Supplementary information

Poly(*para*-phenylene) ionomer membranes: effect of methyl and trifluoromethyl substituents

Fanghua Liu,^a Jinju Ahn,^b Junpei Miyake^c and Kenji Miyatake*,c,d,e

^aGraduate School of Medical, Industrial and Agricultural Science, University of Yamanashi, Kofu, Yamanashi 400-8510, Japan ^bInterdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, Kofu, Yamanashi 400-8510, Japan ^cClean Energy Research Center, University of Yamanashi, Kofu, Yamanashi 400-8510, Japan ^dFuel Cell Nanomaterials Center, University of Yamanashi, Kofu, Yamanashi 400-8510, Japan ^eDepartment 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

¹H and ¹⁹F NMR spectra were measured with a JEOL JNM-ECA/ECX500 using dimethyl sulfoxide (DMSO- d_6) as a solvent and tetramethylsilane (TMS) as an internal reference. The molecular weight was measured via gel permeation chromatography (GPC) equipped with a Jasco 805 UV detector and a Shodex KF-805L column at 50 °C. *N*,*N*-Dimethylformamide (DMF) containing 0.01 M lithium bromide was used as eluent. Molecular weight was calibrated using standard polystyrene samples.

Morphology

Transmission electron microscopic (TEM) images were taken using a Hitachi H-9500 with an acceleration voltage of 200 kV. For TEM measurement, membrane samples were stained with lead ions (Pb²⁺) using PbSO₄. Small-angle X-ray scattering (SAXS, Nano-Viewer, Rigaku) equipped with a temperature/humidity-controlled chamber was used to monitor the morphology of SPP-BP-CH₃ and SPP-BP-CF₃ samples at 80 °C under different relative humidity.

Titrated IEC

Ion exchange capacity (IEC) of the membranes was measured by titration at r.t. A piece of dry membrane in acid form was immersed into 2 M NaCl aqueous solution for at least 24 h. The solution was titrated with standard 0.01 M NaOH aqueous solution. The IEC was calculated using the following equation; IEC (mequiv. g⁻¹) = $\Delta V_{NaOH} \times C_{NaOH} / W_d$, where W_d is weight of dry membrane, ΔV_{NaOH} is consumed volume of the NaOH solution, and C_{NaOH} is the concentration of the NaOH solution.

Water uptake and proton conductivity

The proton conductivity and water uptake were measured with a solid electrolyte analyzer system (MSBAD-V-FC, Bel Japan Co.) equipped with a temperature and humidity controllable chamber. The weight of the membranes at a given humidity was measured by magnetic suspension balance. The water uptake was calculated by the following equation. Water uptake = [(weight of hydrated membrane) – (weight of dry membrane)]/ weight of dry membrane \times 100. The membranes were dried at 80 °C for 3 h under vacuum to obtain the weight of dry membranes and exposed to the set humidity for at least 2 h to obtain the weight of hydrated membranes. The number of absorbed water molecules per sulfonic acid group, λ , was calculated from the water uptake and titrated IEC using the equation: λ = water uptake / (IEC $\times 18$). In-plane proton conductivity (σ) of the membranes was measured by ac impedance spectroscopy (Solartron 1255B and 1287) simultaneously in the same chamber. Ion conducting resistances (R) were determined from the impedance plot measured over the frequency range from 1 to 10⁵ Hz. The proton conductivity was calculated according to the following equation; $\sigma = L / (S \times R)$, where L and S are the distance of the electrodes and the cross-sectional area of the membrane, respectively. The volumetric IEC was calculated using the titrated IEC, dry mass (m_{dry}) and wet volume (V_{wet}) of membrane samples. IECv = (IEC \times m_{dry}) / V_{wet}. The diffusion coefficient (D_{σ}) of the proton (H⁺) in a membrane was calculated from the Nernst-Einstein equation: $D_{\sigma} = \sigma \times R \times T$ / IECv $\times F^2$, where σ is the measured ion conductivity, R is the gas constant, T is the absolute temperature, and F is the Faraday constant.

Mechanical properties

Tensile strength of the membranes was measured with a Shimadzu AGS-J 500N universal test machine attached with a Toshin Kogyo Bethel-3A temperature and humidity controllable chamber at 80 °C and 60% RH at a stretching rate of 10 mm min⁻¹. Stress versus strain curves were obtained for samples cut into a dumbbell shape (DIN-53503-S3, 35 mm × 6 mm (total) and 12 mm × 2 mm (test area)). Dynamic mechanical analyses (DMA) of the membranes (5

mm × 30 mm) were carried out with an ITK DVA-225 dynamic viscoelastic analyzer at 80 °C from 0 to 90% RH at 10 Hz. The storage modulus (E'), loss modulus (E''), and tan δ (= E''/E') of the membranes were measured.

Gas permeability

Hydrogen and oxygen permeability was measured using a GTR-Tech 20XFYC gas permeation measurement apparatus equipped with a Yanaco G2700T gas chromatograph with a Porapak Q column and a thermal conductivity detector to quantify the concentrations of the permeated gases. Argon and helium were used as the carrier gases for the measurement of hydrogen and oxygen, respectively. Membranes were placed in the center of the cells having gas inlet/outlets on both sides of the membranes. The test gas was supplied on one side of the membrane, and the carrier gas was supplied on the other side of the membrane. The same humidity conditions were applied to both test and carrier gases to ensure homogeneous wetting of the membranes. The membrane was equilibrated at the set humidity until stable permeation data were obtained. The gas permeation coefficient, Q [cm³ (STD) cm cm⁻² s⁻¹ cmHg⁻¹], was calculated by the following equation: $Q = 273/T \times 1/A \times B \times 1/t \times 1 \times 1/(76 - P_{H2O})$, where T (K) is the absolute temperature, A (cm²) is the permeation area, B (cm³) is the volume of the permeated test gas, t (s) is the sampling time, 1 (cm) is the thickness of the membrane, and P_{H2O} (cmHg) is the water vapor pressure.

Oxidative stability

To evaluate the oxidative stability of membrane, a membrane was immersed into the Fenton's reagent containing 3% H₂O₂ solution and 2 ppm Fe²⁺ (FeSO₄· 7H₂O) at 80 °C for 1 h. Subsequently, the properties of post-tested membranes were measured.



Scheme S1 Synthesis of 4,4'-dichloro-2,2'-bis(methyl)biphenyl (BP-CH₃) and 4,4'-dichloro-2,2'-bis(trifluoromethyl)biphenyl (BP-CF₃).



Fig. S1 ¹H NMR spectra for BP-CH₃ in DMSO- d_6 at 80 °C.



Fig S2 (a) ¹H and (b) ¹⁹F NNR spectra for BP-CF₃ in DMSO- d_6 at 80 °C.



Fig. S3 SAXS profiles for (a), (b) SPP-BP-CH3 and (c), (d) SPP-BP-CF3 membranes as a function of the q value at 80 °C and different relative humidity.



Fig S4 Background-corrected SAXS profiles for (a), (b) SPP-BP-CH₃-2.9 and -3.3, (c), (d) SPP-BP-CF₃-2.7 and -3.4 membranes as a function of the q value at 80 °C and relative humidity from 30 to 90% RH. The slopes in the Porod region were also included.

Mambrana	Titrated IEC - (mequiv g ⁻¹)	Swelling ratio (%)		
Weinbrane		In-plane	Through-plane	
SPP-BP-CH ₃	2.2	2.1	3.4	
	2.7	3.3	5.3	
	2.9	4.2	6.7	
	3.3	8.9	9.7	
SPP-BP-CF ₃	2.1	1.5	3.8	
	2.6	4.0	4.5	
	2.7	4.6	5.1	
	3.4	5.6	11.8	

Table S1 The swelling ratios of SPP-BP-CH₃ and SPP-BP-CF₃ membranes in fully hydrated conditions at room temperature.



Fig. S5 (a) Water uptake, (b) proton conductivity as a function of IEC and proton diffusion coefficient as a function of (c) volumetric IEC (IECv) and (d) λ at 80 and 100 °C, 20% and 80% RH for SPP-BP-CH₃-3.3 and SPP-BP-CF₃-2.1, -3.7 and -3.4 membrane.



Fig. S6 (a) IEC and (b) molecular weight (M_w) dependence of Young's modulus for SPP-BP-CH₃ and -CF₃ membranes at 80 °C and 60% RH.



Fig. S7 (a) IEC and (b) molecular weight (M_w) dependence of maximum strain for SPP-BP-CH₃ and -CF₃ membranes at 80 °C and 60% RH.



Fig. S8 (a) IEC and (b) molecular weight (M_w) dependence of rupture energy for SPP-BP-CH₃ and -CF₃ membranes at 80 °C and 60% RH.



S11

Fig. S9 Humidity dependence of (a) E', (b) E'' and (c) tan δ of SPP-BP-CH₃ and -CF₃ at 80 °C.



Fig. S10 IEC dependence of (a) E' and (b) E" for SPP-BP-CH₃ and $-CF_3$ membranes at ca. 80 °C and 0% RH (DMA data).

Membrane	Titrated IEC (mequiv. g ⁻ 1)		Integral ratio (aromatic protons /CH ₃ protons)		PDI	
	Before	After	Before	After	Before	After
SPP-BP-CH ₃ - 2.2	2.2	2.1	1.32	1.34	3.00	5.39
SPP-BP-CH ₃ - 2.7	2.7	2.7	1.45	1.64	2.93	5.86
SPP-BP-CH ₃ - 2.9	2.9	3.0	1.58	1.83	3.41	5.13
SPP-BP-CH ₃ - 3.3	3.3	3.3	1.84	2.30	3.46	6.30
SPP-BP-CF ₃ -2.1	2.1	2.1			2.32	2.35
SPP-BP-CF ₃ -2.6	2.6	2.6			2.00	2.00
SPP-BP-CF ₃ -2.7	2.7	2.6			2.12	2.49
SPP-BP-CF ₃ -3.4	3.4	3.3			3.28	3.29

Table S2 Changes of the titrated IECs, integral ratio of aromatic protons to protons of CH_3 groups, and PDI before and after the Fenton's test.



Fig. S11 The ¹H NMR spectra of (a) SPP-BP-CH₃-2.2, (b) -3.3 and ¹H NMR (left) and ¹⁹F NMR (right) spectra of (c) SPP-BP-CF₃-2.7 before (black) and after (red) the Fenton's test.



Fig. S12 (a) Water uptake and (b) proton conductivity of SPP-BP-CF₃ membranes at 80 $^{\circ}$ C before and after the Fenton's test as a function of relative humidity.



Fig. S13 Dynamic mechanical properties of SPP-BP-CF₃ membranes at 80 °C before and after the Fenton's test.



Fig. S14 Stress-strain curves of SPP-BP-CF₃ membranes before and after the Fenton's test at 80 $^{\circ}$ C and 60% RH.