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A clustered sulfonated poly(ether sulfone) based on a new fluorene-based bisphenol monomer

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A new fluorene-based bisphenol monomer containing two pendant phenyl groups, 9,9-bis(3-phenyl-4hydroxy)phenyl-fluorene, was readily synthesized in high yield by a one-step reaction from inexpensive starting materials. A series of poly(ether sulfone)s with clustered sulfonic acid groups was prepared for 10 fuel cell applications by polycondensation of the new monomer with bis(4-hydroxyphenyl)sulfone and

- bis(4-fluorophenyl)sulfone, followed by sulfonation exclusively on the fluorine rings and pendant phenyl rings, using concentrated sulfuric acid at room temperature. The sulfonated polymers gave tough, flexible, and transparent membranes by solvent casting. The ionic exchange capacity (IEC), water-uptake, dimensional stabilities, mechanical properties, thermal and oxidative stabilities as well as proton
- ¹⁵ conductivities and single fuel cell properties of the membranes were investigated. It was found that these membranes show good proton conductivities and fuel cell performance under low humidity conditions, and their proton conductivity also exhibits light humidity dependence..

Introduction

Proton exchange membrane fuel cells (PEMFC) are of interest for ²⁰ their utility in automotive and portable electronic applications because of high efficiency and power density, quiet operation, and low emissions levels.¹⁻³ Perfluorosulfonic acid (PFSA) polymers such as Nafion[®] (DuPont) are the most widely used proton exchange membrane (PEM) materials in fuel cells due to

- ²⁵ their high proton conductivity and chemical stability, but limitations such as cost, fuel crossover, and restricted operation temperature have impeded their widespread adoption in PEMFC. These challenges have driven the investigation of aromatic hydrocarbon polymers as alternative PEM materials.⁴⁻⁶ The most
- ³⁰ widely reported aromatic PEM include sulfonated derivatives of poly(arylene ether ketone)s,⁷⁻⁹ poly(arylene ether sulfone)s,¹⁰⁻¹² poly(arylene ether nitrile)s,^{13,14} poly(arylene sulfide sulfone)s,^{15,16} poly(arylene ether)s,^{17,18} and polyimides.^{19,20} Aromatic PEMs are advantageous in terms of thermal stability and lower gas
- ³⁵ permeability, but they typically require larger amounts of water, and hence sulfonic acid content, in order to achieve proton conductivities comparable to PFSA membranes. In addition, their proton conductivity generally exhibits high humidity dependence and was much lower than that of Nafion under low humidity 40 conditions.

Several approaches have been examined to improve aromatic PEM proton conductivity under conditions of reduced relative humidity and elevated temperatures. One of the effective strategies is the design of multiblock PEMs based on hydrophilic

⁴⁵ and hydrophobic oligomers.²¹⁻²⁸ The sequential block structure of these PEM promotes phase separation between hydrophilic and hydrophobic segments, resulting in much higher proton

conductivity being achieved in a reduced humidity environment in comparison with random sulfonated copolymers. Some ⁵⁰ multiblock PEMs with long hydrophilic and hydrophobic block segments exhibited clear lamellar morphology with wellconnected hydrophilic channels and proton conductivity comparable to that of Nafion 212 at low humidity.²⁵⁻²⁷ The synthetic route for these multiblock copolymers often requires a ⁵⁵ multi-step reaction, and it is not easy to control the length of hydrophilic and hydrophobic block oligomers.

Another approach to enhance PEM performance can be realized by introducing locally and densely sulfonated structures into the aromatic polymer backbone.²⁹⁻³⁵ The large difference in 60 polarity between the locally and densely sulfonated units and hydrophobic units of the polymers results in the formation of well-defined nanophase-separated structures, which induces efficient proton conduction. Ueda and coworkers reported sulfonated poly(ether sulfone)s with ten sulfonic acid groups in 65 each repeating unit by postsulfonation.³³ The sulfonated polymers (IEC=1.96-2.38 mequiv g⁻¹) exhibited good proton conductivity under low humidity conditions, which was comparable to that of Nafion 117 over a wide range of relative humidity (RH). In our previous work, we reported side-chain-type poly(arylene ether 70 sulfone)s containing densely populated flexible butylsulfonic acid pendant units.35 These sulfonated polymers displayed advantageous proton conductivities with relatively low water contents and good conductivity-swelling behavior.

Over the last few years, much research focus has been on ⁷⁵ fluorene-based sulfonated poly(arylene ether)s.^{24,25,36-44} It has been demonstrated that fluorene-based PEM show some attractive properties, not only for chemical, thermal, and mechanical stability, but also good proton conductivities and fuel cell performance over several thousand hours.³⁹ However, the availability of fluorene-based monomers are limited and the resulting fluorene-based PEMs derived from the monomers often contain sulfonic acid groups directly attached to the polymer

- ⁵ main chain. It has demonstrated that aromatic PEMs with pendant sulfophenyl groups generally exhibited a comparatively better balance between proton conductivity and water dimensional swelling than PEM with sulfonic acid groups attached directly onto the aromatic chain. Furthermore, PEMs sulfonated on
- ¹⁰ pendant phenyl groups rather than on the main chain were demonstrated to have a significantly higher thermo-oxidative stability.⁴⁵ In the present work, we report a new easily-prepared and inexpensive fluorene-based monomer containing two pendant phenyl groups and resulting poly(ether sulfone)s with clustered
- ¹⁵ pendant sulfonic acid groups. The membrane properties, such as thermal stability, mechanical stability, oxidative stability, water uptake, morphology, and fuel cell performance were investigated.

Experimental section

Materials

²⁰ 2-Phenylphenol, 9-fluorenone, mercaptopropionic acid (MPA), bis(4-hydroxyphenyl)sulfone (BHPS), and bis(4fluorophenyl)sulfone (BFPS) were purchased from Sigma-Aldrich. N-Methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), and all other solvents and reagents were reagent grade ²⁵ and were used as received.

9,9-Bis(3-phenyl-4-hydroxy)phenyl-fluorene (BPHF)

To a 250 mL four necked round bottom flask, equipped with a reflux condenser, mechanical stirrer, nitrogen inlet and a dropping funnel, 7.20 g (0.04 mol) of 9-fluorenone, 17.02 g (0.1

- $_{30}$ mol) of 2-phenylphenol, 0.1 mL of MPA and 20 mL of toluene were introduced. The reaction mixture was stirred under nitrogen atmosphere at 40 °C for 30 min. 1.5 mL of 98 wt.% $\rm H_2SO_4$ was then added drop-wise over a period of 10 min, and the temperature was thereafter raised to 60 °C for 4–6 h with stirring.
- ³⁵ When the reaction mixture became solid, it was cooled down and transferred into methanol. White solid product was obtained by filtration. Crude product was recrystallized from dimethylacetamide (DMAc) to afford 17.29 g (Yield: 86 %) of pure white powder 9,9-bis(3-phenyl-4-hydroxyphenyl)fluorene,
- ⁴⁰ mp: 268–269 °C. ¹H NMR (300 MHz, DMSO-*d*₆; ppm): 9.37 (s, 2H, -OH), 7.88 (d, *J*=7.2, 2H, H₂), 7.48 (d, *J*=7.2, 2H, H₅), 7.29-7.38 (m, 12H, H₃, H₁₅, H₁₆, H₄), 7.24 (m, 2H, H₁₇), 7.02 (s, 2H, H₉), 6.97 (d, *J*=8.4, 2H, H₁₃), 6.84 (d, *J*=8.4, 2H, H₁₂). ¹C NMR (75 MHz, DMSO-*d*₆; ppm): 153.03 (C₁₁), 151.4 (C₆), 139.4 (C₁),

Synthesis of poly(ether sulfone)s (4-PES-xx)

⁵⁰ A typical synthetic procedure, illustrated by the preparation of 4-PES-38 copolymer (xx: BPHF/BHPS=38/62), is described as follows. 1.146 g (2.28 mmol) BPHF, 0.931 g (3.72 mmol) BHPS, 1.526 g (6 mmol) BFPS, 1.076 g (7.8 mmol) K₂CO₃, 15 mL NMP and 7 mL toluene were added into a 100 mL three-neck flask ⁵⁵ equipped with a mechanical stirrer, a Dean-Stark trap and a nitrogen inlet. The solution was allowed to reflux at 140 °C while the water was azeotropically removed from the reaction mixture. After 4 h, the toluene was removed from the reaction by slowly increasing the temperature to 160 °C, and then the reaction was allowed to continue for another 10-15 h. After the reaction, 5 mL of NMP was added to the mixture to reduce the solution viscosity. The solution was poured into 500 mL deionized water with vigorous stirring. The resulting fibrous copolymer was washed with deionized water and hot methanol several times, and dried at 65 100 °C under vacuum for 24 h.

Sulfonation

12 h.

The sulfonation reaction was conducted according to the method reported in our preceding studies.^{45,46} A typical reaction for 4-SPES-38 is illustrated as follows: To a 100 mL of flask, 1 g of 4-70 PES-38 and 20 mL of concentrated sulfuric acid (98%) were added. After stirring at room temperature for 4 h, the clear and homogeneous viscous solution was poured into a mixture of water and ice to get a silk-like solid. The white solid was washed with water until the water reached neutral pH. Then the 75 sulfonated copolymer was dried in a vacuum oven at 100 °C for

Membrane preparation

The dried sulfonated copolymers were readily dissolved as 10–15 wt % solutions in DMAc at 60 °C. The solutions were filtered, ⁸⁰ cast onto glass plates with a doctor blade, dried at 60 °C for 12 h, and then treated in vacuum at 100 °C for 10 h. The as-cast membranes were immersed into 2.0 M H₂SO₄ solution for 24 h at room temperature and then thoroughly washed with deionized water. Tough, ductile ionomer membranes were prepared with

 $_{85}$ controlled thickness in the range of 50–70 μm , depending on the casting solution concentration.

Measurements

¹H NMR spectra were measured on a 300 MHz Bruker AV 300 spectrometer using DMSO-*d*₆ as solvent. The thermogravimetric ⁹⁰ analyses (TGA) were obtained in nitrogen with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C min⁻¹. The gel permeation chromatographic (GPC) analysis was carried out with Tosoh HLC-8320 instrument (NMP as eluent and polystyrene as standard).

- Ion exchange capacities (IEC) of the membranes were determined by titration. A sample membrane in proton form was immersed in 2M NaCl aqueous solution for 48 h to exchange the H^+ ions with Na⁺ ion. Released protons were titrated by 0.01 M NaOH solution using phenolphthalein as an indicator.
- The humidity dependence of water uptake was measured by placing a membrane in a thermocontrolled humidity chamber for 6 h. Then, the membrane was removed and quickly weighed on a microbalance. Water uptake was calculated from: $WU=(W_w - W_d)/W_d \times 100\%$, where W_d and W_w are the weights of dry and 105 corresponding wet membranes, respectively. The dimensional changes of the membranes were measured in the thickness and inplane direction, which were calculated by $\Delta T = (T_{wet} - T_{dry})/T_{dry}$, $\Delta L = (L_{wet} - L_{dry})/L_{dry}$, where T_{dry} , T_{wet} , L_{dry} , and L_{wet} are the thickness and length of dry and wet samples, respectively.

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The proton conductivity (σ , S/cm) of each membrane coupon (size: 1 cm × 4 cm) was obtained using $\sigma = d/L_s W_s R$ (*d*: distance between reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively). The resistance value (*R*)

- ⁵ was measured over the frequency range from 100 mHz to 100 kHz by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solartron 1260) and an electrochemical interface (Solartron 1287, Farnborough, Farnborough,
- ¹⁰ Hampshire, UK). The membranes were sandwiched between two pairs of gold-plate electrodes. The membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1.0 cm. Conductivity measurements under fully hydrated conditions were carried out in a thermo-controlled ¹⁵ chamber with the cell immersed in liquid water.

For transmission electron microscopy (TEM) observations, the membranes were stained with lead ions by ion exchange of the sulfonic acid groups in 0.5 M lead acetate aqueous solution. After ion exchange, the membranes were rinsed several times

²⁰ with deionized water, and dried in vacuum oven for 12 h. The stained membranes were embedded in epoxy resin, sectioned to 70 nm thickness with a RMCMTX Ultra microtome, and placed on copper grids. Electron micrographs were taken with a Carl Zeiss LIBRA 120 energy-filtering transmission electron ²⁵ microscope using an accelerating voltage of 120 kV.

Membrane electrolyte assemblies (MEAs) were prepared from catalyst inks containing with 20 wt% Pt/C (Johnson Matthey Fuel Cell, USA) and 5 wt% Nafion ionomer (EW=1,100, DuPont, USA) by using the screen printing method.⁴⁷ The active

³⁰ area of MEAs was 5 cm² with Pt catalyst loading of 0.3 mg cm⁻². H₂ / O₂ fuel cell performance of the MEAs was evaluated using a fuel cell test station (SMART I, WonATech, Seoul, Korea). Polarization curves were obtained at 80 °C under 50% and 100% relative humidity (RH) conditions.

35 Results and discussion

Synthesis of monomer

The monomer BPHF was synthesized from 9-fluorenone and 2phenylphenol by a phenol condensation reaction catalyzed using MPA and sulfuric acid (Scheme 1). The reaction is facile to 40 conduct, using inexpensive starting materials, has a high yield,

- and the monomer is readily purified by crystallization. The structure of BPHF was confirmed by NMR spectroscopy. As shown in Fig. 1, the –OH signal appeared at 9.37 ppm and the protons in the pendant phenyl groups (H_{15} , H_{16} and H_{17}) appeared
- ⁴⁵ at 7.24-7.38 ppm. In the ¹³C NMR spectrum, all the 17 carbon atoms had resonances in the region of 60–160 ppm. The unambiguous assignments of each proton and carbon in the

spectra, determined by 2D NMR methods, are in complete agreement with the proposed molecular structure, which indicated 50 the successful preparation of the target new fluorene-based monomer BPHF.



Scheme 1 Synthesis of the monomer BPHF.



Fig. 1 ¹H and ¹C NMR spectra of monomer BPHF.

Synthesis of copolymers and sulfonation

⁶⁰ Poly(ether sulfone) copolymers (4-PES-xx, xx: mole ratio (%) of BPHF) were synthesized by polycondensation using various feed ratios of BPHF/BHPS, resulting in copolymers with different molar percentages of BPHF, as shown in Scheme 2. The polymerization reactions proceeded smoothly to high molecular ⁶⁵ weight ($M_n > 70,000$ g mol⁻¹) after 10-15 h reaction times. Table 1 shows the molecular weight, polydispersity index, and inherent viscosity of 4-PES-xx copolymers, which is consistent with the results of typical polycondensation reactions. The molecular weight of 4-SPES-xx showed a slight increase with increasing ⁷⁰ percentage of BPHF content, indicating that BPHF has a higher reactivity than BHPS.



Scheme 2 Synthesis of copolymers 4-PES-xx and 4-SPES-xx.

5 Table 1	Physical	properties	of 4-PES-xx	and 4-SPES-xx	copolymers
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Copolymers		$\eta_{\rm inh}$ (dL g ⁻¹) ^b	$\eta_{ m inh}$.		
	$M_{\rm n}^{\rm a}$ (×10 ⁴ g mol ⁻¹) $M_{\rm w}$ (×10 ⁴ g mol ⁻¹)		PDI		$(dL g^{-1})^{c}$
4-PES-30	7.25	11.54	1.59	0.51	0.64
4-PES-34	7.69	11.93	1.55	0.52	0.67
4-PES-38	8.52	13.72	1.61	0.55	0.72
4-PES-42	9.80	15.68	1.60	0.60	0.79

^{*a*} Measured at 25 °C using NMP as solvent and polystyrene standards. ^{*b*} Viscosity before sulfonation; 0.5 g dL⁻¹ in NMP solution at 30 °C. ^{*c*} Viscosity after sulfonation; 0.5 g dL⁻¹ in NMP solution at 30 °C.

Electrophilic sulfonation using reagents such as sulfuric acid preferentially introduce sulfonic acid groups onto electron-rich sites of aromatic rings. Our earlier work⁴⁴ has shown that pendent ¹⁰ phenyl rings attached to electron-donating polymer chain sites can be completely sulfonated at the para position, even under mild reaction conditions using sulfuric acid. In the present work, the 4-PES-xx copolymers were sulfonated at room temperature by using concentrated sulfuric acid as both solvent and reagent ¹⁵ according to our preceding studies. In all of the copolymers, full sulfonation at four substitution sites, on the pendant phenyl and fluorenyl rings, was complete in 4 h. The resulting sulfonated copolymers, denoted as 4-SPES-xx, were readily soluble in polar aprotic solvents such as NMP, DMAc and DMSO. The inherent ²⁰ viscosities of the sulfonated copolymers are shown in Table 1 and are higher than those of the corresponding 4-PES-xx copolymers, because of sulfonic acid hydrogen-bonding interactions between polymer chains. Flexible, tough and ductile 4-SPES-xx membranes were obtained by solvent-casting.

The structures of 4-PES-xx and 4-SPES-xx copolymers were determined by NMR spectroscopy. ¹H and ¹C NMR spectra of 4-PES-38 and 4-SPES-38 in DMSO-*d*₆ are displayed in Fig. 2 and 3, respectively. In comparison with the ¹H NMR spectrum of the parent copolymer 4-PES-38, the H₃, H₅ and H₁₆ signals of 4-³⁰ SPES-38 exhibit obvious deshielding due to the strongly electron-withdrawing effects of -SO₃H and appear at 7.83, 7.76 and 7.50 ppm, respectively. Two new signals in the ¹C NMR spectrum of 4-SPES-38 are assigned to the carbon atoms (C₄ and C₁₇) attached to the sulfonic acid groups and appear at 147.99 and 146.74 ppm, respectively. No ¹H and ¹C NMR spectral evidence for partially sulfonated copolymers could be observed and the spectra are in complete agreement with the target structures of the copolymers containing tetrasulfonated units, suggesting that the sulfonation s reaction was selective and complete. Furthermore, the experimental IEC values (Table 2) for all the 4-SPES-xx copolymers were close to the theoretical values, further indicating complete sulfonation.



Fig. 2 1 H and 1 C NMR spectra of 4-PES-38 copolymer.

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Fig. 3 ¹H and ¹C NMR spectra of 4-SPES-38 copolymer.

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Thermal and mechanical properties

- ⁵ The thermal stabilities as measured by TGA 5% weight loss temperatures are listed in Table 2. The TGA curves of all sulfonated copolymers are shown in Fig. 4. A two-step degradation profile was observed for 4-SPES-xx membranes in their acid form. There was no weight loss up to 200 °C because
- ¹⁰ the samples were preheated at 150 °C for 20 min to remove absorbed water. The first weight loss occurred from 300-400 °C, which is associated with the degradation of the sulfonic acid groups, and the initial weight loss increased with increasing the content of sulfuric acid groups. The high decomposition ¹⁵ temperature suggests that sulfonic acid groups attached to pendent phenyl substituents have high thermal stability. The main

weight loss at around 500-600 °C is related to the degradation of



Fig. 4 TGA curves of 4-SPES-xx (acid form) membranes.

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the polymer chain.

Copolymers	$T_{ m d5\%}(^{\circ} m C)^{a}$	Tensile Strength at Break (MPa) ^b	Young's Modulus (GPa)	Elongation at Break (%)
4-SPES-30	369.3	44.8	1.03	22.5
4-SPES-34	357.9	40.6	0.83	19.7
4-SPES-38	353.7	35.9	0.67	17.0
4-SPES-42	336.6	29.6	0.55	13.7

Table 2 Thermal and Mechanical Properties

Good mechanical properties of the membranes are one of the ⁵ necessary requirements for their effective use in PEMFC applications. The mechanical properties of 4-SPES-xx membranes were measured at room temperature and 50% RH. The stress–strain data are presented in Table 2. The membranes have tensile stress at maximum load of 29.6–44.8 MPa and

¹⁰ elongation at break of 13.7–22.5% with the general trend of lower maximum stress for the higher IEC. The results indicated that the membranes were strong and tough for potential use as PEMs materials in a fuel cell.

15 Oxidative stability

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One of the key requirements for PEMs is good oxidativehydrolytic stability under fuel cell operating conditions. Oxidative attack by HO \bullet and HOO \bullet radicals mainly occurs in the hydrophilic domains, resulting in degradation of the polymer

- ²⁰ chains. The oxidative stability of 4-SPES-xx copolymers was evaluated in Fenton's reagent at 80 °C. This method is regarded as one of the standard tests to gauge relative oxidative stability and to simulate accelerated fuel cell operating conditions. As shown in Table 3, over 98 % copolymer weight was retained after
- ²⁵ treatment in Fenton's reagent at 80 °C for 1 h, and dissolution did not occur within 2.5 h treatment at 80 °C. The copolymers exhibited better oxidative resistance in comparison with some fluorene-based PEMs sulfonated directly on the main-chain.^{36,38} The improved oxidative stability is attributed to the introduction
- ³⁰ of the sulfonic acid groups on pendant-phenyl groups on the main chain.⁴⁵

Water uptake and dimensional stabilities

Water uptake of membranes is an important factor for proton conductivity because water molecules play an important role as ³⁵ proton transportation carriers. However, water swelling ratio should be also considered because unrestrained swelling decreases the dimensional stability and mechanical properties of the polymer membranes.

The water uptake data of 4-SPES-xx membranes under the ⁴⁰ hydrated state is shown in Table 3, and the humidity dependence of water uptake is also shown in Fig. 5. The water uptake of 4-SPES-xx membranes is much higher than that of Nafion 212 at 35-100% RH, due to their high IEC values. It is obvious to find that water uptake shows less dependence with IEC values at low ⁴⁵ humidity (<50% RH) but a much larger dependence at high humidity (80-100% RH). For the 4-SPES-30, 4-SPES-34 and 4-SPES-38 membranes, the water uptake increased modestly with increasing IEC values under the hydrated state. However, the highest IEC copolymer 4-SPES-42 shows a relative rapid ⁵⁰ increase in water uptake and attained the highest value, suggesting that 2.23 mequiv g⁻¹ (4-SPES-38) is an upper-limit IEC value. 4-SPES membranes with higher IEC values (unreported) had excessive water uptake.

The dimensional stabilities of 4-SPES-xx membranes were ⁵⁵ evaluated by comparing their hydrated state with the dry state at 80 °C (Table 3). As expected, the dimensional changes had a similar trend with water uptake. Apart from 4-SPES-42, all the membranes had lower or comparable dimensional swelling to Nafion. Considering their relatively high IEC values, 4-SPES-xx ⁶⁰ exhibited acceptable dimensional swelling, which may be attributed to the sulfonic acid groups being located on the rigid fluorene and pendant-phenyl substituents distant from the hydrophobic main chain, rendering the polymer less susceptible to water swelling. In addition, the 4-SPES-xx membranes did not ⁶⁵ exhibit marked anisotropic swelling.



Fig. 5 Relative humidity dependence of water uptake of 4-SPESxx membranes and Nafion 212 at 80 °C.

Copolymers	IEC (mequiv g ⁻¹)		Water uptake ^b	Dimensional Swelling ^b (%)		Proton Conductivity (×10 ⁻² S cm ⁻¹ , 80 °C)		Oxidative Stability	
	calcd	expt ^a	_	Δl	Δt	RH 95%	RH 50%	RW (%) ^c	t (h) ^d
4-SPES-30	1.89	1.87	56.8	10.5	10.9	9.70	0.85	100	>6.0
4-SPES-34	2.06	2.05	62.5	16.5	17.1	11.00	1.15	100	4.5
4-SPES-38	2.23	2.23	79.9	21.2	21.6	12.90	1.56	100	3.5
4-SPES-42	2.38	2.39	124.5	44.1	45.4	13.40	1.83	98	2.5
Nafion 212	0.90	-	30.6	17.7	25.3	13.60	2.10	100	>6.0

Table 3 IEC, Water uptake, Dimensional swelling, Proton conductivity and Oxidative stability of the 4-SPES-xx membranes

^{*a*} Experimentally determined by acid-base titration. ^{*b*} In the hydrated state (80 °C and 100% RH). ^{*c*} Retained weights of membranes after treating in Fenton's reagent 1 h. ^{*d*} The dissolution time of polymer membranes.

5 Proton conductivity

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The proton conductivities of 4-SPES-xx membranes and Nafion 212 were measured at 80 °C in the range of 35–95% RH. As shown in Table 3, 4-SPES-xx membranes had proton conductivities in the range of 9.70×10^{-2} to 13.40×10^{-2} S cm⁻¹ at 10 95% RH and 0.85×10^{-2} to 1.83×10^{-2} S cm⁻¹ at 50% RH. As

- expected, the proton conductivities generally increased with IEC and water uptake. Fig. 6 compares plots the humidity dependence of the proton conductivity of 4-SPES-xx and Nafion 212 membranes. It can be seen that the conductivities did not show a ¹⁵ great dependence on humidity in the range of 50–95% RH, with
- 4-SPES-38 and 4-SPES-42 having a similar trend to that of Nafion 212. This is in contrast to earlier studies, which have shown that the conductivities exhibited a serious dependence on RH for some random aromatic PEMs and alternating aromatic
- ²⁰ PEMs.⁴⁶ The 4-SPES-xx membranes exhibited improved proton conductivities and lesser conductivity-RH dependence, which may be explained by the higher IEC values and the accentuated difference in polarity between clustered pendant-phenyl sulfonated groups and hydrophobic units, resulting in the ²⁵ formation of well-defined phase-separated morphology.



Fig. 6 Proton conductivity of 4-SPES-xx membranes and Nafion 212 at 80 °C as a function of RH.

Hydrophilic/hydrophobic nanophase separation in PEMs ⁴⁵ plays an important role in proton conductivity. In order to investigate the hydrophilic/hydrophobic phase-separated morphology, 4-SPES-38 membrane was studied by TEM and the morphology is shown in Fig. 7. The dark lead-stained regions represent localized ionic domains and the light regions ⁵⁰ correspond to domains formed by the hydrophobic polymer backbone. Clear phase separation is observed, where hydrophilic domains of ~3–7 nm, which could assist proton conduction in the membrane, are surrounded by hydrophobic domains.



Fig. 7 TEM photographs of 4-SPES-38 membrane.

5 PEMFC performance

The H₂/O₂ fuel cell performance of the 4-SPES-38 membrane (50 μ m) and Nafion 212 (50 μ m) were tested at 80 °C. As shown in Fig. 8, 4-SPES-38 membrane displayed good performance had comparable performance to that of Nafion 212. At a cell voltage ¹⁰ of 0.6 V, the current density of 4-SPES-38 membrane was 980 mA cm⁻² at 100% RH and 636 mA cm⁻² at 50% RH. At the effective working potential of 0.6 V, the maximum power density using 4-SPES-38 and Nafion 212 was 570 and 617 mW cm⁻² at 50% RH, respectively. Although the practical fuel-cell operation of 4-SPES-38 membrane had a slightly lower maximum power density than Nafion 212, the test demonstrated that the hydrocarbon PEM could operate within the 50-100% RH range with relatively good performance.



Fig. 8 H₂/O₂ PEMFC performance of 4-SPES-38 and Nafion 212 membranes at 80 °C with humidity at 50% and 100% RH.

Conclusions

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²⁵ A new fluorene-based bisphenol with pendant-phenyl substituents was prepared by a facile synthetic route, from which a series of sulfonated poly(ether sulfone)s with clustered sulfonic acid groups pendant to the main chain were prepared for fuel cell tests. The membranes exhibited good proton conductivity and a low ³⁰ conductivity-humidity dependence. They also exhibited high thermal and oxidative stability, good mechanical properties and acceptable dimensional stability. 4-SPES-38 shows a clear phase-separated morphology of ionic domains of ~3–7 nm size, surrounded by hydrophobic domains and a proton conductivity of ³⁵ 12.90 × 10⁻² S cm⁻¹ at 95% RH and 1.56×10^{-2} S cm⁻¹ at 50% RH at 80 °C. At the effective working potential of 0.6 V, the maximum power density of the fuel cell using 4-SPES-38 (50 µm, the same thickness as Nafion 212) was 570 mW cm⁻² at 50% RH, which is slightly less than that of Nafion 212. Considering the

⁴⁰ facile synthetic route and the overall copolymer properties, this new fluorene-based monomer and the resulting sulfonated poly(ether sulfone)s are promising for exploring larger-scale production and investigation as fuel cell membranes.

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