Electronic Supplementary Information

High performance proton exchange membranes obtained by adjusting the distribution and content of sulfonic acid side groups

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1. Experimental Section

1.1. Materials

Phenylphosphonic dichloride was purchased from Aldrich. 4-Bromofluorobenzene and magnesium chips were obtained from Sinopharm Chemical Reagent Company and used without further purification. 4,4′-(Hexafluoroisopropylidene) diphenol (6FPP) was bought from Sinopharm Chemical Reagents Company and recrystallized from chloroform/toluene prior to use. *N,N*-dimethyl acetamide (DMAc) was dehydrated and distilled under reduced pressure and stored over 4 Å molecular sieves. Tetrahydrofuran (THF) was dehydrated with filamentous sodium and distilled prior to use. Toluene was distilled before use. Potassium carbonate was dried under vacuum at 160°C for 24 h. Other chemicals were obtained from commercial sources and used as received unless otherwise stated. Bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO) and mono-sulfonated bis(4-fluorophenyl)phenyl phosphine oxide (MSPPO) were synthesized according to our previous procedures.[1]

1.2. Synthesis of TSPPO

A 50 mL three-necked round bottom flask with 16 mL fuming sulfuric acid (50%) was immersed in an ice water bath for about 0.5 h. Then, 8 g of BFPPO was slowly added over a period of 1 h. The mixture was stirred at room temperature for 1 h, 60°C for 1 h, 90°C for 4 h and then held at 120°C for several days. After cooling to room temperature, the reaction mixture was poured to the ice water and then neutralized

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with NaOH solution. The crude product was collected by rotary evaporation and then purified by column chromatography using methanol/methylene dichloride mixture as eluent. The pure product was dried *in vacuo* at 160°C for 24 h. Yield: 50%. ^{1}H NMR (DMSO-d_6, ppm): 8.02−7.95 (2H), 7.94−7.88 (1H), 7.87−7.82 (1H), 7.58−7.42 (4H), 7.39−7.32 (2H). FT-IR (KBr, cm^{-1}): 1173 (P=O), 1096, 1050, 639 (–SO_3Na). MS (m/z): 183.8 (⅓M^{3-}), 287 (½M^{3-} + ½Na^+), 597 (M^{3-} + 2Na^+).

1.3. Preparation of polymers

All the polycondensation reactions were performed in a 100 mL three-necked round bottom flask, equipped with a nitrogen inlet/outlet, a mechanical stirrer and a Dean-Stark trap connected with a condenser. The synthesis of msPEPOF-100, tsPEPOF-120 and the corresponding poly(arylene ether phosphine oxide)s (PEPOF) was depicted as typical examples.

Synthesis of msPEPOF-100: A 100 mL flask was charged with 1.2489 g (3 mmol) of MSPPO, 1.0087 g (3 mmol) of 6FPP, 0.4561 g (3.3 mmol) of K_2CO_3, 8 mL of DMAc and 8 mL of toluene. The reaction mixture was stirred at room temperature for 0.5 h and then became homogeneous. The temperature was elevated to 150°C and held at 150°C for 4 h to dehydrate the system by azeotropic distillation, followed by removing toluene. Thereafter, the reaction mixture was held at 165°C for ~3 days, achieving very viscous polymer solution. After cooling to 120°C, the mixture was diluted with 2 mL of DMAc and then poured into 300 mL of deionized water with vigorous stirring to produce the fibrous polymer. The fibrous product was washed with hot deionized water in order to remove inorganic salts. The final product was obtained by drying *in vacuo* at 120°C for 24 h. Yield: 93%.

Synthesis of tsPEPOF-120: 0.7445 g (1.2 mmol) of TSPPO, 0.5657 g (1.8 mmol) of BFPPO, 1.0087 g (3 mmol) of 6FPP, 0.4561 g (3.3 mmol) of K_2CO_3, 8 mL of DMAc and 8 mL of toluene were added into the reaction flask. Thereafter, the reaction procedure and purification process were also similar to those of the synthesis of msPEPOF-100. The resulting product was light yellow and fibre-like. Yield: 95%.

Synthesis of PEPOF: 1.0087 g (3 mmol) 6FPP, 0.9428 g (3 mmol) BFPPO, 0.4561 g (3.3 mmol) K_2CO_3, 8 mL of DMAc and 8 mL of toluene were added to the reaction flask. Similarly, the reaction and purification were carried out like the procedures above. It is worth noting that this resulting reaction mixture was diluted with 6 mL of DMAc so as to fully remove inoraganic salts by pouring to deionized water and then by washing with boiling water. Yield: 98%.

1.4 Preparation and acidification of membranes

The salt-form ionomers were dissolved in DMSO at a concentration of 6% (w/v), and then the solutions were carefully cast onto the dust-free glass plates, followed by drying at 65°C for 48 h. After cooling, they were immersed in deionized water and the membranes peeled off. The acidification of membranes was performed by immersing the salt-form membranes in 0.5 M H_2SO_4 at room temperature for one day and 90°C for 2 hours. Subsequently, the acid-form membranes were soaked in deionized water for one day to remove residual acid and then dried under vacuum at 100°C for 24 h.

1.5 Measurements

NMR spectra were recorded on a Varian MERCURYplus 400 MHz spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent and tetramethylsilane (TMS) as internal standard. Mass spectra of monomers were carried out on a Thermofisher MSQ spectrometer. Fourier transformation infrared (FT-IR) spectra were performed on a Bruker Equinox-55 Fourier transform spectrometer. Intrinsic viscosity was determined in 0.5 g/dL DMSO solution (containing 0.05 mol/L LiBr) at 25°C using an Ubbelohde viscometer. Small-angle X-ray scattering (SAXS) measurements were performed on a SAXSess mc2 instrument with CuKa radiation (Anton Paar). The lead-stained membrane samples were prepared by immersing the acid-form membranes in 0.5 M lead acetate for 24 h, rinsing with deionized water and then drying in vacuum oven for 12 h.[2] The characteristic periodicity (***d***) between the hydrophilic and hydrophobic domains was derived from the equation of $d = 2\pi / q$, the q of which is the scattering vector. Scanning transmission electron microscopy

(STEM) observations were carried out on a JEOL JEM-2100 at an accelerating voltage of 200 kV. The samples for STEM were made of the lead-stained membranes. A strip (1 mm× 3 mm) was cut from the lead-stained membrane, then embedded into an epoxy resin and sectioned to ~120 nm thickness film samples by an ultramicrotome, which were used for STEM observation.

Ion exchange capacity (IEC) of membranes was measured by titration and ^{1}H NMR. Before titration, the membranes were soaked in the saturated NaCl solution for 48 h to liberate the H^+ completely, and then the free H^+ was titrated by 0.01 M NaOH solution with phenolphthalein as an indicator. Additionally, the IEC values of membranes were also determined by their ^{1}H NMR spectra.

The water uptake and swelling of membranes were determined by measuring the change of the weight and length between the dry and wet state. The acid-form membranes (6 cm × 6 cm × ~40 μm) were dried *in vacuo* at 100°C for 24 h. The weight (W_{dry}) and length (l_{dry}) of the dry membranes were measured. Thereafter, the membranes were immersed in deionized water at given temperatures for 24 h, then taken out and wiped off the water on the surface. The weight (W_{wet}) and length (l_{wet}) of the wet membranes were measured. The water uptake and swelling were calculated by the following equations.

$$Water\ uptake = (W_{wet} - W_{dry}) / W_{dry} \times 100\%$$

$$Swelling = (l_{wet} - l_{dry}) / l_{dry} \times 100\%$$

The oxidative stability of membranes was investigated according to a typical procedure.[3,4] The membrane samples (0.5 cm × 1 cm) with a thickness of about 40 μm were tested in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80°C. The oxidative stability of membranes was evaluated by the residual weight after immersing in Fenton's reagent for 1 h and also by the elapsed time when the membrane started to dissolve (τ_1) and dissolved completely (τ_2).

The proton conductivity of membranes was measured by an Autolab PGSTAT 302 (Eco Chemie, Netherland) apparatus with an AC current amplitude of 0.1 mA over a frequency range of 10^6–100 Hz. The membrane sample was clamped between two electrodes of the PTFE mould. Before measurement, the acid-form membrane was washed with ultrapure water several times and immersed in ultrapure water for 24 h in order to be fully hydrated. The proton conductivity (σ) was calculated according to the equation of $\sigma = L/(Rwd)$, where *L, R, w* and *d* are the distance between two electrodes, resistance, width and thickness of the membrane, respectively.

The mechanical properties were measured with a KE XIN WDW 3020 instrument under ambient conditions at a crosshead speed of 2 mm·min^{-1}. The acid-form membranes (0.5cm × 5cm × ~40μm) were equilibrated under room temperature and 50% relative humidity for 24 h before measurement following the previous procedure.[5]

2. Analysis of the chemical structure of monomer/polymers

The dept135 and ^{13}C NMR spectra of TSPPO are indicated in Fig. S1. As shown, Carbon 4 and 7 exhibited a C/P coupling constant of about 100 Hz, which is equivalent to that of the carbon atoms with similar chemical environments.[6] In contrast, Carbon 1 displayed a C/F coupling constant of ~256 Hz. The signal peaks of the carbon atoms of TSPPO were well assigned in Fig. S1.

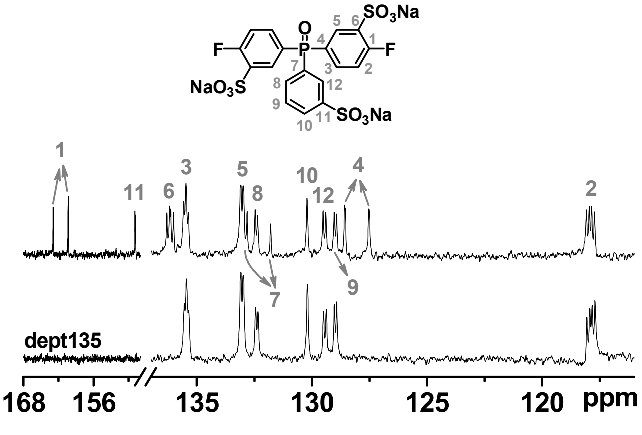

Fig. S1 Dept135 and ^{13}C NMR spectra of TSPPO.

The FT-IR spectra of TSPPO and BFPPO are shown in Fig. S2. By comparison of the IR spectra of TSPPO and BFPPO, it could be found that TSPPO presented the characteristic absorption bands of $-SO_3Na$ at 1096, 1050 and 640 cm^{-1}. The absorptions at 1096 and 1050 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations of $-SO_2-$ in the sulfonate groups, respectively, whereas the band at 640 cm^{-1} is ascribed to the stretching vibration of the S–O in the sulfonate groups.[1,7] Besides, TSPPO also exhibited the 1,3-substituted and 1,2,4- substituted characteristic bands at 1660 and 880 cm^{-1}.

Hence the NMR and FT-IR spectra confirmed the chemical structure of TSPPO.

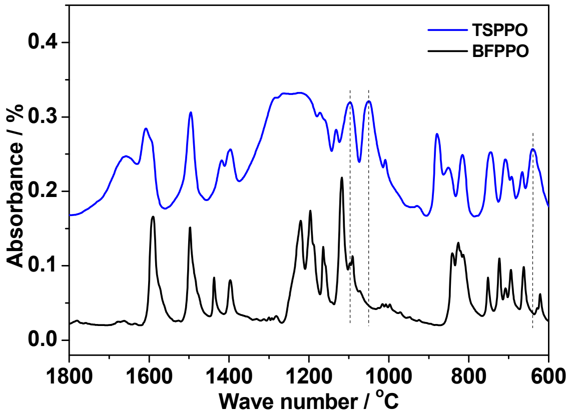

Fig. S2 FT-IR spectra of TSPPO and BFPPO.

The correponding poly(arylene ether phosphine oxide)s (PEPOF) was synthesized as a “model polymer” in order to assist the analysis of the chemical structures of the ionomers. The chemical structures of these three series of polymers are indicated in Fig. S3a. Firstly, the ^{1}H NMR spectrum of PEPOF was analyzed. As shown in Fig. S3c, some of its signal peaks were seriously overlapped, so its HMQC spectra were employed to assist the assignment of the signal peaks of hydrogen atoms, which is exhibited in Fig. S3b. As expected, the signal peaks of the carbon atoms of PEPOF in the ^{13}C NMR spectrum could be assigned (Fig. S3b), thus its signal peaks of hydrogen atoms in the ^{1}H NMR spectrum could be determined by the HMQC spectra. On the other hand, the ^{1}H NMR spectrum of msPEPOF-100 could be well assigned (Fig. S3c). As indicated in Fig. S3a, the non-sulfonated repetitive unit of tsPEPOF-x (including tsPEPOF-100 and -120) is exactly the repetitive unit of PEPOF. Moreover, tsPEPOF-x and msPEPOF-100 possess identical structural moieties, *i.e.* benzenesulfonate side groups and hexafluoroisopropylidene diphenyl moieties. These hydrogen atoms with similar chemical environments have approximate chemical shifts.[7] Therefore, with the assistance of the ^{1}H NMR spectra of PEPOF and msPEPOF-100, the assignment of the ^{1}H NMR spectrum of tsPEPOF-x could be determined, which is displayed in Fig. S3c. As a result, the ^{1}H NMR spectra of PEPOF, msPEPOF-100 and tsPEPOF-x verified their chemical structures.

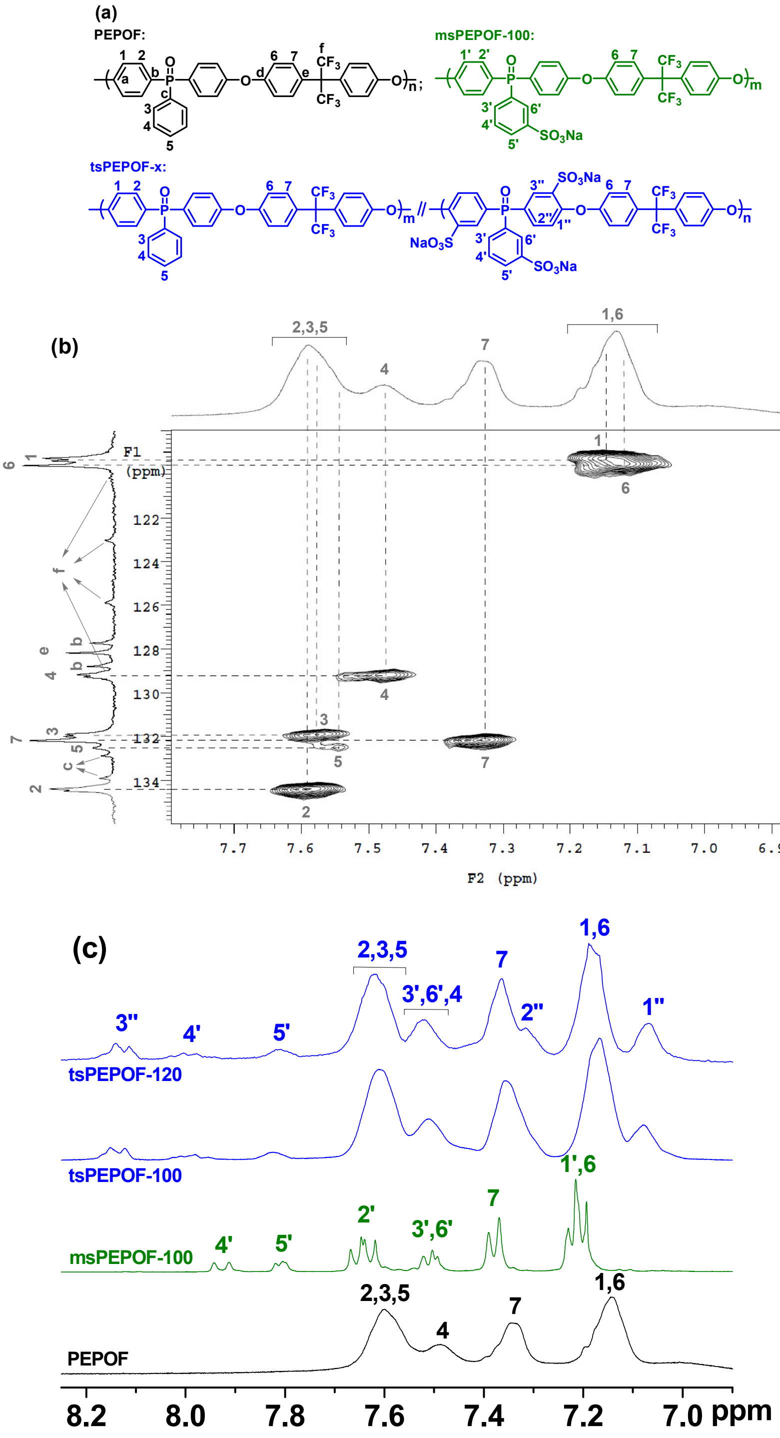

Fig. S3 Chemical structure of PEPOF and sulfonated polymers (a), HMQC spectrum of PEPOF (b), their ^{1}H NMR spectra (c).

The FT-IR spectra of PEPOF, msPEPOF-100 and tsPEPOF-x are shown in Fig. S4. They all exhibited a strong absorption of phosphine oxide groups at ~1176 cm^{-1}. Different from PEPOF, tsPEPOF-x displayed the characteristic absorptions of sulfonate groups at 1084, 1030 and 622 cm^{-1}, whereas msPEPOF-100 presented the characteristic absorptions of sulfonate groups at 1105, 1036 and 622 cm^{-1}.[1,7] The FT-IR spectra of PEPOF, msPEPOF-100, tsPEPOF-x further verified their chemical structures.

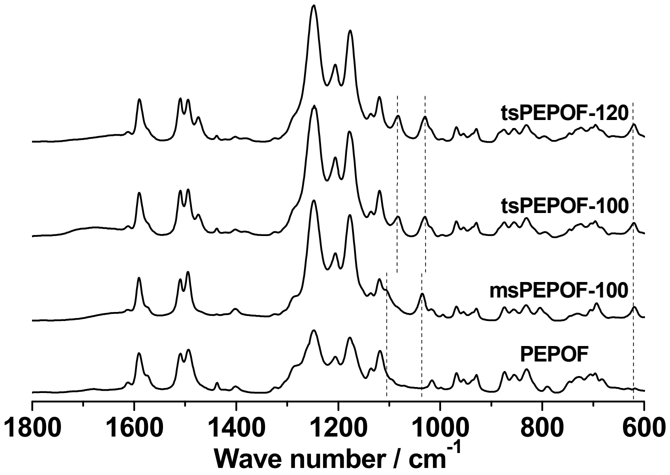

Fig. S4 FT-IR spectra of PEPOF and sulfonated polymers.

3. SAXS of PEPOF

As a contrast, the microstructure of the PEPOF membrane was investigated by SAXS. Its SAXS profile is shown in Fig. S5. As expected, it exhibited no ionomer peak because PEPOF is a homopolymer and doesn't possess phase separation.

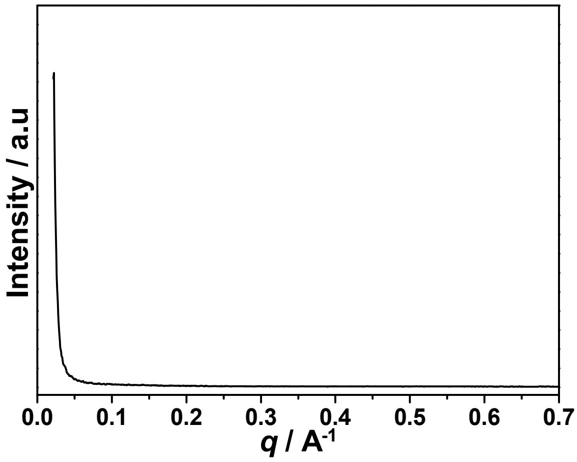

Fig. S5 SAXS profile of PEPOF.

4. Mechanical properties

The mechanical properties of these membranes are compiled in Table S1. The membranes demonstrated a tensile strength of 41.6–45.6 MPa, a Young's modulus of

~1.3 GPa, and an elongation at break of ~6%, which are comparable to the mechanical properties of many other hydrocarbon PEMs.[5,8]

Table S1 Mechanical properties of ionomer membranes.

Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
msPEPOF-100	41.6	1.34	6.1
tsPEPOF-100	41.8	1.35	6.5
tsPEPOF-120	45.6	1.37	6.7

5. Nyquist plots of membranes

The Nyquist plots of membranes were obtained by AC impedance spectroscopy, which were exhibited in Fig. S6. As shown, *Z″* is the imaginary part of the impedance while *Z′* is the real part of the impedance. The impedance (R) with the minimum imaginary parts from those curves was used to calculate the proton conductivity according to the literatures.[9,10]

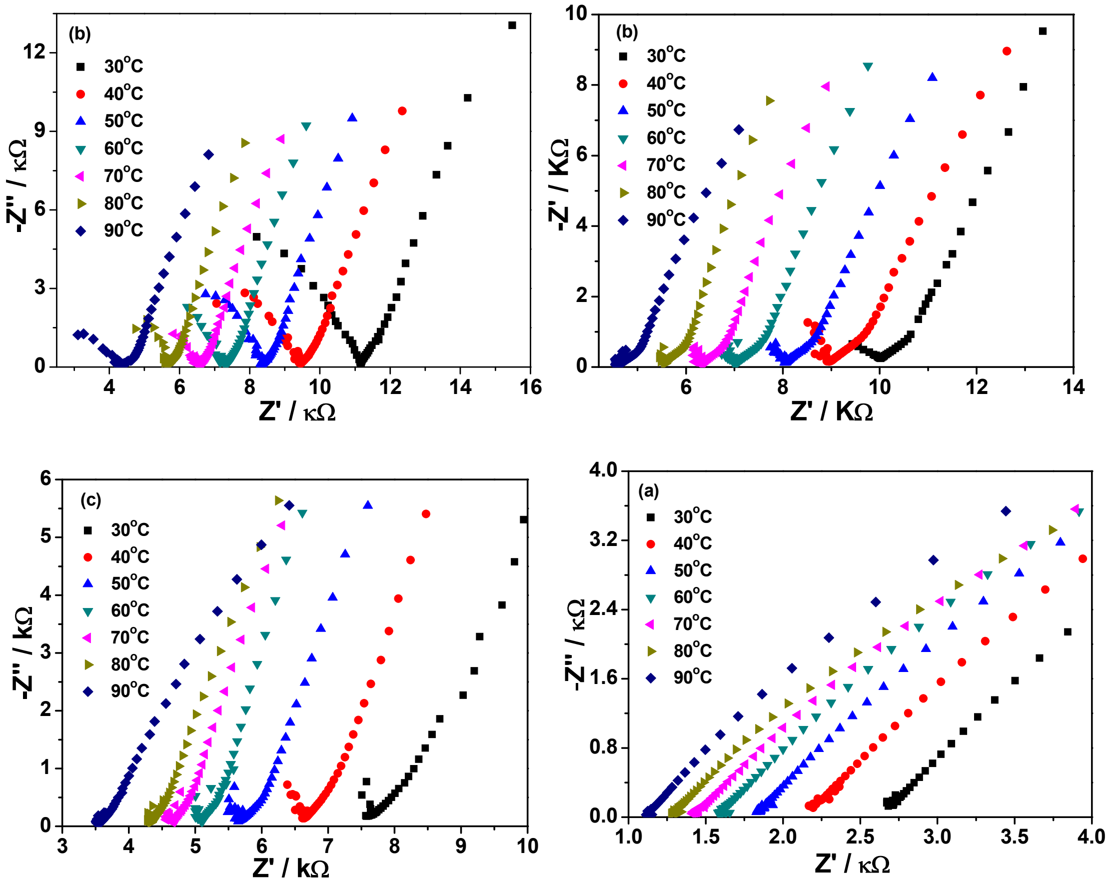

Fig. S6 The Nyquist plots of msPEPOF-100 (a), tsPEPOF-100 (b), tsPEPOF-120 (c) and Nafion 117 (d) at various temperatures.

6. Ion exchange capacity of membranes

The ion exchange capacity (IEC) of sulfonated ionomers is listed in Table S2. The theoretic value was calculated by molecular formula while the experimental value was obtained by titration and ^{1}H NMR.[6,7,11,12] The theoretic values of IEC basically coincides with the experimental ones determined by titration and ^{1}H NMR. In addition, it could also be found that the msPEPOF-100 membrane and the tsPEPOF-100 membrane with equal sulfonation degree showed equal IEC.

Table S2 Sulfonation degree and IEC of ionomer membranes.

Polymer	Sulfonation degree (%)	IEC (meq/g)		
		calculated	measured[a]	measured[b]
msPEPOF-100	100	1.45	1.39	1.38
tsPEPOF-100	100	1.45	1.38	1.37
tsPEPOF-120	120	1.70	1.62	1.79

[a] measured by titration, [b] determined by the ^{1}H NMR spectra.

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