



# Nafion<sup>®</sup>/nitrated sulfonated poly(ether ether ketone) membranes for direct methanol fuel cells

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## ABSTRACT

Sulfonated poly(ether ether ketone)s (SPEEKs) are substituted on the main chain of the polymer by nitro groups and blended with Nafion<sup>®</sup> to attain composite membranes. The sulfonation, nitration and blending are achieved with a simple, inexpensive process, and the blended membranes containing the nitrated SPEEKs reveal a liquid–liquid phase separation. The blended membranes have a lower water uptake compared to recast Nafion<sup>®</sup>, and the methanol permeability is reduced significantly to  $4.29 \times 10^{-7}$ – $5.34 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup> for various contents of nitrated SPEEK for S63N17, and  $4.72 \times 10^{-7}$ – $7.11 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup> for S63N38, with a maximum proton conductivity of  $\sim 0.085$  S cm<sup>-1</sup>. This study examines the single-cell performance at 80 °C of Nafion<sup>®</sup>/nitrated SPEEK membranes with various contents of nitrated SPEEK and a degree of nitration of 23–25 mW cm<sup>-2</sup> for S63N17 and 24–29 mW cm<sup>-2</sup> for S63N38. Both the power density and open circuit voltage are higher than those of Nafion<sup>®</sup> 115 and recast Nafion<sup>®</sup>.

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## 1. Introduction

Fuel cells convert chemical energy directly into electrical energy and represent a promising alternative to electrochemical energy transformers. Direct methanol fuel cells (DMFCs) have attracted significant attention because of their highly efficient energy conversion, low operating temperature, simple design and the use of liquid fuel [1]. Methanol, which has a high specific energy density, is obtained easily from natural sources and is liquid at operating temperatures [2]. Therefore, DMFCs are suitable for stationary as well as portable devices, such as cell phones and laptop computers.

The proton exchange membrane is one of the key components in a fuel cell system. Perfluorosulfonic acid membranes such as Nafion<sup>®</sup> with fluoroalkyl ether side chains and sulfonic acid end groups are the most commonly used materials due to high levels of electrochemical stability, mechanical strength and proton conductivity [3]. However, Nafion<sup>®</sup> membranes are highly permeable to methanol, which passes easily from the anode side, through the membrane, to the cathode side of the cell, where it is oxidized without any contribution to power generation [4]. Additionally, the CO that is formed as an intermediate poisons the cathode, and excessive water flooding limits O<sub>2</sub> access to the catalytic sites on the cathode [5]. Passage of methanol through the membrane separat-

ing the anode from the cathode should be avoided, because it results in low fuel efficiency and a significant loss of performance.

Over the past few years, many polymeric materials have been investigated for the potential to serve as proton-exchange membranes, including sulfonated poly(ether ether ketone) [6], polysulfone [7], and polyimide [8], acid–base blends [4], and inorganic–organic composites [9]. Another approach has been to modify Nafion<sup>®</sup> membranes by the introduction of a component to act as a barrier to methanol. These modifications include partial substitution of the sulfonic acid groups with Cs ions [10], Pd coating [11], sandwiching a Pd foil between two Nafion<sup>®</sup> membranes [12], incorporating inorganic nanoparticles into Nafion<sup>®</sup> [13], blending with poly(vinylidene fluoride) [14], poly(vinyl alcohol) [15], poly(1-vinylimidazole) [16], polypyrrole [17], and polyaniline [3]. Unfortunately, a reduction of methanol permeability is always accompanied by a significant decrease in proton conductivity. Kreuer suggested the possibility of a relationship between the transport properties and the swelling behavior of Nafion<sup>®</sup> and sulfonated poly(ether ether ketone) [18]. It is known that methanol passes through the membrane primarily via ionic channels, and thus methanol permeability is determined by the diameter of these channels and the size of ionic clusters, which are dependent mainly upon the swelling ability of the membrane. Therefore, it should be possible to reduce the swelling by adjusting the morphology of the membrane. Investigation into the relation between the microstructure (i.e. the diameter of proton transfer channels, the size of ionic clusters, etc.) and the transport properties may help to optimize proton-exchange membranes [19]. Kim and

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co-workers studied Nafion<sup>®</sup>/sulfonated poly(arylene ether ketone) blended membranes to prevent methanol permeability, and they confirm that the two-layer morphology obtained by the in situ phase separation affected the properties of the blended membranes [2,20]. The size of the hydrophilic channels increased with increasing content of sulfonated poly(arylene ether ketone) and along the thickness direction to the bottom by the in situ phase separation.

In this study, blended membranes consisting of Nafion<sup>®</sup> and highly nitrated SPEEK were prepared by a simple, inexpensive process. The nitrated main chain was more hydrophobic than native SPEEK, giving rise to a small hydrophobic/hydrophilic interface such as Nafion<sup>®</sup>. Thus, the water-filled channels in nitrated SPEEK are less branched, and have fewer dead-end pockets compared with the native SPEEK membranes. The nitrated SPEEK shows a lower degree of methanol permeability and higher conductivity than SPEEK in our earlier work [21]. Blended membranes based on Nafion<sup>®</sup> can be prepared easily and rapidly by a simple casting method, which is a common process used in the plastics industry. The novel Nafion<sup>®</sup>/nitrated SPEEK composite membranes described here have reduced swelling and methanol permeability compared with membranes composed of recast Nafion<sup>®</sup> alone, resulting in better performance in DMFC applications.

## 2. Experimental

### 2.1. Materials and experimental procedure

#### 2.1.1. Materials

PEEK 450G Victrex<sup>®</sup> from ICI Co. was used as received. Nafion<sup>®</sup> 115 and Nafion<sup>®</sup> solution (5 wt.%, sulfonic acid form) in a 1-propanol/ethanol/water mixture were purchased from E. I. Dupont de Nemours & Co. Concentrated sulfuric acid (95–98%) and nitric acid (70%) were from Aldrich Chemical Co. Dimethylacetamide (DMAc) and methanol were from Mallinckrodt Co. Nafion<sup>®</sup> 115 was treated to completely remove all impurities by boiling in 3% H<sub>2</sub>O<sub>2</sub>, 0.5 M H<sub>2</sub>SO<sub>4</sub> and then in deionized water.

#### 2.1.2. Polymer synthesis

Initially, PEEK was sulfonated in concentrated sulfuric acid at room temperature with vigorous mechanical stirring [22]. The resulting sulfonated polymer solution was decanted into a large excess of ice-cold water. The precipitated polymer was filtered and washed repeatedly with deionized water until the pH was neutral, then dried under vacuum at 100 °C for 24 h (Scheme 1). The degree of sulfonation was determined to be 0.63 and the material was designated SPEEK63.

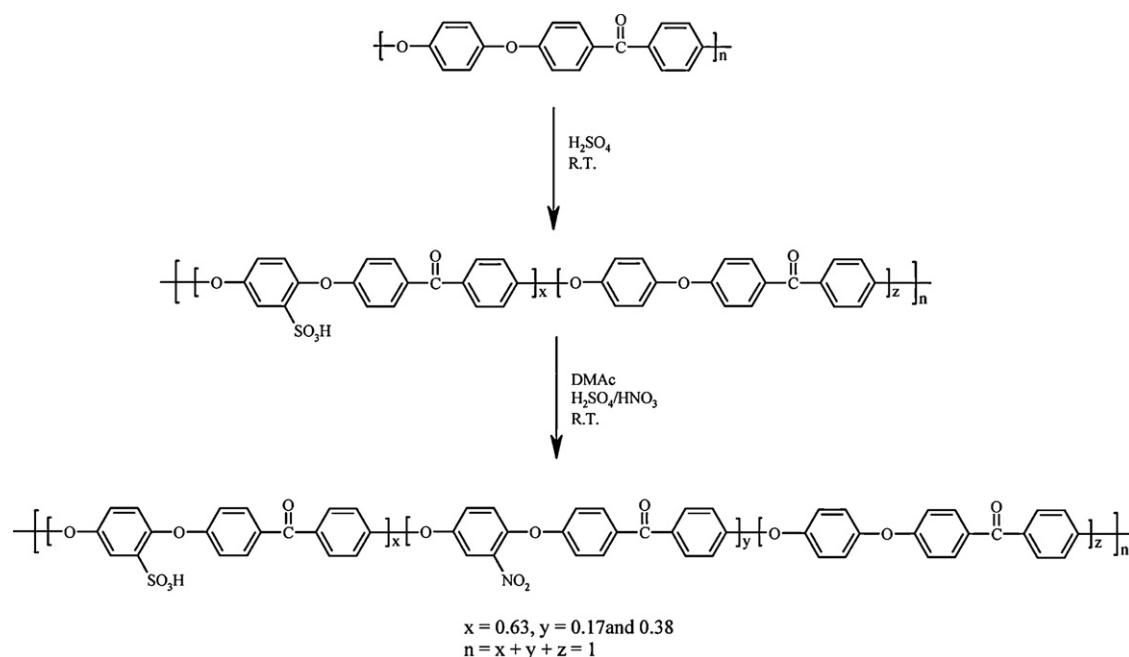
SPEEK63 was nitrated by dissolving it in DMAc with vigorous mechanical stirring, and then sulfuric acid and nitric acid were added drop-wise at room temperature [23,24]. Subsequently, the polymer was isolated by precipitation in deionized water, and the acid was removed by washing repeatedly with deionized water until the pH was neutral. The polymer was dried under vacuum at 100 °C for 24 h. In this study, the degree of nitration was determined to be 0.17 and 0.38 and the materials were designated S63N17 and S63N38, respectively.

#### 2.1.3. Membrane preparation

The composite membranes were prepared by blending nitrated SPEEK and Nafion<sup>®</sup>. The Nafion<sup>®</sup> solution was evaporated to dryness, and then Nafion<sup>®</sup> and nitrated SPEEK were dissolved separately in DMAc to obtain a 15 wt.% solution. The nitrated SPEEK solution was added to the Nafion<sup>®</sup> solution with vigorous stirring. The weight ratios of blends varied from 0.5% to 3% nitrated SPEEK. The mixture was cast onto a glass dish and dried under vacuum at 80 °C. Finally, the cast membrane was dried under vacuum at 120 °C for 2 h, when it had a thickness of ~100 ± 10 μm. The blended membrane was stored in deionized water. The recast Nafion<sup>®</sup> was prepared from commercial Nafion<sup>®</sup> solution with a thickness of ~100 ± 10 μm and was used for comparison of the DMFC properties and performance, while commercial Nafion<sup>®</sup> 115 was used only for comparison of the DMFC performance in this study.

### 2.2. Proton nuclear magnetic resonance (<sup>1</sup>H NMR)

The SPEEK and nitrated SPEEKs were obtained from DMSO-d<sub>6</sub> solution (10 wt.%) at room temperature. The <sup>1</sup>H NMR spectra were



**Scheme 1.** The preparation of SPEEK and nitrated SPEEK via the post aromatic substitution reaction.

obtained with a Varian Unity 600 spectrometer and a Bruker AMX 600 MHz spectrometer.

### 2.3. Fourier transform infrared spectroscopy (FT-IR)

An FT-IR spectrometer with an attenuated total reflection (ATR) attachment was used to confirm the presence of functional groups on the membranes. Spectra were obtained with a Bio-Rad FTS-40A spectrometer in the wavelength range 700–4000  $\text{cm}^{-1}$ . Each spectrum is the average of 48 scans with a resolution of 4  $\text{cm}^{-1}$ .

### 2.4. Scanning electron microscopy (SEM)

All of the specimens were sputter-coated with Pt for 120 s. The morphology of membranes as revealed by freeze-fracture in the cross-section area was observed with a Hitachi S4200 field emission scanning electron microscope.

### 2.5. Thermogravimetric analysis (TGA)

All membranes were heated at 120 °C for 30 min in a furnace to remove moisture. The dynamic TGA experiments were done under a nitrogen atmosphere with a TGA Q50 thermal analyzer (TA Instruments, WI) from 100 °C to 700 °C at a heating rate of 20 °C  $\text{min}^{-1}$ .

### 2.6. Differential scanning calorimetry (DSC)

A Dupont DSC 2910 differential scanning calorimeter was used for the thermal analysis of the thermal transition behavior of the blended membranes from 30 °C to 250 °C at a heating rate of 10 °C  $\text{min}^{-1}$  under a nitrogen atmosphere.

### 2.7. Water uptake by membranes

Membranes were dried to constant weight under vacuum at 120 °C. The water uptake was measured by immersing the membranes in deionized water and heating from 30 °C to 80 °C. The weight of equilibrium water uptake was determined as:

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

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

### 2.8. Methanol permeability

The methanol permeability of the membranes was determined using a diaphragm diffusion cell. The membranes were equilibrated in deionized water overnight with stirring. The initial concentration of methanol in one side of the cell (compartment A) was 2 M, while the other side of the cell (compartment B) contained deionized water. The increase in the concentration of methanol with time was determined by gas chromatography. The methanol permeability was calculated from the slope of a least-squares linear fit:

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

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

### 2.9. Proton conductivity measurement

The proton conductivity cell was immersed in water at a constant temperature from 30 °C to 80 °C. The conductivity of the blended membranes in the in-plane direction was determined with an electrochemical cell. A stainless steel blocking electrode was used for the measurement. AC impedance analysis was done 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. The proton conductivity of membranes was determined as follows:

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

where  $\sigma$  is the proton conductivity,  $l$  is the distance between the electrodes,  $R$  is the membrane resistance obtained by impedance analysis, and  $A$  is the membrane area.

### 2.10. Single-cell performance

Nafion® 115, recast Nafion®, and the blended membranes were used as proton exchange membranes in fuel cells, and the catalysts for the anode and the cathode were applied to carbon paper by spread. The anode and cathode consisted of commercial 20 wt.% Pt/Ru (1:1) in Vulcan carbon (E-TEK) with a Pt loading of 1.2  $\text{mg cm}^{-2}$  and 0.6  $\text{mg cm}^{-2}$ , respectively. Methanol (2 M) was supplied to the anode with a micro-pump at 2  $\text{mL min}^{-1}$ , while the cathode was supplied with dry  $\text{O}_2$  at a rate of 100  $\text{mL min}^{-1}$ . Single-cell performance was evaluated using a DMFC unit with a cross-section area of 4  $\text{cm}^2$ .

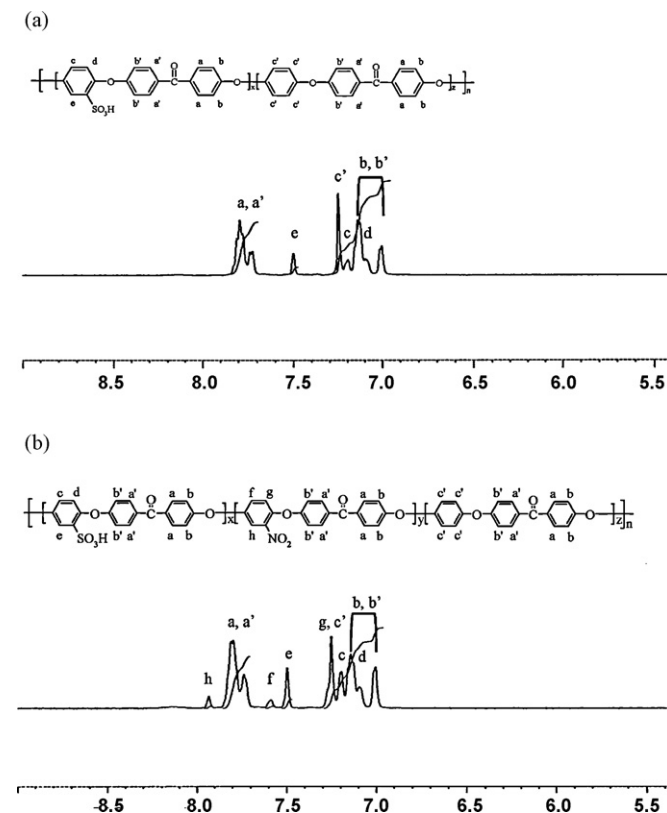
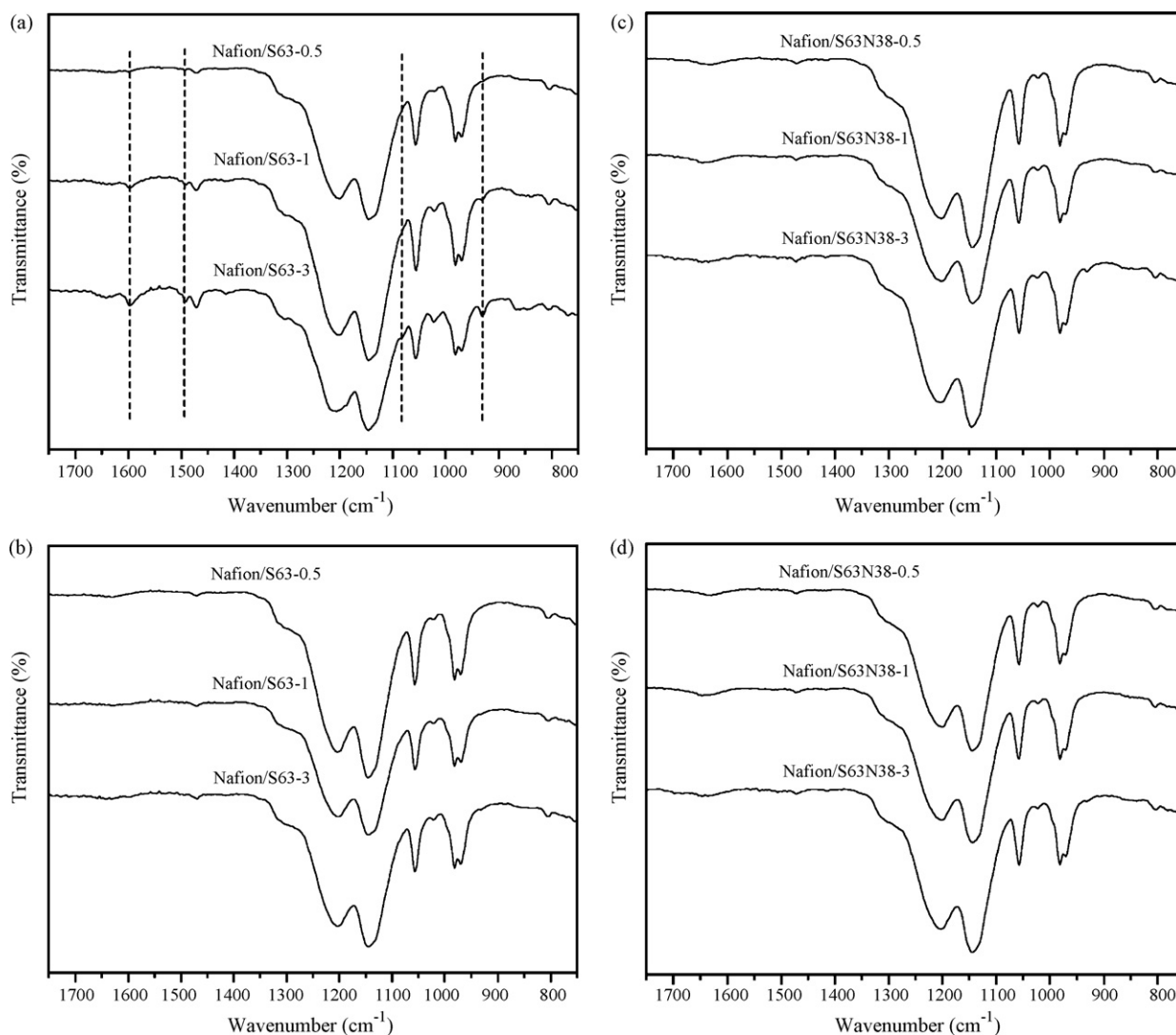


Fig. 1. The  $^1\text{H}$  NMR spectrum for (a) SPEEK and (b) nitrated SPEEK.



**Fig. 2.** The FT-IR ATR spectra for (a) front surface of Nafion<sup>®</sup>/SPEEK, (b) back surface of Nafion<sup>®</sup>/SPEEK, (c) front surface of Nafion<sup>®</sup>/nitrated SPEEK and (d) back surface of Nafion<sup>®</sup>/nitrated SPEEK.

### 3. Results and discussion

#### 3.1. Polymer characteristics

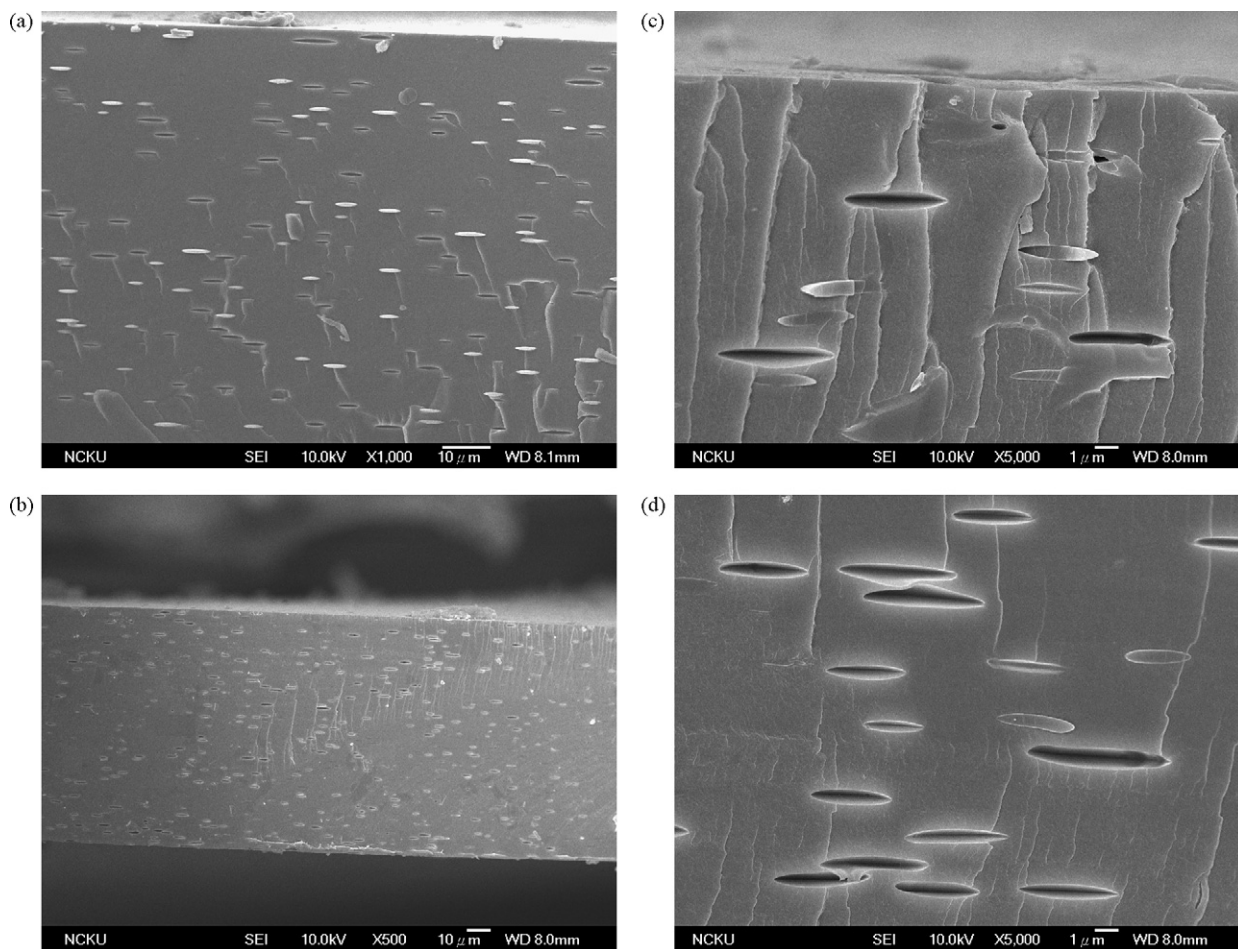
<sup>1</sup>H NMR spectroscopy was used to provide structural confirmation, and to determine the degree of sulfonation and nitration. Fig. 1(a) shows the <sup>1</sup>H NMR spectrum of SPEEK dissolved in DMSO-d<sub>6</sub>. The degree of substitution was derived from the ratio between the peak area of the H<sub>e</sub> signal and the integrated peak area of the signals corresponding to the other aromatic hydrogen atoms [25]. In this study, the degree of sulfonation was 0.63 (SPEEK63). Fig. 1(b) shows the <sup>1</sup>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<sub>f</sub>, H<sub>g</sub>, and H<sub>h</sub> in the hydroquinone ring at 7.59 ppm, 7.27 ppm and 7.93 ppm, respectively, and the intensity of those signals increased with the increasing degree of nitration [21,26]. Sulfonation cannot react further in this step, and the degree of nitration was derived from the ratio between the peak area of the H<sub>h</sub> signal and the integrated peak area of the signals corresponding to the other aromatic hydrogen atoms, except the corresponding hydrogen atoms of sulfonation. The degree of nitration was 0.17 (S63N17) and 0.38 (S63N38) for SPEEK63. These results were compatible with the results of elemental analysis.

The FT-IR ATR spectra which were used to confirm the homogeneity of Nafion<sup>®</sup>/SPEEK and Nafion<sup>®</sup>/nitrated SPEEK on the front and back surface are shown in Fig. 2(a)–(d). Compare the front surface Fig. 2(a) with back surface (b) of various SPEEK content, the new absorption bands appeared at 1595 cm<sup>-1</sup>, 926 cm<sup>-1</sup> and 1080 cm<sup>-1</sup> which can be assigned to the symmetric stretching vibrations of the sulfonic groups. The aromatic C–C band was observed at 1493 cm<sup>-1</sup>. With the increment of SPEEK content in the blended membranes, the intensities of these characteristic peaks increased on the front surface, however no relative peaks appeared on the back surface. These characteristic peaks indicated that the homogeneity was different therein. In Nafion<sup>®</sup>/nitrated SPEEK, the density of nitrated SPEEK was higher than that of SPEEK and came closer to Nafion<sup>®</sup>. It showed more homogenized on the front surface Fig. 2(c) and back surface (d) due to the density difference.

#### 3.2. Morphology

SEM was used to study the morphology of the recast Nafion<sup>®</sup> and blended membranes. The freeze-fractured cross-section morphology in SEM micrographs of the blended membrane with SPEEK and nitrated SPEEK is shown in Fig. 3(a)–(d). The morphology of cross-sections revealed that phase separation between two immiscible





**Fig. 3.** The SEM images for (a) Nafion®/SPEEK, (b) Nafion®/nitrated SPEEK, (c) top layer of Nafion®/nitrated SPEEK and (d) bottom layer of Nafion®/nitrated SPEEK.

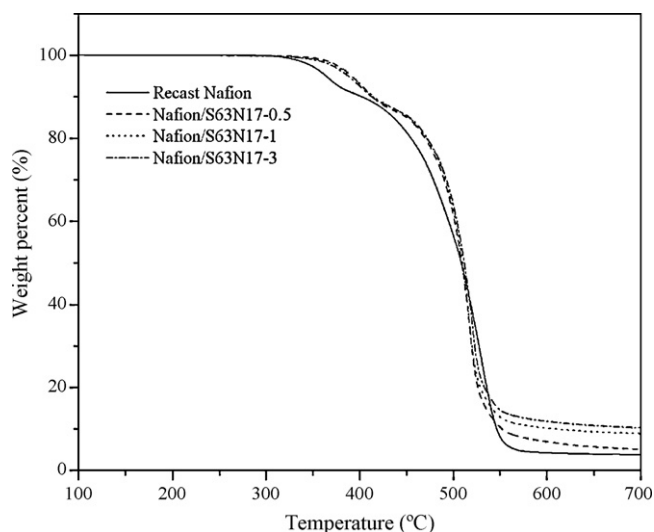
polymers including SPEEK and nitrated SPEEK in Fig. 3(a) and (b). In both Nafion®/SPEEK and Nafion®/nitrated SPEEK blended membranes, the phase separation occurred in two steps [2,20,27], finally a sea-island morphology was formed in the top layer and bottom layer, which is shown in Fig. 3(c) and (d).

### 3.3. Thermal characteristics

The thermal stability of the recast Nafion® and the blended membranes was investigated by TGA. Nafion® is known to be thermally stable, and has a 5 wt.% loss temperature ( $T_{d5}$ ) of 364 °C. According to the literature [3], thermogravimetric curves recorded under a nitrogen atmosphere are characterized by four steps: (i) a gradual loss of water from 25–290 °C; (ii) desulfonation accompanied by decomposition of the ether groups on the side chains from 290–400 °C; (iii) decomposition of side chains from 400–470 °C; and (iv) degradation of the PTFE backbone at 470–560 °C. Fig. 4 shows the loss temperature of blended membranes,  $T_{d5}$  was shifted to a higher temperature with the introduction of nitrated SPEEK. In the blended membranes,  $T_{d5}$  was increased to 399 °C, 394 °C, and 399 °C with 0.5%, 1%, and 3% S63N17, respectively, and to 392 °C, 391 °C, and 388 °C with 0.5%, 1%, and 3% S63N38, respectively. The incorporation of nitrated SPEEK profoundly affected the thermal degradation of Nafion® and has a higher  $T_{d5}$  than that of Nafion®/SPEEK blends (~364 °C) which is summarized in Table 1. The improvement in thermal stability was attributed to the inhibition of desulfonation.

DSC analysis was used to characterize the thermal transition for recast Nafion® and blended membranes. Fig. 5 shows the transition

temperature present in the DSC curves of the recast Nafion® and the blended membranes. In recast Nafion®, the endothermic peak appeared at about 110 °C, which may be interpreted as the cluster transition temperature [28]. With the introduction of nitrated SPEEK into the Nafion® membrane, the cluster transition temperature was increased with increasing content of nitrated SPEEK. In the blended membranes, the cluster transition temperature increased



**Fig. 4.** The 5% loss temperature of Nafion®/nitrated SPEEK.

**Table 1**  
Properties of blended membranes.

Membranes	Thermal degradation temperature, $T_{d5}$ (°C)	Water uptake (%) $\pm 1$		Methanol permeability, $P$ ( $\times 10^{-7}$ cm $^2$ s $^{-1}$ )	Conductivity, $\sigma$ (S cm $^{-1}$ )	
		30 °C	80 °C		30 °C	80 °C
Recast Nafion®	364	27	36	20.62	0.093	0.146
Nafion®/S63-0.5	367	21	26	17.02	0.052	0.099
Nafion®/S63-1	367	22	31	13.96	0.047	0.097
Nafion®/S63-3	364	24	34	12.75	0.042	0.089
Nafion®/S63N17-0.5	399	17	24	4.29	0.079	0.136
Nafion®/S63N17-1	394	17	25	4.54	0.078	0.135
Nafion®/S63N17-3	399	19	25	5.34	0.077	0.134
Nafion®/S63N38-0.5	392	18	25	4.72	0.085	0.139
Nafion®/S63N38-1	391	19	25	6.03	0.084	0.138
Nafion®/S63N38-3	388	20	26	7.11	0.082	0.137

to 110 °C, 110 °C, and 112 °C with 0.5%, 1%, and 3% S63N17, respectively, and to 117 °C, 134 °C, and 162 °C with 0.5%, 1%, and 3% S63N38, respectively.

### 3.4. Water uptake

It is well known that the proton conductivity and methanol permeability of the membrane are strongly related to the presence of water. An adequate level of water uptake is needed to maintain good proton conductivity; however, water uptake should be minimized to reduce methanol permeability. Consequently, maintaining the appropriate level of water uptake is very important. The water uptake of nitrated SPEEK, which was more hydrophobic [21,29], showed a relatively low uptake at 30 °C of 34% and 37% for S63N17 and S63N38, respectively, compared with native SPEEK63. Table 1 shows the water uptake by blended membranes as a function of temperature. The water uptake by the introduction of nitrated SPEEK was 17–20% lower than that of SPEEK (21–24%) at the same content levels, and it was 27% for recast Nafion® at 30 °C. Although the water uptake of nitrated SPEEK was greater than that of recast Nafion®, the introduction of hydrophobic nitrated SPEEK decreased the water uptake of the blends and had a lower water uptake than Nafion®/SPEEK. Consequently, the diameter of the transfer channels and the size of the ionic clusters were reduced by adjusting the morphology of the membrane [20]. Furthermore, the water uptake increased with increasing content of nitrated SPEEK. At temperatures up to 80 °C, water uptake increased sharply to 24%, 25%, and 25% for 0.5%, 1%, and 3% S63N17, respectively, and to 25%, 25%, and

26% for 0.5%, 1%, and 3% S63N38, respectively. This was perhaps due to the formation of ionic clusters. When the temperature and the degree of nitration were high, the dispersed sulfonic groups can readily form ion domains, which are hydrophilic and mainly responsible for water uptake [30].

### 3.5. Methanol permeability

The methanol permeability of nitrated SPEEK membranes increased with increasing degree of nitration from  $1.86 \times 10^{-7}$  cm $^2$  s $^{-1}$  to  $2.40 \times 10^{-7}$  cm $^2$  s $^{-1}$  for S63N17 and S63N38, respectively. The nitrated SPEEK was more hydrophobic than native SPEEK, giving rise to a small hydrophobic/hydrophilic interface. These values were all lower than that of native SPEEK63 ( $3.44 \times 10^{-7}$  cm $^2$  s $^{-1}$ ) and recast Nafion® ( $20.62 \times 10^{-7}$  cm $^2$  s $^{-1}$ ). The sulfonic groups aggregate to form ion clusters in the presence of water, and the hydrophilic domains are further interconnected within the membrane. The absorbent water has a major role in the transport of methanol through the membrane by hydration with the ionizable sulfonic groups. The methanol permeability of the Nafion®/nitrated SPEEK blended membranes was less than that of Nafion® and Nafion®/SPEEK blended membranes, which is summarized in Table 1. The methanol permeability of blended membranes increased with the increase of nitrated SPEEK content and the substitution of nitro groups, with relatively low methanol permeability at 30 °C of  $4.29 \times 10^{-7}$  cm $^2$  s $^{-1}$ ,  $4.54 \times 10^{-7}$  cm $^2$  s $^{-1}$ , and  $5.34 \times 10^{-7}$  cm $^2$  s $^{-1}$  for an S63N17 content of 0.5%, 1%, and 3%, respectively, and  $4.72 \times 10^{-7}$  cm $^2$  s $^{-1}$ ,  $6.03 \times 10^{-7}$  cm $^2$  s $^{-1}$ , and  $7.11 \times 10^{-7}$  cm $^2$  s $^{-1}$  for an S63N38 content of 0.5%, 1%, and 3%, respectively. This showed that a significant reduction in methanol crossover was achieved by the introduction of nitrated SPEEK into the Nafion® membrane. Changes of the methanol permeability and water uptake of the blended membranes were similar. The incorporation of nitrated SPEEK changed the morphology of blended membranes by increasing the number of hydrophobic substitutions. This significant reduction in methanol crossover is favorable for DMFC applications.

### 3.6. Proton conductivity

The performance of a DMFC is determined mainly by proton conductivity and methanol crossover. In general, a good performance needs high proton conductivity and low methanol crossover. Table 1 shows the proton conductivity of recast Nafion® and the blended membranes as a function of temperature. In Table 1, the proton conductivity of the blend membranes from 30 °C to 80 °C was increased to 0.079–0.136 S cm $^{-1}$ , 0.078–0.135 S cm $^{-1}$ , and 0.077–0.134 S cm $^{-1}$  for an S63N17 content of 0.5%, 1%, and 3%, respectively, and to 0.085–0.139 S cm $^{-1}$ , 0.084–0.138 S cm $^{-1}$ , and 0.082–0.137 S cm $^{-1}$  for an S63N38 content of 0.5%, 1%, and 3%, respectively. The proton conductivity of the blended membranes decreased with increas-

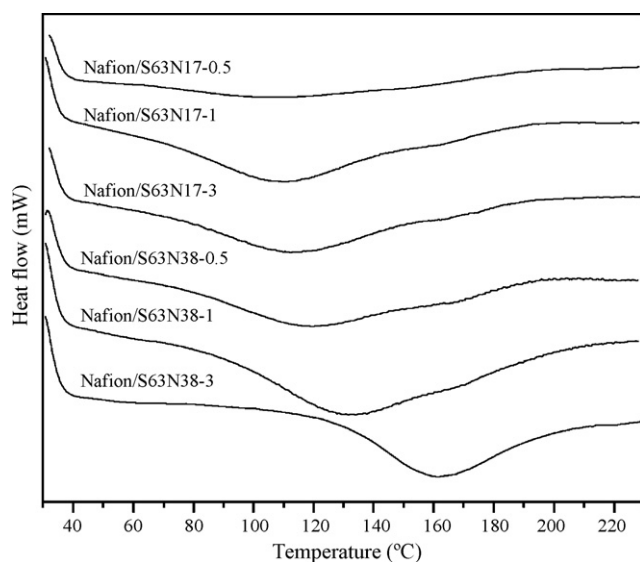


Fig. 5. The transition temperature of Nafion®/nitrated SPEEK.

ing content of nitrated SPEEK. These values were lower than that for recast Nafion® (0.093 S cm<sup>-1</sup>) measured at 30 °C. It was likely that the lower conductivity of nitrated SPEEK caused a decrease in proton conductivity. The proton transport in membranes requires well-connected channels formed by ionic clusters of hydrophilic sulfonic groups. By contrast, it was apparent that the higher degree of nitration (S63N38) increased the proton conductivity at the same level of content [21]. The introduction of nitrated SPEEK improved the morphology of the blended membranes.

The activation energy,  $E_a$ , the minimum energy required for proton transport across the membrane, was calculated by fitting to the Arrhenius equation:

$$\sigma = A \times e^{-E_a/RT} \quad (4)$$

where  $\sigma$  is the proton conductivity (S cm<sup>-1</sup>),  $E_a$  is the activation energy (kJ mol<sup>-1</sup>),  $R$  is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), and  $T$  is the absolute temperature (K). Activation energy values were estimated from the slopes of the plots. All membranes had linear Arrhenius behavior between 30 °C and

80 °C. Recast Nafion® and the blended membranes had an activation energy of 8.14 kJ mol<sup>-1</sup> and 8.92–11.15 kJ mol<sup>-1</sup>, respectively.

### 3.7. Single-cell performance

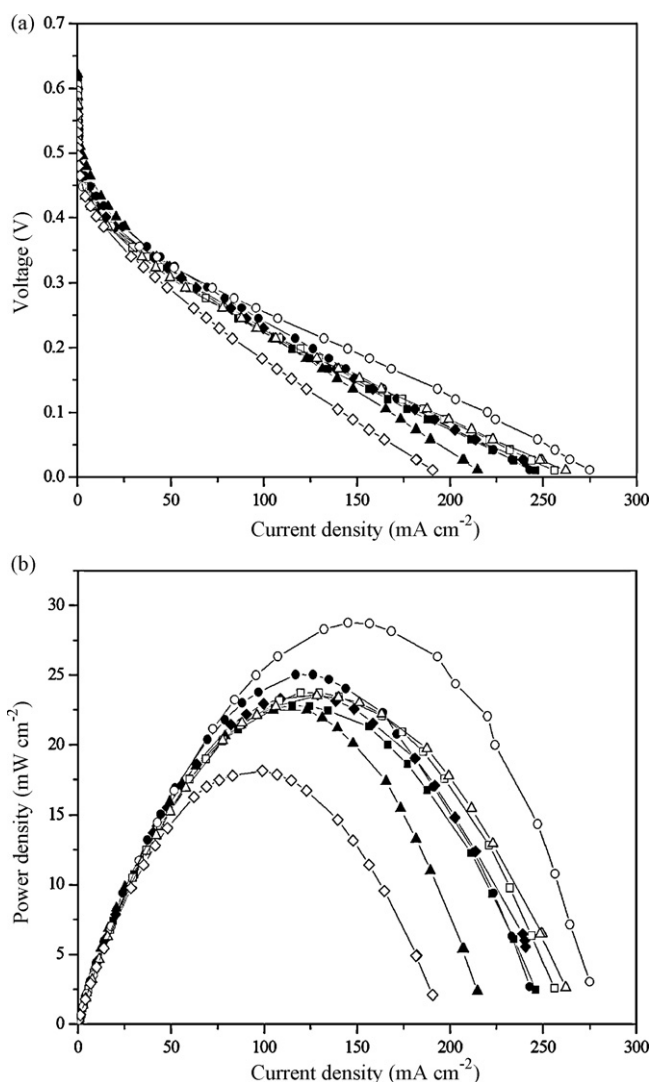
Nafion® 115, recast Nafion® and blended membranes were used in DMFCs. Fig. 6 shows the performance with polarization (a) and power density (b) as a function of current density with various contents of nitrated SPEEK. All the characteristic curves displayed similar polarization behavior. In the region of low current density, activation control caused a large drop of potential, which was decreased further by the intrinsic ohmic resistance at intermediate current density. Although all these factors contribute to a lower output in the context of a load applied to the system, only methanol crossover actively decreases the open circuit voltage. Nafion® 115 has a thickness of 127  $\mu\text{m}$ , while the blended membranes are  $\sim 100 \mu\text{m}$ . In theory, Nafion® 115 is preferred in DMFCs because of its thickness: thicker membranes guarantee a limited methanol crossover rate. However, single cells with any of the blended membranes had a higher open circuit voltage (OCV 0.556–0.621 V) and power density than Nafion® 115 (OCV 0.527 V). The higher OCV indicated clearly that the introduction of nitrated SPEEK decreased the rate of methanol crossover significantly in the DMFC applications due to the relatively low methanol permeability. Although the conductivity of the blended membranes was lower than that of Nafion®, the DMFC performance can be improved by a reduction in methanol crossover. As the nitrated SPEEK content of blended membranes was increased to 3%, the ohmic resistance increased and the performance decreased. The blended membrane with a content of 1% S63N38 had the highest power density (29 mW cm<sup>-2</sup>), which was better than that of the other blended membranes and Nafion® 115 (24 mW cm<sup>-2</sup>). As shown in Fig. 6, the performance of the single cell improved with increasing nitro groups at the same nitrated SPEEK content due to higher proton conductivity. The maximum power density at 80 °C of blended membranes with various contents of nitrated SPEEK and a degree of nitration was 23–25 mW cm<sup>-2</sup> for S63N17 and 24–29 mW cm<sup>-2</sup> for S63N38.

## 4. Conclusion

In this study, nitrated SPEEK and Nafion® were used to prepare blended membranes, which were characterized using <sup>1</sup>H NMR, FT-IR ATR, SEM, TGA, DSC, water uptake, methanol permeability, conductivity, and single-cell performance. <sup>1</sup>H NMR was used to confirm the nitrated substitution of SPEEK, and FT-IR ATR determined the homogeneity of the blended membranes. The degree of nitration could be controlled simply, and the content of nitrated SPEEK could be adjusted easily by blending. The incorporation of nitrated SPEEK in Nafion® decreased the methanol permeability of the membrane; suppressed methanol-crossover significantly, decreased the water uptake, and retained a reasonable thermal property. Although the conductivity was decreased, the resistance of the blended membranes could be decreased as the result of reduced thickness. The blended membranes exhibited higher OCV and superior single-cell performance compared with that of Nafion® 115.

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**Fig. 6.** The performance curves of Nafion® and blended membranes: (a) Polarization curve: (◆) Nafion® 115, (◇) Recast Nafion®, (■) Nafion®/S63N17-0.5, (●) Nafion®/S63N17-1, (▲) Nafion®/S63N17-3, (□) Nafion®/S63N38-0.5, (○) Nafion®/S63N38-1, and (△) Nafion®/S63N38-3. (b) Power density curve: (◆) Nafion® 115, (◇) Recast Nafion®, (■) Nafion®/S63N17-0.5, (●) Nafion®/S63N17-1, (▲) Nafion®/S63N17-3, (□) Nafion®/S63N38-0.5, (○) Nafion®/S63N38-1, and (△) Nafion®/S63N38-3.

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