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Structural influence of hydrophobic diamine in sulfonated
poly(sulfide sulfone imide) copolymers on medium temperature PEM
fuel cell

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Abstract

Sulfonated poly(sulfide sulfone imide) copolymers containing flexible sulfide bond and six-membered imide ring were synthesized by random polycondensation. Two types of membranes were prepared by using different non-sulfonated diamines to investigate the effects of the hydrophobic component. IEC_w values were controlled to 1.51–1.94 meq.g⁻¹ depending on the degree of sulfonation (DS) which was in the range of 50 to 80%. The membrane series showed good thermal stability ($T_{d5\%}$: > 310 °C) and mechanical properties (tensile strength > 30 MPa). Dimensional stabilities of the membranes were excellent with 23–35% increases, even at 100 °C. Proton conductivities of two types of membranes composed of different hydrophobic diamines display a relatively good correlation with water content, morphology. In fuel cell tests, the S-PSI60 membrane shows relatively high current density of 250 mA cm⁻² at 0.6 V and maximum power density of 175 mW cm⁻² at 120 °C, 35% RH, 1.5 atm.

Keywords: Medium temperature PEMFC, polymer electrolyte membrane, sulfonated polyimide, poly(phenylene sulfide sulfone imide), hydrophobic component

Introduction

Much attention has been paid to polymer electrolyte membrane fuel cells (PEMFC)s as promising alternative power sources due to advantages such as high power density, high efficiency and zero emission. Consequently, PEMFCs are being considered as potential energy sources for stationary, automotive and mobile devices [1-4]. While perfluorosulfonic acid ionomers (PFSA) like Nafion[®] have been widely used in practical fuel cell applications in the past few decades due to their high proton conductivity, good mechanical strength and chemical stability, they suffer from well-recognized drawbacks of high cost, low application temperatures ($< 100\text{ }^{\circ}\text{C}$) and high fuel permeability [5, 6].

Recent research has focused on the development of PEMFCs that operate at medium–high temperature ($100 - 200\text{ }^{\circ}\text{C}$) [7-12]. The medium–high temperature PEMFCs offer several advantages, such as reduced catalyst poisoning by CO, higher reaction efficiencies, more effective heat management, high fuel diffusion rate and lower cost. However, the relatively low glass transition temperature ($T_g = 111\text{ }^{\circ}\text{C}$ for H^+ form), susceptibility to dehydration and conductivity loss of Nafion[®] limits operating it in the medium–high temperature range [5, 13]. As replacements for ionomers, sulfonated hydrocarbon membranes, acid-doped polybenzimidazole (PBI) membranes, inorganic additive composite membranes, pore-filling reinforced membranes and blend membranes have been studied for medium – high temperature PEMFCs [9, 14, 15].

Recently, sulfonated hydrocarbon membranes have been studied for medium temperature applications ($100\text{ }^{\circ}\text{C} - 120\text{ }^{\circ}\text{C}$), to overcome the performance degradation of PFSA membranes and the concerns about acid leakage of acid-doped PBI membranes. Various hydrocarbon membranes such as sulfonated polymers derived from poly(phenylene oxide), poly(sulfone), poly(arylene ether sulfone), poly(phenylene sulfide sulfone), poly(ether ether ketone), poly(arylene ether nitrile) and polyimide have been studied [7, 9, 10]. Common

characteristics of these polymers are good mechanical strength, thermal stability, chemical resistance and low cost. However, these polymer membranes rely on water as a proton carrier, so water uptake and retention properties are important issues. In addition, sufficient proton conductivity and control of dimensional changes at medium temperature remain challenges.

As previously reported, aromatic sulfonated polyimide (SPI) membranes are promising candidates for use in medium temperature PEMFC (MT-PEMFC) applications, because they possess good thermal and mechanical properties, excellent dimensional stability, thermo-oxidative stability, and superior solvent resistance [16-20]. In particular, dimensional stability is an essential property for MT-PEMFC [11]. However, SPI membranes have several drawbacks, such as low hydrolytic stability. To overcome these drawbacks, several approaches have been studied. One approach is to incorporate a crosslinkable amine monomer like tris-amine into SPI membranes [21, 22], which showed better hydrolytic stability after crosslinking. Another approach to enhance SPI membrane stability is by introducing a flexible sulfonic acid side chain group to reduce hydrolysis of the main chain [23]. In this case, the water surrounding sulfonic acid groups exists distant from the polymer main chain. Thus, hydrolytic stability of the membranes is enhanced. Similar in concept to the side chain type sulfonic acid groups is the introduction of spacer groups [24, 25]. The existence of a spacer group within the main chain between sulfonic acid groups and imide linkage improves resistance to imide hydrolysis.

In our previous study, sulfonated poly(phenylene sulfide sulfone nitrile) (SPSSN) was synthesized [26-28]. The sulfide groups can be oxidized to sulfone groups during the PEM operation by reaction with hydroxyl radicals. This change can improve the oxidative stability and long term stability [26, 29-31]. Using this concept, we designed copolymers with sulfide linkage and spacer groups. In order to compare morphological effects, two types of copolymer structures were prepared from two different hydrophobic diamines, 4,4'-

diaminodiphenyl sulfide (TDA) and 4,4'-bis(4-aminophenylthio)diphenylsulfone (BAPTPS).

In the present study, sulfonated poly(sulfide sulfone imide) copolymers containing flexible sulfide linkages and six-membered imide rings were synthesized. The effects of membrane morphology and polymer chain structure due to different hydrophobic monomers were characterized. It is our goal to evaluate this copolymer membrane as polymer electrolyte membranes for medium temperature (120 °C, 35% RH).

Experimental section

Materials

1 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA), 4,4'-diaminodiphenyl sulfide
2 (TDA), 4-aminothiophenol, 4,4'-dichlorodiphenyl sulfone (DCDPS), *m*-cresol, 1-methyl-2-
3 pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc), isopropanol
4 (IPA), triethylamine (TEA), benzoic acid, toluene, and potassium carbonate were purchased
5 from Sigma Aldrich Co. 3,3'-Disulfonate-4,4'-dichlorodiphenyl sulfone (SDCDPS) was
6 synthesized by sulfonation of DCDPS with fuming sulfuric acid (30% free SO₃, Sigma
7 Aldrich, WI, USA) as previously reported [32]. NTDA, SDCDPS and potassium carbonate
8 were dried at 120 °C in a vacuum oven for 24 h before use. Other reagents were used as
9 received.

10 4,4'-Bis(4-aminophenylthio)diphenylsulfone-3,3'-disulfonic acid (BAPTPSDS) as
11 hydrophilic sulfonated diamine and 4,4'-bis(4-aminophenylthio)diphenylsulfone (BAPTPS)
12 as hydrophobic diamine monomers were prepared by substitution reaction of 4-
13 aminothiophenol with SDCDPS or DCDPS according to previous literature, respectively [33,
14 34].

15 **Synthesis of sulfonated polyimide copolymers**

16 The synthetic procedure for the sulfonated poly(sulfide sulfone imide) copolymers was
17 similar to that of SPIs, as reported in previous studies [16-18, 22-24]. For convenience in this
18 study, the S-PSI refers to a copolymer composed of NTDA, BAPTPSDS and TDA, and S-
19 PSFI refers to one composed of NTDA, BAPTPSDS and BAPTPS. The S-PSI50 is given as a
20 representative example, where 50 refers to DS. To a 100 mL three-neck flask equipped with a
21 mechanical stirrer, and a cooling condenser, 1.56 g (2.5 mmol) of BAPTPSDS and 15 mL of
22 *m*-cresol were added under nitrogen atmosphere. After adding 2.1 mL (15 mmol) of TEA, the
23 reaction mixture became clear due to the formation sulfonic acid—TEA salt. Then, 0.54 g (2.5
24 mmol) of TDA, 1.56 g (5 mmol) of NTDA, 1.22 g (10 mmol) of benzoic acid and an
25 additional 15 mL of *m*-cresol were added, successively. The reaction mixture was heated to

80 °C for 6 h and 180 °C for 20 h and then cooled to room temperature. The viscous brown mixture was precipitated into acetone. The resulting fiberlike precipitate was washed with acetone several times. The obtained S-PSI50 copolymer was dried under vacuum at 80 °C for 24 h. S-PSI60 and 70 copolymers were prepared by controlling the DS by the monomer feed ratio. S-PSFI60, 70 and 80 copolymers composed of BAPTPS were also obtained using the same synthetic route.

Membrane preparation

The SPIs in their TEA salt form were dissolved in DMSO to 12 wt% concentration. The polymer solutions were filtered with a 0.45 µm PTFE syringe filter. The two series of SPI membranes were fabricated by casting the polymer solutions onto clean glass plates followed by heating at 80 °C for 12 h, and dried in vacuum at 100 °C for 2 h, 120 °C for 2 h and 200 °C for 2 h to remove solvent and anneal the membranes. The obtained membranes were acidified in 1.0 N hydrochloric acid at room temperature for 2 days, then washed with deionized water until the pH value was 7. The resulting proton form membranes were dried in vacuum at 100 °C for 12 h. The thickness of the membranes were ~ 60 µm.

Measurements

The structure of SPIs was analyzed by ¹H nuclear magnetic resonance spectra (NMR, Mercury Plus 300 MHz, Varian, USA) with dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) as a solvent. The molecular weights of SPI series were measured by gel permeation chromatography (GPC, Waters, MA, USA) with Styragel[®] columns and Waters 2414 refractive index detector with NMP containing 0.05 M LiBr as an eluent. Molecular weights were calculated against polymethylmethacrylate (PMMA) standard.

The thermal stability of the membranes was performed under nitrogen flow using thermogravimetric analysis (TGA, Q500, TA Instrument, DE, USA). Thermogravimetric experiments were carried out at a heating rate of 10 °C/min to 850 °C. Differential scanning

calorimetry (DSC, Q20, TA Instrument, DE, USA) was used for determining glass transition temperature (T_g) and the thermal properties. The membranes density of proton form was measured after they were dried completely. 2,2,4-Trimethylpentane (density = 0.692 g cm⁻³) was used as the measurement solvent. The tensile strength and elongation of membranes were measured using universal testing machine (Shimazu, AGS-500NJ, Tokyo, Japan) following ASTM (ISO37-4). Dried and hydrated membranes were measured several times, and the average value was taken. Under hydrated condition, samples were supplied with humidification continuously.

Transmission electron microscopy (TEM) was used to investigate morphology of membranes. The membranes were stained with lead ion (Pb²⁺) by immersing in 0.5 M lead(II) acetate aqueous solution, and rinsed several times with deionized water, and then dried completely under vacuum. The stained samples were embedded in epoxy resin, sectioned to 70 nm thickness with a RMCMTX Ultra microtome, and placed on copper grids. TEM images were obtained using a Carl Zeiss LIBRA 120 energy-filtering transmission electron microscope operating at an accelerating voltage of 120 kV.

The molecular structure of SPIs was simulated using the Material Studio program (Accelry, San Diego, CA, USA) to confirm three-dimensional (3D) structures of the S-PSI and the S-PSFI copolymers. Molecular simulation was carried out using the COMPASS force field. This method is suitable for estimation of polymer structure and conformational properties. After constructing hydrophilic and hydrophobic repeating units, S-PSI and S-PSFI random copolymers were built according to DS values and molecular weight. Energy minimization was performed to eliminate any energy artifacts of the repeating units and polymer chain matrix.

Oxidative stability and hydrolytic stability

The oxidative stability of membranes was determined by the following procedure. Small

pieces of membrane samples with weight of approximately 0.02 g were soaked in Fenton's reagent (2 ppm FeSO₄ in 3 wt% H₂O₂) at 80 °C for 1 h. The residual weight change of samples was measured. In addition, the dissolution time at room temperature (τ) was recorded when the membranes were dissolved completely. The hydrolytic stability was evaluated by treating the membrane samples (1 × 4 cm) in water (100 °C) until their mechanical properties were lost. The soaking time was recorded when each membrane was broken by the bending on the both end sides of samples.

Water uptake, retention and dimensional stability

Water uptake (WU) and water retention were determined by measuring the weight of proton form membranes before and after hydration. Before measurement, the membranes were dried under vacuum at 120 °C for 12 h to measure the weight of dry membranes (W_{dry}). For the weight of hydrated membranes (W_{wet}), the membranes were immersed in deionized water for 24 h to reach equilibrium at given temperature (30 °C and 100 °C). Weight-based water uptake (WU_w) and volumetric water uptake (WU_v) were calculated using the following equations. Volumetric water uptake (WU_v) was determined with density of water (δ_w) and dried membranes (δ_M).

$$WU_w \text{ (wt\%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100$$

$$WU_v \text{ (vol\%)} = \frac{(W_{wet} - W_{dry})/\delta_w}{(W_{dry}/\delta_M)} \times 100$$

In addition, the water retention measurement was carried out in order to confirm the water contents amount and desorption behavior [35, 36]. The fully hydrated samples at 100 °C were maintained for 2 h at 100 °C under 35 % RH in the chamber and were weighed ($W_{wet, 2h}$). Water retention was calculated by the following equation.

$$\text{Water retention (wt\%)} = \frac{W_{wet, 2h} - W_{dry}}{W_{dry}} \times 100$$

Dimensional stability of membranes was determined by measuring area (in-plane swelling) and thickness (through-plane swelling) changes in the membranes at the same conditions of water uptake.

$$\text{In-plane swelling (\%)} = \frac{A_{wet} - A_{dry}}{A_{dry}} \times 100$$

$$\text{Through-plane swelling (\%)} = \frac{l_{wet} - l_{dry}}{l_{dry}} \times 100$$

Where A_{dry} and A_{wet} are the area of dried and wet membranes and l_{dry} and l_{wet} are the thickness of dried and wet membranes, respectively.

Ion exchange capacity and proton conductivity

The weight-based ion exchange capacity (IEC_w) of membranes was determined by acid-base titration. The proton form membrane samples were soaked in a 1.0 M NaCl solution for 24 h to exchange H^+ ions with Na^+ ions, and then released H^+ ions were titrated by 0.01 M NaOH solution using phenolphthalein as an indicator. Volumetric IEC values of dried membranes ($IEC_{v(dry)}$) were calculated by multiplying the IEC_w and the membrane density. The IEC values of hydrated membranes ($IEC_{v(wet)}$) were calculated based on measured water uptake using the following equations.

$$IEC_{v(dry)} = IEC_w \times \text{density}$$

$$IEC_{v(wet)} = \frac{IEC_{v(dry)}}{1 + 0.01 WU_v}$$

The proton conductivity of each membrane sample (size: 1 cm × 4 cm) was characterized at 80 °C under 100% RH, 100 °C under 85% RH, and 120 °C under 35% RH in a two-probe type conductivity cell by using alternating current (AC) impedance spectrometer (Solartron 1260, Farnborough, Hampshire, UK). The temperature and RH were controlled by Fuel cell station (CNL, Seoul, Korea) under nitrogen flow. Furthermore, the conductivity cell was back pressurized at 1.5 atm to maintain hydrated status. All the membrane samples were measured

for in-plane and through-plane conductivity, respectively. The proton conductivity (σ) was calculated from the following equation.

$$\sigma = \frac{L}{RS}$$

Where L is the distance between the counter electrodes and the working electrode, R is the impedance of membrane and S is the cross-sectional surface area of membrane samples (cm^2).

MEA preparation and single cell performance

Membrane electrode assemblies (MEAs) were fabricated by a catalyst coated substrate (CCS) method. Nafion[®] ionomer solution (20 wt% in IPA and water, DuPont, DE, USA) and 20 wt% Pt/C (Johnson Matthey Fuel Cell, London, UK) were mixed in water. The catalyst slurry was coated on gas diffusion layers (GDLs) both anode and cathode sides until the weight of Pt loading reached 0.5 mg cm^{-2} . MEAs were fabricated by sandwiching the membranes between the anode and cathode electrodes and hot pressed at 130°C under a pressure of 50 bar for 7 min. The prepared MEAs were tested in a single-cell fixture (with an active area of 5 cm^2). The PEMFC test was performed on test station (Won-A-Tech, SMART1, Seoul, Korea). Electrochemical performances of S-PSI and S-PSFI series were evaluated by following conditions. H_2 and air were fed at a flow rate of 100 mL min^{-1} at 80°C under 100% RH, 100°C under 85% RH, and 120°C under 35% RH respectively. In addition, all operation conditions were back pressurized in the same way as conductivity measurements.

Results and discussion

Synthesis of monomers and copolymers

The synthetic procedure for sulfonated poly(sulfide sulfone imide) copolymers is shown in

Scheme 1. Two types of copolymers with various DS composed of hydrophobic diamine monomers TDA or BAPTPS were synthesized in *m*-cresol with TEA as base and benzoic acid as acid catalyst for carbonyl group in NTDA. Molar percentage of BAPTPSDS was targeted as 50, 60 and 70 for S-PSI copolymer and 60, 70 and 80 for S-PSFI copolymer in order to compare between S-PSI (containing TDA) and S-PSFI (containing BAPTPS) copolymers as a function of similar IEC_w.

The structure of synthesized SPI copolymers series (TEA salt form) was confirmed by ¹H NMR spectroscopy, as shown in Figure 1. The aromatic proton signals of S-PSI and S-PSFI copolymers were assigned. The signals corresponding to NTDA appeared at 8.75 ppm, and the H_d, H_e and H_f signals were observed at 8.23, 7.02 and 7.78 ppm, respectively. The S-PSFI copolymer showed two additional signals when compared with that of the S-PSI copolymer. Signals at 7.43 ppm (H_g) and 7.92 ppm (H_h) were observed by influence of the sulfone group in BAPTPS.

All the SPI copolymers were obtained as brown fiberlike solids. The high molecular weights were measured by GPC and are shown in Table 1. The weight-average molecular weights (*M_w*) of SPI copolymers were higher than 77 kDa, and the polydispersity indices (PDI) were lower than 3. The SPI copolymer membranes were fabricated by solution casting and were ultimately treated at 200 °C for 2 h for thermal annealing. In previous studies [27, 37, 38], it was observed that thermally annealed polymer electrolyte membranes showed effective morphology for proton conduction and exhibited better electrochemical performance and dimensional stability.

Thermal and mechanical properties

In the thermal stability tests of SPI membranes (proton form), the first degradation step was observed at around 320–330 °C due to thermal degradation of sulfonic acid groups and the polymer main chain decomposed at around 500–580 °C, as shown in Figure 2. All the

membranes exhibit good stabilities with high $T_{d5\%}$ (The 5 % weight loss temperature) in the range of 313–320 °C. In addition, the T_g s of SPI membranes were investigated by DSC, and the values were dependent on the DS. Note that the S-PSI membranes show higher T_g (308–310 °C) than S-PSFI membranes (286–289 °C).

The mechanical properties of the S-PSI and S-PSFI membranes under dry and wet conditions are summarized in Table 1. Under dry conditions, the S-PSFI membranes exhibit higher maximum tensile strength than the S-PSI membranes, in the range of 42.2–56.8 MPa, whereas the S-PSI membranes show slightly higher elongation at break than S-PSFI membranes, in the range of 17–21 %. Under wet conditions, the elongation of S-PSFI membranes was significantly increased, but the S-PSFI membranes exhibit lower tensile strengths than the S-PSI membranes. Note that in both the dry and wet conditions, the two different copolymer structures (S-PSI and S-PSFI), derived from the hydrophobic diamine monomers TDA and BAPTPS respectively, affect the polymer chain matrix, morphology, and ion clusters. Thus, the mechanical properties under dry and wet conditions display different behavior. In summary, the S-PSI and S-PSFI series show good tensile strength but low elongation when compared with Nafion[®] 212.

Oxidative stability and hydrolytic stability

The oxidative stability of the SPI PEMs was evaluated in Fenton's reagent at 80 °C for 1 h by measuring their weight changes after exposure. Fenton's test provides an indication of relative durability of PEM from free radical attack under fuel cell operating conditions [5]. The dissolution times (τ) were also measured at 30 °C, and are listed in Table 1. All the samples except S-PSFI80 showed a slight weight gain as a result of oxidation from –S– to –SO– and –SO₂– [26, 29-31]. At the same time, membranes with high DS values exhibited a faster degradation trend, as expected. Furthermore, the dissolution time (τ) of SPI

membranes occurred after more than 100 h, except for S-PSFI80. In general, the S-PSI series were comparatively more stable in oxidative conditions than the S-PSFI series.

The stability of SPI membranes in water is one of the key issues, because the imide linkage is relatively easy to hydrolyze at elevated temperature and humidity [39-41]. In previous studies [24, 25, 33, 42], use of in-chain spacer groups between sulfonic acid groups and imide linkages demonstrated improved stability in water. The six-membered imide ring has higher hydrolytic stability than five-membered imide ring [39]. For these reasons, the copolymers were designed with six-membered dianhydride (NTDA) and sulfonated diamine containing *p*-aminothiophenyl spacer groups (BAPTPSDS). The hydrolytic stabilities of S-PSI and S-PSFI membranes were tested in water at 100 °C, and the time to membrane breakage when both ends of samples were bent are listed in Table 1. The stability of membranes appeared to be closely affected by DS and IEC values. The S-PSI70 and S-PSFI80 were broken after 53 h and 48 h, respectively. However, the S-PSI50, 60 and the S-PSFI60, 70 exhibited relatively good properties (87–112 h) compared to other SPI membranes [16, 19, 25].

Membranes morphology and molecular simulation

In order to observe nano-phase separation of membranes, transmission electron microscopy (TEM) images were taken as shown in Figure 3. Although both S-PSI and S-PSFI are random copolymers, well separated hydrophilic/hydrophobic morphology was observed, unlike common random copolymers. The two types of membrane confirmed an increasing trend of hydrophilic domain (dark area) with DS values. In particular, S-PSI60, 70 and S-PSFI70, 80 ($IEC_w \geq 1.73 \text{ meq cm}^{-2}$) showed connected hydrophilic ionic clustered morphology (S-PSI60 $\approx$ 8 nm, S-PSI70 $\approx$ 12 nm, S-PSFI70 $\approx$ 13 nm and S-PSFI80 $\approx$ 15 nm channel widths). Well-connected hydrophilic clusters with 8 nm size of the S-PSI60 should be helpful to have capillary water retention effect, as discussed in our previous research [36]. S-PSI membranes showed more closely linked hydrophilic clusters compared

with S-PSFI membranes, despite having similar IEC_w values. The distance between formed hydrophilic clusters in S-PSIs and S-PSFIs are 10–17 nm, 13–40 nm, respectively.

The three-dimensional (3D) polymer chain structures of the S-PSI60 and the S-PSFI70 copolymers were visualized by molecular simulation as shown in Figure 4. The hydrophobic repeating unit of S-PSI (containing TDA) showed a torsional angle of 83° whereas the repeating unit of S-PSFI (containing BAPTPS) showed a torsional angle of 23° . Chain length of SPI series was controlled with number of repeating unit ($RU = 60$), which corresponded to minimum weight average molecular weight ($M_w > 70$ kDa) of synthesized polymer, as shown in Table 1. The S-PSI60 copolymer containing TDA as hydrophobic diamine showed a comparatively ordered helical structure, whereas the S-PSFI70 copolymer exhibited slightly entangled helical structure. These results might be influenced by differences of torsional angle between S-PSI60 and S-PSFI70. Molecular simulation data was largely consistent with the experimental data. A well-ordered helical structure could be helpful to facilitate dense packing of hydrophilic domains, as identified in the TEM images. Thus the S-PSI60 membranes exhibited higher T_g , lower water uptake and better dimensional stability than those of the S-PSFI70 membranes.

Water uptake, retention and dimensional stability

Water uptake and dimensional stability of PEMs are typically a function of IEC_w due to DS. Water uptake and dimensional stability of sulfonated hydrocarbon membranes, when water is primarily the proton carrier, are particularly important, unlike acid-doped PBI membranes and ionic liquid composite electrolyte membranes. Furthermore, at medium temperature (100 °C – 120 °C) PEMFC operation conditions, water retention properties and good dimensional stability of membranes are essential [7, 9, 14].

Table 2 compares the density, IEC, water uptake and water retention of fabricated SPI membranes. As expected, water uptake of both S-PSI and S-PSFI membranes increased with

temperature, IEC_w , and $IEC_{v(dry)}$, due to the increased DS. All the membranes showed similar water uptake behavior between weight% and volume% due to their density (1.45–1.48 g cm⁻³). Also the volume-based IEC_v showed a very similar trend as the weight-based IEC_w . The S-PSI70 and S-PSFI80 samples exhibited the highest water uptake in weight% and volume% (40 wt% and 59 vol%) at 100 °C among all the samples. In general, the S-PSFI membrane series exhibited higher water uptake than S-PSI. For example, with the same IEC_w of 1.73 meq cm⁻², S-PSFI70 showed a larger water uptake (38 wt% and 55 vol%) than S-PSI60 (35 wt% and 52 vol%). In contrast to the water uptake, the S-PSI membranes showed superior water retention than the S-PSFI membranes when compared to samples having similar IEC_w values. Among them, the S-PSI60 retained about 5.3% after a water retention test, although slightly lower than Nafion[®] 212 (5.7%). Considering these points, the S-PSI membranes have more favorable morphology to retain water than the S-PSFI membranes at medium temperature (≥ 100 °C) and low humidity operation conditions.

Figure 5 compares the IEC_w dependence of dimensional swelling ratio and relationship between in-plane and through-plane changes at 100 °C for S-PSI and S-PSFI membranes. As expected, the dimension of two types of PEM membranes was swelled by increasing IEC_w . For all the samples, in-plane changes were larger than through-plane changes. However, the S-PSI membranes exhibited a smaller gap between in-plane and through-plane than the S-PSFI membranes. Despite the S-PSFI membranes showing larger in-plane swelling, the through-plane swelling of the S-PSI membranes was higher than the S-PSFI membranes. This indicates that the S-PSI membranes have more efficient water channel in the through-plane directions. In addition, all the fabricated SPI membranes achieved excellent dimensional stability (in-plane: < 38% and through-plane: < 24%) in comparison with many sulfonated hydrocarbon PEMs [14]. Accordingly, good dimensional stability of synthesized SPI membranes could be obtained for medium temperature fuel cell operation.

Proton conductivity

Proton conductivity is the most significant characteristic of fuel cell performance. Figure 6 shows the in-plane ($\sigma_{//}$) and through-plane ($\sigma_{\perp}$) conductivity of S-PSI and S-PSFI membranes as a function of IEC_w at 80 °C under 100% RH, 100 °C under 85% RH and 120 °C under 35% RH. For comparison, Nafion[®] 212 data are included as a reference. A conductivity cell fixture was used to control temperature and hydration conditions by connecting into the fuel cell stations. In addition, conductivity cell was back pressurized to 1.5 atm, and the relative humidity (RH) was calculated and controlled by the temperature of the humidifier. N₂ was supplied at flow rate 0.1 mL min⁻¹ in order to prevent any extraneous chemical reactions.

Proton conductivities decreased with increasing temperature above 80 °C. $\sigma_{//}$ of all the membranes was higher than $\sigma_{\perp}$. The S-PSFI membrane series showed higher conductivity than S-PSI membranes series. From these results, it is clear that the water uptake, IEC, and proton conductivity are closely related. However, at 120 °C under 35% RH, the numerical differences between the S-PSI and the S-PSFI series were reduced. In particular, different polymer structure from hydrophobic diamines (TDA and BAPTPS) resulted in a decrease of the conductivity gap between $\sigma_{//}$ and $\sigma_{\perp}$. Among them, the S-PSI60 and the S-PSI70 membranes exhibited isotropic conducting behavior at 120 °C under 35% RH. Furthermore, the membranes with high IEC_w (1.7 and 1.9) were observed to have better proton conductivity than Nafion[®] 212. The S-PSFI80 membrane showed the highest values ($\sigma_{//} = 0.051 \text{ S cm}^{-1}$, $\sigma_{\perp} = 0.038 \text{ S cm}^{-1}$) at 120 °C among all the samples.

Single cell performance

The achievement of superior performance of polymer electrolyte fuel cells is predicated on a combination of PEM material properties such as high proton conductivity, appropriate water uptake, good dimensional stability, mechanical properties, and chemical resistance [4, 43]. In particular, at medium temperature operation conditions, the role of dimensional

1 stability is essential [44]. As water is a proton carrier, moisture retention ability as well as the
2 amount of water uptake is also important.

3 All single cells were assembled using the same methodology and electrode composition for
4 a fair comparison as reported before [45]. Figure 7 shows the current–voltage polarization
5 curves of the S-PSI and the S-PSFI membranes, obtained at 80 °C, 100 °C and 120 °C,
6 respectively. In typical fuel cell operating conditions (80 °C, 100% RH, 1.5 atm), single cell
7 performance of all the membranes depends on proton conductivity, which is a function of
8 IEC and DS. The S-PSFI membranes were observed to have higher current density (520 –
9 649 mA cm⁻²) than the S-PSI membranes (415–540 mA cm⁻²) measured at 0.6 V. Note that
10 the morphology of the S-PSFI membranes is more efficient for proton transfer through the
11 membranes having high water uptake and relatively large ion clusters (13–20 nm).

12 However, when the operation temperature was increased to 100 °C and RH was reduced to
13 85 %, the tendency was quite reversed when comparing between the two PEM series having
14 similar IEC_w. For example, the S-PSI60 showed higher performance (current density (at 0.6
15 V) = 498 mA cm⁻² and maximum power density = 314 mW cm⁻²) than that of S-PSFI70
16 (current density (at 0.6 V) = 435 mA cm⁻² and maximum power density = 284 mW cm⁻²)
17 at 100 °C, 85% RH which is inverted from the results of 80 °C, 100% RH.

18 When the cell temperature and RH were changed from 100 °C and 85% RH to 120 °C and
19 35% RH, the difference was even more pronounced. Single cell performances of SPI
20 membranes series at 0.6 V were considerably decreased except S-PSI60. For example, current
21 density and maximum power density of the S-PSI70 decreased from 477 mA cm⁻² and 305
22 mW cm⁻² to 206 mA cm⁻² and 151 mW cm⁻², and also those of the S-PSFI80 decreased from
23 462 mA cm⁻² and 303 mW cm⁻² to 181 mA cm⁻² and 138 mW cm⁻², respectively. Interestingly,
24 in the case of S-PSI60, the extent of reduction of performance was comparatively low, and
25 achieved good cell performance at 120 °C under 35% RH (current density (at 0.6 V) = 250

1 mA cm⁻² and maximum power density = 175 mW cm⁻²). These results indicate that a moderate level of DS is one of the key factors and water moisture retention ability as well as water uptake in membranes is considerably important. In particular, efficient morphology of the membrane to allow proton transport and moisture retention capability due to narrow ion clusters plays a significant role on the PEM performance at medium temperature, which is probably controlled by different hydrophobic monomers.

8 Conclusions

9 A series of sulfonated poly(sulfide sulfone imide) copolymers (S-PSI and S-PSFI) were
10 successfully synthesized by facile polycondensation. All the membranes showed good
11 thermal stability and high mechanical strength as well as excellent dimensional stability of
12 membranes even at 100 °C. Two types of copolymer membranes composed of different
13 hydrophobic diamines (TDA and BAPTPS) displayed different morphology, evidenced by
14 TEM images and molecular dynamics simulation, due to polymer chain arrangement. This
15 correlated well with dimensional stability and mechanical properties. In particular, the
16 dimensional swelling ratio between in-plane and through-plane directions is closely related to
17 proton conductivity. In this regard, efficient ion clustered morphology in the through-plane
18 directions is controlled by polymer chain structure. In addition, to improve the fuel cell
19 performance, moderate IEC values as well as efficient morphology are essential. The amount
20 of water uptake is also important but the capacity to retain moisture is significant at medium
21 temperature (100 °C–120 °C). Considering fuel cell operation conditions, the S-PSI60 is a
22 promising candidate for MT-PEMFC due to its closely packed morphology and suitable
23 narrow conducting clusters (8 nm). In comparison with other sulfonated hydrocarbon
24 membranes, the S-PSI60 membrane achieved the expected cell performances at 120 °C under

35 % RH (current density (at 0.6 V) = 250 mA cm⁻² and maximum power density = 175 mW cm⁻² at 0.6 V), and showed the possibility of further applications.

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Scheme 1. Synthetic procedure of Sulfonated poly(sulfide sulfone imide) copolymers

(a) S-PSI60

(b) S-PSFI70

Figure 1. ¹H-NMR analysis of (a) S-PSI and (b) S-PSFI copolymers (DMSO-*d*₆)

1 **Table 1.** Molecular weight, mechanical properties, hydrolytic and oxidative stability of S-PSI and S-PSFI membranes

Membranes	M_w^a (kDa)	PDI ^a	Tensile strength ^b (MPa)		Elongation at break ^b (%)		Hydrolytic stability ^c (h)	Oxidative stability ^d (wt%)	τ^e (h)
			Dry	Wet	Dry	Wet			
S-PSI50	102.6	2.7	47.2 ± 5.4	21.1 ± 6.8	16.8 ± 5.3	22.2 ± 6.2	108	101.4	159
S-PSI60	77.0	2.8	40.1 ± 4.6	14.8 ± 4.3	13.7 ± 5.4	21.9 ± 6.7	87	101.2	140
S-PSI70	82.2	3.0	35.9 ± 5.1	13.5 ± 2.3	21.4 ± 4.2	23.5 ± 8.9	53	100.5	108
S-PSFI60	136.3	2.9	56.8 ± 8.3	29.1 ± 6.2	12.4 ± 3.5	21.7 ± 7.4	112	101.9	151
S-PSFI70	155.9	2.3	44.7 ± 5.6	18.3 ± 4.2	22.5 ± 7.5	47.2 ± 13.2	91	100.2	125
S-PSFI80	110.6	2.8	42.2 ± 6.7	14.4 ± 4.1	16.5 ± 8.8	56.8 ± 15.5	48	98.6	94
Nafion 212	—	—	22.5 ± 2.9	19.5 ± 0.3	200.4 ± 12.3	224.6 ± 10.6	—	98.0	—

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3 ^a Determined by GPC using NMP with 0.05 M LiBr. ^b Measured at 30 °C. ^c The time of membranes maintain mechanical properties at 100 °C
4 in water. ^d Retained weight percent of membranes after Fenton`s test. <sup>e</sup> The time at which the membranes dissolved completely in Fenton`s
5 reagent at 30 °C.
6

Figure 2. TGA curves of S-PSI and S-PSFI copolymers under N₂ atmosphere

Figure 3. TEM phase images of S-PSI and S-PSFI membranes

Figure 4. Chemical structure and 3D models of (a) S-PSI60 and (b) S-PSFI70 copolymers with 60 repeating units

1 **Table 2.** Density, ion exchange capacity (IEC), water uptake and retention of S-PSI and S-PSFI membranes

Membranes	Density ^a (g cm ⁻³)	IEC _w (meq.g ⁻¹)		IEC _v (meq.cm ⁻³)		WU (wt%)		WU (Vol%)		Water retention (%)
		cal ^b	tit ^c	dry	wet	30 °C	100 °C	30 °C	100 °C	
S-PSI50	1.45	1.53	1.49	2.17	1.67	20.9	29.3	30.2	42.5	3.49
S-PSI60	1.47	1.73	1.71	2.51	1.84	24.6	35.4	36.2	52.0	5.31
S-PSI70	1.48	1.91	1.87	2.77	1.97	27.3	40	40.4	59.2	4.91
S-PSFI60	1.45	1.51	1.47	2.13	1.63	21.2	34.9	30.7	50.5	3.25
S-PSFI70	1.46	1.73	1.70	2.48	1.82	24.8	37.9	36.2	55.3	3.85
S-PSFI80	1.46	1.94	1.89	2.76	1.97	27.7	40.3	40.4	58.8	4.14
Nafion 212	1.97	0.92	0.98	1.93	1.28	21.6	—	42.6	—	5.69

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3 ^a Measured at 30 °C. ^b Calculated ion exchange capacity (IEC) values. ^c Determined by titration.
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Figure 5. IEC_w dependence of dimensional swelling ratio and relationship between in-plane and through-plane changes at 100 °C

Figure 6. In-plane and through-plane proton conductivity of S-PSI and S-PSFI membranes as a function of IEC_w at 80 °C , 100 % RH (1.5 atm), (b) 100 °C, 85% RH (1.5 atm) and (c) 120 °C, 35% RH (1.5 atm), (★, ☆ indicates in-plane and through-plane conductivity of Nafion 212 respectively)

1

2 **Figure 7.** H₂/air Single cell performances of S-PSI and S-PSFI membranes as a function of
 3 the current density at various temperature and RH