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Supplementary information

Proton exchange membranes containing densely sulfonated quinquephenylene groups for high performance and durable fuel cells

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EXPERIMENTAL SECTION

Materials. Dimethylacetamide (DMAc) (KANTO Chemical), oleum (30% SO_3) (KANTO Chemical), hydrochloric acid (KANTO Chemical), 2,2'-bipyridine (TCI), bis(1,5-cyclooctadiene)nickel(0) ($Ni(cod)_2$) (KANTO Chemical), lead(II) acetate ($Pb(OAc)_2$) trihydrate (KANTO Chemical) and sodium chloride (NaCl) (KANTO Chemical) were purchased and used as received. 1,6-Diiodoperfluorohexane was kindly supplied by Tosoh Finechem Co. Bis(3-chlorophenyl)perfluorohexane (PAF)[1] and quinquephenylene (QP)[2] monomers were synthesized according to our previous reports.

Spectroscopy. ^1H (500 MHz), ^{13}C (125 MHz), and ^{19}F (471 MHz) NMR spectra were obtained by a JEOL JNM-ECA 500 spectrometer using $CDCl_3$ or DMSO-d_6 as a solvent and tetramethylsilane as an internal reference.

Titration. The ion exchange capacity (IEC) of the membranes was measured by acid/base titration at r.t. Ca. 20 mg of dry membrane was immersed in 2 M NaCl aqueous solution for 24 h at r.t., and then was titrated with standard 0.01 M NaOH aqueous solution.

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

Morphology. For transmission electron microscopy (TEM), the membrane samples were stained in 0.5 M $Pb(OAc)_2$ aqueous solution, embedded in epoxy resin, sectioned to 50 nm thickness and placed on copper grids. Images were obtained with Hitachi H-9500 microscope with an accelerating voltage of 200 kV.

Water Uptake and Proton Conductivity. Water uptake and in-plane proton conductivity of the membranes were measured simultaneously at 80 ºC with a solid electrolyte analyzer system (MSBAD-V-FC, Bel Japan Co.) in a temperature/humidity-controllable chamber. The weight was measured by a magnetic suspension balance. The dry weight of a membrane was provided after drying at 80 ºC under reduced pressure for 3 h and the wet weight of a membrane was obtained after exposure to the testing humidity for more than 2 h. The water uptake was calculated from the equation: (wet weight - dry weight)/dry weight × 100. The in-plane proton conductivity was tested with a four-probe conductivity cell connected with an ac impedance analyzer (Solartron 1255B and 1287, Solartron Inc.). Ion-conducting resistance was obtained in the frequency range of 1 to 10^5 Hz. The proton conductivity (δ) was calculated from the following equation: $\delta = l/(A \times R)$, where l is the distance between the two reference electrodes, A is the cross-sectional area, and R is the ion-conducting resistance.

Dynamic Mechanical Analysis (DMA). DMA was carried out with an ITK DVA-225 dynamic viscoelastic analyzer to evaluate the temperature (heating rate of 1 ºC min^{-1} from r.t. to 100 ºC at 60% RH) or humidity (humidification rate of 1% RH min^{-1} from 0 to 90% RH at 80 ºC) dependence of the storage moduli (E′), loss moduli (E″), and tan δ (= E″/E′) of the membranes.

Tensile Test. The tensile property was measured with a Shimadzu AGS-J 500N universal testing instrument attached with a Toshin Kogyo Bethel-3A temperature/humidity-controllable chamber at 80 ºC and 60% RH or 20% RH. Samples were cut into a dumbbell shape [DIN-53504-S3, 35 mm × 6 mm (total) and 12 mm × 2 mm (test area)]. After equilibrating under the tested conditions for at least 2 h, the stress-strain curves were obtained at a stretching rate of 10 mm min^{-1}.

Preparation of Catalyst-Coated Membrane (CCM). A catalyst paste was prepared by mixing Pt/CB catalyst (TEC10E50E, Tanaka Kikinzoku Kogyo K. K.), Nafion dispersion (IEC = 0.95-1.03 meq g^{-1}, D-521, Du Pont), deionized water and ethanol by ball-milling for 30 min. The mass ratio of Nafion ionomer to the carbon support (I/C) was adjusted to 0.7. Catalyst-coated membranes (CCMs) were prepared by spraying the catalyst paste on both sides of the membrane (NRE211, SPAF-MM or SPAF-QP) by pulse swirl spray (PSS) technique. The CCMs were dried at 60 ºC overnight and hot-pressed at 140 ºC and 1.0 MPa for 3 min. The geometric area and the Pt loading amount in the catalyst layer (CL) were 4.41 cm^2 and 0.50 ± 0.02 mg cm^{-2}, respectively.

Fuel Cell Operation. Linear sweep voltammetry (LSV) was measured to evaluate the hydrogen permeability from the anode to the cathode through the ionomer membranes. LSV measurement was carried out at 30 or 100% RH and 80 ºC. Prior to the LSV measurements, H_2 (100 mL min^{-1}) and N_2 (100 mL min^{-1}) were supplied to the anode and the cathode, respectively. The cathode potential was swept from 0.15 to 0.6 V at a sweep rate of 0.5 mV s^{-1}. To evaluate the fuel cell performance, the polarization curves were measured at 30 or 100% RH and 80 ºC. Pure H_2 and O_2 (or air) were supplied to the anode and the cathode, respectively. The gas utilizations at the anode and the cathode were 70% and 40%, respectively. The high frequency resistance (HFR) of the cell was measured with an ac milliohmmeter (Model 3356 Tsuruga Electric Corporation) at 1.0 kHz. The open circuit voltage (OCV) hold test was carried out at 80 ºC and 30% RH with H_2 for the anode and air for the cathode at a gas flow rate of 100 mL min^{-1}. The OCV hold test was continued for 1000 h.

Table S1. Synthesis condition, yield and molecular weight of PAF-QP

	m:n[a]	PAF	QP	Ni(cod)$_2$	2,2’-bipyridine	DMAc	Yield (%)	M_w[b] (kDa)	M_n[b] (kDa)	M_w/M_n[b]
PAF-QP	1:0.15	0.941 g (1.80 mmol)	0.122 g (0.27 mmol)	1.33 g (5.18 mmol)	0.849 g (5.43 mmol)	5.5 mL	93	26.9	7.39	3.63
PAF-QP	1:0.22	0.941 g (1.80 mmol)	0.179 g (0.40 mmol)	1.41 g (5.49 mmol)	0.900 g (5.77 mmol)	5.9 mL	91	72.4	25.6	2.83
PAF-QP	1:0.5	0.941 g (1.80 mmol)	0.408 g (0.90 mmol)	1.73 g (6.75 mmol)	1.107 (7.09 mmol)	7.2 mL	95	41.3	10.8	3.82

[a] Calculated from the feed comonomer ratio. [b] Determined by GPC.

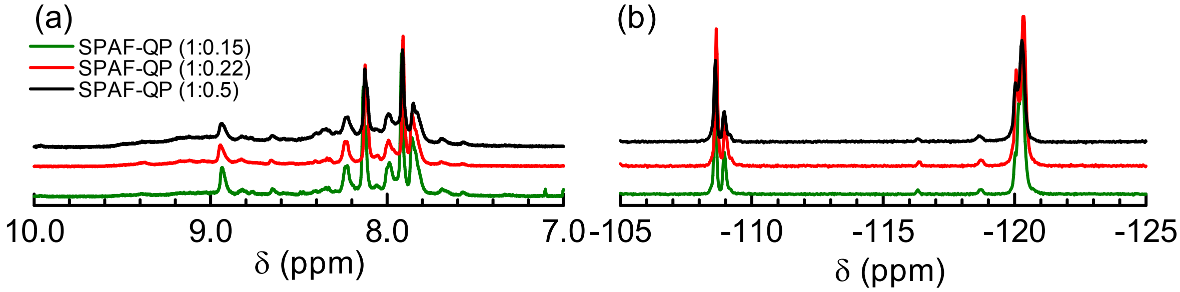

Fig. S1. (a) ^{1}H and (b) ^{19}F NMR spectra of SPAF-QP in DMSO-d_6 at 80 °C.

Table S2. Integral percentage of the aromatic peaks (P_m) in the ^{1}H NMR spectra of SPAF-QP[a]

P_m	P_1	P_2	P_3	P_4	P_5	P_6
δ (ppm)	8.97-8.88	8.27-8.18	8.16-8.08	8.02-7.94	7.94-7.87	7.87-7.75
SPAF-QP (1:0.15)	8.62	11.69	23.07	12.33	23.40	20.89
SPAF-QP (1:0.22)	9.35	10.74	22.46	13.24	21.99	22.22
SPAF-QP (1:0.5)	10.31	15.23	21.10	15.58	20.03	17.85

[a] $P_m = I_m/(I_1+I_2+I_3+I_4+I_5+I_6)\times100\%$ (m=1, 2, 3, 4, 5, 6), where P was the integral percentage, I was the integration of the peak.

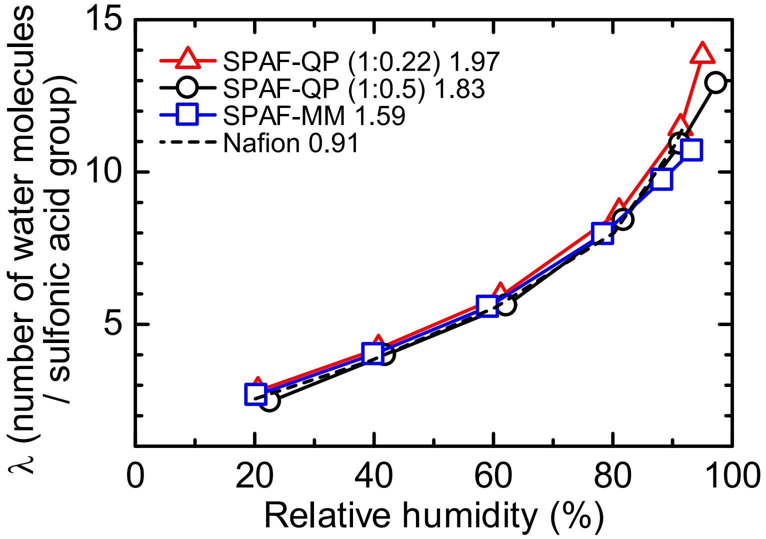

Fig. S2. Relative humidity dependence of the number of absorbed water molecules per sulfonic acid group (λ) of SPAF-QP, SPAF-MM and Nafion membranes at 80 °C.

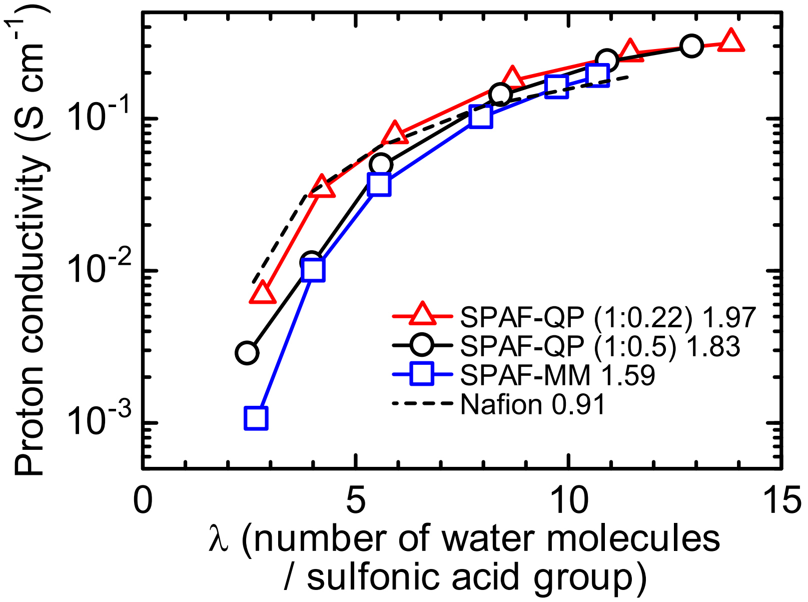

Fig. S3. Proton conductivity of SPAF-QP, SPAF-MM and Nafion membranes as function of the number of absorbed water molecules per sulfonic acid group (λ) at 80 °C.

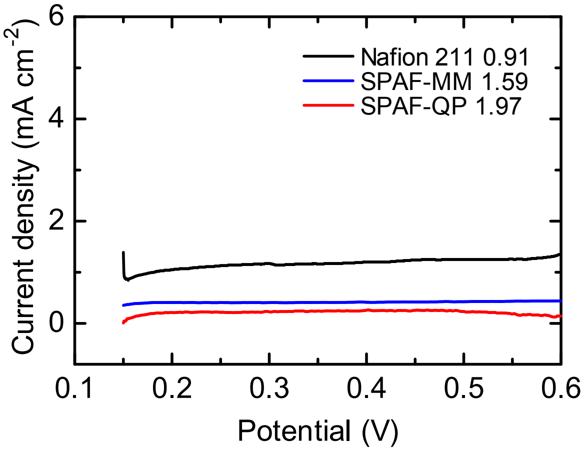

Fig. S4. Linear sweep voltammograms (LSVs) of fuel cell with Nafion, SPAF-MM and SPAF-QP (1:0.22) membranes at 80 °C and 100% RH. Pure hydrogen and nitrogen were supplied to the anode and cathode, respectively.

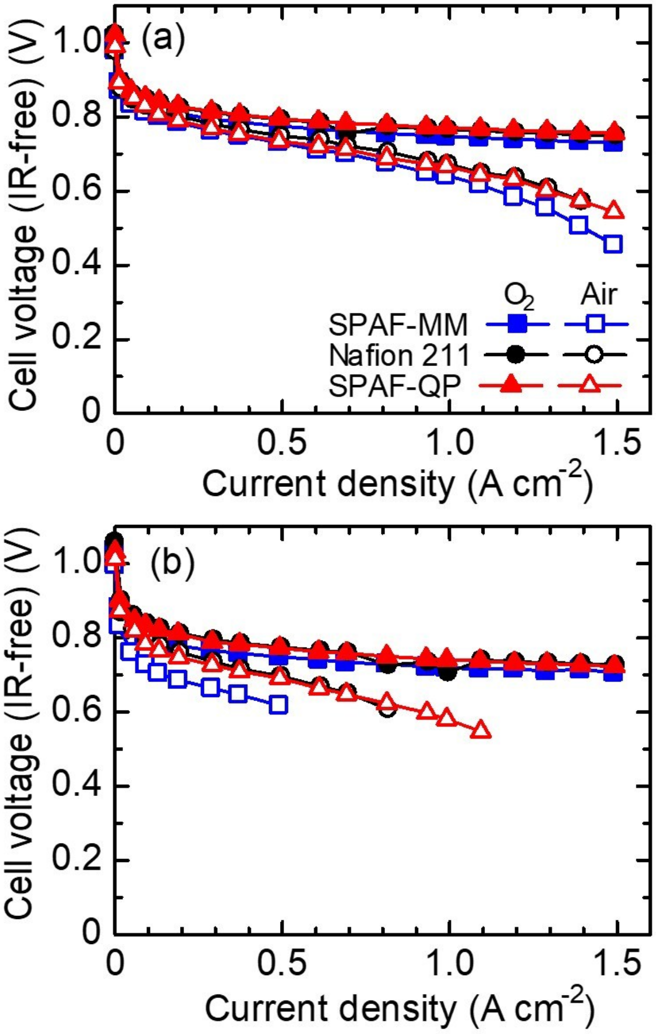

Fig. S5. *IR*-free polarization curves and ohmic resistances for the SPAF-MM (1.59 meq g^{-1}, 28 μm), Nafion (0.91 meq g^{-1}, 25 μm), and SPAF-QP (1.97 meq g^{-1}, 26 μm) cells at 80 ºC and (a) 100% and (b) 30% RH. The Pt loading amounts were 0.5 ± 0.05 mg cm^{-2} for both electrodes. Pure hydrogen and oxygen or air were supplied to the anode and cathode, respectively, without back pressure. The gas utilizations at the anode and the cathode were 70% and 40%, respectively.

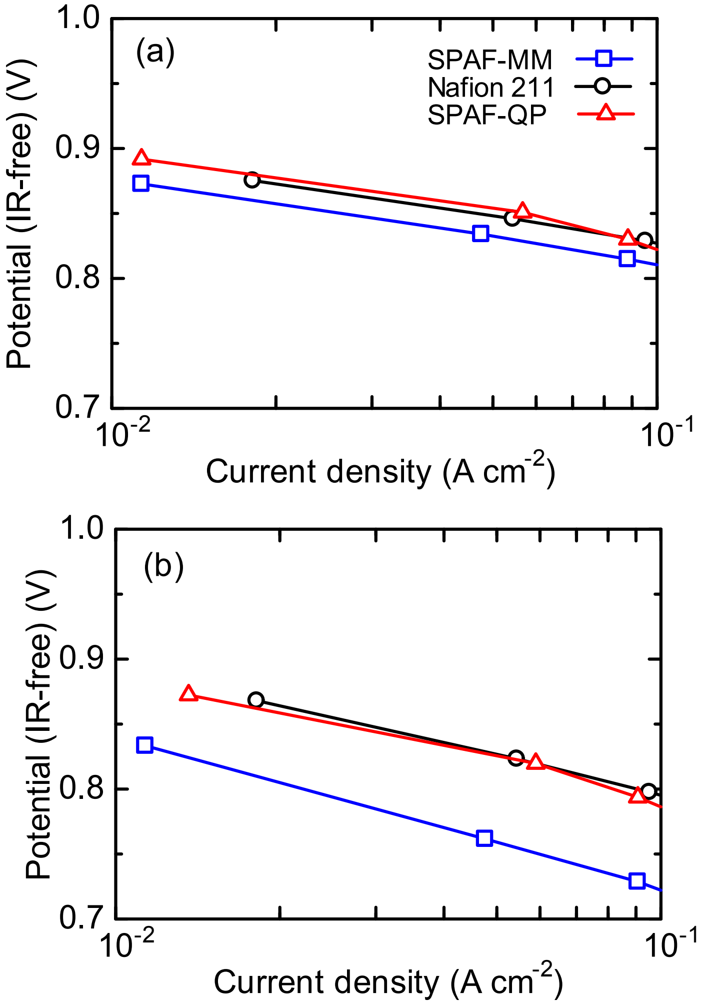

Fig. S6. Tafel curves of SPAF-MM (1.59 meq g^{-1}, 28 μm), Nafion (0.91 meq g^{-1}, 25 μm), and SPAF-QP (1.97 meq g^{-1}, 26 μm) cells with H_2/air at 80 ºC and (a) 100% and (b) 30% RH.

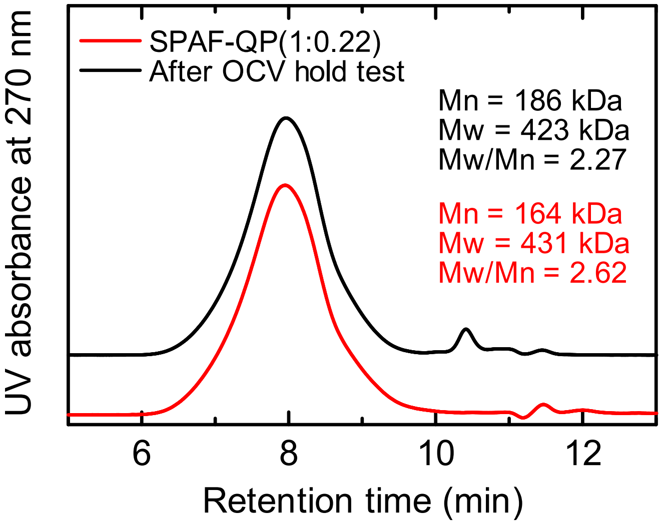

Fig. S7. GPC profiles of SPAF-QP, pristine and after the OCV hold test for 1000 h.

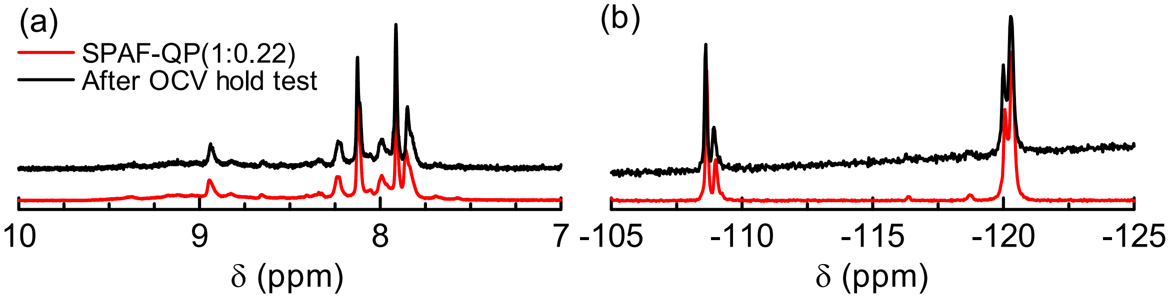

Fig. S8. (a) ^{1}H and (b) ^{19}F NMR spectra of SPAF-QP, pristine and after the OCV hold test for 1000 h in DMSO-d_6 at 80 °C.

References

[1] Junpei Miyake, Ryunosuke Taki, Takashi Mochizuki, Ryo Shimizu, Ryo Akiyama, Makoto Uchida, Kenji Miyatake, Design of flexible polyphenylene proton-conducting membrane for next-generation fuel cells, Sci. Adv. 2017;3: eaao047.

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