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ARTICLE

Polymer Electrolyte Membranes Based on Cross-Linked Highly Sulfonated Multiblock Copoly(ether sulfone)s

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ABSTRACT: Polymer electrolyte membranes based on cross-linked highly sulfonated multiblock copoly(ether sulfone)s (IEC = 2.99−3.40 mequiv/g) were prepared successfully by the reaction between the sulfonic acid groups in the main chains and 1,4-diphenoxybenzene as a cross-linker in the presence of the condensation agent. The **HSPx1−3** membranes, which represent the cross-linked **HSP1−3** membranes, demonstrated good mechanical strength in the dry state regardless of their high IEC values and the introduction of the cross-linking structure. Additionally, the multiblock polymer and the cross-linking structure suppressed unacceptable water uptake and dimensional change of the **HSPx1−3** membranes even in the hydrated state, while maintaining relatively high water uptake under low relative humidity (10.3−17.6 wt % at 30% RH) due to their high IEC values. The **HSPx1−3** membranes showed higher proton conductivity than that of Nafion 117 in the range of 30−95% RH (at 80 °C). Especially, the **HSPx3** membrane with the highest IEC value (3.40 mequiv/g) showed 2.4−3.6 times higher proton conductivity compared to Nafion 117 in the whole range of 30−95% RH and still maintained excellent proton conductivity of 1.0×10^{-2} S/cm even at 80 °C and 30% RH.

Introduction

Polymer electrolyte membranes (PEMs) are key materials for polymer electrolyte fuel cells (PEFCs) which are one of the clean and efficient energy sources as alternatives to limited fossil fuel resources. Up to now, perfluorinated polymers, such as Nafion and Flemion, have been widely used as PEM materials because of their excellent chemical and physical stability and high proton conductivity.[1,2] However, they have certain drawbacks, such as high cost, high methanol permeation property, and low operation temperature (< 80 °C), which restrict their practical use in PEFCs. Hence, a number of acid-functionalized aromatic hydrocarbon polymers have been developed as altermatives to perfluorinated PEM materials.[3−19] However, in spite of numerous efforts, the performance of hydrocarbon PEM materials, especially their proton conductivity under low relative humidity, is still inferior to that of perfluorinated PEM materials. Consequently, further improvement of the hydrocarbon PEM performance is essential for the realization of PEFCs.

As for hydrocarbon PEM materials, several approaches to improve proton conductivity have been debated so far,[20−31] which include sulfonated multiblock copolymers,[20−26] highly sulfonated polymers,[27−29] and so on. Sulfonated multiblock copolymers can control both hydrophilic and hydrophobic domains simultaneously to improve proton conductivity and durability of membranes, such as water resistance and mechanical strength due to the defined phase-separated structure between hydrophilic and hydrophobic domains. However, ion exchange capacity (IEC) values of reported sulfonated multiblock copolymers prepared by the nucleophilic coupling reaction of telechelic hydrophilic and hydrophobic oligomers with equivalent molar ratios have been relatively low (~2.00 mequiv/g) so far.[21−26] Such low IEC values may hinder drastic improvement of proton conductivity because water uptake and proton conductivity of membranes are generally improved by increasing IEC values of polymers. On the other hand, according to previous reports, highly sulfonated polymers (IEC > 3.00 mequiv/g) accomplished high proton conductivity even under low relative humidity due to their high IEC values.[27,28] Although these results proved that IEC values were an important factor for proton conductivity, high IEC values generally induce low durability of membranes, such as unacceptable water swelling and low mechanical strength, or such membranes may dissolve in water.[27]

To realize both high proton conductivity and high durability of membranes, we previously proposed the combination of multiblock polymer structure and high IEC values for high-performance PEM materials. Highly sulfonated multiblock copoly(ether sulfone)s (IEC = 2.75 mequiv/g) were successfully prepared by the nucleophilic coupling reaction of hydroxyl-terminated hydrophilic and hydrophobic oligomers in the presence of highly reactive decafluorobiphenyl (DFB) as a chain extender, followed by postsulfonation with concentrated sulfuric acid.[29] Membranes prepared by solution-casting demonstrated relatively high water uptake even under low relative humidity due to their high IEC values, which led to high proton conductivity (2.3×10^{-3} S/cm) even at 80 °C and 30% RH. Additionally, regardless of their high IEC values, unacceptable water uptake and a decrease in mechanical strength could be suppressed due to the multiblock polymer structure. These results revealed that the combination of multiblock polymer structure and high IEC values was a promising approach for high-performance hydrocarbon PEM materials. Thus, based on this accomplishment, our next target was to prepare higher performance PEM materials from higher sulfonated multiblock copolymers (IEC > 3.00 mequiv/g). Even multiblock copolymers, however, can show much water swelling or partially dissolve in water in the cases of IEC > 3.00 mequiv/g. To overcome this problem, herein we report PEM materials based on cross-linked highly sulfonated multiblock copoly(ether sulfone)s

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(IEC = 2.99−3.40 mequiv/g). Cross-linked membranes were successfully prepared by the chemical reaction of sulfonic acid groups in the polymers and 1,4-diphenoxybenzene in the presence of phosphorus pentoxide:methanesulfonic acid (1:10 by weight, PPMA). The resulting cross-linked membranes showed considerably higher proton conductivity than that of Nafion 117 in the wide range of 30−95% RH. In particular, proton conductivity of the membrane with the IEC value of 3.40 mequiv/g reached 1.0×10^{-2} S/cm at 80 °C and 30% RH, which was 2.4 times higher than that of Nafion 117 under the same conditions. Additionally, the properties of the cross-linked membranes such as water uptake, oxidative stability, thermal stability, and mechanical strength are also discussed in detail.

Experimental Section

Materials. Highly sulfonated multiblock copoly(ether sulfone)s were prepared according to the previous report.[29] *N*-Methyl-2-pyrrolidinone (NMP) was distilled from calcium hydride before use. Other solvents and reagents were used as received.

Characterization. FT-IR spectra were measured on a Horiba FT-720 spectrometer. Inherent viscosity was determined on 0.5 g/dL concentration of polymer in DMF with an Ubbelohde capillary viscometer at 30 °C. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG) and differential thermal analysis (DTA). Dynamic mechanical analysis (DMA) was performed on the film specimens (length, 30 mm; width, 10 mm; thickness, 50 μm) by using the Seiko DMS 6300 at a heating rate of 2 °C/min with a load frequency of 1 Hz under a nitrogen atmosphere.

Preparation of Cross-Linked Membranes and Ion Exchange Capacity (IEC). The optimized condition to prepare the cross-linked membranes is as follows: NMP solutions of each polymer containing 5 wt % of 1,4-diphenoxybenzene were casted onto a flat glass plate. Drying the solution at 80 °C for 12 h under reduced pressure gave transparent, flexible, and tough membranes. The obtained membranes were immersed into phosphorus pentoxide:methanesulfonic acid (1:10 by weight, PPMA) for 10 s and cured on a hot plate at 80 °C for 24 h under a nitrogen atmosphere to give the transparent cross-linked membranes (40−50 μm). IEC values of the cross-linked membranes after protonation (in 1 M H_2SO_4(aq) at room temperature for 2 days) were determined by titration with 0.02 M NaOH(aq). Additionally, the degree of the cross-linking (DCL) was calculated from

$$\mathrm{DLC} = N_c/N_b \times 100\%$$

where N_c and N_b are the numbers of sulfonic acid groups consumed in the cross-linking reaction and before the cross-linking reaction, respectively.

Water Uptake and Dimensional Change. The humidity dependence of water uptake was measured by placing the membrane in a thermo-controlled humidity chamber for 3−4 h. Then the membrane was taken out and quickly weighed on a microbalance. Water uptake was calculated from

$$\mathrm{WU} = (W_s - W_d)/W_d \times 100 \text{ wt\%}$$

where W_s and W_d are the weights of wet and dried membrane, respectively. The humidity dependence of water uptake was measured by placing the membrane in a thermo-controlled humidity chamber for several hours. Then the membrane was taken out and quickly weighed on a microbalance. Dimensional change of a hydrated membrane was also investigated by placing the membrane in a thermo-controlled humidity chamber (80 °C and 95% RH) for several hours, and the changes of thickness and length were calculated from

$$\Delta \mathrm{t} = (t - t_s)/t_s$$
$$\Delta \mathrm{l} = (l - l_s)/l_s$$

where t_s and l_s are the thickness and length of the dried membrane, respectively; t and l refer to those of the hydrated membrane.

Proton Conductivity. Proton conductivity in plane direction of the membrane was determined using an electrochemical impedance spectroscopy technique over the frequency from 5 Hz to 1 MHz (Hioki 3532-80). A two-point-probe conductivity cell with two platinum plate electrodes was fabricated. The cell was placed under a thermocontrolled humid chamber. Proton conductivity (σ) was calculated from

$$\sigma = d/(L_s w_s R)$$

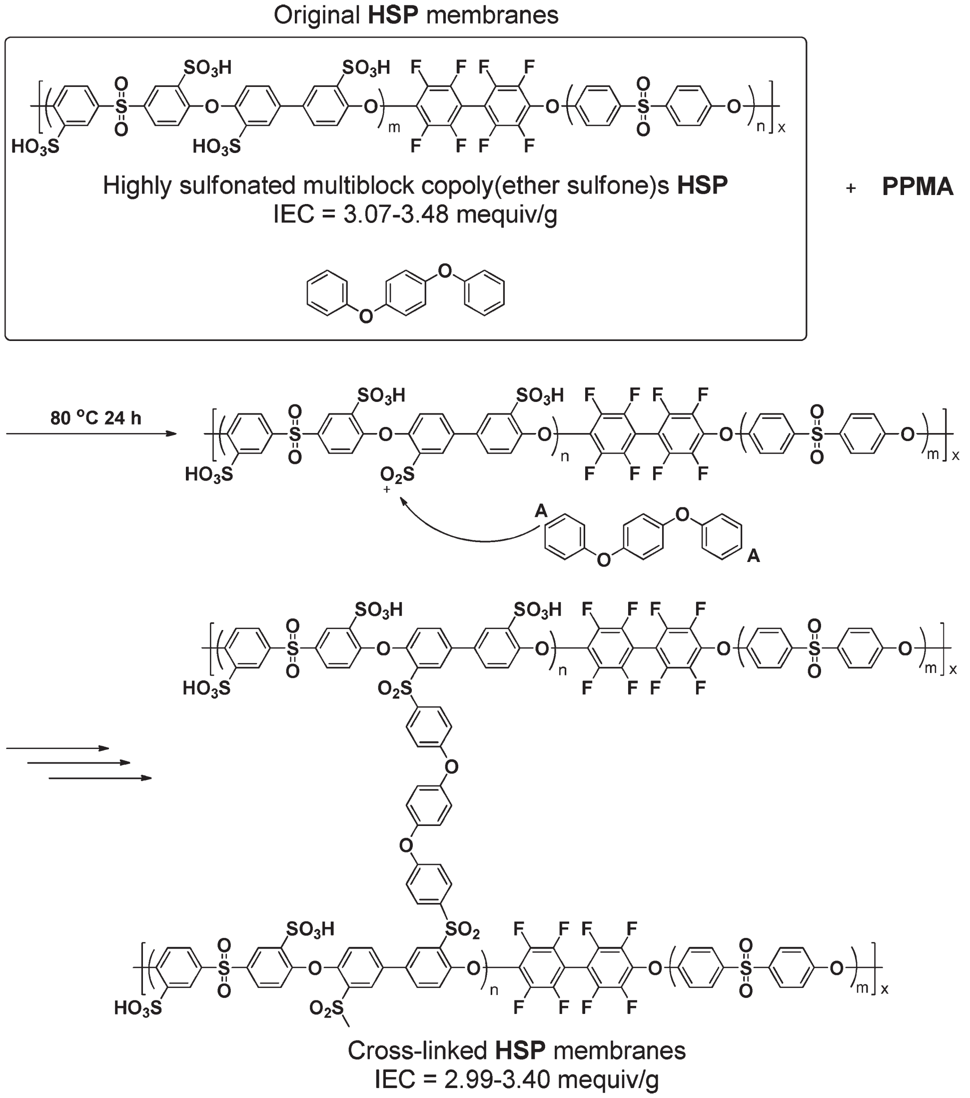
where d is the distance between the two electrodes, L_s and w_s are the thickness and width of the membrane, and R is the resistance value measured.

Oxidative Stability. Oxidative stability of the membranes was tested by immersing the films into Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80 °C. The dissolution time of the membranes into the reagent was used to evaluate their oxidative stability.

Results and Discussion

Preparation of Cross-Linked Membranes. Highly sulfonated multiblock copoly(ether sulfone)s **HSPs** (IEC = 3.07−3.48 mequiv/g) were prepared by the coupling reaction of hydroxyl-terminated hydrophilic (M_n = 10 000) and hydrophobic (M_n = 4500) oligomers in the presence of DFB as a chain extender, followed by postsulfonation with concentrated sulfuric acid according to a previous report.[29] The inherent viscosity values of **HSP1−3** were in the range of 0.98−1.33 dL/g in DMF at 30 °C, and their IEC values estimated from ^{1}H NMR spectra were 3.07, 3.28, and 3.48 mequiv/g, respectively. The preparation of the cross-linked **HSP** membranes is based on the chemical reaction of the sulfonic acid groups in **HSPs** and 1,4-diphenoxybenzene in the presence of the condensation agent (PPMA), and the formed cross-linking bonds are the stable sulfonyl bonds. Previously, it was reported that many diaryl sulfones could be readily prepared by the condensation reaction of arenesulfonic acids and aromatic compounds in PPMA, and sodium 4-phenoxybenzenesulfonate could even carry out self-condensation polymerization in PPMA to give high molecular weight poly(ether sulfone).[30,31] Additionally, Okamoto et al. prepared cross-linked sulfonated polyimide membranes successfully in this system.[32] Hence, we followed this system to prepare **HSPx** membranes (**HSPx** represent cross-linked **HSP**). NMP solutions of each polymer containing 1,4-diphenoxybenzene were cast on a glass plate and dried under reduced pressure to give the original **HSP** membranes. As a result of optimization of the cross-linking reaction conditions, such as the amount of 1,4-diphenoxybenzene, reaction time, and reaction temperature, the transparent and flexible **HSPx** membranes could be prepared as follows: the original **HSP** membranes containing 5 wt % of 1,4-diphenoxybenzene were immersed in PPMA for 10 s and cured on a hot plate at 80 °C for 24 h under a nitrogen atmosphere. As shown in Scheme 1, the cross-linking reaction should be carried out between the sulfonic acid groups in **HSPs** and the most electrophilic hydrogen atoms of 1,4-diphenoxybenzene (marked **A** in Scheme 1). Figure 1 shows the FT-IR spectra of

Scheme 1. Preparation of HSPx Membranes



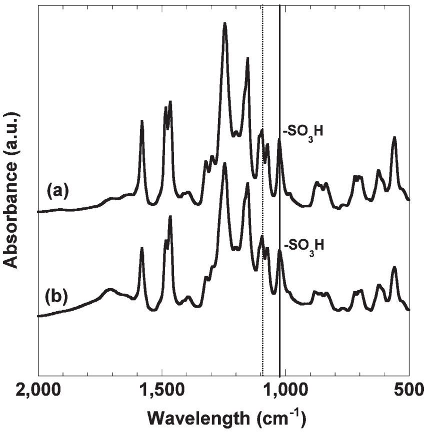


Figure 1. FT-IR spectra of **HSP2** membrane (a) before and (b) after the cross-linking reaction.

the **HSP2** membrane before and after the cross-linking reaction, which were normalized by the intensity of the absorption band at 1100 cm^{-1} (dotted line) corresponding to the aryl fluoride moiety. No specific change is observed between these two spectra except that the relative intensity of the absorption band at 1026 cm^{-1} corresponding to the stretch vibration of the sulfonic acid groups decreases after the cross-linking reaction, indicating that some sulfonic acid groups were consumed to form the sulfonyl bonds by the cross-linking reaction. Moreover, the IEC values of the **HSPx** membranes and their DCL are summarized in Table 1. Compared to the IEC values before the cross-linking reaction, the IEC values of the **HSPx** membranes decreased by 0.08−0.10 mequiv/g, which corresponds to DCL of 3.33−4.20%. The durability of the **HSPx** membranes for hot water was also improved compared to the original **HSP** membranes (e.g., the dissolution time of the **HSP2** membrane in hot water was improved from 1 h to > 10 h by the cross-linking reaction). These aforementioned results indicate that

Table 1. IEC Values, DLC, and Inherent Viscosity of HSPx Membranes

	initial IEC (mequiv/g)[a]	IEC (mequiv/g)[b]	DCL (%)[c]	η_{inh} (dL/g)[d]
HSPx1	3.07	2.99	3.33	1.09
HSPx2	3.30	3.20	4.20	1.33
HSPx3	3.48	3.40	3.34	0.98

[a] Before the cross-linking reaction. [b] After the cross-linking reaction. [c] Degree of cross-linking (DCL) was calculated from DLC = $N_c/N_b \times 100\%$ (see Experimental Section). [d] Inherent viscosity values were measured in DMF at 30 °C.

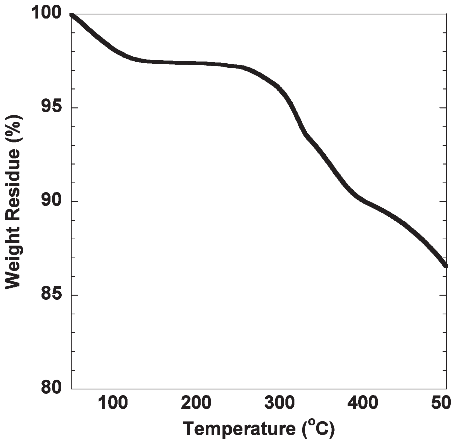


Figure 2. TG curve of **HSPx2** membrane.

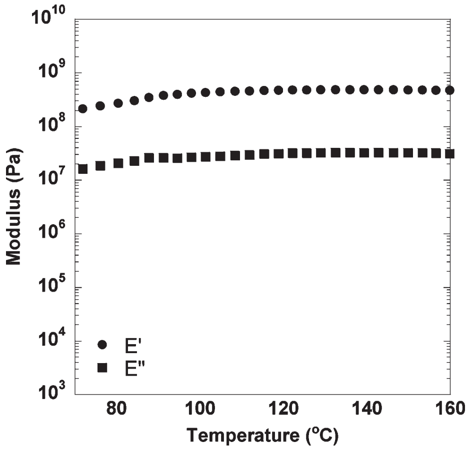


Figure 3. DMA traces of **HSPx2** membrane.

the consumption of some sulfonic acid groups in the cross-linking reaction to obtain the **HSPx** membranes successfully.

Thermal Stability. The thermal stability of the **HSPx** membrane was evaluated by TG analysis. Figure 2 shows the TG curve of the **HSPx2** membrane, where a three-step weight loss is observed from 50 to 150 °C, from 250 to 400 °C, and above 400 °C. The first weight loss is due to the evaporation of hydrated water, the second is attributed to the decomposition of the sulfonic acid groups, and the third is assigned to the decomposition of the polymer main chains and the cross-linking bonds. As the mentioned above, the sulfonyl bonds formed by the cross-linking reaction are very stable, which contributed to the high thermal stability of the **HSPx** membranes.

Mechanical Strength. DMA was carried out for the dry **HSPx** membrane at a heating rate of 2 °C/min under a nitrogen atmosphere. Figure 3 shows the variation in the storage modules (E') and loss modules (E'') of the **HSPx2** membrane at different temperatures. The E' and E'' values of 600 and 50 MPa are maintained up to 160 °C. The **HSPx1** and **HSPx3** membranes demonstrated almost the same E' and E'' values as well. Generally, membranes with high IEC values can be brittle in the dry state,[27] and additionally the cross-linked structure can also induce poor mechanical strength. The **HSPx1−3** membranes, however, demonstrated good mechanical strength in spite of their high IEC values and the cross-linked structure. The multiblock polymer structure and low DCL values should contribute to good mechanical strength.

Table 2. Properties of HSPx Membarnes

	IEC (mequiv/g)[a]	water uptake (wt %)[b]	Δl[b]	Δt[b]	τ (h)[c]
HSPx1	2.99	66.1	0.15	0.65	10
HSPx2	3.20	67.3	0.15	0.67	9
HSPx3	3.40	80.0	0.20	0.70	6

[a] After the cross-linking reaction. [b] In the hydrated state (80 °C and 95% RH). [c] Dissolution time of membranes in Fenton's reagent (a 3 wt % H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80 °C.

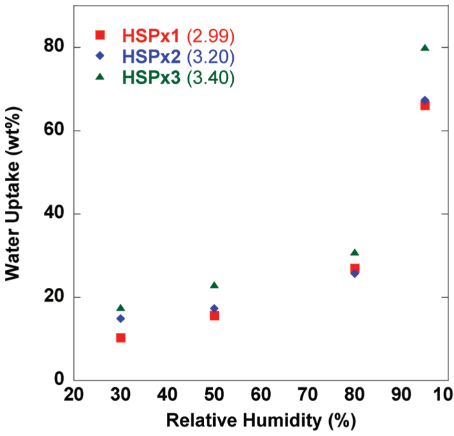


Figure 4. Humidity dependence on water uptake of **HSPx1−3** membranes at 80 °C.

Oxidative Stability. The oxidative stability of the **HSPx** membranes was evaluated in Fenton's reagent (a 3 wt % H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80 °C as an accelerated test (Table 2). The **HSPx1−3** membranes maintained the shapes of the membranes in Fenton's reagent for 6−10 h, which demonstrates that the **HSPx** membranes have relatively high stability against Fenton's reagent regardless of their high IEC values.[33,34] Oxidative degradation is likely to occur at carbon atoms linking the ether bond by the attack of hydroxyl radicals due to the high electron density at these positions.[35] The higher oxidative stability of the **HSPx** membrane should be derived from the cross-linking structure.

Water Uptake and Dimensional Change. Water uptake of membranes is a significant factor for proton conductivity because water molecules behave as proton transportation carriers in membranes. However, excessive water uptake induces unacceptable dimensional changes and a decrease in the mechanical property. The humidity dependence on water uptake was investigated for the **HSPx1−3** membranes at 80 °C. As shown in Figure 4, the **HSPx1−3** membranes showed relatively high water uptake (66.1−80.0 wt %) and larger dimensional change in the thickness direction than in the length direction of the membranes in the hydrated state (80 °C and 95% RH). The strong anisotropic membrane swelling indicates the presence of anisotropic morphology with some degree of in-plane orientation of polymer chains. Considering their high IEC values (2.99−3.40 mequiv/g), these water uptake and dimensional change are acceptable values, indicating that the multiblock polymer structure and introduction of the cross-linked structure should suppress unacceptable water uptake. Additionally, these values of the **HSPx** membranes under high relative humidity (> 80% RH) would not be a problem for PEM materials because practical usage of PEFCs is assumed under high temperature (> 110 °C) and low relative humidity (< 30% RH) conditions. The **HSPx1−3** membranes show good water uptake under low relative humidity, and in particular, the **HSPx2**

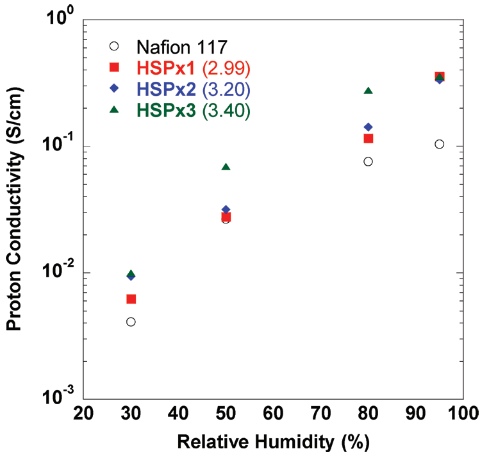


Figure 5. Humidity dependence of proton conductivity of **HSPx1−3** and Nafion 117 membranes at 80 °C.

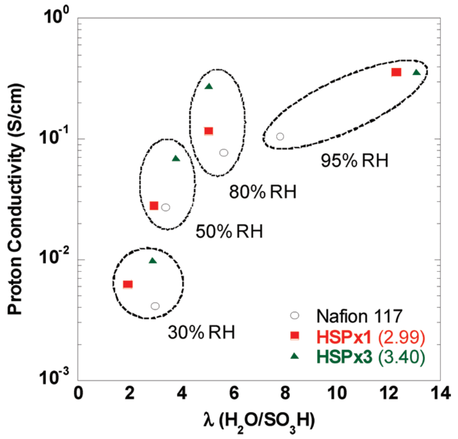


Figure 6. Relationship between proton conductivity and hydration number (λ) of **HSPx1**, **HSPx3**, and Nafion 117 membranes at 80 °C.

and **HSPx3** membranes maintain high water uptake of 14.9 and 17.6 wt %, respectively, even at 30% RH. These water uptake values respectively correspond to 2.59 and 2.88 water molecules per a sulfonic acid group (λ), whereas the λ value of Nafion 117 is 2.99 under the same conditions. As for sulfonated hydrocarbon polymers, low λ values cause deficient proton conduction under low relative humidity. The **HSPx2** and **HSPx3** membranes demonstrated not only high water uptake but also high λ values comparable to those of Nafion 117 and therefore are expected to show high and effective proton conduction even under low relative humidity as well as perfluorinated polymers.

Proton Conductivity. The humidity dependence of proton conductivity was measured for the **HSPx** and Nafion 117 membranes at 80 °C. Generally, proton conductivity is considered to play an important role in the performance of fuel cells. High levels of proton conductivity can achieve high power densities. As shown in Figure 5, the **HSPx1−3** membranes show quite higher proton conductivity ($(3.4-3.6) \times 10^{-1}$ S/cm) than that of Nafion 117 (1.0×10^{-1} S/cm) at 95% RH. Although most sulfonated hydrocarbon polymers can achieve higher proton conductivity than that of Nafion 117 under high relative humidity (95% RH), the problem is how to maintain high proton conductivity even under low relative humidity (30−50% RH). Low proton conductivity of sulfonated hydrocarbon polymers under low relative humidity is a critical issue that has to be overcome.[9,10,12,13] As for the **HSPx1−3** membranes, high level of proton conductivity is maintained from 30 to 95% RH. The **HSPx3** membrane, especially, shows 2.4−3.6 times higher proton conductivity in the whole range of 30−95% RH compared to Nafion 117, and excellent proton conductivity of 1.0×10^{-2} S/cm is observed even at 30% RH. High water uptake of the **HSPx3** membrane in the whole range of relative humidity led to such excellent proton conductivity. Even the **HSPx1** membrane with the lowest IEC value (2.99 mequiv/g) shows high proton conductivity in the range of 30−95% RH. In a previous report, we revealed that PEM materials based on a combination of a multiblock polymer structure and high IEC values were promising candidates to achieve high and efficient proton conduction. Compared to the previous report (IEC = 2.75 mequiv/g),[29] the proton conductivity of the **HSPx1−3** membranes (IEC = 2.99−3.40 mequiv/g) was drastically improved, and especially, the **HSPx3** membrane with the highest IEC value (3.40 mequiv/g) could achieve excellent proton conductivity. Furthermore, good mechanical strength and reasonable dimensional change were observed simultaneously, regardless of quite high IEC values. These results indicate that the strategy of the combination of the multiblock polymer structure with high IEC values works effectively for high-performance PEM materials which have both high proton conductivity and high water resistance.

The relationship between water uptake and proton conductivity of the **HSPx1**, **HSPx3**, and Nafion 117 membranes was investigated. In Figure 6, proton conductivity is plotted against hydration number (λ). All membranes tend to increase their proton conductivity with increasing λ values. The **HSPx3** membrane shows higher λ values than those of the **HSPx1** membrane in the range of 30−95% RH due to its higher IEC value, which is reflected in their proton conductivity (Figure 5). Additionally, the **HSPx3** membrane shows almost the same λ values as Nafion 117 in the range of 30−80% RH. These high λ values, like perfluorinated polymers, led to high and effective proton conduction of the **HSPx1−3** membranes even under low relative humidity.

Conclusions

Hydrocarbon PEM materials based on cross-linked highly sulfonated multiblock copoly(ether sulfone)s (IEC = 2.99−3.40 mequiv/g) were prepared successfully by the chemical reaction of sulfonic acid groups and 1,4-diphenoxybenzene in the presence of the condensation agent (PPMA). DMA demonstrated that the **HSPx1−3** membranes had good mechanical strength in the dry state regardless of high IEC values and the cross-linked structure. The **HSPx1−3** membranes maintained high water uptake even under low relative humidity and showed high proton conductivity in a wide range of relative humidity. The **HSPx3** membrane, especially, showed 2.4−3.6 times higher proton conductivity in the whole range of 30−95% RH compared to Nafion 117, and excellent proton conductivity of 1.0×10^{-2} S/cm was observed even at 30% RH. Consequently, these results demonstrated that the strategy to combine the cross-linked multiblock polymer structure with the high IEC value was promising for high-performance PEM materials which have both high proton conductivity and high water resistance.

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