NRC Publications Archive
Archives des publications du CNRC

Durable sulfonated poly(arylene sulfide sulfone nitrile)s containing naphthalene units for direct methanol fuel cells (DMFCs)
Shin, Dong Won; Lee, So Young; Kang, Na Rae; Lee, Kang Hyuck; Guiver, Michael D.; Lee, Young Moo

This publication could be one of several versions: author’s original, accepted manuscript or the publisher’s version. / La version de cette publication peut être l’une des suivantes : la version prépublication de l’auteur, la version acceptée du manuscrit ou la version de l’éditeur.
For the publisher’s version, please access the DOI link below./ Pour consulter la version de l’éditeur, utilisez le lien DOI ci-dessous.

Publisher’s version / Version de l'éditeur:
https://doi.org/10.1021/ma400154t
Macromolecules, 46, 9, pp. 3452-3460, 2013-04-24

NRC Publications Record / Notice d'Archives des publications de CNRC:
https://nrc-publications.canada.ca/eng/view/object/?id=e60179f7-d893-4823-81bf-ded0a8a782ef
https://publications-cnrc.canada.ca/fra/voir/objet/?id=e60179f7-d893-4823-81bf-ded0a8a782ef

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at
https://nrc-publications.canada.ca/eng/copyright
READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L’accès à ce site Web et l’utilisation de son contenu sont assujettis aux conditions présentées dans le site
https://publications-cnrc.canada.ca/fra/droits
LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D’UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at
PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n’arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

National Research Council Canada
Conseil national de recherches Canada

Durable Sulfonated Poly(arylene sulfide sulfone nitrile)s Containing Naphthalene Units for Direct Methanol Fuel Cells (DMFCs)

Journal:	*Macromolecules*
Manuscript ID:	Draft
Manuscript Type:	Article
Date Submitted by the Author:	n/a
Complete List of Authors:	Shin, Dong Won; Hanyang University, Department of Chemical Engineering Lee, So; Hanyang University, Chemical Engineering Kang, Na Rae; Hanyang University, WCU Department of Energy Engineering Lee, Kang Hyuck; Hanyang University, WCU Department of Energy Engineering Guiver, Michael; National Research Council of Canada, Institute for Chemical Process & Environmental Technology Lee, Young Moo; Hanyang University, School of Chemical Engineering, College of Engineering

Durable Sulfonated Poly(arylene sulfide sulfone nitrile)s Containing Naphthalene Units for Direct Methanol Fuel Cells (DMFCs)

Dong Won Shin[1], So Young Lee[1], Na Rae Kang[2], Kang Hyuck Lee[2], Michael D. Guiver[2,3], Young Moo Lee[1,2,*]

[1]Department of Chemical Engineering, College of Engineering, Hanyang University, Seoul, Korea, 133-791.

[2]WCU Department of Energy Engineering, College of Engineering, Hanyang University, Seoul, Korea, 133-791.

[3]National Research Council, Ottawa, Ontario, Canada, K1A 0 R6.

[Insert Running title of <72 characters]

Abstract

Sulfonated poly(arylene sulfide sulfone nitrile)s (SN) were synthesized to investigate the effects of naphthalene units in the polymer backbone on membrane properties. The small and planar naphthalene in the main chain induced semi-crystallinity in the polymer, as confirmed by molecular simulations and wide angle X-ray diffraction patterns. The semi-crystalline SN polymer membranes exhibited excellent chemical and mechanical properties, better than those of their phenylene counterpart (SP). In particular, the water uptake and swelling ratio of the SN membranes were much lower than those of the SP membranes. Furthermore, the SN membranes exhibited a greatly reduced methanol permeability (9-17 × 10^{-8} cm^2 s^{-1}) compared to Nafion® 117 (240 × 10^{-8} cm^2 s^{-1}) at 30°C in 10 M methanol. Moreover, sulfide- and naphthalene-based chemical structure and semi-crystalline nature of the SN membranes enhanced their DMFC single cell performance and long-term stability during fuel cell operation.

Keywords

Direct methanol fuel cell (DMFC), Proton exchange membrane (PEM), Sulfonated poly(arylene sulfide sulfone nitrile), Naphthalene units

Introduction

Direct methanol fuel cells (DMFCs) are actively pursued as an alternative power source for portable applications due to their high energy density, system simplicity, and environmental friendliness. [1] Proton exchange membranes (PEMs) play a key role in DMFC systems because the protons are transported through the membranes and the fuel and oxidant are separated by the membranes, which ultimately affects the fuel cell performance. PEMs usually require a high proton conductivity, excellent chemical and mechanical stabilities, and low fuel permeability. Perfluorosulfonic acid polymers (PFSAs) such as Nafion®, Aciplex®, and Flemion® are considered state-of-the-art PEMs because of their excellent chemical and mechanical stabilities and high proton conductivities. However, PFSA membranes have high fuel permeabilities especially with liquid fuels, because liquids are easily transported together with solvated protons through the water-filled ion cluster channels in polymer membranes, resulting in poor performance during fuel cell operation. In addition, the high cost, difficult synthetic procedure, and environmental concerns of fluorine limit their commercial use.[2,3]

Hydrocarbon-based aromatic polymers have been extensively investigated to overcome the drawbacks of PFSAs.[4] Many research groups have developed various hydrocarbon-based PEMs such as sulfonated poly(arylene ether)s (SPAEs)[5-8], sulfonated polyimides (SPIs)[9-14], and polybenzimidazoles (PBIs)[15-19] due to their excellent stabilities, low fuel permeabilities, and low cost. However, their proton conductivities are relatively lower than those of PFSAs because rigid polymer chains hinder ionic channel formation. For these reasons, many studies of inorganic composite membranes[20-24], block copolymers[25-32], pendent or comb-shape copolymers[11,33-38], and highly sulfonated copolymers[39-45] have been carried out to enhance proton conductivity.

Proton conductivity and methanol permeability are regarded as the most important factors that contribute to DMFC performance. However, there is a trade-off relationship between the proton conductivity and the methanol barrier property since methanol may enlarge the hydrophilic ionic cluster of the membranes resulting in enhanced transport of both protons and methanol. In order to increase the selectivity, i.e., the ratio of the proton conductivity to the methanol permeability, extensive efforts have been made to develop highly selective membranes.[33,36,37,46,47] The water uptake and swelling ratio of the membranes are also critical factors which affect the DMFC performance since a high water uptake and swelling ratio increases methanol crossover and diminishes the mechanical properties. Therefore, the optimization of the polymer structure to result in a high proton conductivity, low fuel permeability, low water uptake, and low swelling ratio is important to achieve a high DMFC performance.

In order to develop advanced PEMs, further detailed understanding of the relationship between the chemical structure and properties of the polymers is necessary. Sulfonated polymers containing sulfur atoms (-S-, -SO-, and $-SO_{2-}$) are considered promising PEMs due to their good film-forming capabilities, hydrophilicity, outstanding electrical insulation, and excellent thermal, chemical, and physical stabilities.[44,48-51] In particular, the electron-donating sulfide linkages play an important role as a free-radical-scavenging moiety in fuel cell systems by converting sulfide to electron-withdrawing sulfoxide or sulfone during fuel cell operation. In addition, electron-withdrawing sulfone linkages located close to sulfonic acid groups enhance their acidity, resulting in improved proton conductivity. For these reasons, sulfonated poly(arylene thioether)s are expected to enhance fuel cell performance and their long-term stability.

It has been reported that strongly polar nitrile groups decreased the water uptake and membrane swelling because the dipole-dipole force of nitrile groups increased inter-chain interactions resulting in physical cross-linking.[52] Furthermore, nitrile groups are known to strengthen the interactions with heteropolyacid and inorganic compounds in composite membranes. Also, the strong dipole forces of the nitrile group potentially promote the adhesive properties of the membrane to a catalyst layer.[53,54]

Sulfonated aromatic polymers containing naphthalene units in the backbone are expected to exhibit relatively low water uptake, water swelling ratio, and fuel permeability values because the rigid and planar naphthalene groups augment chain aggregation.[55] Furthermore, naphthalene groups in the backbone induce well-developed hydrophilic ionic clusters in the polymer since the small and planar naphthalene groups are likely to associate with each other and accordingly, facilitate aggregation of the hydrophilic sulfonic acid groups. For these reasons, naphthalene units were incorporated into sulfonated aromatic polymers in order to improve the chemical stability and proton conductivity.[52,55-57]

Here, we report the synthesis, structure, and properties of novel sulfonated aromatic polymers composed of sulfide, nitrile, and naphthalene units in the polymer backbone to clarify the effects of the functional groups on membrane properties including proton conductivity, methanol permeability, and single cell performance for DMFC application. The sulfide linkage is expected to offer stability and enhance the hydrophilicity of sulfonic acid groups, while the nitrile group and naphthalene units are intended to reduce the water uptake, swelling ratio, and methanol permeability. In addition, the combination of these unique units is anticipated to induce a semi-crystalline structure into the polymer due to the shallow rotational conformation energy of the sulfide linkage, strong dipole interaction of the nitrile group, and small and planar naphthalene unit.

Experimental Details

Materials. 4,4'-Dichlorodiphenyl sulfone (DCDPS), 2,6-dichlorobenzonitrile (DCBN), potassium carbonate, 1-methyl-2-pyrrolidinone (NMP), and toluene were purchased from Sigma-Aldrich (St. Louis, MO, USA). 2,6-Naphthalenedithiol (NDT) was obtained from Yanjin Technology (Tianjin, China). The other solvents and reagents including 2-propanol, ethanol, and dichloromethane were extra pure grade and supplied by Daejung Chemicals & Metals (Korea). DCBN was purified with ethanol and NDT was recrystallized using dichloromethane to remove impurities. The other chemicals were used as received without further purification. 3,3'-Disulfonated-4,4'-dichlorodiphenyl sulfone (SDCDPS) was prepared by following a reported procedure.[58]

Polymer synthesis. Sulfonated poly(phenylene sulfide sulfone nitrile) (SP) random copolymer was synthesized according to a procedure reported in our previous work.[50] Sulfonated poly(naphthalene sulfide sulfone nitrile) (SN) random copolymer was synthesized by a nucleophilic aromatic substitution reaction in a four-necked round-bottom flask equipped with a nitrogen inlet, thermometer, mechanical stirrer, and Dean-Stark trap with a reflux condenser. 3,3’-Disulfonated-4,4’-dichlorodiphenyl sulfone (SDCDPS), 2,6-dichlorobenzonitrile (DCBN), and 2,6-naphthalenedithiol (NDT) were introduced and NMP was added to the flask. The molar ratio of SDCDPS/DCBN was varied to achieve the desired degree of sulfonation. The reaction mixture was heated to 80^{o}C to completely dissolve the monomer and then, the reaction temperature was slowly increased to 140^{o}C to activate the monomer and remove water in the presence of potassium carbonate and toluene as a catalyst and azeotropic reagent, respectively. After removing the water and toluene, the reaction temperature was elevated to 170^{o}C and held for 24 h to obtain a viscous polymer solution. The polymer solution was then cooled to room temperature and filtered using 5 μm filter paper (Advantec, Dublin, CA, USA) to remove the salt. The filtered solution was precipitated in a 2-propanol and water mixture, washed several times to remove the remaining salt and solvent, and then dried at 120^{o}C under vacuum.

Membrane Preparation. Dried SN and SP random copolymers were dissolved as a 15 wt % solution in NMP. The polymer solution was filtered using a 0.45 μm PTFE filter to remove impurities and then cast onto a clean glass plate. After removing the solvent under vacuum, the membranes were peeled off from the glass plate by immersing into deionized water. The membranes were boiled in a 1 M H_2SO_4 aqueous solution for 2 h, followed by washing with boiled deionized water for 2 h to protonate the sulfonic acid groups in the polymer. The Nafion® 117 membrane was purchased from DuPont® and used after acidification.

Characterization and Measurements. *Nuclear Magnetic Resonance (NMR) Spectrocopy.* To confirm the chemical structures of the SN and SP random copolymers, ^{1}H NMR spectra were recorded on a 300 MHz Bruker AV 300 spectrometer using DMSO-d_6 as a solvent.

Molecular Weight and Inherent Viscosity Determinations. To verify the molecular weights of the SN and SP random copolymers, gel permeation chromatography (GPC) was conducted using a Waters 2414 refractive index detector equipped with Styragel® HR 3 and 4 columns. NMP was used as the mobile phase and LiBr was added to control the ionic aggregates associated with the sulfonated copolymers and to minimize the ionic effect.[59] The inherent viscosities of the SN and SP copolymers were measured by a Ubbelohde viscometer at 25°C.

Molecular Structure Analysis. The molecular structure was simulated using the Materials Studio program (Accelrys, San Diego, CA, USA) to confirm the three-dimensional structures of the monomers and polymers. Wide angle X-ray diffraction (WAXD) was conducted using a CuKα radiation source to identify the semi-crystalline structure of the Nafion®, SN, and SP copolymers. All samples were dried at 120°C under vacuum for 12 h to remove any remaining water.

Chemical and Mechanical Stabilities. Fenton's test was performed to verify the chemical stability of the Nafion®, SN, and SP copolymers. The retained weight (RW) was calculated after immersion in Fenton's reagent containing 3% H_2O_2 and 2 ppm $FeSO_4$ at 80°C for 1 h. The dissolution time (τ) was measured by submerging the membranes in Fenton's reagent at 30°C. The elongation and tensile strength of the membranes were measured using a universal test machine (AGS-J 500N, Shimadzu, Kyoto, Japan) at room temperature following the ASTM D882 method.

Water Uptake (WU) and Swelling Ratio (SR) Measurements. The water uptake (WU) and swelling ratio (SR) were calculated from the mass and volume ratios between the dry and wet states. Before the measurements, all samples were dried at 120°C under vacuum to remove water and then immersed into deionized water at 80°C for 12 h to stabilize the membrane.

Proton Conducting Parameters. The density of the membranes was measured by the floatation method using a microbalance. 2,2,4-Trimethylpentane was used as a reference liquid. The weight-based ion exchange capacity (IEC_w) was determined using a conventional titration method. The acidified membranes were immersed into a NaCl solution to substitute the H^+ of sulfonic acid groups with Na^+. The solution was titrated with a NaOH solution using phenolphthalein as an indicator. The volume-based IEC values of the Nafion®, SN, and SP membranes under dry ($IEC_{v(dry)}$) and wet ($IEC_{v(wet)}$) states were calculated by multiplying the IEC_w values by the dry and wet membrane densities, respectively. The hydration number (λ), which is the ratio of the water molecules to sulfonic acid groups, was obtained based on the water uptake and IEC_w values. The molar volume per charge of the fully hydrated membranes ($MVC_{(wet)}$), which is an estimated volume per mole equivalent of acid groups, was calculated by simply counting the van der Waals volume increments of composing atoms or structure groups of the polymers and the hydration number of the membranes. The percent conducting volume (PCV), which is the ratio of the volume of the hydrophilic conducting domain per acid site to the total volume of the hydrated membrane per acid site, was calculated from the molar volume of water, hydration number, and $MVC_{(wet)}$.

Methanol Permeability. The methanol permeability was measured using a homemade diffusion cell consisting of two reservoirs. The membrane sample was sandwiched between two reservoirs which contained deionized water and a 10 M methanol solution. The methanol concentration change in the deionized water reservoir was monitored using gas chromatography (GC-14B, Shimadzu, Kyoto, Japan) as a function of time under continuous stirring and was then converted to the methanol permeability.

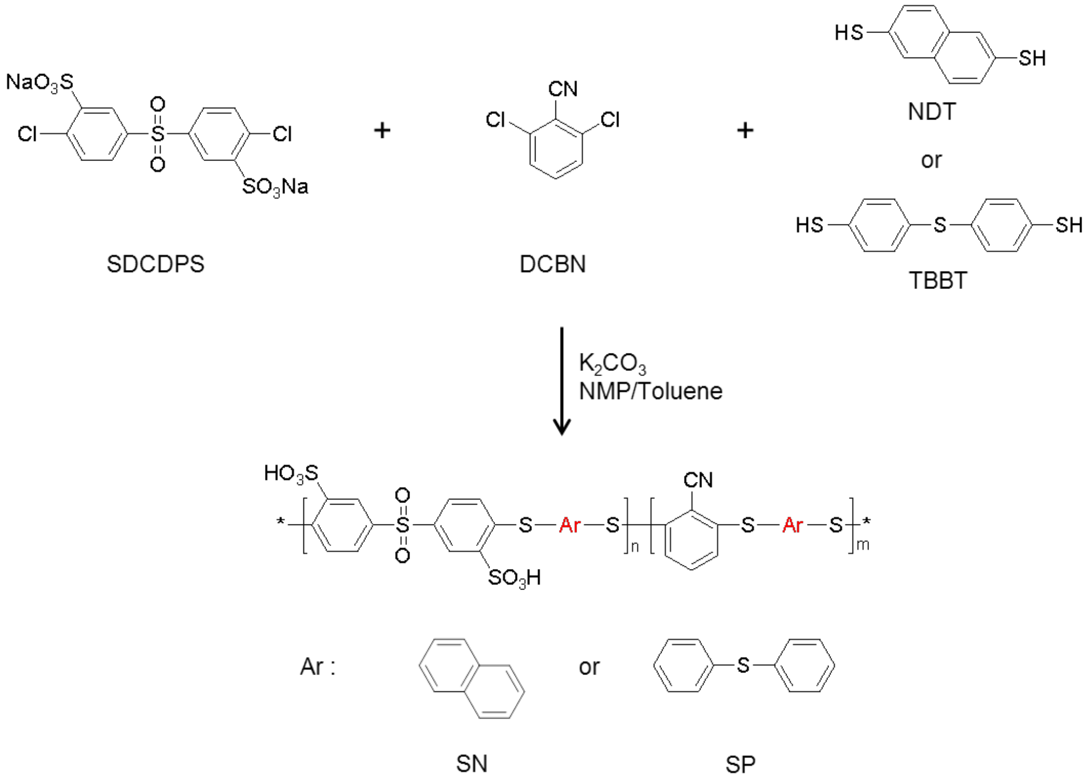
Proton Conductivity. The proton conductivity of the membranes was measured using two different homemade cells. A reservoir type conductivity cell connected to a temperature control chamber was used for the in-plane conductivity measurements under fully hydrated conditions (immersion in deionized water) as a function of temperature. Meanwhile, a single cell type conductivity cell was used to obtain the in-plane and through-plane conductivities of the membranes at 80^{o}C in the fully hydrated state (RH 100%) connected with a PEMFC single cell test station (CNL, Seoul, Korea). The proton conductivity was obtained from the resistance between the working and counter electrodes. The resistance of the membranes was measured over the frequency range from 100 mHz to 100 kHz using an electrode system connected with an impedance/gain-phase analyzer (Solartron 1260, Farnborough, Hampshire, UK) and an electrochemical interface (Solartron 1287).

DMFC Performance. The electrocatalysts used in the anode and cathode were a Pt/Ru alloy (50 at% Pt and 50 at% Ru, HiSPEC® 6000, Alfa Aesar, USA) and Pt black (HiSPEC® 1000, Alfa Aesar, USA), respectively. 5 wt% Nafion® ionomer (Sigma Aldrich, USA) was used as a binder. The catalyst was loaded onto a membrane by a spraying method and then the membrane electrode assembly (MEA) was prepared by hot-pressing the catalyst-coated membrane with carbon paper, which plays the role as a gas diffusion layer. A DMFC single cell test was performed at 80^{o}C using a fuel cell test station (WonATech, Seoul, Korea). The active area of the MEAs was 5 cm^2 with an overall Pt loading of 3 mg/cm^2. Methanol and oxygen were used as a fuel and oxidant, respectively. Also, in the accelerated test, the DMFC single cell was continuously operated at a constant 0.4 V to estimate the long-term stability of the membranes.

Results and Discussion

Polymer Synthesis. Sulfonated poly(naphthalene sulfide sulfone nitrile) (SNxx, xx: mole ratio (%) of SDCDPS) and sulfonated poly(phenylene sulfide sulfone nitrile) (SPxx) random copolymers were successfully synthesized by polycondensation with various feed ratios of SDCDPS to DCBN, resulting in copolymers with different degrees of sulfonation, as shown in Scheme 1. Viscous polymer solutions were obtained after a reaction time of 24 h. Table 1 shows the molecular weights, polydispersities, and inherent viscosities of the SN and SP random copolymers.

The chemical structures of the SN and SP copolymers were confirmed by ^{1}H NMR spectroscopy, providing good agreement to the designed structure, as shown in Figure 1.



Scheme 1. Synthesis procedure of SN and SP random copolymers.

Table 1. Molecular weight and inherent viscosity of SN and SP copolymers.

	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI	η_{inh} (dL g^{-1})
SN30	66	120	1.82	0.92
SN35	64	109	1.70	0.88
SN40	60	103	1.72	0.76
SP35	75	134	1.79	0.89
SP40	69	129	1.84	0.89
SP50	63	118	1.87	0.82

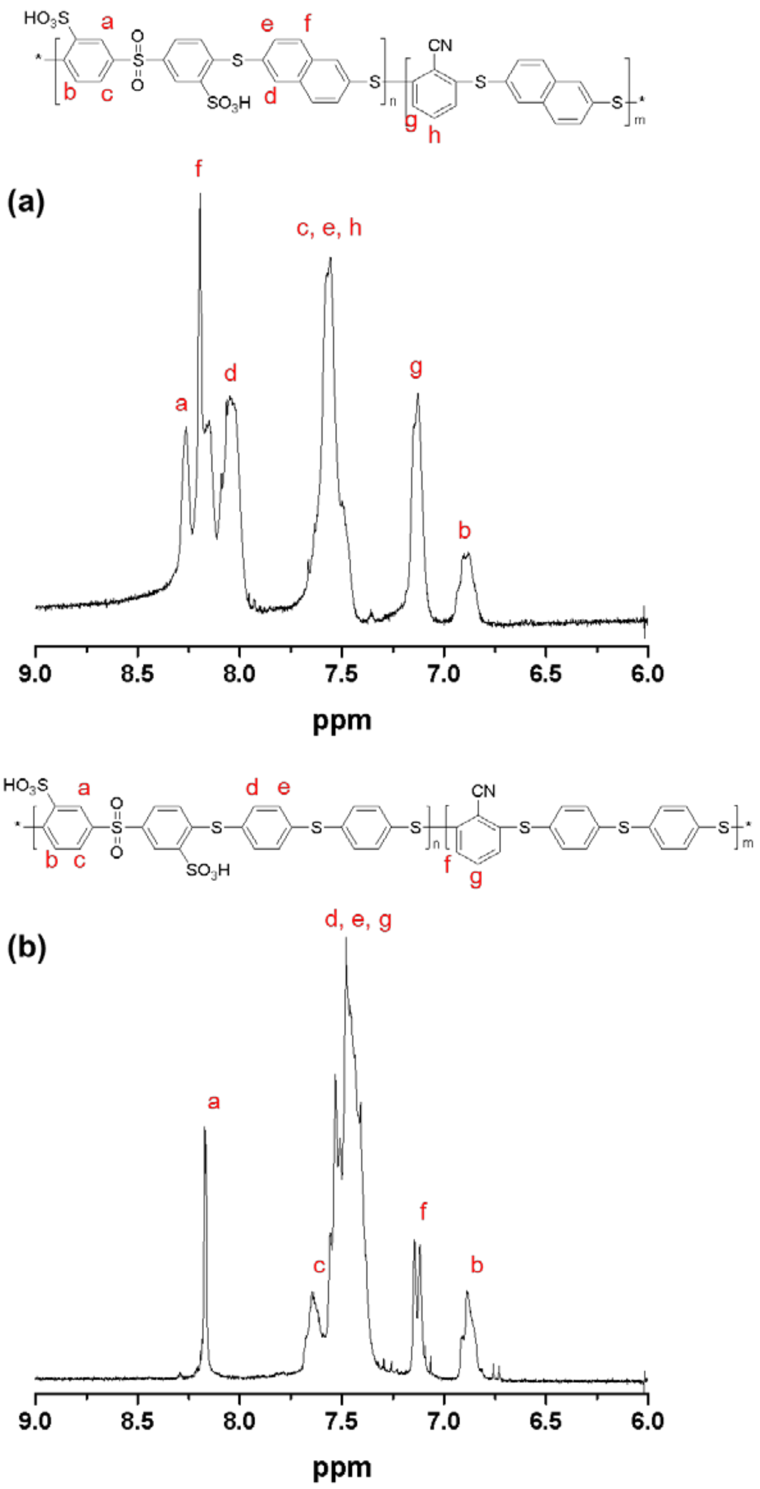


Figure 1. ^{1}H NMR spectra of (a) SN and (b) SP random copolymer.

Molecular Structure. The three-dimensional molecular structures of the sulfide-based monomers (NDT and TBBT) and polymers (SN and SP) were visualized by molecular simulation, as shown in Figure 2. The NDT (torsion angle = 8^o) monomer was planar, whereas the TBBT (torsion angle = 14^o) was slightly tilted to stabilize the structure, as expected. Also, the SN polymers tend to aggregate due to the small and planar naphthalene unit, while the SP polymers had more dispersed benzene rings because flexible sulfide linkages are present between the aromatic groups. This behavior was clearly manifested in the long polymer chain length (number of repeating units > 30). The SN polymers exhibited well-packed hydrophilic ionic clusters whereas the sulfonic acid groups in the SP polymers were randomly distributed. For these reasons, the distance between the sulfonic acid groups in the SP polymers may be farther than that in the SN polymers, which consequently affects the polymer structure and hopping transport of protons through the sulfonic acid groups.

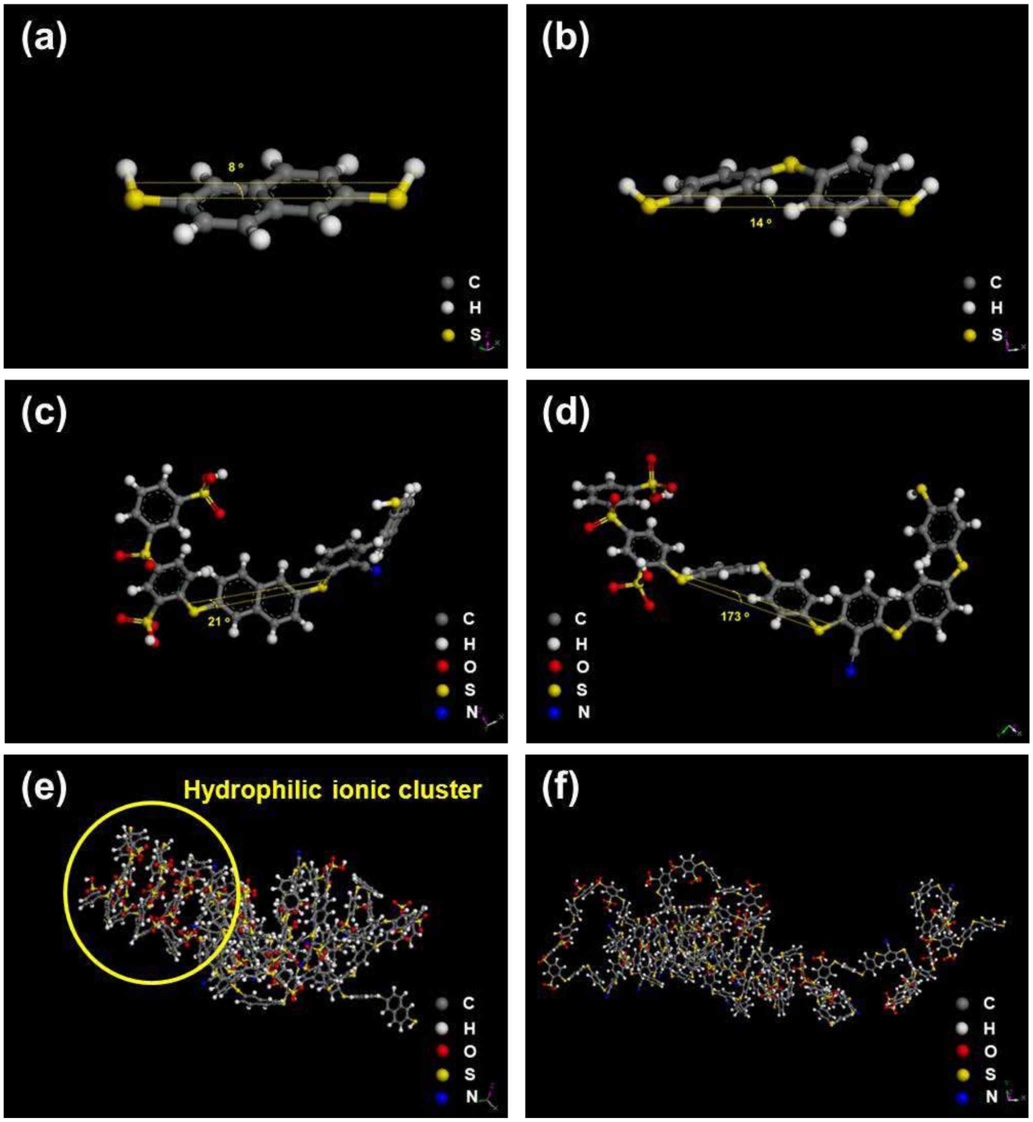


Figure 2. Three-dimensional molecular structures of (a) NDT, (b) TBBT, (c) one repeat unit of SN, (d) SP, (e) 30 repeat units of SN and (f) SP.

WAXD was performed to study the semi-crystalline structures of the SN, SP, and Nafion® membranes, as shown in Figure 3. The Nafion® membrane exhibited four peaks at around 2θ = 17, 21, 24, and 26°, due to the amorphous and orthorhombic crystal structure.[60] Most sulfonated hydrocarbon polymers are amorphous because bulky sulfonic acid groups hinder their chain packing. However, the SN copolymers showed similar WAXD patterns as Nafion® membrane whereas the SP copolymers exhibited smooth and amorphous patterns. This behavior indicates that the π-π interaction of small and planar naphthalene unit enhanced the polymer chain aggregation, resulting in semi-crystalline structure formation.

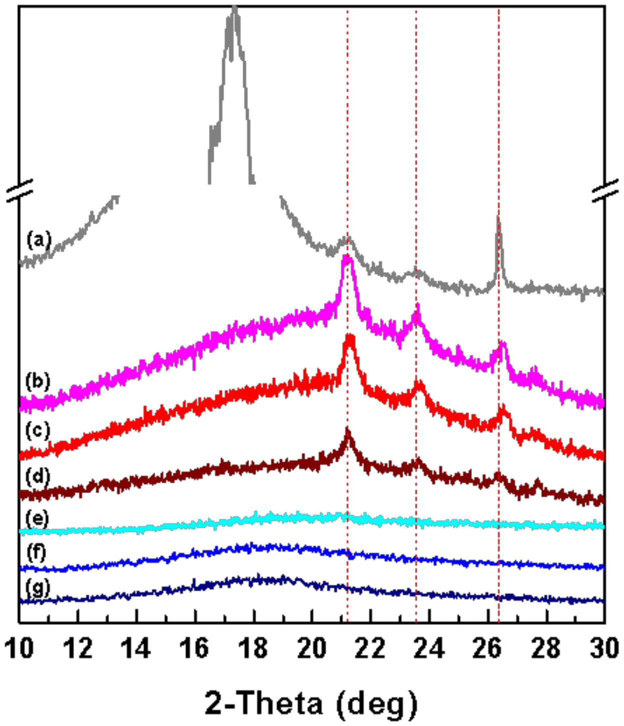


Figure 3. WAXD patterns of (a) Nafion®, (b) SN30, (c) SN35, (d) SN40, (e) SP35, (f) SP40, and (g) SP50.

Chemical and Mechanical Stabilities. Excellent chemical and mechanical stabilities are necessary requirements for ideal polyelectrolyte membranes because the chemical and mechanical properties affect the fabrication conditions and fuel cell performance. Generally, amorphous polymers have less good chemical and physical stabilities compared with semi-crystalline polymers, which limit their use in engineering applications. However, semi-crystalline polymers possess outstanding stabilities because periodically stacked rigid crystalline regions play an important role to physically crosslink the amorphous regions. Thus, SN copolymers are chemically more stable and robust than SP copolymers, as shown in Table 2. In particular, the retained weights of the SN and SP membranes were slightly increased after immersion in Fenton's reagent since sulfide linkages are oxidized to sulfoxide or sulfone. The enhanced chemical stability of the SN membranes is attributed to the introduction of the naphthalene units and sulfide linkage in the polymer backbone. The chemical stability of sulfide-based polymers is expected to result in improved fuel cell performance. Although the elongation of the SN membranes (10–21%) was lower than that of the SP membranes (19–65%), the SN membranes had much higher tensile strengths (58–78 MPa) than the SP membranes (42–58 MPa) because the semi-crystalline structure of SN hinders chain extension while the flexible sulfide linkage enhances their ductility.

Table 2. Chemical and mechanical properties of SN, SP, and Nafion®.

	RW (%)	τ (h)	Elongation at break (%)	Tensile strength (MPa)
SN30	111	70	10 ± 2	78 ± 7
SN35	112	63	12 ± 4	60 ± 10
SN40	114	48	21 ± 4	58 ± 6
SP35	107	65	19 ± 3	46 ± 6
SP40	110	55	47 ± 5	42 ± 4
SP50	109	40	65 ± 8	35 ± 4
Nafion® 117	98	50	198 ± 11	20 ± 3

Swelling Ratio and Water Uptake. The swelling ratio was measured as a function of temperature in the range of 30 to 80^{o}C, as shown in Figure 4(a). The swelling ratio of the SN and SP membranes increased with increasing degree of sulfonation, since the sulfonic acid groups enhance the ionic nature of the sulfonated polymers. The SN copolymers had a much smaller swelling ratio than the SP copolymers due to the planar naphthalene unit, which induces polymer chain aggregation and interrupts membrane swelling. For example, the swelling ratio of SN40 was 75 vol%, while that of SP50 was 381 vol% at 80^{o}C despite their similar IEC$_w$ values (1.93 and 1.99 meq g^{-1}, respectively, as shown in Table 3). As a result, modification of the polymer structure using the planar naphthalene unit can effectively improve the dimensional stability.

Water uptake is a critical factor for PEMs because of its critical influence on the proton conductivity and mechanical properties. Water molecules are important in sulfonated membranes because they act as proton carriers. A lack of water in the polymer membrane leads to a decrease of the proton conductivity. However, an excess of water may dilute the concentration of sulfonic acid groups and decrease the proton conductivity. Also, excessive water leads to instability of the polymer chain resulting in a large swelling ratio and deterioration in the mechanical properties. Furthermore, excessive water around the membrane causes flooding during fuel cell operation resulting in a significant performance drop in the high current density region. The water uptakes of the SN and SP membranes also increased with increasing degree of sulfonation because hydrophilic sulfonic acid groups are strongly associated with water molecules, as shown in Figure 4(b). SN PEMs had a reasonable water uptake values in the range of 28-60 wt%, while the water uptake of the SP membranes was considerably higher (75–270 wt% at 80^{o}C).

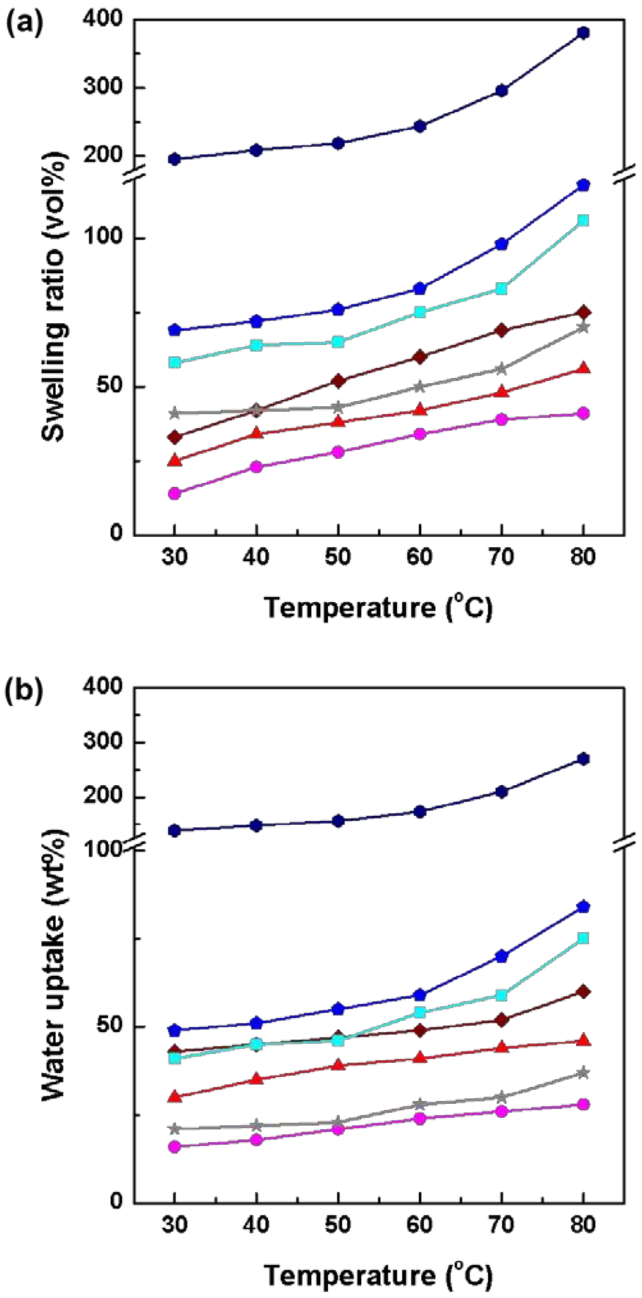


Figure 4. Swelling ratio and water uptake of SP50 (⬢), SP40 (⬟), SP35 (■), SN40 (◆), SN35 (▲), SN30 (●), and Nafion® (★).

The SN and SP membranes exhibited increased swelling ratios and water uptakes as the temperature increased, particularly above 60°C. A sudden increase of the swelling ratio and water uptake of SP was observed as $IEC_{v(wet)}$ increased, as shown in Figure 5(a) and (b). However, the swelling ratio and water uptake of the SN membranes continuously increased with increasing $IEC_{v(wet)}$, whereas those of the SP membranes showed an inflection point at around an $IEC_{v(wet)}$ value of 1.4. These results indicate that the SN copolymers have a higher proton conduction capacity than the SP copolymers with a high degree of sulfonation.

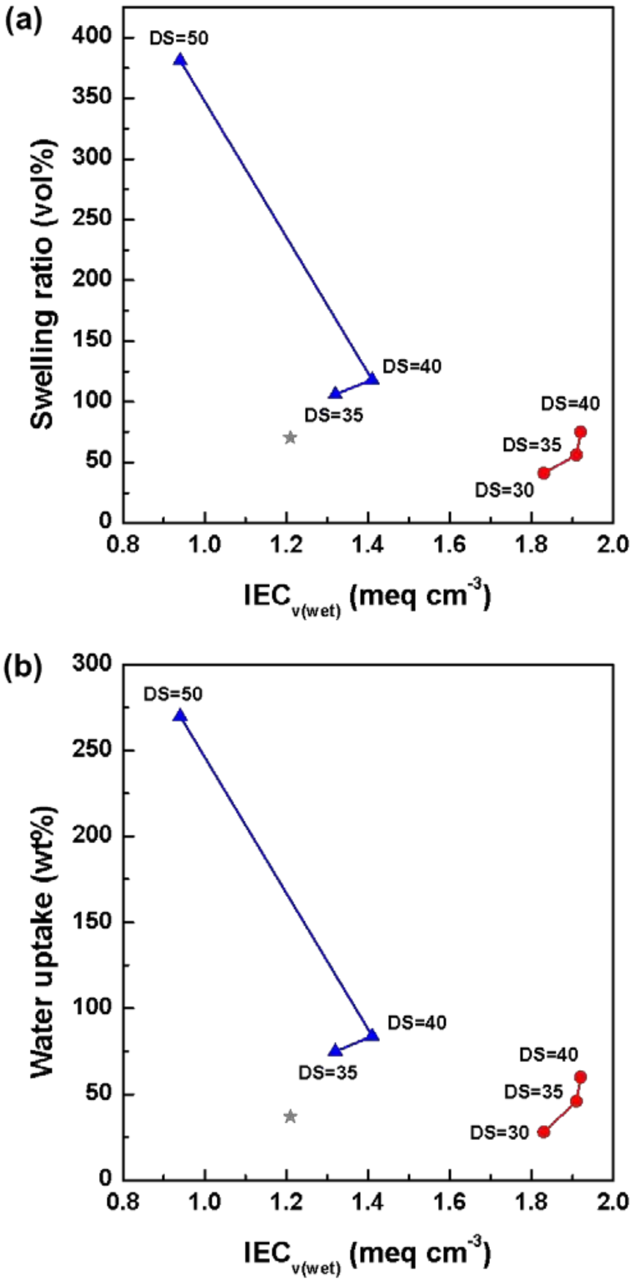


Figure 5. (a) Swelling ratio and (b) water uptake of SN (●), SP (▲), and Nafion® (★) as a function of IEC$_{v(wet)}$ values.

Proton Conducting Parameters. The proton conducting parameters based on the mass and volume of the membranes including the IEC, MVC, and PCV values of the SN and SP membranes were obtained to estimate their potential as a PEM. The values were compared to Nafion® as a reference and are displayed in Table 3. Traditionally, only weight-based parameters are considered to estimate fuel cell performance. However, Kim and Pivovar suggested volume-based parameters because weight-based parameters have significant limitations when correlated to fuel cell performance.[61] The limitations result from the different densities of various polymers. Also, proton transport through membranes occurs over length scales represented by volume rather than mass. For these reasons, volume-based parameters are reported, since they are more relevant to estimate fuel cell performance.

Weight-based IEC values (IEC_w) were first measured by a titration method and they corresponded well with the IEC values calculated from the chemical structure. As expected, IEC_w increased with increasing degree of sulfonation. The volume-based IEC values of the dry membranes ($IEC_{v(dry)}$) also increased with increasing degree of sulfonation because the densities of the SN and SP membranes were quite similar despite their different chemical structures and degrees of sulfonation. However, the volume-based IEC values of the wet membranes ($IEC_{v(wet)}$) exhibited different trends than the IEC_w and $IEC_{v(dry)}$ values because the SN and SP membranes showed an inflection point (or percolation threshold) in the water uptake and swelling ratio at around an $IEC_{v(wet)}$ of about 1.4. For these reasons, the $IEC_{v(wet)}$ of SP50, located above the inflection point, was significantly lower than that of SP 40 due to its large water uptake and swelling ratio. However, the SN40 membrane exhibited almost the same $IEC_{v(wet)}$ value as SN35 since it maintained much of its original weight and volume despite the high degree of sulfonation. The trend of $MVC_{(wet)}$ of the sulfide-based polymer membranes was quite similar to that of their water uptake because $MVC_{(wet)}$ depends heavily on the chemical structure and hydration number (λ). The SN membranes showed higher $IEC_{v(wet)}$ and smaller $MVC_{(wet)}$ values than the SP membranes, indicating the potentially high proton conductivity of SN compared to SP. However, the proton conductivity of the SN membranes was actually lower than that of the SP membranes because water is only regarded as a volume element in $\mathrm{IEC}_{\mathrm{v(wet)}}$ and $\mathrm{MVC}_{\mathrm{(wet)}}$ despite the fact that water is very important for proton transfer. On the other hand, PCV, defined as the ratio of the volume of the hydrophilic conducting domain per acid site to the total volume of the hydrated membrane per acid site, is well correlated with the IEC and degree of sulfonation and thus, the proton conductivity.

Table 3. Proton conducting parameters of SN, SP, and Nafion®.

	IEC_{cal} (meq g^{-1})	IEC_{tit} (meq g^{-1})	Density (g cm^{-3})	$IEC_{v(dry)}$ (meq cm^{-3})	$IEC_{v(wet)}$ (meq cm^{-3})	λ	$MVC_{(wet)}$ (cm^3 mol^{-1})	PCV
SN30	1.60	1.53	1.36	2.08	1.83	6	568	0.18
SN35	1.81	1.74	1.37	2.38	1.91	10	581	0.30
SN40	1.99	1.93	1.32	2.55	1.92	12	591	0.38
SP35	1.57	1.52	1.37	2.08	1.32	15	731	0.37
SP40	1.74	1.71	1.39	2.38	1.41	19	755	0.45
SP50	2.05	1.99	1.40	2.79	0.94	39	1045	0.67
Nafion® 117	0.90	0.91	2.07	1.80	1.21	15	799	0.34

Proton Conductivity. The proton conductivity is one of the most important properties for fuel cell applications. The in-plane and through-plane proton conductivities of the wet membranes were measured as a function of temperature, as shown in Figure 6. As expected, the proton conductivity increased with increasing temperature because water activity in the membrane that affects proton transport is drastically enhanced by increasing temperature. However, the SN membranes exhibited much lower proton conductivities than the SP membranes in the hydrated state while the IEC values of the SN membranes were much higher than those of the SP membranes. This phenomenon may arise from the small water uptake and semi-crystalline characteristics of SN resulting in an insufficient proton conducting phase. Although the semi-crystalline structure interrupts proton transport, the SN membranes exhibited an isotropic proton conductivity (in-plane/through-plane ≈ 1) similar to the SP and Nafion® membranes, indicating that the semi-crystalline structure was randomly distributed in SN.

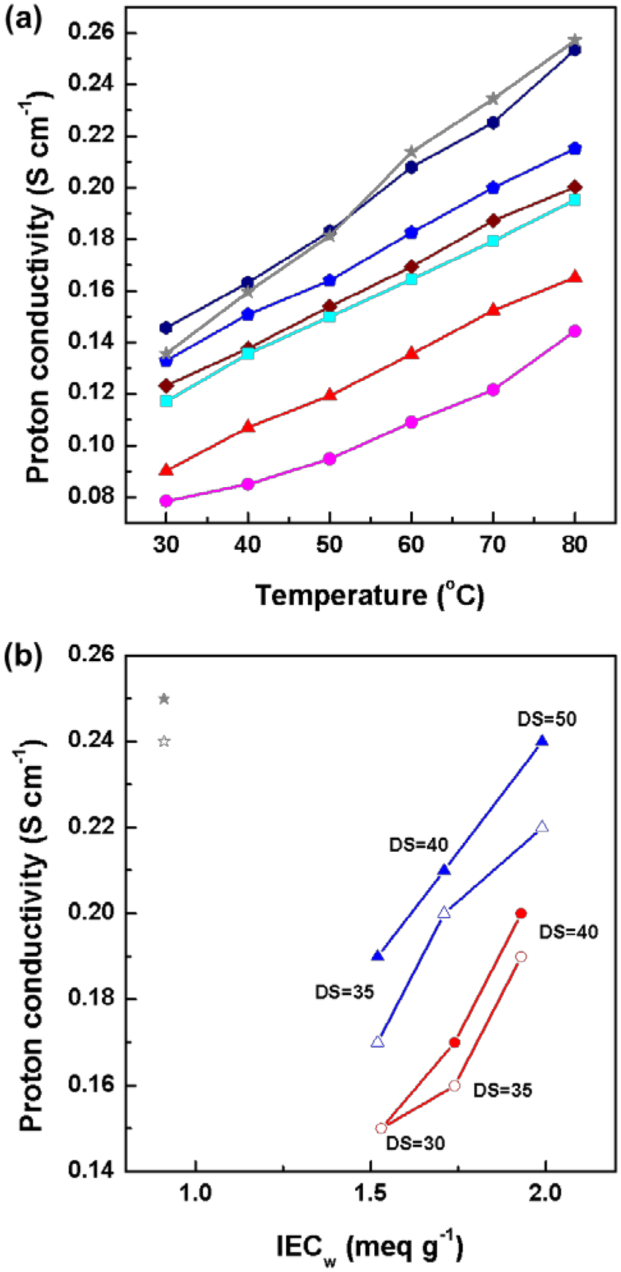


Figure 6. (a) Proton conductivity of SP50 (⬢), SP40 (⬟), SP35 (■), SN40 (◆), SN35 (▲), SN30 (●), and Nafion® (★) as a function of temperature and (b) in-plane (solid) and through-plane (open) proton conductivity of SP (▲,△), SN (●, ○), and Nafion® (★, ☆) as a function of IEC$_w$ value.

Methanol Permeability and Selectivity. Methanol permeability is one of the critical factors for DMFC applications because methanol crossover reduces the fuel cell performance. The methanol permeabilities of the SN, SP, and Nafion® membranes at room temperature are listed in Table 4. The SN and SP membranes showed much lower methanol permeabilities (9–99 × 10^{-8} cm^2 s^{-1}) than Nafion® (240 × 10^{-8} cm^2 s^{-1}). In particular, the methanol permeability was significantly reduced by incorporating the naphthalene unit in SN, which acts as a fuel barrier. The selectivity is defined as the ratio of the proton conductivity to the methanol permeability of the membrane and is often used to estimate the DMFC performance. Generally, membranes with a higher selectivity exhibit better DMFC performance.[20,40] As shown in Table 4, the SN (738–899 × 10^3 s S cm^{-3}) and SP (147–325 × 10^3 s S cm^{-3}) membranes demonstrated higher selectivities than the Nafion® membrane (57 × 10^3 s S cm^{-3}). In particular, the SN membranes possessed the highest selectivities among the membranes tested due to their excellent methanol barrier property. These results demonstrate that the sulfide linkage, nitrile group, and naphthalene unit contributed to improved selectivities and fuel cell performances.

Table 4. Proton conductivity, methanol permeability and selectivity of SN, SP, and Nafion® at 30°C.

	Proton conductivity (mS cm^{-1})	Methanol permeability (10^{-8} cm^2 s^{-1})	Selectivity (10^3 s S cm^{-3})	Relative selectivity[a]
SN30	79	9	899	16
SN35	90	12	751	13
SN40	123	17	738	13
SP35	117	36	325	6
SP40	133	62	216	4
SP50	146	99	147	3
Nafion® 117	136	240	57	1

[a] Ratio of selectivity of sample to that of Nafion®.

Fuel Cell Performances. MEAs with SN and SP membranes (thickness = 40~60 μm) were successfully fabricated by hot-pressing the membranes due to their excellent mechanical properties. A DMFC single cell test was performed at 80°C using 2 M methanol solutions and oxygen as a fuel and oxidant, respectively, as shown in Figure 7. The maximum power densities of the SN40 and SP50 membranes were 115 and 102 mW cm^{-2} , respectively, which are higher than that of the Nafion® membrane (54 mW cm^{-2}). This is presumably due to the high methanol permeability of Nafion®, and consequently the high methanol cross-over in the fuel cell.

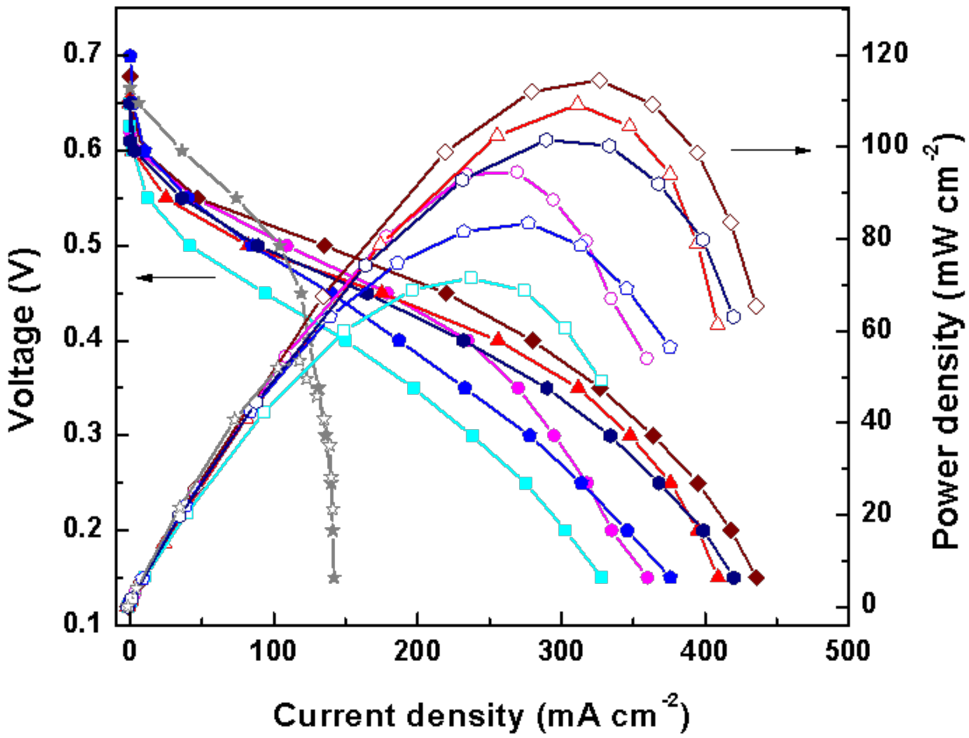


Figure 7. DMFC single cell performance of SN40 (◆), SN35 (▲), SN30 (●), SP50 (⬢), SP40 (⬟), SP35 (■), and Nafion® (★) at 80°C using 2 M methanol and oxygen as a fuel and oxidant.

The long-term stability of the membranes was estimated by conducting accelerated durability testing of the SN40 and SP50 membranes using 2 M methanol and an excess amount of oxygen, as shown in Figure 8. The SN40 membrane maintained a current density of over 80% of its initial performance for 320 h, whereas the SP50 and Nafion® membranes kept this level for 120 and 80 h, respectively. By comparison, Cheng *et al.* reported that the open circuit voltage (OCV) of Nafion® declined from 0.627 to 0.527 V after 200 h operation at 60 °C (non-accelerated test condition).[62] This result demonstrates the beneficial effects of the naphthalene unit in SN polymer membranes on the chemical and mechanical stabilities of the PEMs during fuel cell operation.

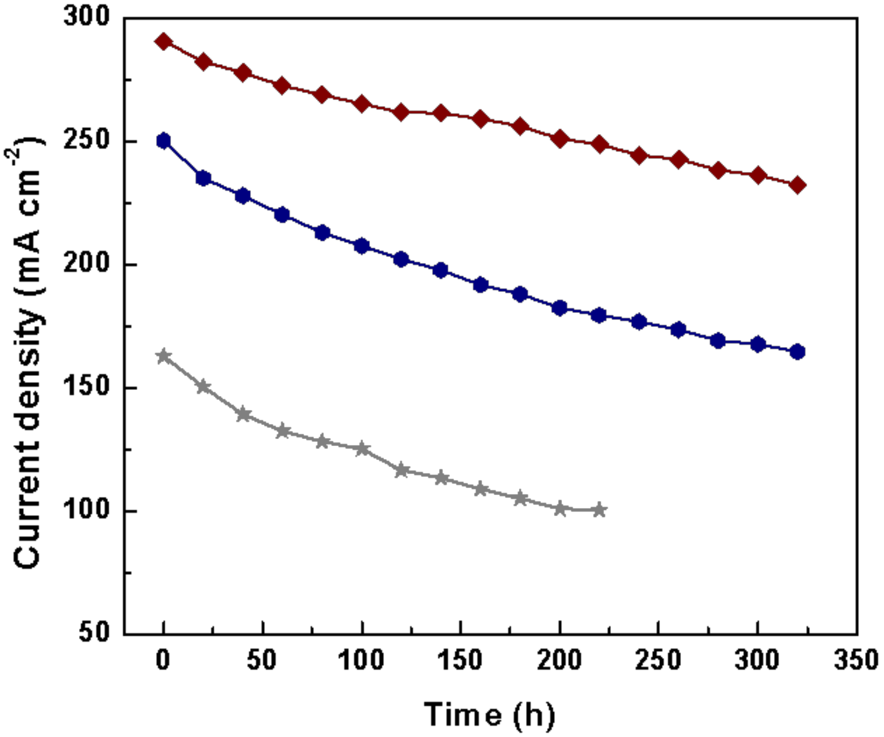


Figure 8. Accelerated DMFC durability testing of SN40 (◆), SP50 (⬢), Nafion® (★).

Conclusions

Novel sulfonated polymers (SN) were successfully synthesized containing a sulfide linkage, nitrile group, and naphthalene unit. This unique chemical structure of the SN polymer formed a semi-crystalline structure, as confirmed by the molecular simulations and WAXD analysis. The SN membranes showed excellent chemical and mechanical properties compared to the SP and Nafion® membranes. In particular, the retained weight of the sulfide-based polymers after immersing in Fenton’s reagent increased while that of Nafion® slightly decreased due to the oxidation of the sulfide linkage to sulfoxide or sulfone moieties. The SN polymer membranes also exhibited a significantly reduced water uptake and swelling ratio compared to the SP membranes despite their similar IEC values since the planar naphthalene moiety was easily packed and thus, hindered the absorption of water molecules. For similar reasons, the methanol permeability of the SN membranes was much lower than those of the SP and Nafion® membranes. Although the semi-crystalline SN membrane had a decreased proton conductivity, the overall selectivity of the SN membrane was improved. The relative selectivity of the SN membranes was up to sixteen times compared with the Nafion® membrane. As a result, the SN membranes demonstrated a two times higher DMFC single cell performance compared to Nafion®, particularly at a higher methanol concentration of 2 M. It was clearly proven that the long-term fuel cell performance was improved by inducing naphthalene units in the sulfide-containing aromatic hydrocarbon membranes.

Acknowledgements

This work was supported by the WCU(World Class University) (R31-2008-000-10092) and Nano·Meterial Technology Development (2012M3A7B4049745) program through the National Research Foundation funded by the Ministry of Education, Science and Technology.

References

(1) Tripathi, B. P.; Shahi, V. K. *Prog Polym Sci* **2011**, *36*, 945.

(2) Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem Rev* **2004**, *104*, 4587.

(3) Zhang, H. W.; Shen, P. K. *Chem Rev* **2012**, *112*, 2780.

(4) Park, C. H.; Lee, C. H.; Guiver, M. D.; Lee, Y. M. *Prog Polym Sci* **2011**, *36*, 1443.

(5) Wang, Z.; Ni, H. Z.; Zhang, M. Y.; Zhao, C. J.; Na, H. *Desalination* **2009**, *242*, 236.

(6) Bae, B.; Miyatake, K.; Watanabe, M. *J Membrane Sci* **2008**, *310*, 110.

(7) Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. *J Membrane Sci* **2002**, *197*, 231.

(8) Arnett, N. Y.; Harrison, W. L.; Adami, A. S. B.; Roy, A.; Lane, O.; Cromer, F.; Dong, L.; McGrath, J. E. *J Power Sources* **2007**, *172*, 20.

(9) Asano, N.; Miyatake, K.; Watanabe, M. *Chem Mater* **2004**, *16*, 2841.

(10) Chen, X. B.; Yin, Y.; Chen, P.; Kita, H.; Okamoto, K. I. *J Membrane Sci* **2008**, *313*, 106.

(11) Lee, C. H.; Park, C. H.; Lee, Y. M. *J Membrane Sci* **2008**, *313*, 199.

(12) Zhai, F. X.; Guo, X. X.; Fang, J. H.; Xu, H. J. *J Membrane Sci* **2007**, *296*, 102.

(13) Li, N. W.; Cui, Z. M.; Zhang, S. B.; Li, S. H.; Zhang, F. *J Power Sources* **2007**, *172*, 511.

(14) Yan, J. L.; Liu, C. P.; Wang, Z.; Xing, W.; Ding, M. M. *Polymer* **2007**, *48*, 6210.

(15) Yu, S.; Xiao, L.; Benicewicz, B. C. *Fuel Cells* **2008**, *8*, 165.

(16) Qian, G. Q.; Benicewicz, B. C. *J Polym Sci Pol Chem* **2009**, *47*, 4064.

(17) Diaz, L. A.; Abuin, G. C.; Corti, H. R. *J Power Sources* **2009**, *188*, 45.

(18) Kim, T. H.; Lim, T. W.; Lee, J. C. *J Power Sources* **2007**, *172*, 172.

(19) Lin, H. L.; Hsieh, Y. S.; Chiu, C. W.; Yu, T. L.; Chen, L. C. *J Power Sources* **2009**, *193*, 170.

(20) Chen, Z. W.; Holmberg, B.; Li, W. Z.; Wang, X.; Deng, W. Q.; Munoz, R.; Yan, Y. S. *Chem Mater* **2006**, *18*, 5669.

(21) Mistry, M. K.; Choudhury, N. R.; Dutta, N. K.; Knott, R.; Shi, Z. Q.; Holdcroft, S. *Chem Mater* **2008**, *20*, 6857.

(22) Pereira, F.; Valle, K.; Belleville, P.; Morin, A.; Lambert, S.; Sanchez, C. *Chem Mater* **2008**, *20*, 1710.

(23) Kim, Y. S.; Wang, F.; Hickner, M.; Zawodzinski, T. A.; McGrath, J. E. *J Membrane Sci* **2003**, *212*, 263.

(24) Staiti, P.; Arico, A. S.; Baglio, V.; Lufrano, F.; Passalacqua, E.; Antonucci, V. *Solid State Ionics* **2001**, *145*, 101.

(25) Takamuku, S.; Jannasch, P. *Adv Energy Mater* **2012**, *2*, 129.

(26) Einsla, M. L.; Kim, Y. S.; Hawley, M.; Lee, H. S.; McGrath, J. E.; Liu, B. J.; Guiver, M. D.; Pivovar, B. S. *Chem Mater* **2008**, *20*, 5636.

(27) Badami, A. S.; Lane, O.; Lee, H. S.; Roy, A.; McGrath, J. E. *J Membrane Sci* **2009**, *333*, 1.

(28) Lee, H. S.; Badami, A. S.; Roy, A.; Mcgrath, J. E. *J Polym Sci Pol Chem* **2007**, *45*, 4879.

(29) Ghassemi, H.; McGrath, J. E.; Zawodzinski, T. A. *Polymer* **2006**, *47*, 4132.

(30) Lee, H. S.; Roy, A.; Lane, O.; Dunn, S.; McGrath, J. E. *Polymer* **2008**, *49*, 715.

(31) Lee, H. S.; Roy, A.; Lane, O.; McGrath, J. E. *Polymer* **2008**, *49*, 5387.

(32) Li, N.; Lee, S. Y.; Liu, Y. L.; Lee, Y. M.; Guiver, M. D. *Energy & Environmental Science* **2012**, *5*, 5346.

(33) Wang, C.; Shin, D. W.; Lee, S. Y.; Kang, N. R.; Lee, Y. M.; Guiver, M. D. *J Membrane Sci* **2012**, *405*, 68.

(34) Park, C. H.; Shin, D. W.; Lee, Y. M.; Kang, P. H.; Nho, Y. C. *Macromol Res* **2009**, *17*, 825.

(35) Kim, D. S.; Robertson, G. P.; Guiver, M. D. *Macromolecules* **2008**, *41*, 2126.

(36) Li, N. W.; Shin, D. W.; Hwang, D. S.; Lee, Y. M.; Guiver, M. D. *Macromolecules* **2010**, *43*, 9810.

(37) Wang, C. Y.; Li, N.; Shin, D. W.; Lee, S. Y.; Kang, N. R.; Lee, Y. M.; Guiver, M. D. *Macromolecules* **2011**, *44*, 7296.

(38) Li, N.; Wang, C.; Lee, S. Y.; Park, C. H.; Lee, Y. M.; Guiver, M. D. *Angew Chem Int Edit* **2011**, *50*, 9158.

(39) Bae, B.; Yoda, T.; Miyatake, K.; Uchida, H.; Watanabe, M. *Angew Chem Int Edit* **2010**, *49*, 317.

(40) Lee, K. S.; Jeong, M. H.; Kim, Y. J.; Lee, S. B.; Lee, J. S. *Chem Mater* **2012**, *24*, 1443.

(41) Lee, K. S.; Jeong, M. H.; Lee, J. P.; Kim, Y. J.; Lee, J. S. *Chem Mater* **2010**, *22*, 5500.

(42) Matsumura, S.; Hlil, A. R.; Al-Souz, M. A. K.; Gaudet, J.; Guay, D.; Hay, A. S. *J Polym Sci Polym Chem* **2009**, *47*, 5461.

(43) Miyatake, K.; Chikashige, Y.; Higuchi, E.; Watanabe, M. *J Am Chem Soc* **2007**, *129*, 3879.

(44) Schuster, M.; Kreuer, K. D.; Andersen, H. T.; Maier, J. *Macromolecules* **2007**, *40*, 598.

(45) Lee, S. Y.; Kang, N. R.; Shin, D. W.; Lee, C. H.; Lee, K.-S.; Guiver, M. D.; Li, N.; Lee, Y. M. *Energy & Environmental Science* **2012**, *5*, 9795.

(46) Jeong, M. H.; Lee, K. S.; Lee, J. S. *Macromolecules* **2009**, *42*, 1652.

(47) Lee, K. S.; Jeong, M. H.; Lee, J. P.; Lee, J. S. *Macromolecules* **2009**, *42*, 584.

(48) Zhao, D.; Li, J. H.; Song, M. K.; Yi, B. L.; Zhang, H. M.; Liu, M. L. *Adv Energy Mater* **2011**, *1*, 203.

(49) Barique, M. A.; Wu, L. B.; Takimoto, N.; Kidena, K.; Ohira, A. *J Phys Chem B* **2009**, *113*, 15921.

(50) Phu, D. S.; Lee, C. H.; Park, C. H.; Lee, S. Y.; Lee, Y. M. *Macromol Rapid Comm* **2009**, *30*, 64.

(51) Schuster, M.; de Araujo, C. C.; Atanasov, V.; Andersen, H. T.; Kreuer, K. D.; Maier, J. *Macromolecules* **2009**, *42*, 3129.

(52) Gao, Y.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Li, X.; Kaliaguine, S. *Polymer* **2006**, *47*, 808.

(53) Gao, Y.; Robertson, G. P.; Guiver, M. D.; Wang, G.; Jian, X.; Mikhailenko, S. D.; Li, X.; Kaliaguine, S. *J Membrane Sci* **2006**, *278*, 26.

(54) Gao, Y.; Robertson, G. P.; Kim, D. S.; Guiver, M. D.; Mikhailenko, S. D.; Li, X.; Kaliaguine, S. *Macromolecules* **2007**, *40*, 1512.

(55) Bae, B.; Miyatake, K.; Watanabe, M. *Macromolecules* **2009**, *42*, 1873.

(56) Kim, D. S.; Kim, Y. S.; Guiver, M. D.; Pivovar, B. S. *J Membrane Sci* **2008**, *321*, 199.

(57) Xing, P. X.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Kaliaguine, S. *J Polym Sci Polym Chem* **2004**, *42*, 2866.

(58) Li, Y. X.; VanHouten, R. A.; Brink, A. E.; McGrath, J. E. *Polymer* **2008**, *49*, 3014.

(59) Savard, O.; Peckham, T. J.; Yang, Y.; Holdcroft, S. *Polymer* **2008**, *49*, 4949.

(60) Porat, Z.; Fryer, J. R.; Huxham, M.; Rubinstein, I. *J Phys Chem-Us* **1995**, *99*, 4667.

(61) Kim, Y. S.; Pivovar, B. S. *Annu Rev Chem Biomol* **2010**, *1*, 123.

(62) Cheng, X.; Peng, C.; You, M. D.; Liu, L.; Zhang, Y.; Fan, Q. B. *Electrochim Acta* **2006**, *51*, 4620.

Legends

Scheme 1. Synthesis procedure of SN and SP random copolymers.

Figure 1. ^{1}H NMR spectra of (a) SN and (b) SP random copolymer.

Figure 2. Three-dimensional molecular structures of (a) NDT, (b) TBBT, (c) one repeat unit of SN, (d) SP, (e) 30 repeat units of SN and (f) SP.

Figure 3. WAXD patterns of (a) Nafion®, (b) SN30, (c) SN35, (d) SN40, (e) SP35, (f) SP40, and (g) SP50.

Figure 4. Swelling ratio and water uptake of SP50 (⬢), SP40 (⬟), SP35 (■), SN40 (◆), SN35 (▲), SN30 (●), and Nafion® (★).

Figure 5. (a) Swelling ratio and (b) water uptake of SN (●), SP (▲), and Nafion® (★) as a function of $\text{IEC}_{v(wet)}$ values.

Figure 6. (a) Proton conductivity of SP50 (⬢), SP40 (⬟), SP35 (■), SN40 (◆), SN35 (▲), SN30 (●), and Nafion® (★) as a function of temperature and (b) in-plane (solid) and through-plane (open) proton conductivity of SP (▲,△), SN (●, ○), and Nafion ® (★, ☆) as a function of IEC_w value.

Figure 7. DMFC single cell performance of SN40 (◆), SN35 (▲), SN30 (●), SP50 (⬢), SP40 (⬟), SP35 (■), and Nafion® (★) at 80°C using 2 M methanol and oxygen as a fuel and oxidant.

Figure 8. Accelerated DMFC durability testing of SN40 (◆), SP50 (⬢), Nafion® (★).

Tables

Table 1. Molecular weight and inherent viscosity of SN and SP copolymers.

Table 2. Chemical and mechanical properties of SN, SP, and Nafion®.

Table 3. Proton conducting parameters of SN, SP, and Nafion®.

Table 4. Proton conductivity, methanol permeability and selectivity of SN, SP, and Nafion® at 30°C.

For Table of Contents Use Only

Durable Sulfonated Poly(arylene sulfide sulfone nitrile)s Containing Naphthalene Units for Direct Methanol Fuel Cells (DMFCs)

Dong Won Shin, So Young Lee, Na Rae Kang, Kang Hyuck Lee, Michael D. Guiver, Young Moo Lee*