

Terminally-Crosslinked Sulfonated Poly(fluorenyl ether sulfone) as a Polymer Electrolyte Membrane for both PEMFC and DMFC Application

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Experimental

Materials. Bis-(4-fluorophenyl)-sulfone (FPS) and hydroquinone sulfonic acid potassium salt (HQS) were obtained from Aldrich Chemical Co. 4,4'-(9-fluorenylidene)biphenol (FBP) was obtained from Fluka and recrystallized from water and ethanol. HQS was recrystallized from water. Potassium carbonate, FPS and FBP were dried under vacuum at 60 °C for 24 h prior to the polymerization. All the other chemicals were obtained from commercial sources and used without further purification.

Characterization. ¹H NMR spectra were recorded on a Bruker Advance DPX-500 instrument using DMSO-*d*₆ (or otherwise mentioned) as a reference or internal deuterium lock. FTIR spectra were recorded on a Nicolet MAGNA 560-FTIR spectrometer.

Synthesis of sulfonated poly(fluorenyl ether sulfone) copolymers.

Synthesis of hydroxy-terminated PFES-50 (1): Bis-(4-fluorophenyl)-sulfone (6 g, 23.60 mmol), hydroquinone sulfonic acid (3.23 g, 14.16 mmol), 4,4'-(9-fluorenylidene)biphenol (3.64 g, 10.38 mmol) and potassium carbonate (6.85 g, 49.56 mmol) were added to a mixture of dimethyl acetamide (45 mL) and toluene (35 mL) in a 250 mL round bottom flask which was equipped with a Dean-stark apparatus. The reaction mixture was heated at 150 °C for 4 h until the water was essentially removed by azeotropic distillation and toluene was distilled out. The temperature of the reaction mixture was then raised to 180 °C and allowed to stir at this temperature for another 24 h under a nitrogen atmosphere. After this time, the mixture was cooled to room temperature and dissolved in DMF (15 mL), followed by pouring into methanol (500 mL). The product was collected by filtration, washed several times with deionized water to remove residual inorganic materials, and dried at 60 °C under vacuum for at least 48 h to give 5.26 g (41%) of the hydroxyl-terminated PFES-50 (1) as white beads. ¹H-NMR (DMSO-*d*₆) δ 7.8-7.9 (br signal, 10H, ArH), 7.3-7.4 (br signal, 7H, ArH), and 6.9-7.1 (br signal, 18H, ArH); IR (KBr) cm⁻¹ 3447, 3066, 1580, 1473, 1306, 1153, 1024, 872 and 833.

Synthesis of allyl-terminated PFES-50 (2): Sodium hydride (60% w/w dispersion in mineral oil; 0.36 g, 9.01 mmol) was added in a DMF (17 mL) solution of the hydroxyl-terminated PFES polymer 1 (4.52 g, 4.48 mmol) at 0 °C under nitrogen. This was left to stir for 1 h at this temperature before allyl bromide (0.38 mL, 4.48 mmol) was added. The reaction mixture was stirred at room temperature overnight and then precipi-

tated into 500 mL of ethanol. The filtrate was collected, washed with deionized water several times to give a white powder, which was further treated with NaOH solution (15% in water) at 80 °C for 3 h, HCl (10% in water) and deionized water at the same conditions for the deallylation of the sulfonate ester. Finally, the polymer obtained was washed repeatedly with deionized water and dried at 60 °C under vacuum to produce 4.16 g (92.04%) of the allyl-terminated PFES-70 (2) as a white powder; ¹H-NMR (DMSO-*d*₆) δ 7.8-7.9 (br signal, 10H, ArH), 7.4-7.4 (br signal, 5H, ArH), 7.3 (br signal, 2H, ArH_a), 6.9-7.1 (br signal, 18H, ArH), 5.9-6.1 (m, 2H, CH), 5.5-5.6 (m, 4H, CH₂) and 3.8-3.9 (m, 4H, CH₂); IR (KBr) cm⁻¹ 3447, 3065, 1588, 1473, 1298, 1153, 1405, 1305, 1252, 1115, 1084, 917, and 841.

Fabrication of crosslinked membranes. All membranes were prepared in a DMF solution of the corresponding polymers using the solution-casting method, and the film thickness was controlled by means of a doctor blade. The crosslinked PFES-50 membrane was obtained by addition of the 2,6-bis(4-azido-benzylidene)-4-methyl-cyclohexanone 3 (30 wt % compared to polymer 2) in a stirred DMF solution of the allyl-terminated poly(fluorenyl ether sulfone) (20%, w/v). The solution was then poured onto a glass plate and the cast film was dried in a vacuum oven at 180 °C for 18 h to complete crosslinking. The membrane on the glass was soaked in water at room temperature to remove residual solvent, and peeled off by immersion in deionized water. The thermally-cured membrane was immersed in NaOH solution (15% in water) at 80 °C for 4 h, followed by HCl (10% in water) at 80 °C for 3 h, and deionized water at 80 °C for 3 h. Finally, the membrane was washed repeatedly with deionized water. For comparison, sulfonated poly(fluorenyl ether sulfone) (PFES-50n) was also prepared in the same method except the addition of the crosslinker 3 during the film casting.

Proton conductivity. Proton conductivity (σ) of each membrane coupon (size: 1 cm × 4 cm) was obtained using $\sigma = l/RA$ (l : distance between reference electrodes, A : cross-sectional area of a membrane coupon). Here, ohmic resistance (R) was measured by four-point probe alternating current (ac) impedance spectroscopy using an electrode systems connected with an impedance/gain-phase analyzer (SI-1260) and an electrochemical interface (SI-1287) over the frequency range from 0.1 to 2000 kHz. The proton conductivity value was obtained by the average of at least 4 different tests. The conductivity measurements were performed from rt to 100 °C, and the film samples were placed in a closed cell to keep the relative humidity at 100%.

Methanol diffusion coefficient. Methanol permeability of the membranes was measured at room temperature using a

liquid permeability cell. The cell consisted of two reservoirs, which were separated by a vertical membrane coupon with a diameter of 1.5 cm of test area. 3% of methanol solution in water was placed on one side of the cell ($V_A = 13$ mL) and deionized water was filled on the other side ($V_B = 13$ mL). The magnetic stirrers were used continuously during the measurements. The concentration-driven diffusion of methanol from compartment A to B across the membrane was monitored as a function of time, by a differential refractive index using a RI-750F refractometer. Prior testing, all membranes were immersed in deionized water for 24 h.

Dimensional stabilities. Dimensional change of the membranes was evaluated from measuring the swelling ratio of the

membranes, which was investigated by immersing the round-shaped membranes into water at room temperature and 80 °C, respectively, and the changes of both in-plane and through-plane direction were calculated using the following equations:

$$\Delta t (\%) = (t - t_{\text{dry}}) / t_{\text{dry}} \times 100$$

$$\Delta l (\%) = (l - l_{\text{dry}}) / l_{\text{dry}} \times 100,$$

where t_{dry} and l_{dry} are the thickness and diameter of the dried membranes, respectively, and t and l refer to those of the membranes immersed in water for 24 h. The dried membranes were prepared by placing membranes under vacuum at 60 °C for 24 h prior to the measurement.

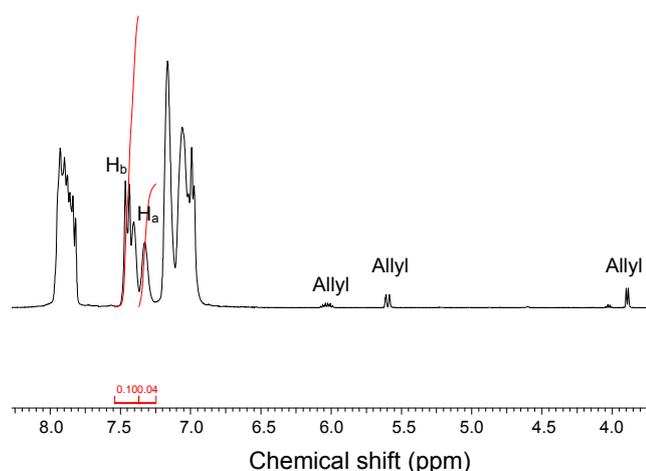


Figure S1. $^1\text{H-NMR}$ spectra of the allylated PFES-50 (2) in $\text{DMSO-}d_6$.

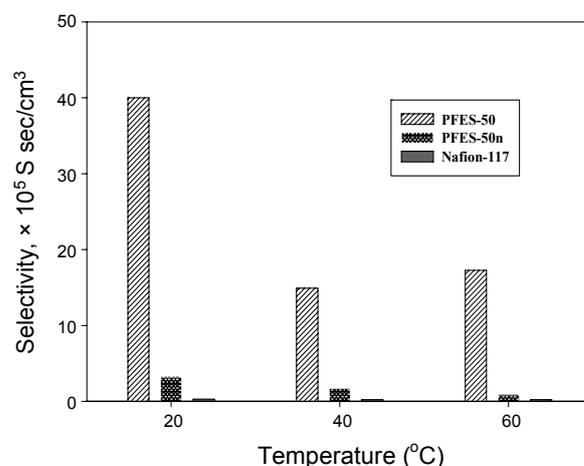


Figure S2. Selectivity of the crosslinked PFES-50, its non-crosslinked counterpart PFES-50n and Nafion[®]-117 at 20, 40 and 60 °C.

Table S1. Proton conductivity and IEC of the crosslinked membrane (PFES-50), its azide-free counterpart (PFES-50n) and Nafion[®]-117

Membrane	proton conductivity, σ (S/cm)					IEC (meq/g)
	20 °C	40 °C	60 °C	80 °C	100 °C	
PFES-50	0.040	0.082	0.152	0.201	0.285	0.88 (1.23) ^a
PFES-50n	0.064	0.091	0.127	0.169	0.201	1.22 (1.23) ^a
Nafion [®] -117	0.08	0.1	0.14	0.16	0.17	0.91

^aTheoretical IEC calculated from degree of sulfonation determined by $^1\text{H-NMR}$

Table S2. Methanol diffusion coefficient for PFES-50, PFES-50n and Nafion[®]-117 at different temperature

Membrane	Methanol permeability, $\times 10^{-8}$ cm ² /sec		
	20 °C	40 °C	60 °C
PFES-50	1	5.5	8.8
PFES-50n	19.8	52.6	146
Nafion [®] -117	279.1	477.5	657.1