Solution-blown SPEEK/POSS nanofiber–nafion hybrid composite membranes for direct methanol fuel cells

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ABSTRACT: This study aims to develop novel hybrid composite membranes (NHMs) by impregnating Nafion solution into the porous sulfonated poly(ether ether ketone)/polyhedral oligomeric silsesquioxanes (SPEEK/POSS) nanofibers (NFs). The composite membrane was prepared by solution blowing of a mixture of SPEEK/POSS solution. The characteristics of the SPEEK/POSS NFs and the NHMs, including morphology, thermal stability, and performance of membrane as PEMs, were investigated. The performance of NHMs was compared with that of Nafion117 and SPEEK/Nafion composite membranes. Results showed that the introduction of POSS improved the proton conductivity, water swelling, and methanol permeability of membranes. A maximum proton conductivity of 0.163 S cm^{-1} was obtained when the POSS content was 6 wt % at 80°C, which was higher than that of Nafion117 and SPEEK/Nafion. NHMs could be used as proton exchange membranes (PEMs) for fuel cell applications. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42843.

INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) have attracted increasing attention because of their use in clean and efficient power sources.[1] Perfluorosulfonic acid membranes (e.g., DuPont's Nafion series) are typically used as proton exchange membranes (PEMs) because of their good chemical and physical stabilities, as well as high proton conductivity under high humidity conditions.[2] However, Nafion have several disadvantages, such as high production cost, extensive swelling, and high methanol crossover. Moreover, its applications in PEMFCs is limited, particularly in direct methanol fuel cells (DMFCs) that are promising candidates as power generators for portable devices.[3]

The Nafion membrane has been modified to meet the requirements for DMFC applications. Among various attempts to achieve these requirements, mechanically reinforcing nanofibers (NFs) in Nafion has been used to prepare a NF composite membrane (NCM).[4,5] Chien *et al.*[6] prepared a high-water-uptake activated carbon/Nafion composite membrane. The membrane showed superior current density and peak power density than the commercial Nafion 211 at various relative humidities. Mollá[3] prepared a PVA/Nafion composite membrane by impregnating PVA mat into the Nafion dispersion. These composite Nafion/PVA membranes exhibited relatively low methanol crossover owing to the barrier property of the PVA NFs. The main focus in these works was to obtain reinforced NCMs, and NFs that can induce the formation of proton-conducting channels as a skeleton, thereby improving the mechanical properties.

Recently, various inorganic materials have been used for the preparation of the organic–inorganic composite PEMs.[7] Such hydrophilic materials include SiO2, TiO2, and ZrO2, these fillers enhance both water retention and thermal stability, and contribute to lower methanol permeability. Therefore, organic–inorganic materials have gained considerable attention. Polyhedral oligomeric silsesquioxanes (POSS) compounds are a new generation of hybrid materials that have several advantages, such as monodisperse size, low density, and synthetically well-controlled functionalities over silica, silicones, and other conventional inorganic fillers.[8] Because of the organic functional groups, the POSS cage is naturally compatible with organic hosts, such as polymers, and can be incorporated into polymer systems by blending or by chemical grafting.[9] Wang *et al.*[10] found that a small POSS concentration (≤6%) could significantly improve the properties of nanocomposites. Furthermore, the POSS hollow cage structure can retain water molecules, therefore high water uptake could maintain heightened proton conductivity.[11]

This study developed new NF hybrid composite membranes (NHM) reinforced with curled sulfonated poly(ether ether ketone) (SPEEK)/POSS NFs. It was expected that the introduction of POSS could improve the proton conductivity, chemical and thermal stabilities, methanol permeability of composite membrane. The NFs were obtained by solution blowing, which was reported as a promising NF spinning process.[12] Solution blowing is suitable for almost all types of polymers, especially polymers with extremely high melt viscosities. Solution-blown NFs are commonly curled in three dimensions; a large number of crimped fibers are closely entangled to form a stable structure conducive to blocking methanol crossover after formation of the composite.

In this study, SPEEK/POSS/Nafion membranes with different content of POSS were prepared and characterized. The water uptake (WU), proton conductivities, and methanol permeability varied with different contents of SPEEK/POSS in the composite membrane. The membranes were characterized through scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD).

EXPERIMENTAL

Materials
Victrex PEEK was purchased from ICI and was sulfonated using 98% sulphuric acid. Nafion (5 wt % solution) was obtained from DuPont Co., and N, N-Dimethylformamide (DMF) was obtained from Tianjin Kermel Chemical Reagents. All chemicals were analytical grade.

Syntheses of SPEEK
PEEK was sulfonated using 98% sulphuric acid, and details of the SPEEK synthesis are described in our previous work.[13] The degree of sulfonation of the SPEEK obtained was 62%, which was determined by titration. SPEEK (1–2 g) was placed in 1 M aqueous NaCl and kept for 1 day. The solution was titrated with 0.1 M NaOH until pH = 7. DS was calculated using the following equations: IEC = $V_{NaOH} C_{NaOH}/m$; DS % = M_{PEEK}IEC/ (1-M_{-SO3H}IEC), where V_{NaOH} and C_{NaOH} are volume and molar concentration of NaOH, respectively; m is mass of SPEEK; M_{PEEK} and M_{SO3H} are molar mass of PEEK and -SO$_3$H, respectively.

Preparation of SPEEK/POSS NFs
The experimental set-up used to prepare nonwoven NFs was shown in our previous work.[14] SPEEK was dissolved in DMF (18 wt %) and POSS (2, 4, and 6 wt %) were mixed to obtain the spinning solution. The spinning processes are briefed in the following: the solution was loaded into a syringe as spinneret. A syringe pump was used to squeeze out the spinning solution at a speed of 16 mL h^{-1} through a 0.38 mm inner diameter needle coaxially surrounded by a gas cavity. High-velocity airflow was supplied to the gas cavity. The air pressure was 0.06 MPa. After the solution streams were pressed out of the syringe needle, the spinning solution was blown and attenuated into ultrafine fibers. The nonwoven NFs were collected on a collector to form a fibrous mat, and the collecting distance was 60 cm.

Preparation of SPEEK/POSS/Nafion NHM
The solution-blown SPEEK/POSS NF mat was peeled off from the collector, and mechanically compressed with a hot-presser (CB-950Z5 hot-presser, China) at 30°C and 6 MPa for 3 min. Then, a SPEEK nonwoven mat was impregnated into a 5% Nafion solution to form a pore-filled and fully dense NF hybrid composite membrane. All NHMs contained 10 wt % of NFs and were designated as SPN-2%, SPN-4%, and SPN-6% (2, 4, and 6 wt % POSS, respectively). In addition, pure Nafion, and SPEEK/Nafion-10 was prepared by solvent-casting method for a comparison.

Characterization
Structure and Morphology of SPEEK/POSS NFs and NHMs. The morphologies of SPEEK/POSS NFs and NHMs were characterized using a SEM (Hitachi S-4800). Before SEM observations, all samples were gold coated using a sputter coater. The membrane cross sections were obtained by immersing samples in liquid nitrogen. Besides, the SPEEK/POSS NFs were examined using a SEM from HITACHI equipped with an EDX spectrometer. The diameter of nanofiber is measured with Image-Pro Plus version 6.0.0(Media Cybernetics), and data were analyzed by origin 8.0 (OriginLab Corporation) to obtain diameter distribution.

XRD was performed using an XRD spectrometer (D8 Discover with GADDS, 40 kV, 40 mA) from 10 to 60 with a CuKa radiation (λ = 1.541 Å).

Thermal Behavior. The thermal degradation of all the samples were investigated by high resolution thermogravimetric analysis (TGA), which was performed using TGA instruments (STA409PC).

Water Uptake (WU) and Swelling Ratio (SR). WU, SR of membranes were measured. Rectangular shaped membranes (about 2 × 2 cm^2) were dried in a vacuum oven at 90°C for 10 h. Their weight and area were then measured accurately. After immersion in distilled water for 24 h at the desired temperature, the membranes were removed and wiped with an absorbent paper quickly. The weight and area were rapidly measured. WU and SR were calculated using the following equations:

$$WU = (W_w - W_d)/W_d \times 100\%$$

$$SR = (S_w - S_d)/S_d \times 100\%$$

where W_w and W_d are the water swollen membrane weight and the dry membrane weight, respectively. S_w and S_d are the water swollen membrane area and the dry membrane area, respectively.

Proton Conductivity. The proton conductivity of samples was measured using four electrodes. The proton conductivity was measured by electrochemical impedance spectroscopy using a electrochemical workstation (CHI660D, 1-10^5 Hz). The proton conductivity was calculated from the $\sigma = L\ A^{-1}\ R^{-1}$ formula, where L, A, and R are the membrane thickness, the cross sectional area(were calculated from $A = W\ d$, where W and d are the width and thickness of the membrane, respectively), and the resistance of the membrane, respectively. The proton
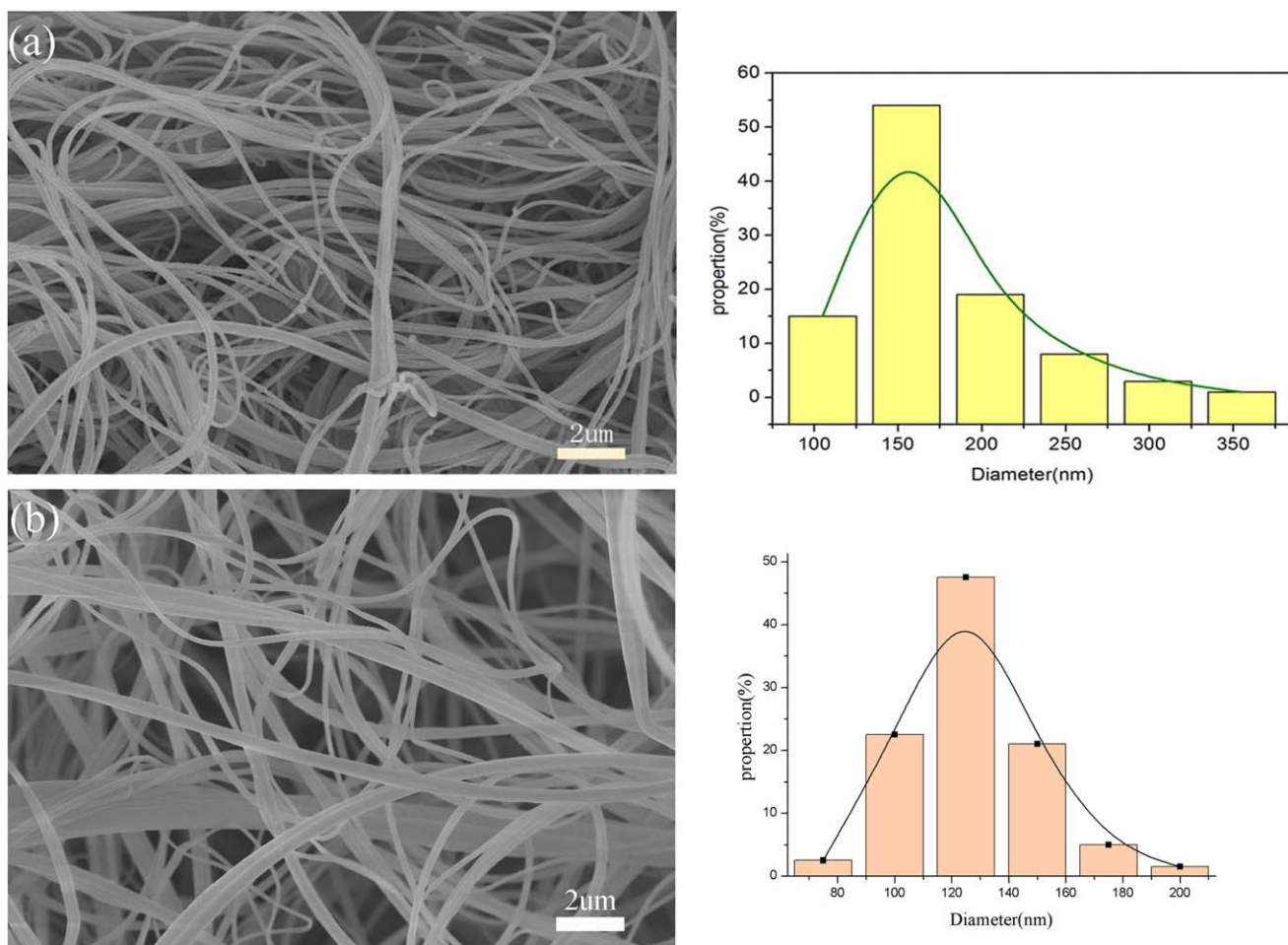
Figure 1. (a) SEM images of SPEEK/POSS NF and the corresponding diameter distribution map. (b) SEM images of SPEEK NF and the corresponding diameter distribution map. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conductivity of the membranes are measured at different temperatures, and temperature are controlled by a constant temperature and humidity box (GP/GPS-D, shanghai Guangpin Equipment Co).

Methanol Permeability. The methanol diffusion coefficient through the membrane was measured using diffusing equipment with two glass compartments, which were separated by the test membrane. A certain volume of 10 M methanol solution was added to one side. The same volume of deionized water was added to the other side. Magnetic stirrers were used on each compartment to ensure uniformity. Methanol concentration within the water cell was monitored by gas chromatography. The methanol diffusion coefficients were calculated by Fick's first law,[15] that is:

$$C_{B(t)} = A \ V_B^{-1} DK \ L^{-1} C_A(t - t_0)$$

where C_A and C_B are the methanol concentrations of methanol feed side and water side, respectively; A, L, and V_B are the effective area, the thickness of membrane and the volume of permeated compartment, respectively; DK defined is the methanol permeability; t is time.

RESULTS AND DISCUSSION

Structure and Morphology of SPEEK/POSS NFs and NHMs

SPEEK/POSS NFs were fabricated by solution blowing. Figure 1 shows the SEM micrographs and the corresponding diameter distribution map of solution-blown SPEEK/POSS NFs and SPEEK NFs. As shown in Figure 1, the solution-blown NF mat consists of droplet-free NFs, and the NFs are commonly curled in three dimensions and closely entangled like the SPEEK NFs in our previous work. The SPEEK nanofibers with diameters ranged between 80 nm and 210 nm, whereas the diameter of SPEEK/POSS is between 100 nm and 350 nm. This may be due to the introduction of POSS that increases the viscosity of the spinning solution.

Figure 2(a,b, and c) show SEM images of the cross section of SPN-2%, SPN-4%, and SPN-6%, respectively. The images show complete reinforcement of fiber embedded in a Nafion matrix. No significant crack is observed, indicating good compatibility between SPEEK/POSS NFs and the Nafion phase. Figure 2(d) shows a surface image of SPN-2% with no porosity, possibly indicating that the membrane is totally compact, and the surface of NHMs is smooth. The SEM images demonstrate good impregnation of Nafion matrix into the pores of SPEEK/POSS NFs.
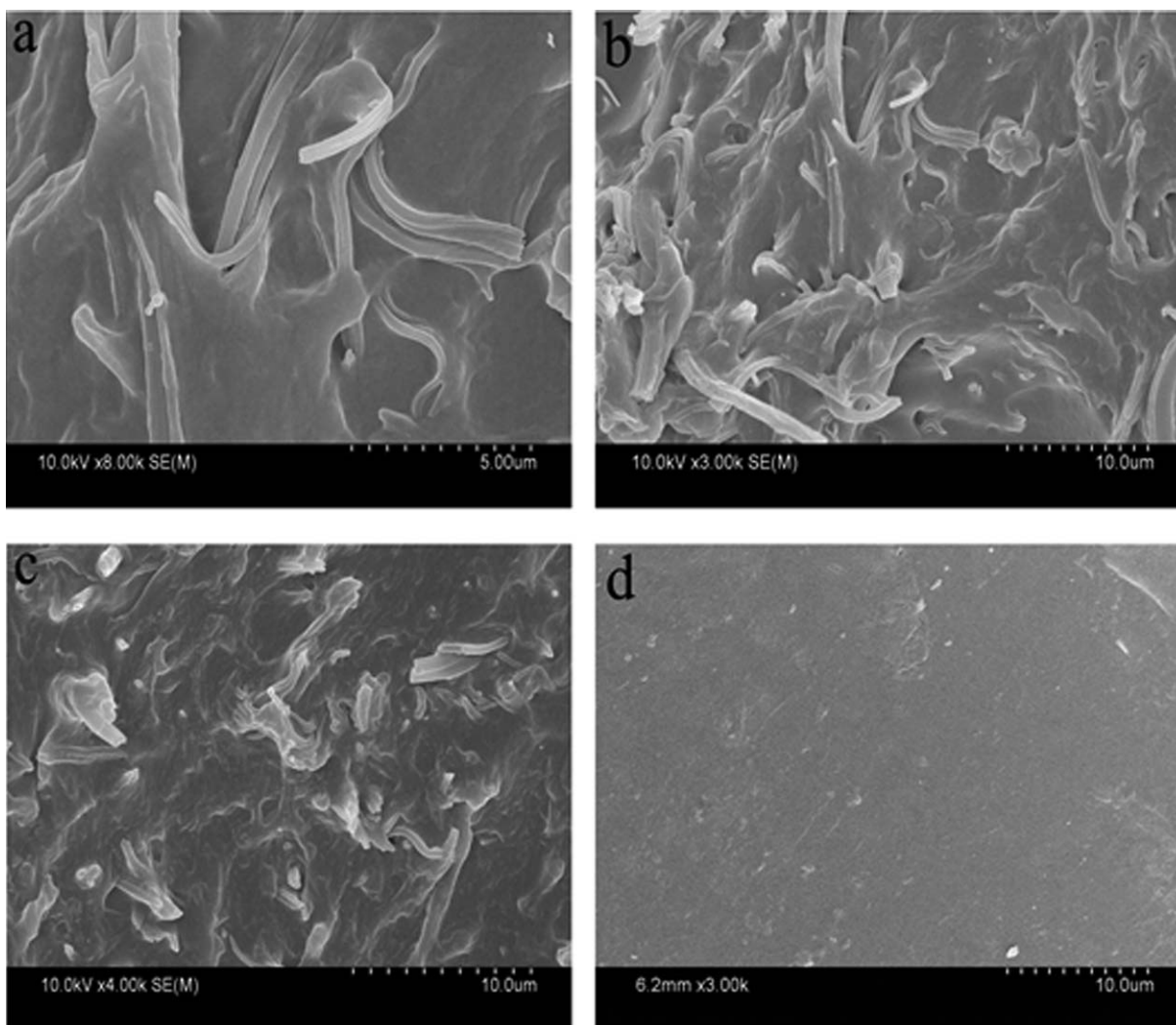
Figure 2. Micrographs of composite membrane, (a, b and c) SEM images of the cross-section of SPN-2%, SPN-4%, and SPN-6%, respectively. (d) The surface image of the SPN-2%.

Figure 3 shows the EDX spectrum of the SPEEK/POSS (1:0.06) NFs, which shows the presence of Si, thereby indicating the existence of POSS.

The XRD curves of Nafion, SPEEK and NHMs are shown in Figure 4. For comparison, the curves of NHMs with different ratio, as well as Nafion and SPEEK NFs, are given in the same figure. The peaks for POSS are sharp with three characteristic peaks at 8°, 13°, and 19°, indicating good crystallization property of POSS. The peak of Nafion and SPEEK occurs at 17° and 19°, respectively. The peak for the hybrid membranes shifted along the direction of 2θ caused by the SPEEK/POSS NFs redistribution in Nafion and reveals the good compatibility of the materials. Moreover, a broad peak occurs at 2θ of 18° for all the hybrid membranes. Only SPN-6% has a characteristic peak at 8° perhaps because of little introduction of POSS.

Thermal Behavior

Figure 5 shows the behavior of membranes in terms of temperature for the evaluation of the thermal stability of obtained membranes. The curves exhibit three main degradation stages for all samples. The initial weight loss below 200°C is attributed to the loss of evaporation of residual solvent and water. The second transition occurs over temperature ranging from 300°C to 370°C, corresponding to loss of sulfonic acid groups. The third step weight loss of the composite membranes occurs at ~450°C, which represents the main chain degradation of polymers. These curves exhibit that the introduction of SPEEK/POSS improves the thermal stability of Nafion. The thermal stability enhancement exhibited by SPEEK/POSS nanofiber is believed to be due to the restriction of the thermal motions of the tethered SPEEK/POSS macromolecular chain structure, reducing the organic decomposition pathways accessible to the tether. In addition, the inorganic POSS component provides additional heat capacity thereby stabilizing the materials against thermal decomposition. The presence of Si—O—Si inorganic backbone on the POSS structure contributes to the increase of the thermostability due to the high Si—O bond dissociation energy (460 kJ mol^{-1}) compared with the C—O (345 kJ mol^{-1}) or even with Si—C (318 kJ mol^{-1}) bonds.[8] In addition, the NHMs present a distinctly lower mass loss because POSS
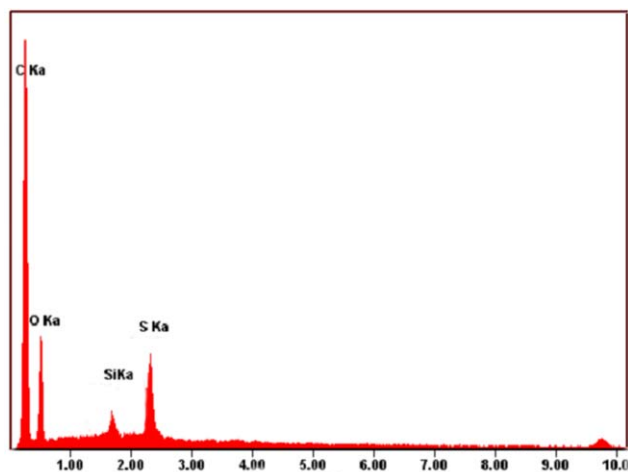
Figure 3. EDX measurement of SPEEK/POSS (POSS-6%) NFs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. TGA of Nafion117, SPEEK casting membranes, and NHMs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

possesses a better thermal stability. TGA experiments demonstrate that the NHMs have sufficient thermal stability for fuel cell applications.

Water Uptake and Swelling Ratio

WU is closely related to the basic properties of a membrane and plays an essential role in the membrane behavior. In general, a high WU is a prerequisite for a good proton-conducting
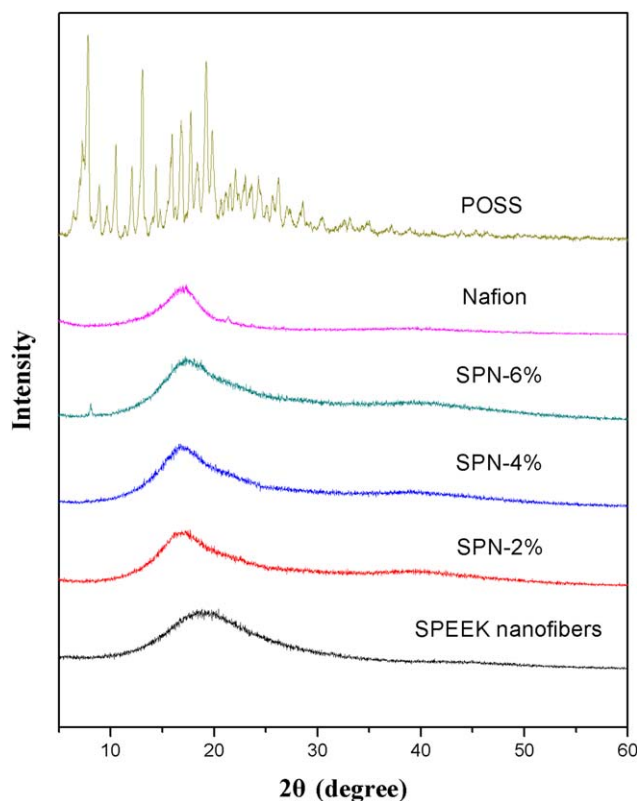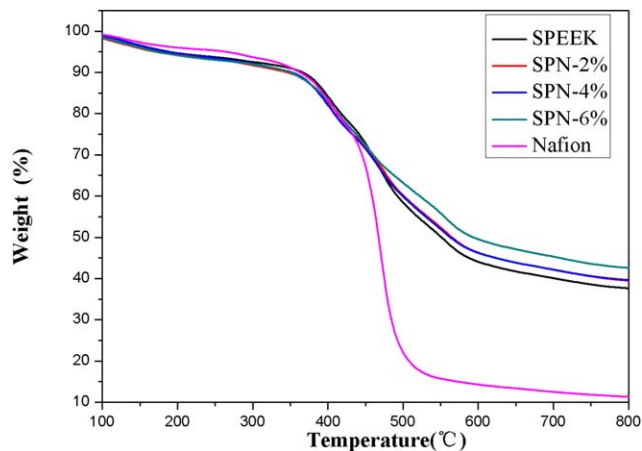
membrane; however, excessive WU in a PEM leads to unacceptable dimensional change. Consequently, higher swelling ratio (SR) leads to high methanol permeability. Hence, the optimization of WU and SR is required for the successful operation in a fuel cell[16] The WU and SR of different membranes are shown in Figures 6 and 7, respectively.

All of the membranes exhibit a significant increase in WU with the increase in temperature, and the WU of all the NHMs is higher than that of SPEEK/Nafion-10 at the same temperature. The WU increased with the increase of POSS in NHMs. This increase in WU can be attributed to the inclusion of SPEEK has enhanced WU because of the higher hydrophilic character of the polar sulfonic acid groups in this case, and water could get into POSS through hydroxyl, then the cage-like structure of POSS that can entrap water molecules further increase the water uptake of the membranes[17]
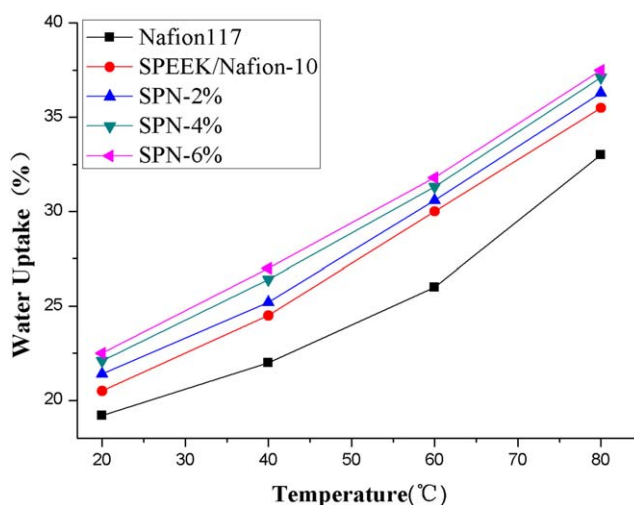

Figure 4. XRD patterns of Nafion117, SPEEK, and NHMs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. WU of Nafion117, SPEEK/Nafion-10, and NHMs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
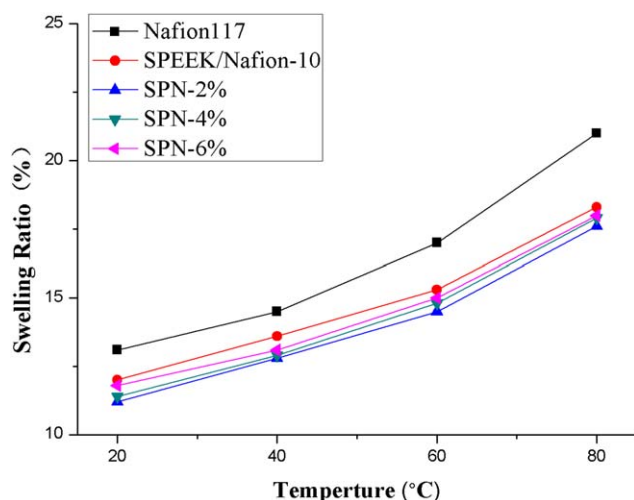
Figure 7. SR of Nafion117, SPEEK/Nafion-10, and NHMs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The temperature dependence of SR is shown in Figure 7. The SR of SPEEK/Nafion-10 and NHMs is both lower than Nafion. This phenomenon is the reinforcing effect, and NFs resist excessive swelling. Furthermore, although the WU of NHMs is higher than that of Nafion117 and SPEEK/Nafion, the SR of NHMs is lower than that of Nafion117 and SPEEK/Nafion-10. Thus, the NHMs exhibited improved dimensional stability by incorporation of POSS into the Nafion matrix. However, the SR increases with the increase of POSS in hybrid membranes because high content of POSS leads to high WU, thereby causing a relative increase in SR. Overall, the SR of NHMs is within a controllable range.

Proton Conductivity

Proton conduction capability is the most important characteristic of PEM for methanol fuel cell applications.[18] Figure 7 illustrates the proton conductivity–temperature relationship of the
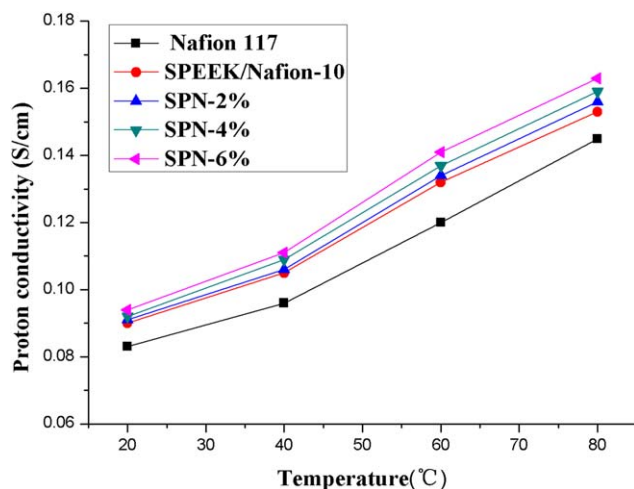

Figure 8. Proton conductivity–temperature relationship of Nafion117, SPEEK/Nafion-10, and NHMs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Methanol Permeability and Selectivity of Nafion, SPEEK/Nafion-10, and NHMs

Sample	Methanol permeability $\times 10^{-7}$ (cm^2 s^{-1})	Selectivity 10^4 (S s cm^{-3})
Nafion117	14.1	5.7
SPEEK/Nafion-10	9.9	9.2
SPN-2%	8.6	10.6
SPN-4%	8.0	11.5
SPN-6%	7.3	12.8

NHMs in comparison with that of Nafion117 and SPEEK/Nafion-10. Proton conductivity is improved for all the samples by increasing the temperature, which indicated that proton conduction is a thermally activated process. As seen, in the temperatures range (20–80°C), the proton conductivity of all the NHMs is better than that of Nafion117 and SPEEK/Nafion-10 and increases with increase in the content of POSS. This result is initially ascribed to the fact that the existence of SPEEK/POSS playing a positive role for proton conduction. Second, the POSS hollow cage structure can retain water molecules; therefore, a large number of bond water is attached to SPEEK/POSS nanofiber, the high WU, hence the proton conductivity increases. To conclude, the highest proton conductivity of SPN-6% is significantly superior to that of Nafion117 membranes in the temperatures range, with a highest 17.5% increase compared with that of Nafion117. However, the increase of SPEEK/Nafion-10 is only 5.5% higher than the Nafion117. The highest conductivity of SPN-6% is 0.163 S cm^{-1} at 80°C. Therefore, the SPEEK/POSS improves the proton conductivity of NHMs, and NHMs are suitable materials for DMFC.

Methanol Permeability

To prevent fuel from penetrating, PEMs used in DMFCs should possess a high methanol resistance property. Nevertheless, methanol crossover is a common problem in DMFC, especially in Nafion.

The methanol permeability of various membranes is measured at room temperature and the results are illustrated in Table I. As displayed in Table I, the methanol permeability of the NHMs is lower than the membranes without POSS, and decreases dramatically by increasing the POSS content. This result can be explained by the presence of inorganic materials of POSS that introduce tortuous diffusion pathways against methanol across the membrane, and consequently decrease the methanol permeation rate.

The selectivity parameter is defined as the ratio of proton conductivity to methanol diffusion coefficient.[18] It is usually a crucial factor for polymer electrolyte membrane in DMFC application. Accordingly, higher selectivity could allow superior membrane performance. The room-temperature selectivity values of all samples are also shown in Table I. Among all the membranes, SPN-6% exhibits the highest selectivity; nevertheless, all the NHMs show higher selectivity than SPEEK/Nafion-10.

The improvement in selectivity results from the incorporation of POSS into the membranes.

CONCLUSIONS

The SPEEK/POSS NF mats were prepared by solution blowing of mixed solutions of 10 wt % SPEEK and POSS. The prepared NFs were bead-free. Results showed that the presence of inorganic POSS in the nanofibrous skeleton was advantageous in attracting more water compared with SPEEK/Nafion-10 without POSS. In addition, the organic–inorganic nanofibrous skeleton showed a better reinforcing effect for the composite membrane than the SPEEK/Nafion-10. The NHMs showed significantly reduced membrane swelling and methanol permeability. The proton conductivity of the NHMs was superior to SPEEK/Nafion-10 owing to its relatively high water retention and resistance to swelling. The results suggested that the NHMs have significantly improved the properties when compared with SPEEK/Nafion-10 and that they could be used in fuel cells.

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