Preparation of nitrated sulfonated poly(ether ether ketone) membranes for reducing methanol permeability in direct methanol fuel cell applications

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ABSTRACT

Sulfonated poly(ether ether ketone)s (SPEEKs) were further substituted on the polymer main chain by nitration. All sulfonation and nitration were achieved with an inexpensive and simple post substitute reaction. The nitrated SPEEKs have a high glass transition temperature and thermal decomposition temperature, and a lower water uptake than SPEEK, which provides sufficient mechanical strength without swelling in the direct methanol fuel cell (DMFC) application. The methanol permeability of nitrated SPEEKS is reduced to $1.76 \times 10^{-7} \, cm^2 \, s^{-1}$ for S53N22 and $1.86 \times 10^{-7} \, cm^2 \, s^{-1}$ for S63N17 with no loss of conductivity in the DMFC application, and a proton conductivity that reached $0.026 \, S \, cm^{-1}$. The nitrated SPEEK membranes satisfy the requirements of proton-exchange membranes for the DMFC.

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1. Introduction

The fuel cell is a promising alternative to an electrochemical energy transformer, converting chemical energy directly into electrical energy. Proton-exchange membrane cells have attracted significant attention because of the simple design, the ability to produce energy efficiently at low operating temperatures, and without the emission of harmful pollutants [1]. Proton-exchange membrane fuel cells represent a promising energy source for portable devices, automobiles, and stationary applications [2]. The proton-exchange membrane is one of the key components that have to meet several demanding requirements: i.e. high proton conductivity, long-term stability in high levels of humidity and temperature, low permeability to fuel (methanol or hydrogen), simple manufacturing process, and low cost.

Perfluorosulfonic acid membranes, such as Nafion, with fluoroalkyl ether side chains and sulfonic acid end groups are the most commonly used material. However, Nafion membranes have several drawbacks [3]: (i) the production process is complicated and expensive; (ii) the proton conductivity depends strongly on the ambient relative humidity; (iii) they have poor thermal stability and shrink at high temperatures, resulting in poor contact and proton conductivity; (iv) they have high methanol permeability, which reduces fuel utilization and cathode performance in a direct methanol fuel cell (DMFC).

Several attempts have been made to replace the Nafion membranes in proton-exchange membrane fuel cells by cheaper and ecologically more acceptable materials. Attempts to optimize and develop of proton-exchange membranes have involved mainly the synthesis of new hydrocarbon-based aromatic polymer membranes, such as sulfonated poly(ether ether ketone) (PEEK) [4–7], poly(ether sulfone) (PES) [8–10], polybenzimidazole (PBI) [11,12], and polyimide (PI) [13,14]. Sulfonated PEEKs have been studied extensively and tested for fuel cell application. Membranes made of PEEKs have many desirable properties, such as high mechanical strength, resistance to heat-induced distortion, good long-term thermal stability, and low gas and liquid (water and methanol) permeability. Crivello [15] and Daly et al. [16] prepared nitrated polymers by using ammonium nitrate and trifluoroacetic anhydride as nitrating agents. Naik et al. [17] described the preparation and the properties of amination on poly(ether sulfone) and poly(ether ether sulfone) (PEES) main chains. Before the amination reaction, the polymer was prepared by nitration using nitric acid and sulfonic acid in nitrobenzene. Karcha and Porter [18] prepared nitrated poly(ether ether ketone) (PEEK-NO₂) by dissolving PEEK in methanesulfonic acid and subsequently nitration in concentrated nitric acid.

In this study, novel nitrated SPEEK membranes were synthesized for proton-exchange membrane applications. SPEEK was prepared via the post-sulfonatization method with concentrated sulfonic acid. Subsequently, SPEEK was nitrated by adding concentrated nitric acid and a sulfonic acid solution. The degree of substitution can be controlled in the simple, relatively inexpensive sulfonation and nitration. All nitrated SPEEKS were characterized by

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x = 0.53, y = 0.22, 0.31, and 0.45
x = 0.63, y = 0.17, 0.22, and 0.38
n = x + y + z = 1
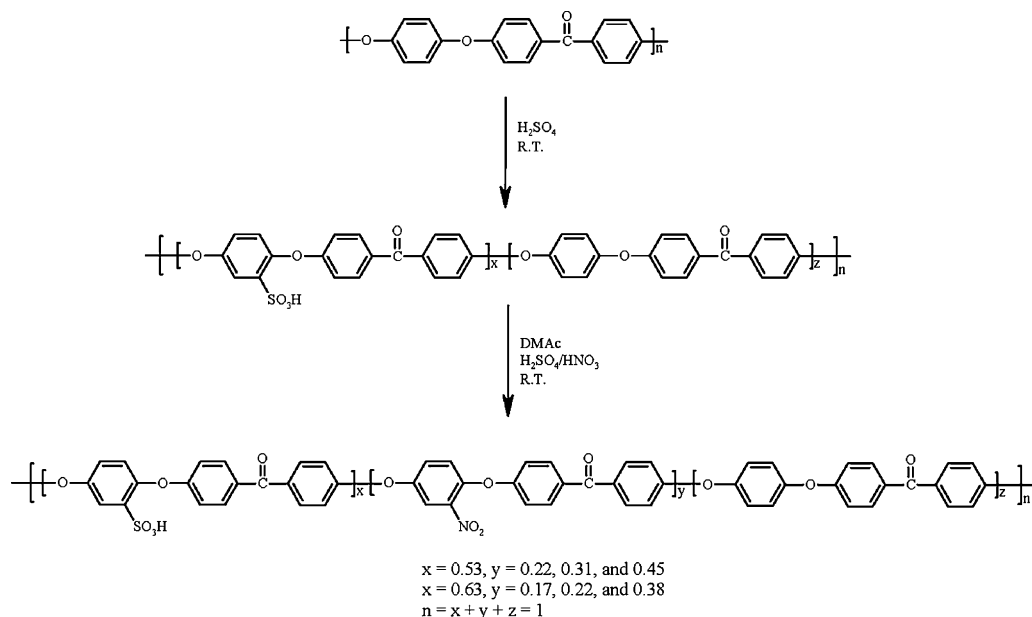
Scheme 1. The preparation of SPEEK and nitrated SPEEK via the post aromatic substitution reaction.

proton nuclear magnetic resonance, elemental analysis (EA), Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetric analysis, water uptake, methanol permeability, proton conductivity, and DMFC single-cell performance. It was expected that the novel nitrated SPEEK membranes would decrease water uptake and methanol permeability, without loss of conductivity or performance in the DMFC application.

2. Experimental

2.1. Materials and experiments

2.1.1. Materials
All reagents were used as received. PEEK 450G Victrex® was provided by ICI Corp. Concentrated sulfonic acid (95–98%) and nitric acid (70%) were obtained from Aldrich Chemical Corp. *N,N*-dimethylacetamide (DMAc) and methanol were obtained from Mallinckrodt Corp.

2.1.2. Polymer synthesis
PEEK was sulfonated in concentrated sulfuric acid and kept at room temperature for the desired length of time with vigorous mechanical stirring [4–7]. The resulting sulfonated polymer solution was decanted into a large excess of ice-cold water. The precipitated polymer was filtered and washed with distilled water several times until the pH was neutral, and then dried under vacuum at 100 °C for 24 h, as shown in Scheme 1. Nitration of SPEEK was done by an inexpensive process; the sulfonated polymer was dissolved in DMAc with vigorous mechanical stirring, and then sulfonic acid and nitric acid were added drop-wise [19–21]. The polymer solution was kept at room temperature for the desired length of time. Subsequently, the polymer was isolated by precipitation in water, and the acid was removed by washing with distilled water several times until the pH was neutral. The polymer was dried under vacuum at 100 °C for 24 h.

2.1.3. Membrane preparation
All SPEEK and nitrated SPEEK membranes were prepared by dissolving the sample in DMAc to form a 5% (w/w) solution. Membranes with different degrees of sulfonation and nitration were cast by heating and evaporating the solvent from the solution in a glass

Petri dish at 120 °C for 3 h. The membranes were obtained by adding deionized water to the surface and peeling the membranes from the dish. The thickness of membranes was controlled at $100 \pm 10 \, \mu m$.

2.2. Proton nuclear magnetic resonance (^1H NMR)

SPEEK and nitrated SPEEK were obtained from DMSO-d_6 solution (10%, w/v) at room temperature. The ^1H NMR spectra were obtained with a Varian Unity 600 spectrometer and a Bruker AMX 600 spectrometer.

2.3. Fourier transform infrared spectroscopy (FT-IR)

SPEEK and nitrated SPEEK were dissolved in DMAc (5%, w/v) solution and dropped onto a KBr specimen to form a thin film, which was dried under vacuum. Spectra in the range 600–4000 cm^{-1} were recorded with a BioRad, FTS-40A spectrometer.

2.4. Thermogravimetric analysis (TGA)

All polymers were heated at 100 °C for 30 min in a furnace to remove moisture. Then the dynamic TGA experiments were measured from 100 °C to 700 °C at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere. Thermogravimetric analysis was done with a TGA Q50 thermal analyzer (TA Instruments, WI).

2.5. Differential scanning calorimetry (DSC)

Thermal analysis was carried out in a Dupont DSC 2910 differential scanning calorimeter from 30 °C to 250 °C at a heating rate of 10 °C min^{-1} to study the thermal transition behavior of the polymers. The glass transition temperature (T_g) was collected in the second trace of the heating history.

2.6. Water uptake of membranes

Before the measurement of equilibrium water uptake, membranes were dried under vacuum at 140 °C to constant weight. The equilibrium water uptake for membranes was obtained by immersion in deionized water from 30 °C to 80 °C. The amount of water uptake was measured at predetermined time intervals to constant
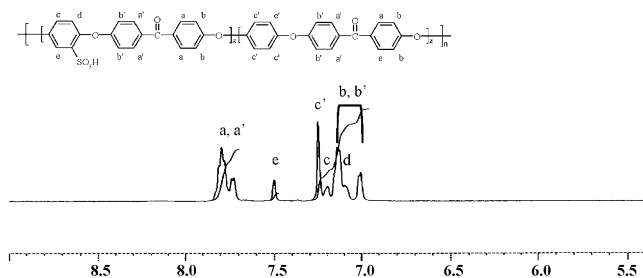
Fig. 1. The ^{1}H NMR spectrum of SPEEK.

Sample designation	Elemental analysis (wt.%)					
	C	H	N	S	DS[a]	DS[b]
S53N22	66.65	3.43	1.06	4.96	0.26	0.22
S53N31	65.87	3.37	1.42	4.90	0.35	0.31
S53N45	64.89	3.28	1.89	4.78	0.48	0.45
S63N17	65.46	3.38	0.88	5.79	0.22	0.17
S63N22	65.12	3.35	1.04	5.76	0.26	0.22
S63N38	64.41	3.28	1.58	5.42	0.42	0.38

[a] The degree of nitration calculated from the elemental analysis.
[b] The degree of nitration calculated from the ^{1}H NMR spectra.

weight. The weight of equilibrium water uptake was determined as follows:

$$\text{Water uptake}\,(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \qquad (1)$$

where W_{wet} and W_{dry} are the weights of the wet membrane and the dry membrane, respectively.

2.7. Methanol permeability

The methanol permeability of membranes was determined using a diaphragm diffusion cell, which consisted of two identical compartments separated by a vertical test membrane clamped between the two compartments. Before the experiment, the membranes were equilibrated in deionized water overnight. The initial concentration of methanol in compartment A was 2 M, while compartment B contained deionized water. The contents of both compartments were stirred by a magnetic follower at room temperature throughout the permeation experiment. The increase in the concentration of methanol with time in compartment B was obtained by gas chromatography. Methanol permeability was calculated from the slope of the linear fit based on the equation:

$$C_B(t) = \frac{A}{V_B} \frac{P}{L} C_A(t - t_0) \qquad (2)$$

where A is the effective membrane area, L is the membrane thickness, C_A and C_B are the initial concentration of methanol in compartment A and B, respectively, and V_B is the volume of compartment B.

2.8. Proton conductivity measurement

The proton conductivity of the membranes was obtained with an electrochemical cell. Impedance analysis was used from 30 °C to 80 °C with Autolab PGSTAT 30 equipment (Eco Chemie B.V., Netherlands). The frequency response analysis (FRA) software used an oscillation potential of 10 mV from 100 kHz to 10 Hz in a thermostatically controlled cell. The proton conductivity of the membranes
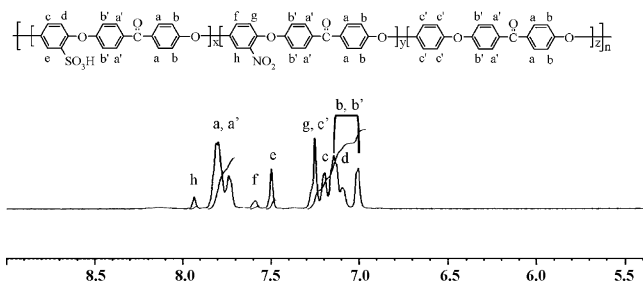
was determined as follows:

$$\sigma = \frac{l}{RA} \qquad (3)$$

where σ is the proton conductivity, l is the membrane thickness, R is the membrane resistance obtained from impedance analysis, and A is the membrane area.

2.9. Single-cell performance

Nitrated SPEEKs were used as proton-exchange membranes, the catalysts for the anode and the cathode were applied to carbon paper by brushing. The anode and cathode consisted of commercial 20 wt.% Pt/Ru (1:1) in Vulcan carbon (E-TEK) with a Pt loading of 0.6 mg cm^{-2}. Methanol at a concentration of 2 M was supplied to the anode with a micropump at 2 mL min^{-1}, while the cathode was supplied with dried O$_2$ at a rate of 100 mL min^{-1}. Single-cell performance was evaluated using a DMFC unit with a cross-section area of 4 cm^2.

3. Results and discussion

3.1. Polymer characteristics

^{1}H NMR spectroscopy was used to provide structural confirmation, and to determine the composition of sulfonation and nitration of the synthesized SPEEK and nitrated SPEEK. Fig. 1 shows the ^{1}H NMR spectrum of SPEEK dissolved in DMSO-d_6. All characteristic peaks of H$_a$ and H$_{a'}$ protons appeared at low field because of the de-shielding effect of the carbonyl group. The H$_b$ protons located at 7.14 ppm were shifted upward by the increase of sulfonic groups and H$_{b'}$ protons located at 7.00 ppm. The H$_{c'}$ protons of the unsubstituted hydroquinone ring appeared as a characteristic singlet at 7.25 ppm. The sulfonic groups were introduced into the hydroquinone ring activated for electrophilic substitution and caused a significant downfield shift of the hydrogen signals of H$_c$, H$_d$, and H$_e$ in the hydroquinone ring at 7.20 ppm, 7.09 ppm, and 7.50 ppm, respectively. The intensity of the H$_e$ signal corresponding to the hydrogen atoms located adjacent to the sulfonic groups was equivalent to the sulfonic group contents. The degree of substitution can be derived from the ratio between the peak area of the H$_e$ signal and the integrated peak area of the signals corresponding to the other aromatic hydrogen atoms [4,22,23]. The degree of substitution of sulfonic groups was 0.53 (S53) and 0.63 (S63).

Fig. 2 shows the ^{1}H NMR spectrum for nitrated SPEEK. It was found that the presence of the nitro groups resulted in a distinct and significant shift of the hydrogen signals of H$_f$, H$_g$, and H$_h$ in the hydroquinone ring at 7.59 ppm, 7.27 ppm, and 7.93 ppm [20], respectively, and the intensity of those signals increased with the increasing degree of substitution. The degree of substitution can be derived from the ratio between the peak area of the H$_h$ signal and the integrated peak area of the signals corresponding to the other aromatic hydrogen atoms, except the corresponding
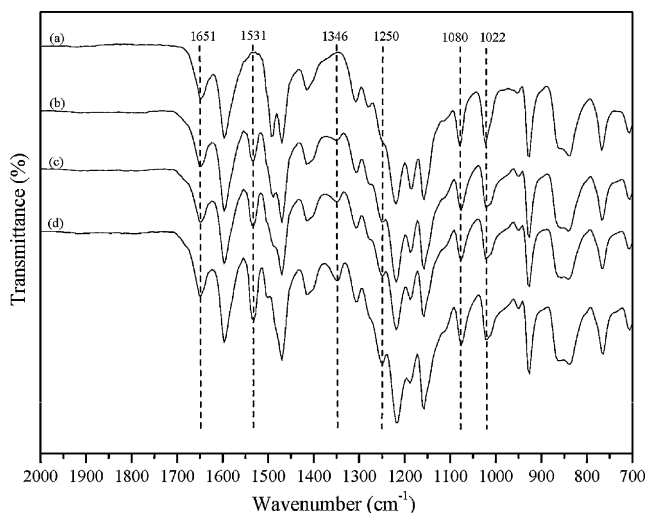

Fig. 2. The ^{1}H NMR spectrum of nitrated SPEEK.

Fig. 3. The comparative FT-IR spectra of SPEEK and nitrated SPEEK: (a) S53, (b) S53N22, (c) S53N31, and (d) S53N45.

Fig. 5. The DSC traces of SPEEK and nitrated SPEEK: (a) S53, (b) S53N22, (c) S53N31, (d) S53N45, (e) S63, (f) S63N17, (g) S63N22, and (h) S63N38.

hydrogen atoms of sulfonation. The degree of substitution was 0.22 (S53N22), 0.31 (S53N31), and 0.45 (S53N45) for SPEEK53, and 0.17 (S63N17), 0.22 (S63N22), and 0.38 (S63N38) for SPEEK63, respectively. These results were approximated to the elemental analysis, which is summarized in Table 1.

The comparative FT-IR spectra of SPEEK and nitrated SPEEK are shown in Fig. 3. The broad band appearing at ∼3460 cm^{-1} was assigned to O–H vibration, indicating that sulfonic groups in SPEEK or/and nitrated SPEEK interacted with H$_2$O. The aromatic C–C band was observed to split into two peaks, 1470 cm^{-1} and 1493 cm^{-1}, due to the substitution achieved by sulfonation and nitration. The absorption peak at 1022 cm^{-1} was assigned to S=O stretching vibration. The absorption peaks at 1080 cm^{-1} and at 1250 cm^{-1} can be assigned to the symmetrical O=S=O stretching vibration, and the asymmetric stretching vibration of the sulfonic acid group [23,24], respectively. The absorption at 1651 cm^{-1} was assigned to the backbone carbonyl stretching band. In the spectra of nitrated SPEEK, the NO$_2$ groups could be characterized easily by the asymmetric stretching at 1531 cm^{-1} and the symmetric stretching at 1346 cm^{-1} [21,25], respectively. This result indicated clearly that the nitro groups were incorporated into the polymer chain, and the absorption increased proportionally with the increasing nitro groups relative to the backbone carbonyl group at 1651 cm^{-1}.
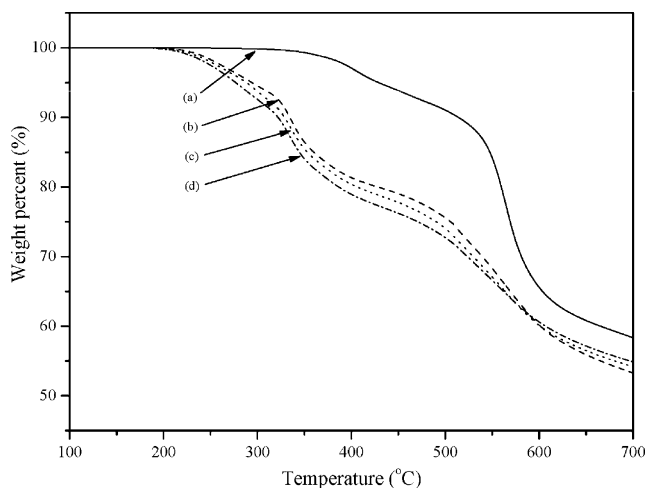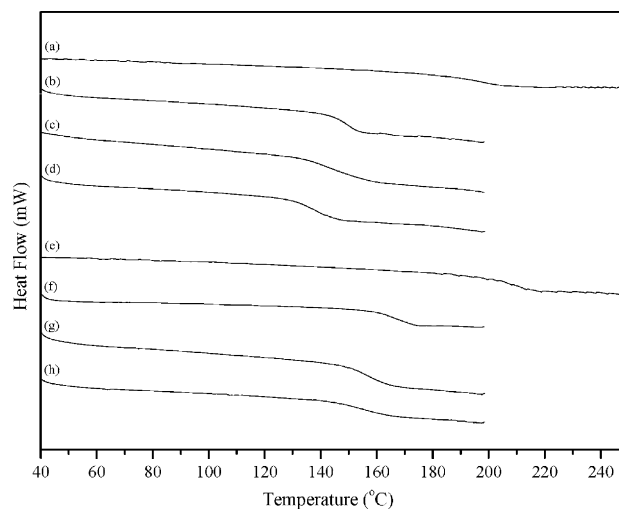
3.2. Thermal characteristics

The thermal stability of SPEEK and nitrated SPEEK was investigated by TGA. Fig. 4 shows the 5% (w/w) loss temperature (T_{d5}) of SPEEK and nitrated SPEEK, and the data are summarized in Table 2. The controlled PEEK is well known to be a thermally stable polymer and had a T_{d5} of 581 °C. Both SPEEK and nitrated SPEEK had two steps of weight loss; S53 and S63 revealed a lower T_{d5} at 429 °C and 350 °C, respectively, compared with the control PEEK. The first weight loss step was assigned to the loss of –SO$_3$H groups by evolution of SO and SO$_2$, and the second step contributed to the degradation of the polymer main chain. This indicated that the degradation of SPEEK started with the desulfonation of sulfonic groups. The thermal stability was decreased further when nitrated. T_{d5} was 294 °C, 288 °C, and 277 °C for S53N22, S53N31, and S53N45, respectively, and was 292 °C, 278 °C, and 269 °C for S63N17, S63N22, and S63N38, respectively.

Differential scanning calorimetry (DSC) was used to characterize the thermal transition for SPEEK and nitrated SPEEK, and the data are summarized in Table 2. Fig. 5 shows the DSC traces of SPEEK and nitrated SPEEK, where T_g values for S53 and S63 are 195 °C and 207 °C, respectively, resulting from the hydrogen interaction of the bulky sulfonic group within SPEEK. On the other hand, T_g was decreased in nitrated SPEEK; 165 °C, 155 °C, and 150 °C for S63N17, S63N22, and S63N38, respectively. The incorporation of a nitro group would lower the T_g values, but was thought not to be involved in the intermolecular interaction [18].

3.3. Water uptake

It is well known that the proton conductivity and mechanical stability of a membrane are related strongly to the presence of water. It is necessary to have an adequate level of water uptake to promote good proton conductivity. However, water uptake should be minimized to provide the membrane with mechanical stability and to avoid swelling. In the presence of water, the hydrophilic domains are hydrated and provide good proton conductivity, while the hydrophobic domains provide the membranes with good morphological and mechanical stability. Consequently, it is very important to maintain a sulfonated membrane with an appropriate level of water uptake. Both sulfonation and nitration affect the water uptake of membranes.

Fig. 6 shows a plot of the water uptake of SPEEK and nitrated SPEEK membranes versus temperature. It was found that the water

Fig. 4. The 5% (w/w) loss temperature (T_{d5}) of SPEEK and nitrated SPEEK: (a) S53, (b) S53N22, (c) S53N31, and (d) S53N45.

Table 2
Properties of SPEEK and nitrated SPEEK according to the degree of sulfonation and nitration.

	SPEEK and nitrated SPEEK							
	S53	S53N22	S53N31	S53N45	S63	S63N17	S63N22	S63N38
Thermal degradation temperature, T_{d5} (°C)	429	294	288	277	350	292	278	269
Glass transition temperature, T_g (°C)	195	150	145	139	207	165	155	150
Water uptake[a] (%)	31	25	28	30	38	34	36	37
Methanol permeability[a], P ($\times 10^7$ cm^2 s^{-1})	3.14	1.76	1.89	2.25	3.44	1.86	2.10	2.40
Conductivity[a], σ ($\times 10^2$ S cm^{-1})	0.8	1.1	1.1	1.1	2.4	2.5	2.6	2.6
Activation energy, E_a (kJ mol^{-1})	19.45	18.77	21.79	21.75	8.62	9.60	9.13	10.50

[a] Values measured at 30 °C.

uptake of SPEEK membranes at 30 °C increased from 31% for S53 to 38% for S63. The sulfonic group is hydrophilic, hence membranes with sulfonation can absorb more water due to the increase of hydrophilicity. The water uptake of all membranes was increased with the increase of temperature, especially for the S63 series. On the other hand, the water uptake of nitrated SPEEK, which had more hydrophobic nitro groups than sulfonic groups [26], showed a relatively lower uptake of 25% in S53N22, and 34% in S63N17.

When the temperature was ~80 °C, the mobility of the polymer chain and the free volume for water absorption were increased and, as a result, nitrated SPEEK membranes were more swollen at 80 °C than pure SPEEK membranes. As the degree of nitration increased, the water uptake increased sharply to 49%, 51%, and 53% for S63N17, S63N22, and S63N38, respectively, reflecting the formation of ion clusters [4,27]. When the temperature and/or degree of nitration increased, the dispersed sulfonic groups readily form ion domains, which are hydrophilic and mainly responsible for water uptake. The incorporation of nitro groups was not required for the mechanical stability of the membranes in this study.

3.4. Methanol permeability

The methanol permeability of SPEEK and nitrated SPEEK membranes is shown in Table 2. The methanol permeability of SPEEK membranes increased with increasing degree of sulfonation from 3.14×10^{-7} cm^2 s^{-1} to 3.44×10^{-7} cm^2 s^{-1} for S53 and S63, respectively. These values are far lower than that of the Nafion® 117 membrane (2×10^{-6} cm^2 s^{-1}), which is characterized by the extremely high hydrophobicity of the perfluorinated backbone and the hydrophilicity of the sulfonic side chain. These sulfonic groups aggregate to form ion clusters in the presence of water, and these

hydrophilic domains are interconnected within the membrane. However, the morphology of SPEEK membranes was found to be distinctly different; the backbone of the SPEEK membrane was less hydrophobic, and the sulfonic groups were less acidic, giving rise to a larger hydrophobic/hydrophilic interface corresponding to highly disperse sulfonic groups and less nano-phase separation. Thus, the water-filled channels in SPEEK membranes are more branched, and have more dead-end pockets compared with the Nafion membrane® [22,28], which is responsible for the reduction of methanol permeability in the SPEEK membranes. The methanol permeability of the nitrated SPEEK membranes was lower than that of the pure SPEEK membranes, with values of 1.76×10^{-7} cm^2 s^{-1}, 1.89×10^{-7} cm^2 s^{-1}, and 2.25×10^{-7} cm^2 s^{-1} for a S53N22, S53N31, and S53N45, respectively, and 1.86×10^{-7} cm^2 s^{-1}, 2.10×10^{-7} cm^2 s^{-1}, 2.40×10^{-7} cm^2 s^{-1} for S63N17, S63N22, and S63N38, respectively, at 30 °C. This showed that a significant reduction in methanol crossover was achieved by the introduction of nitro groups into nitrated SPEEK membranes. These results could be attributed to the decrease of hydrophobic nitro groups, and to a greater mobility of the polymer backbone with an increase of nitro groups. The addition of nitro groups changed the morphology of the hydrophobic/hydrophilic domains in membranes, and these changes enhanced the hydrodynamic solvent transport. The methanol permeability values were about one order of magnitude lower than that of the Nafion® membrane at the same temperature.

3.5. Proton conductivity

Fig. 7 shows the proton conductivity of SPEEK and nitrated SPEEK membranes as a function of temperature and degree of substitution. The proton conductivity of S53–S63 membranes at 30–80 °C was 0.008–0.024 S cm^{-1} and 0.024–0.039 S cm^{-1}, respectively. It is
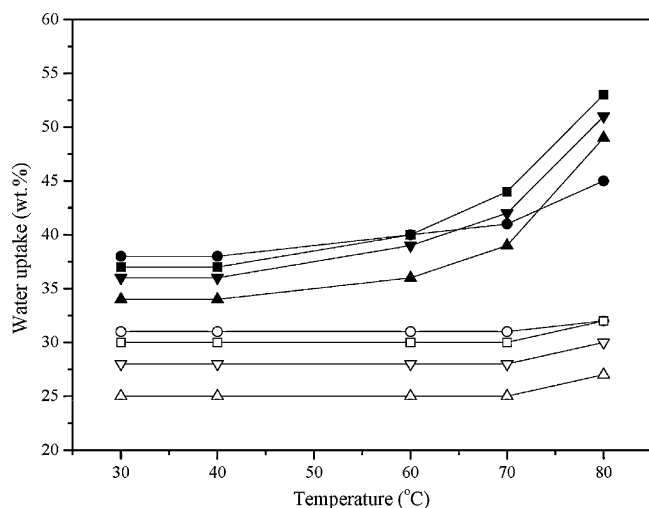

Fig. 6. The water uptake of SPEEK and nitrated SPEEK membranes versus temperature: (○) S53, (△) S53N22, (▽) S53N31, (□) S53N45, (●) S63, (▲) S63N17, (▼) S63N22, and (■) S63N38.
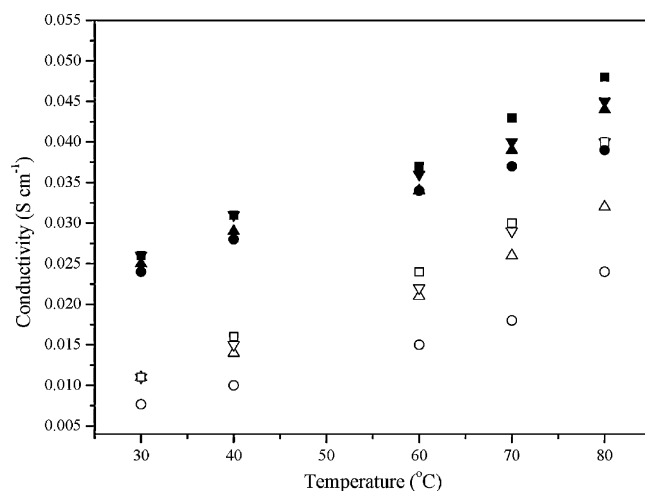

Fig. 7. The proton conductivity of SPEEK and nitrated SPEEK membranes versus temperature: (○) S53, (△) S53N22, (▽) S53N31, (□) S53N45, (●) S63, (▲) S63N17, (▼) S63N22, and (■) S63N38.
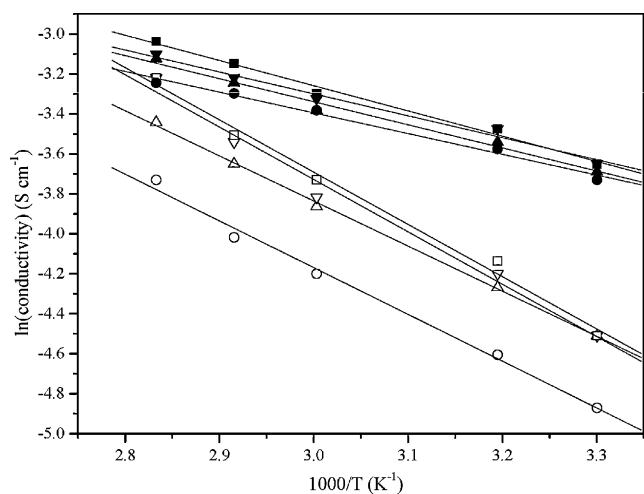
Fig. 8. Arrhenius plots of proton conductivity for SPEEK and nitrated SPEEK membranes: (○) S53, (△) S53N22, (▽) S53N31, (□) S53N45, (●) S63, (▲) S63N17, (▼) S63N22, and (■) S63N38.

well known that the proton conductivity of ionomer membranes increases with increased sulfonic group content, temperature and water content. In Fig. 7, the proton conductivity of nitrated SPEEK membranes at 30–80 °C was increased to 0.011–0.040 S cm⁻¹ for nitration of SPEEK53, and to 0.025–0.048 S cm⁻¹ for nitration of SPEEK63. It was apparent that the addition of nitro groups increased the proton conductivity, causing a different distribution of ion domains in the membrane that provides more effective phase separation morphology. For nitrated SPEEK membranes, the hydrophilic sulfonic groups may aggregate into hydrophilic ionic domains, which are dispersed throughout the hydrophobic polymer domains. The hydrophilic domains were isolated in the continuous hydrophobic domains when the sulfonic group content was low. However, the incorporation of nitro groups increased the mobility of the polymer chain and increased the density of sulfonic groups in the nitrated SPEEK membranes. These ionic domains were aggregated when the sulfonic group content increased, leading to a percolation of ion channels with good connectivity through which protons can be transported rapidly, even though the water uptake of the nitrated SPEEK membrane was lower than that of the SPEEK membrane [4,29].

The proton conduction mechanism in these membranes is known to occur by two routes: (i) the first route is a hopping or jumping mechanism, also known as the Grotthuss model, in which a proton is passed through a channel of water molecules; the protons are transferred from one vehicle to the other by hydrogen bonds. (ii) The second route is a vehicle mechanism, wherein a proton combines with solvent molecules, producing a complex such as H_3O^+, $H_5O_2^+$, $H_7O_3^+$ or $CH_3OH_2^+$, which diffuses through the membrane. The activation energy (E_a), the minimum energy required for proton transport across the membrane, was calculated by fitting to the Arrhenius equation:

$$\sigma = A \times e^{-E_a/RT} \tag{4}$$

where σ is the proton conductivity (S cm⁻¹), E_a is the activation energy (kJ mol⁻¹), R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), and T is the absolute temperature (K). Activation energy values were estimated from the slopes of the plots and are summarized in Table 2. Fig. 8 shows the Arrhenius plots of SPEEK and nitrated SPEEK membranes; all membranes had linear Arrhenius behavior between 30 °C and 80 °C. SPEEK, nitrated SPEEK, and Nafion® 117 membranes had an activation energy of 8.62 kJ mol⁻¹, 21.79 kJ mol⁻¹, and 9.28 kJ mol⁻¹, respectively [3,30]. For the hopping mechanism, the activation energy for proton con-

ductivity should be around 14–40 kJ mol⁻¹, and the results of this study were close to those values.

3.6. Single-cell performance

DMFC performance was evaluated for SPEEK and nitrated SPEEK membranes to observe the methanol crossover from open circuit voltage (OCV) by a relatively low loading of electrocatalyst. Fig. 9 shows the performance results with polarization (a) and power density (b) as a function of current density. The single cell with nitrated SPEEK membranes had higher OCV (0.621–0.623 V) with low loading of electrocatalyst and power density than that of SPEEK membranes (OCV = 0.594 V). The higher OCV indicated clearly that the nitro groups incorporated into the SPEEK membrane truly decreased the rate of methanol crossover in the DMFC application due to the relatively low methanol permeability, and the higher maximal power density indicated a better performance of nitrated SPEEK than SPEEK. The S63N38 membrane shows a higher performance than S63N17 or S63N22. The performance of the single cell improved slightly with increasing content of nitro groups, as shown in Fig. 9. The maximum power density was 12 mW cm⁻² at 66 mA cm⁻² when the S63N38 membrane was used, and 11 mW cm⁻² at 60 mA cm⁻² or 63 mA cm⁻² when the S63N17 or S63N22 membrane was used, respectively.
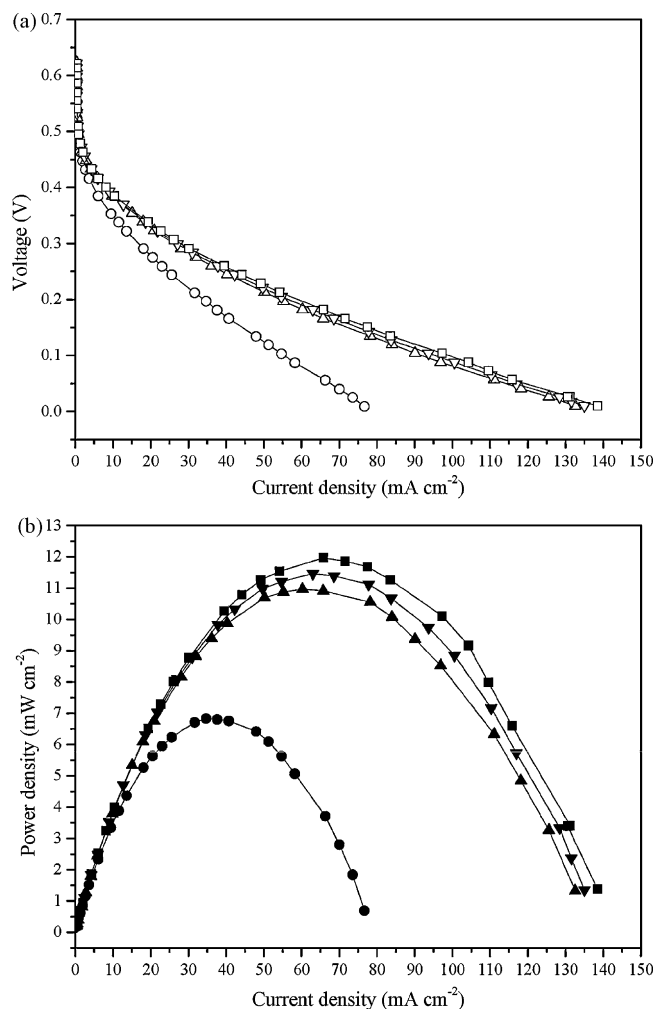

Fig. 9. The performance curves of SPEEK63 and nitrated SPEEK63 membranes: (a) Polarization curves: (○) S63, (△) S63N17, (▽) S63N22, and (□) S63N38. (b) Power density curves: (●) S63, (▲) S63N17, (▼) S63N22, and (■) S63N38.

4. Conclusion

In this study, nitrated SPEEK membranes were prepared by incorporation of nitro groups into SPEEK. The membranes were characterized using ^{1}H NMR, EA, FT-IR, TGA, DSC, water uptake, permeability, conductivity, and fuel cell performance. ^{1}H NMR, EA, and FT-IR were used for structural and compositional determinations of the sulfonation and nitration substitution. The degree of substitution could be controlled simply by altering the length of time for the sulfonation and nitration reactions. The incorporation of nitro groups into the SPEEK main chain improved the water uptake of membranes allowing the maintenance of excellent mechanical property, increased the conductivity and retained a reasonable thermal property. Furthermore, the methanol permeability was suppressed without loss of conductivity. Compared with the SPEEK membranes, the nitrated SPEEK membranes had higher conductivity and superior single-cell performance. The nitrated SPEEK membranes were simple to prepare by an inexpensive process. The low methanol permeability, high conductivity and high single-cell performance mean that substituted SPEEK membranes warrant consideration for use in DMFC applications.

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