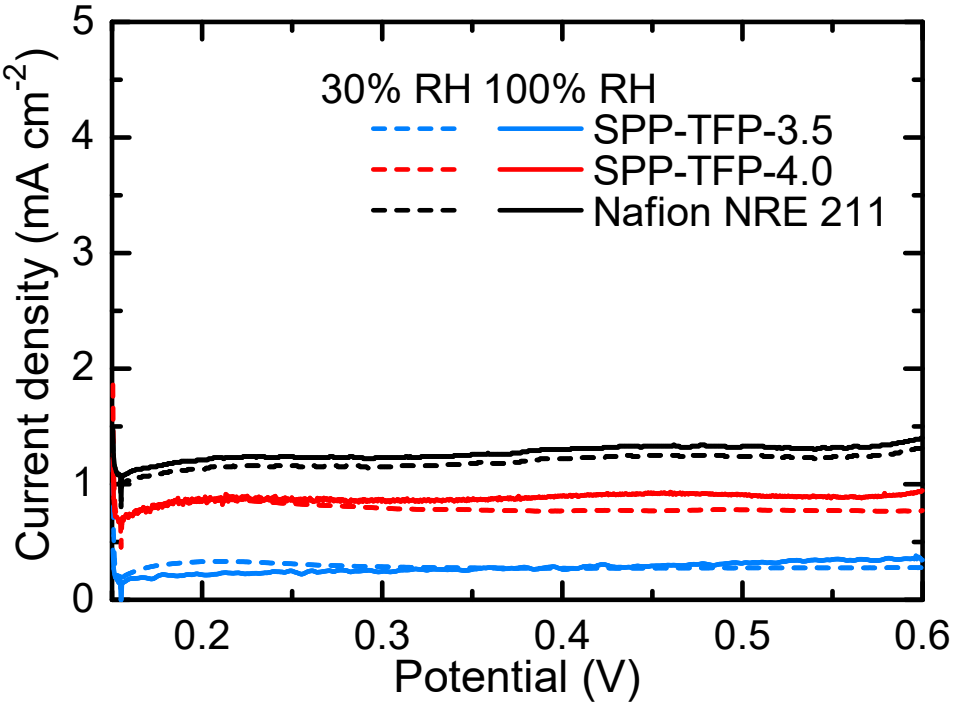


Fig. S10 Linear sweep voltammograms (LSVs) of SPP-TFP-3.5, -4.0 and Nafion NRE 211 cells at 80 °C under 30% and 100% RH supplying pure hydrogen (0.1 L min^{-1}) and nitrogen (0.1 L min^{-1}) at the anode and the cathode, respectively.

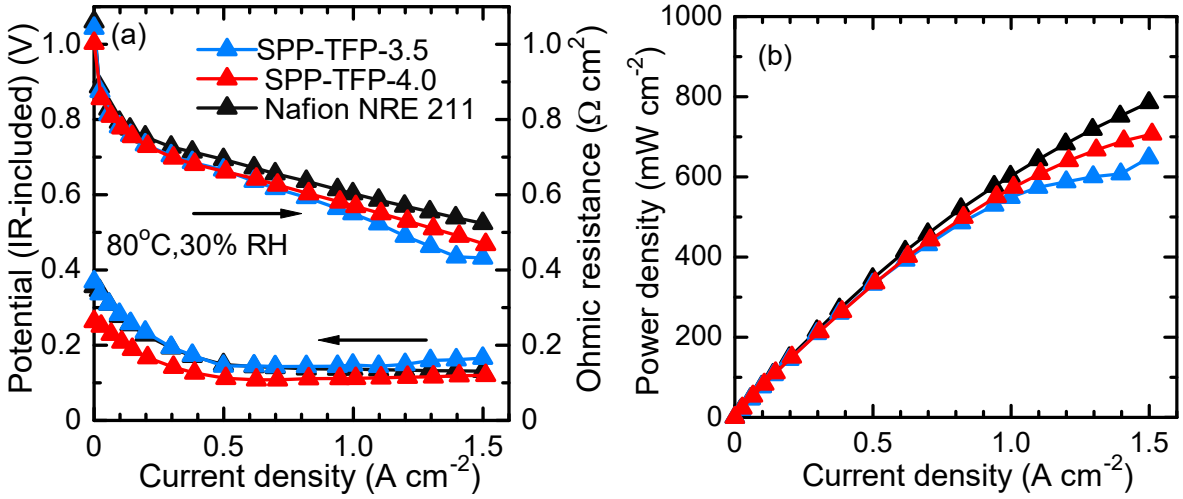


Fig. S11 (a) IR-included polarization curves and ohmic resistances as well as (b) power density of SPP-TFP-3.5 (31 μm), -4.0 (28 μm) and Nafion NRE 211 (25 μm) cells under H_2/ O_2, at 80 °C and 30% RH.

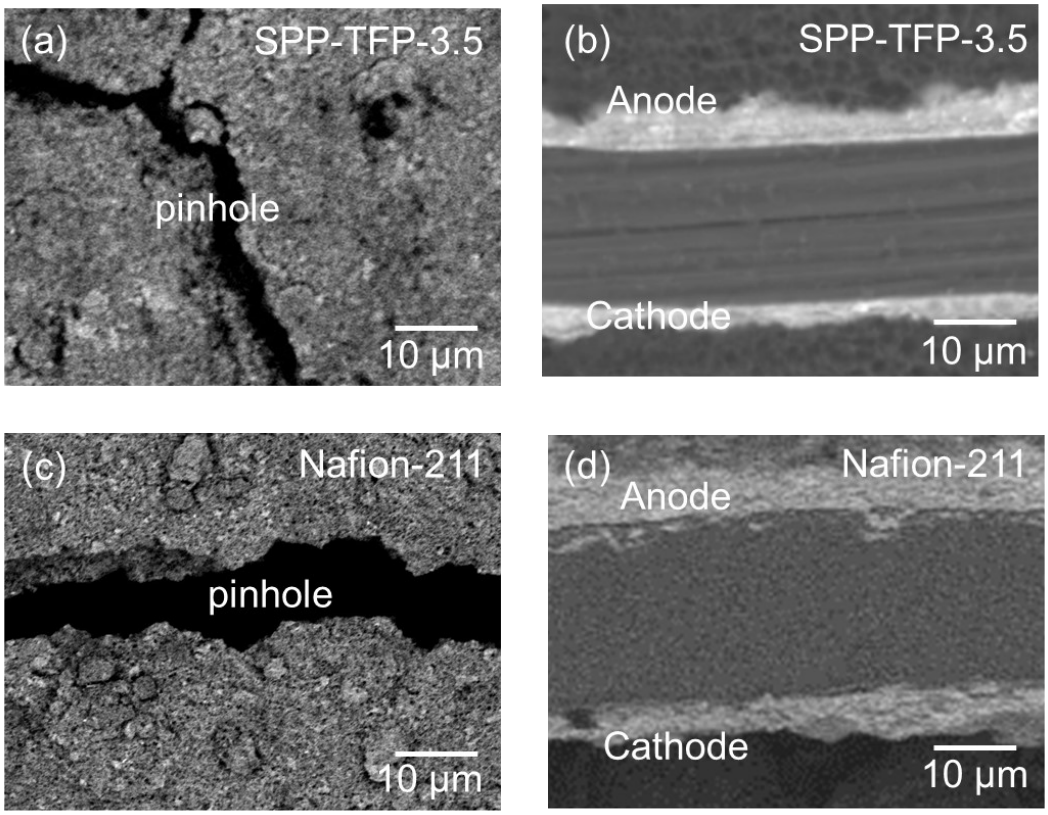


Fig. S12 SEM images of the membranes after the combined chemical and mechanical durability test; (a) surface and (b) cross-sectional for SPP-TFP-3.5 and (c) surface and (d) cross-sectional for Nafion NRE 211.

Table S3. Combined chemical (OCV hold) and mechanical (relative humidity cycling) durability test of SPP-TFP-3.5 and Nafion NRE 211 membranes.

Membrane	Duration (s)	Ohmic resistance (Ω cm^2)	Pt loading amount (mg cm^{-2})	Test time (h)	Cycle number (N)	Molecular weight (kDa)		Remaining M_w (%)
	Wet/ dry	Wet/ dry	Anode/cathode			M_n	M_w	
SPP-TFP-3.5	15/ 2	0.24/ 0.61	0.2/ 0.1	46.5	9847	14.1	358.2	67.9
Nafion NRE 211	15/ 2	0.27/ 0.75	0.2/ 0.1	41.5	8788	--	--	--

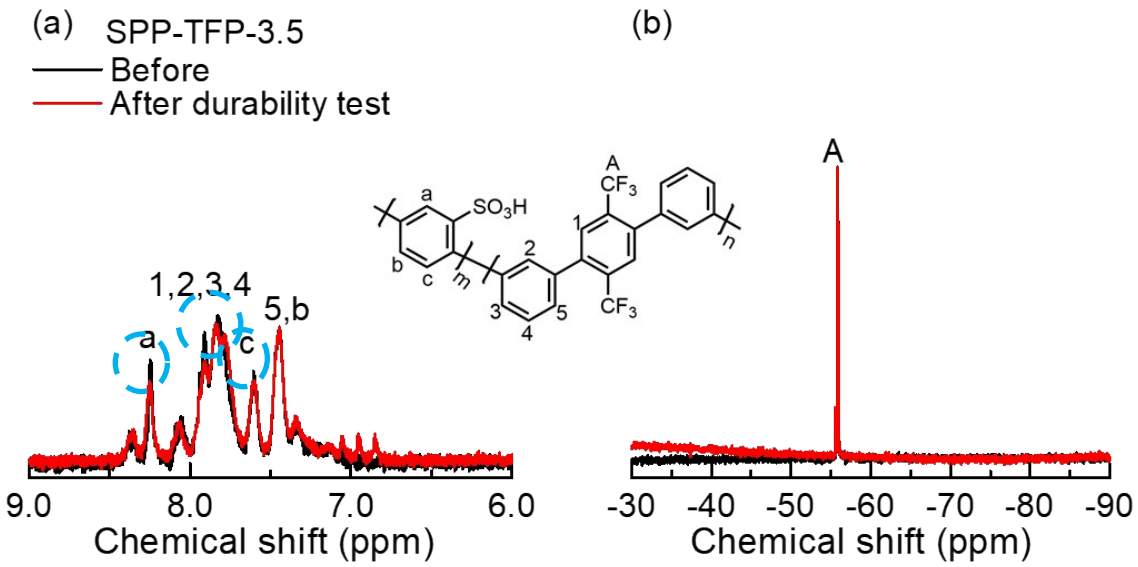


Fig. S13 (a) ^{1}H and (b) ^{19}F NMR spectra of SPP-TFP-3.5 in DMSO-d_6 at 80 °C before and after the combined chemical and mechanical durability test.

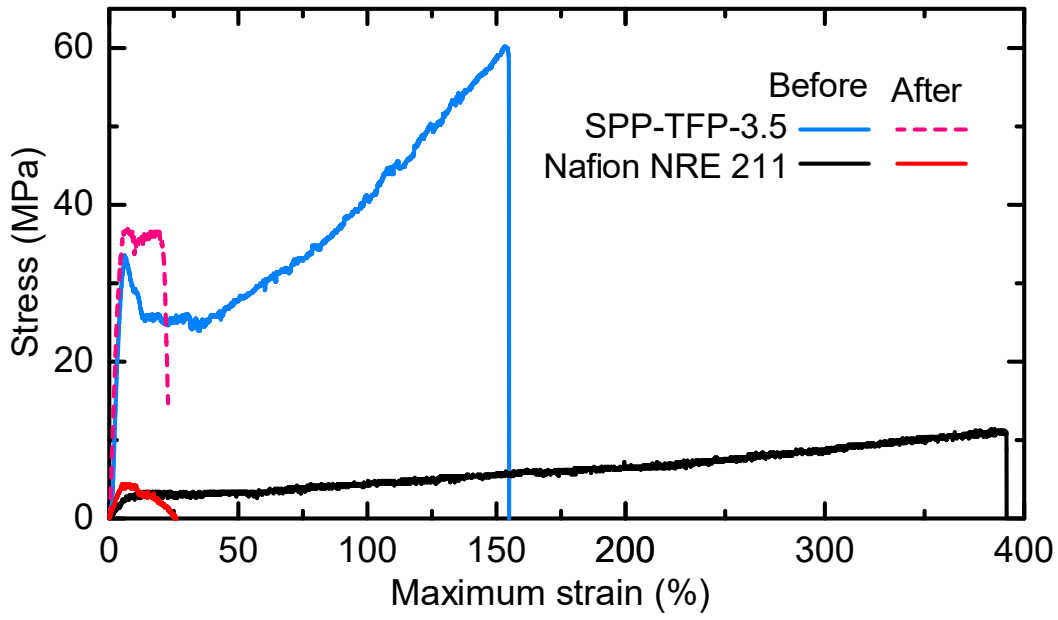


Fig. S14 Mechanical properties of SPP-TFP-3.5 and Nafion NRE 211 at 80 °C under 60% RH before and after the combined chemical and mechanical durability test.

Reference

1 R. Mukundan, A. M. Baker, A. Kusoglu, P. Beattie, S. Knights, A. Z. Weber and R. L. Borup, *J. Electrochem. Soc.* 2018, **165**, F3085-F3093.

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