



Semi-interpenetrating polymer network electrolyte membranes composed of sulfonated poly(ether ether ketone) and organosiloxane-based hybrid network

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ABSTRACT

A semi-interpenetrating polymer network (semi-IPN) proton exchange membrane is prepared from the sulfonated poly(ether ether ketone) (sPEEK) and organosiloxane-based organic/inorganic hybrid network (organosiloxane network). The organosiloxane network is synthesized from 3-glycidyloxypropyltrimethoxysilane and 1-hydroxyethane-1,1-diphosphonic acid. The semi-IPN membranes prepared were stable up to 300 °C without any degradation. The methanol permeability is much lower than Nafion® 117 under addition of the organosiloxane network. The proton conductivity of semi-IPN membranes increases with an increase the organosiloxane network content; the membrane containing the 20–24 wt% organosiloxane network shows higher conductivity than Nafion® 117. The power density of the MEA fabricated with the semi-IPN membrane with 24 wt% organosiloxane network is 135 mW cm⁻², much better than that of the pristine sPEEK membrane, 85 mW cm⁻². Chemical synthesis of the semi-IPN membranes is identified using FTIR, and its ion cluster dimension examined using SAXS. The dimensional stability associated with water swelling and dissolution is investigated at different temperatures, and the semi IPN membranes dimensionally stable in water at elevated temperature.

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1. Introduction

Nafion® series membranes are the most well known commercially available proton exchange membranes for fuel cell applications because they possess high proton conductivity and good chemical and mechanical properties. However, Nafion® membranes have some problems associated with high methanol permeability and high cost. Because of these problems, several types of hydrocarbon proton exchange membranes have been studied for development as alternatives to Nafion® membranes [1–5].

Recently, the organosiloxane-based organic/inorganic hybrid network materials (organosiloxane network) have been recognized as promising electrolyte membranes [6–12]. In general, organosiloxane networks consist of siloxane linkages and organic chains with phosphoric acid. The phosphoric acid is considered an excellent proton carrier given its good proton donating and accepting properties. Among the several organic reagents that bear a phosphoric acid, 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) is known to have very powerful proton conducting properties, as it possesses two phosphoric acids and thus four protons in a mole [6]. This type of organosiloxane network, however, has severely weak

mechanical (brittle) properties, rendering it near-ineffectual fuel cell membrane applications.

Sulfonated poly(ether ether ketone) (sPEEK) has been noted as a membrane replacement for Nafion® given its low cost, low methanol permeability, and good mechanical and thermal properties. However, utilization of sPEEK as a fuel cell membrane presents with an obstacle, as its proton conductivity strongly depends on the degree of sulfonation (DS). The sPEEK membranes with high DS, above 65%, are greatly swollen or sometimes easily dissolved in hot water, generally above 70 °C, even though its proton conductivity is relatively high, whereas the sPEEK membranes with low DS, below 55%, would have a low conductivity. In order to prevent the sPEEK membrane with a high DS from large swelling or dissolution in hot water, sPEEK membranes have been modified by crosslinking [13,14], this would sacrifice proton conductivity, however.

In other to improve the conductivity of the proton exchange membranes, the sulfuric acid-functionalized silica materials were occasionally introduced [15–17] as fillers or blending components, but it usually led to deterioration of other properties, especially, mechanical properties. In this study, semi-interpenetrating polymer networks (semi-IPN) were prepared from the two components mentioned above, the organosiloxane network and sPEEK. As the molecular structure of this membrane system is quite different from the previous ones in association with an entangled network structure, it is expected to show improvements in both proton conductivity and mechanical properties. The interpenetrating

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network structure between sPEEK and organosiloxane possibly makes membrane flexible but still strong in harsh fuel cell atmosphere. While sPEEK with 65% DS (sPEEK65) provides advantageous properties, low methanol permeability, superior chemical, mechanical, and dimensional stability, the organosiloxane network provides high proton conductivity. By the provisions of these two supportive properties, the semi-IPN membranes prepared are expected to cure the drawbacks associated with each component material, resulting in high proton conductivity, low methanol permeability, and good thermal and mechanical properties, along with good cell performance.

2. Experimental

2.1. Materials

The PEEK powder ($M_n = 100,000 \text{ g mol}^{-1}$, Victrex® 450PF, ICI, London, England, UK) was used as a basic polymer matrix for the semi-IPN membranes. Its average particle size was $100 \mu\text{m}$. Methylsulfonic acid (MSA) (Aldrich) was used as a solvent for dissolution of the PEEK powders to enable homogeneous sulfonation. *N,N*-Dimethyl acetamide (DMAc) (Aldrich) was used as a casting solvent for fabrication of sPEEK membranes. 3-Glycidyloxypropyltrimethoxysilane (GPTMS) and 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) were purchased from (TCI, Tokyo, Japan) and used to synthesize the organosiloxane networks. Hydrochloric acid solution (37% wt%) (Aldrich) and sulfuric acid (97%) (Aldrich) were used for protonation and sulfonation of PEEK, respectively.

2.2. Preparation of semi-IPN membranes

Sulfonation of the PEEK powder was conducted by dissolving 10.0 g of PEEK in 50 mL of methylsulfonic acid under vigorous stirring for 4 h, followed by addition of 400 mL 97 wt% sulfuric acid in a 3-neck flask under nitrogen at 30°C . After the reaction was complete, the sPEEK was washed with de-ionized water several times and dried in an oven for 5 h at 100°C . The DS was controlled by sulfonation time; in this research the sPEEKs, with a series of DS, 65, 70, 75, and 80%, were prepared. Among them, the sPEEK in a DS of 65% (IEC of 1.85) was used to synthesize the semi-IPNs. The IEC value of the sPEEK was determined by back titration of the sPEEK with sodium hydroxide solution. The sPEEK particles, 0.1 g, were placed in 20 mL 0.05 N NaOH aqueous solution and kept for 3 days. The solution was then titrated with 0.05 N HCl aqueous solution using a pH meter. The molar number of the sPEEK repeat unit, x , and IEC value, IEC, were calculated from the following equations:

$$x = V_{\text{NaOH}} * M_{\text{NaOH}} - V_{\text{HCl}} * M_{\text{HCl}} \quad (1)$$

$$\text{IEC} = \frac{x * 1000}{\text{sPEEK}_{\text{mass}}} \quad (2)$$

Here V_{NaOH} and M_{NaOH} are volume and concentration of NaOH aqueous solution and V_{HCl} and M_{HCl} those of HCl aqueous solution, $\text{sPEEK}_{\text{mass}}$ the mass of sPEEK (g), respectively.

The organosiloxane network/sPEEK65 semi-IPN membrane was prepared using DMAc, a casting solvent. sPEEK65 (0.3 g) was dissolved in 9.7 g DMAc under stirring until a homogeneous phase was obtained (solution 1). The organosiloxane network was prepared from GPTMS and HEDPA in a 1:1 molar ratio. The GPTMS (0.95 g) and HEDPA (60%) (1.4 g) were dissolved in 5.0 mL of DMAc under stirring for 20 min, followed by addition of 1.0 mL de-ionized water and a drop of concentrated hydrochloric acid to yield a homogenous solution (solution 2). Solutions 1 and 2 were mixed together to prepare a series of mixtures with different organosiloxane concentrations of 4, 8, 12, 16, 20, and 24 wt%. As the overall

membrane properties were not enhanced or became even poorer beyond 24 wt%, preparation of the samples containing greater than 24 wt% were not further considered. Each mixture was stirred for 8 h at room temperature and then cast onto a glass dish, followed by curing and drying at 80°C for 10 h. The semi-IPN membranes were obtained after further drying at 120°C for 2 h under vacuum.

2.3. Characterizations of semi-IPN membranes

2.3.1. Chemical structure

The Fourier transform infrared (FTIR) spectra were obtained using a Bruker IFS-66 ATR-FTIR spectrometer (Bruker, Germany). The measurement was conducted at the resolution of 2 cm^{-1} in the spectral range of $4000\text{--}400 \text{ cm}^{-1}$.

2.3.2. Water uptake

The weight of the membrane was measured after it was dried at 100°C for 24 h under vacuum. The membrane was soaked in water for 12 h to promote swelling up to equilibrium. After achievement of equilibrium, the membrane surface was wiped with a clean tissue to remove any trace of liquid, and the swollen membrane then weighed. The % water uptake was defined by:

$$\text{Wt\%} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (3)$$

where W_{wet} and W_{dry} are the weights of swollen and dry membranes, respectively. The swelling experiments were carried out at room temperature.

2.3.3. Proton conductivity

The ohmic resistance of the membrane was measured using an impedance measurement unit (Zahner, IM6eX, Germany) with a Bekktech cell (BT-115, USA) at different temperatures from 40 to 90°C and at a fixed humidity of 95%. Before each measurement, the membrane sample was fully hydrated by immersion in de-ionized water for 10 h. The conductivity cell had a nominal internal volume of 55 cm^3 . The hydrogen gas flow rate was 990 SCCM to avoid water precipitation of the membrane. The ion conductivity of the membrane was calculated from the ohmic resistance measured by Eq. (4):

$$\sigma(\text{Scm}^{-1}) = \frac{L}{R \times W \times T} \quad (4)$$

where W and T are the respective width and thickness of the membrane; R the resistance of the membrane; L the distance in the direction of ion flow between the voltage measurement probes.

2.3.4. Methanol permeability

Methanol permeability was measured using a diaphragm cell at room temperature. The glass cell consisted of two identical compartments separated by test membranes. One compartment contained 2.0 M methanol and the other de-ionized water. Both compartments were magnetically stirred during the permeation experiments. Concentration of the permeated methanol was measured by a refractive index (RI) detector (RI750F Younglin Instrument, Korea). Methanol permeability was calculated from the slope of the linear plot of the methanol concentration versus permeation time. A more detailed measurement methodology and procedure was previously reported [18].

2.3.5. Ion cluster structure

The small angle X-ray scattering (SAXS) technique was employed to investigate the radial structure of the particles and the average ionic cluster dimension of the membrane. The membrane sample was first immersed in a 1.0 M CsCl solution for 24 h to exchange the protons in the sulfonic groups with the ionic

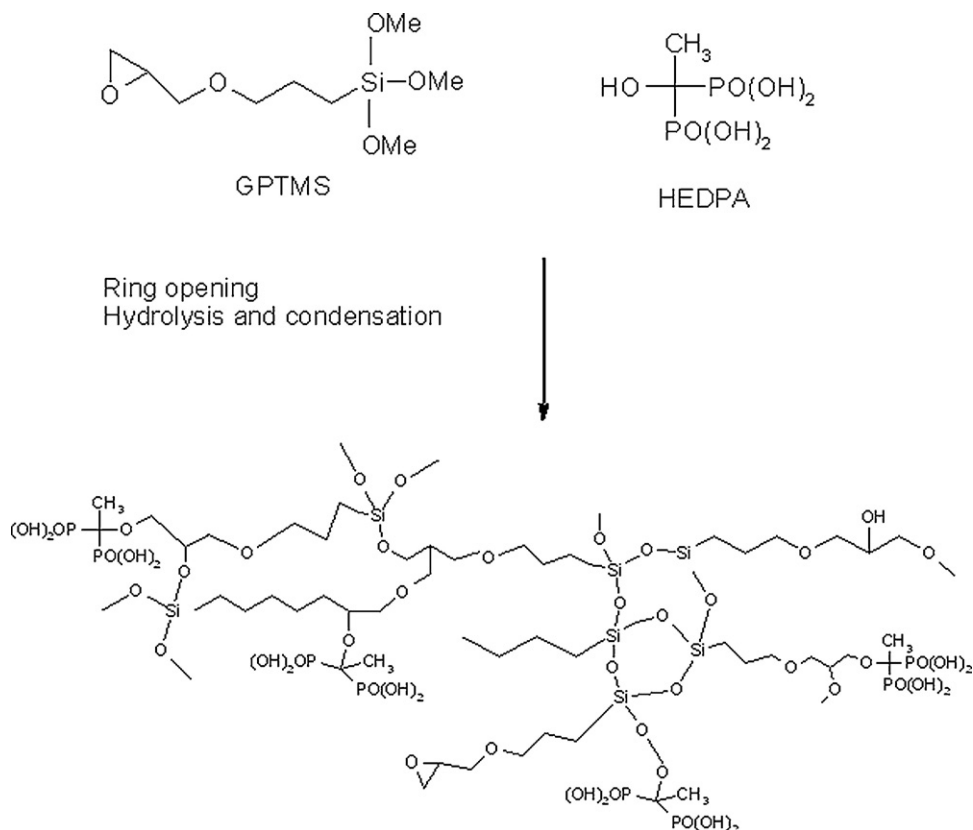


Fig. 1. Synthetic scheme of organosiloxane network.

cesium. All the samples were washed with de-ionized water prior to measurement. All SAXS experiments were performed using Synchrotron radiation with $\lambda = 1.608 \text{ \AA}$ at the 4C1 lines of Pohang Accelerator Laboratory in POSTECH. The distance between each sample and detector was fixed at 50 cm and the sample exposure time was approximately 60 s per sample. Data were obtained by converting signals collected by a 2D detector using 2D data processing software in the range of the small angle region. The average ion cluster dimension of the membrane was calculated from the following formula:

$$d = \frac{2\pi}{q} \quad (5)$$

where d is the average ion cluster dimension of the membrane (angstrom) and q the scattering vector (angstrom), respectively.

2.3.6. Thermal and mechanical properties

Thermogravimetric analyzer and differential thermal analyzer (TGA-DTA, TA Instrument SDT 2960, Seico, Japan) were employed to investigate the thermal behavior of the membranes in a temperature range from 50 to 600 °C and at a ramping rate of 10 °C min⁻¹ under a nitrogen atmosphere.

The tensile strength of both sPEEK and semi-IPN membranes were measured using a universal tensile machine (UTM model 5565, Lloyd, Fareham, UK). Samples 10 mm in width and 50 mm in length were stretched with a 250 N load cell and pulled at 10 mm min⁻¹ within 21 cm of gauge length. The measurements were conducted at least three times and the average value taken for determination.

2.4. MEA fabrication and cell performance

The membrane electrode assemblies (MEAs) were prepared by hot pressing the membranes between 2 electrodes. The catalysts

of Pt-Ru (Pt/Ru = 1/1) and Pt (Jonson Matthey, London, England, UK) were loaded at the anode and cathode, respectively, with a loading content of 3 mg cm⁻² for anode side and 2 mg cm⁻² for cathode side. A Nafion® solution was used as a binder between the membrane and catalyst on both electrodes. The semi-IPN membrane was sandwiched between 2 electrodes by hot pressing for 1 min at 105 °C and 6.9 MPa. A 2.0 M methanol solution was fed to the anode at a flow rate of 5.0 mL min⁻¹. Oxygen gas was supplied at cathode side at the cathode pressure of 0.2 MPa. The active cell area was 6.25 cm², and the cell was operated at 80 °C.

3. Results and discussion

3.1. Synthesis of semi IPN membranes

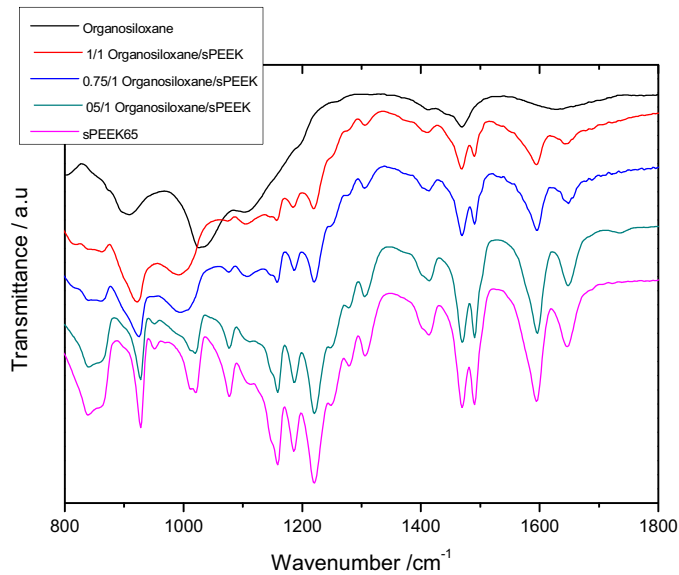
The organosiloxane network was synthesized from GPTMS and HEDPA via sol-gel reactions [7]. The hydroxyl groups of the HEDPA react with the epoxide groups of GPTMS to create ring-opened products. Alkoxy silanes of the GPTMS undergo condensation to make Si-O bonds during the hydrolysis and drying processes, resulting in the formation of a crosslinked siloxane network as shown in Fig. 1. When the sPEEK molecules are present during this curing reaction between GPTMS and HEDPA, the sPEEK molecules are interpenetrated into the siloxane network, forming the semi-IPN structure. The thickness of the membranes prepared is 200–230 μm.

3.2. FTIR analysis

Fig. 2 shows the FTIR spectra of semi-IPN membranes, along with the bare organosiloxane network, and pure sPEEK65 materials. The pristine organosiloxane network illustrates two characteristic peaks at 1030 and 1110 cm⁻¹, where the first arises from the

Table 1
Water uptake of semi-IPN membranes.

Temperature (°C)	Organosiloxane content						
	sPEEK65	4%	8%	12%	16%	20%	24%
40	17.5	23.6	25.6	29.1	29.6	31.7	33.8
50	22.3	27.4	30.2	32.0	34.1	35.0	36.6
60	26.4	32.4	34.8	37.7	38.0	39.6	42.2
70	31.5	40.0	43.2	45.5	47.5	49.6	51.8
80	76.1	80.1	82.7	84.2	87.6	90.2	92.4

**Fig. 2.** FTIR spectra of the organosiloxane and semi-IPN membranes.

Si–O–Si bond formed by the sol–gel condensation and the second from the Si–O–C [19–21]. In the FTIR spectra of the bare sPEEK65, the absorption at 1078 cm^{-1} was ascribed to the symmetric O=S=O vibration, and the absorptions at 1200 and 1020 cm^{-1} to the sulfonic acid group, respectively. With an increase of organosiloxane content, the absorption bands of sulfonic acid in sPEEK65 slightly shifted to the left from 1020 cm^{-1} due to a hydrophilic interaction between the sulfonic acid groups of sPEEK and Si–O–Si groups of organosiloxane.

3.3. Water uptake

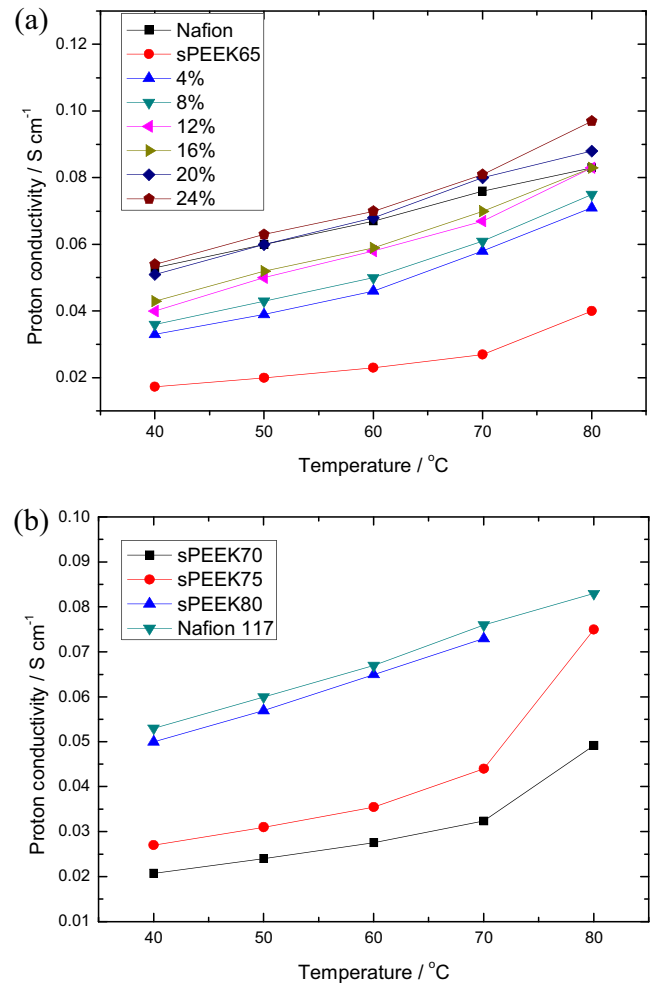
The water uptake of the semi-IPN membranes with various organosiloxane network contents is shown in Table 1. Water uptake of the membranes increased with an increasing organosiloxane network content because of its high hydrophilic property, its room temperature water uptake is 62 wt%. However, the temperature dependence of the water uptake for the IPN systems was not as strong as that for the pristine sPEEK65 system; the water uptake of the IPN system (24%) was nearly twice that of pristine sPEEK65 at $40\text{ }^{\circ}\text{C}$, but slightly higher at $80\text{ }^{\circ}\text{C}$. This is because molecular mobility of IPN system is diminished by the crosslinks, and thus the temperature has relatively less influence on the water absorption. Table 2 shows a water uptake for a series of pristine sPEEK membranes with different DS for comparison with that of semi IPN membranes.

3.4. Proton conductivity

The organosiloxane network concentration effect on the proton conductivity of semi-IPN membranes is shown in Fig. 3a. The proton conductivity of the semi-IPN membranes increases considerably upon increase of the organosiloxane concentration. The semi-IPN

Table 2
Water uptake of pristine sPEEK membranes with different degrees of sulfonation.

Temperature (°C)	Water uptake			
	sPEEK65	sPEEK70	sPEEK75	sPEEK80
40	17.5	26.2	30.2	33.2
60	26.4	32.4	46.0	65.4
70	31.5	50.0	56.7	110
80	76.1	98.2	Dissolved	Dissolved

**Fig. 3.** Proton conductivity of (a) semi-IPN membranes and (b) sPEEK membranes with different degrees of sulfonation.

membranes with a 20 and 24% siloxane network show a proton conductivity even higher than that of Nafion®. It is attributed to the excellent conducting properties of the organosiloxane network associated in the presence of a number of phosphoric acid groups, the proton carriers. If the pristine sPEEK membrane needs to be comparable to Nafion® in terms of proton conductivity, very high DS, over 80%, is thus prerequisite, as shown in Fig. 3b. However, the sPEEK80 membrane swells too much or is dissolved in hot water, above $70\text{ }^{\circ}\text{C}$; as shown in Table 2, this membrane cannot be used in a fuel cell for extended periods of time. In comparison with the sPEEK80, the semi IPN membranes with 24% organosiloxane shows even higher proton conductivity than Nafion® 117, but much lower water uptake than sPEEK80 (see Table 1). In conclusion, preparation of the semi membranes using the two basic components, organosiloxane network and sPEEK65, enhances proton conductivity significantly without noticeable loss of dimensional stability caused by water swelling and dissolution.

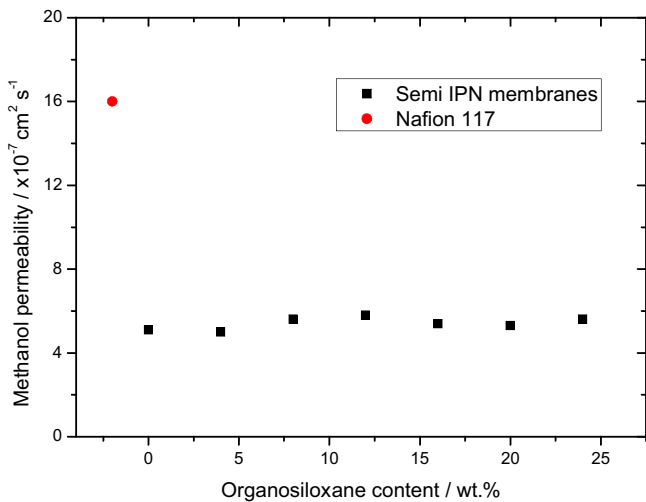


Fig. 4. Methanol permeability of semi-IPN and Nafion® membranes.

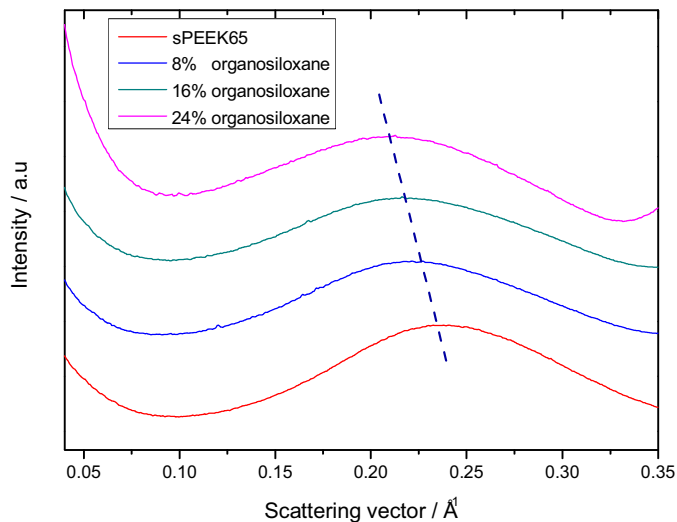


Fig. 5. SAXS patterns of semi-IPN membranes with different organosiloxane content.

3.5. Methanol permeability

Incorporation of the organosiloxane component has negligible influence on the methanol permeability of membranes as shown in Fig. 4. As the semi-IPN membranes show very low methanol permeability, nearly the same as that of pristine sPEEK65 and about one third that of Nafion® 117, those can be promisingly applied in DMFC. Even if the hydrophilic properties increase and thus allow accommodation of more water in the membranes upon addition of the organosiloxane component, the inherent immobile network structure prevents facile permeability of the methanol molecules.

3.6. SAXS analysis

Fig. 5 illustrates the small angle X-ray scattering (SAXS) patterns for semi-IPN membranes prepared after hydration to equilibrium at room temperature. In Fig. 5, the scattering vector of the semi-IPN membranes shifted to the left with an increasing organosiloxane network content, indicating that the average ionic cluster size of the membrane increases with organosiloxane concentration as shown in Table 3. Increased water uptake and proton conductivity by formation of the semi-IPN structure was associated with this ionic cluster size change.

Table 3
Scattering vector and ionic cluster size of semi-IPN membranes.

% of organosiloxane	24	16	8	0
Scattering vector (Å)	0.207	0.216	0.226	0.241
Ionic cluster size (nm)	3.03	2.91	2.78	2.61

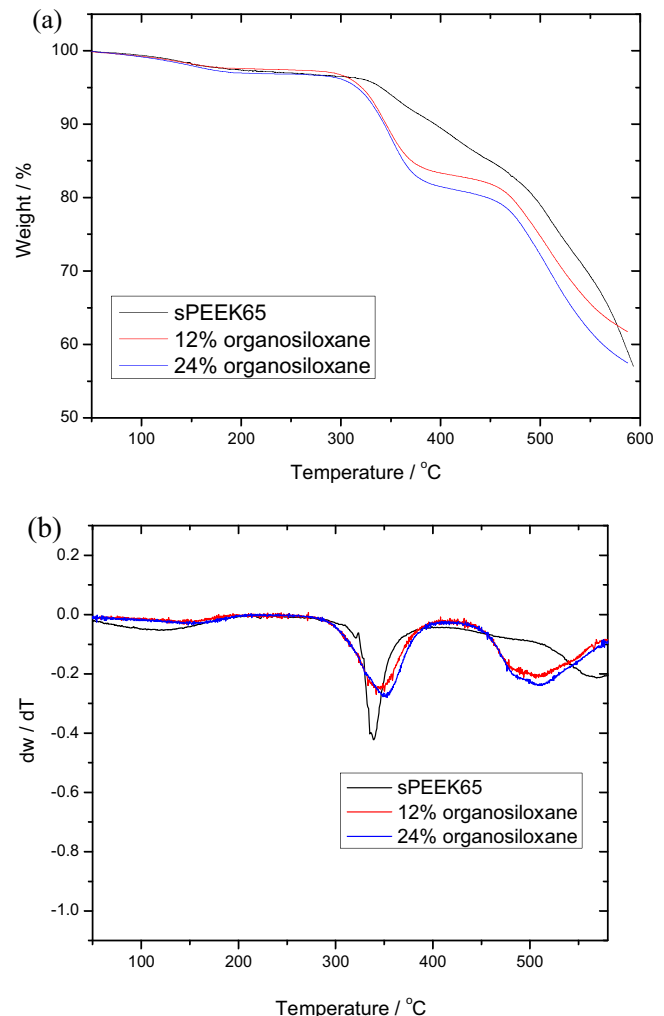


Fig. 6. (a) TGA and (b) DTG curves for sPEEK65 and semi-IPN membranes.

3.7. Thermal and mechanical properties

Fig. 6a and b show the TGA and DTG curves of semi-IPN membranes with different organosiloxane network content. For the pristine sPEEK65 membrane, the first weight loss up to 200 °C is caused by evaporation of water, which was initially absorbed into the sample from the atmosphere, whereas the second weight loss from approximately 330 °C occurs by decomposition of sulfonic acid group, and the third from approximately 470 °C, decomposition of the polymer backbone. For the semi-IPN membranes shown in Fig. 6a and b, the weight loss from 300 to 370 °C is caused by decomposition of both sulfonic acid and phosphoric acid groups, and that from 370 to 470 °C by organic groups contained within the organosiloxane network, followed by decomposition of the PEEK backbone from 470 °C. This analysis confirms that the semi-IPN membranes prepared are thermally utilizable up to 300 °C.

The stress versus strain curves of the semi-IPN membranes are shown in Fig. 7. The tensile strength of the semi-IPN

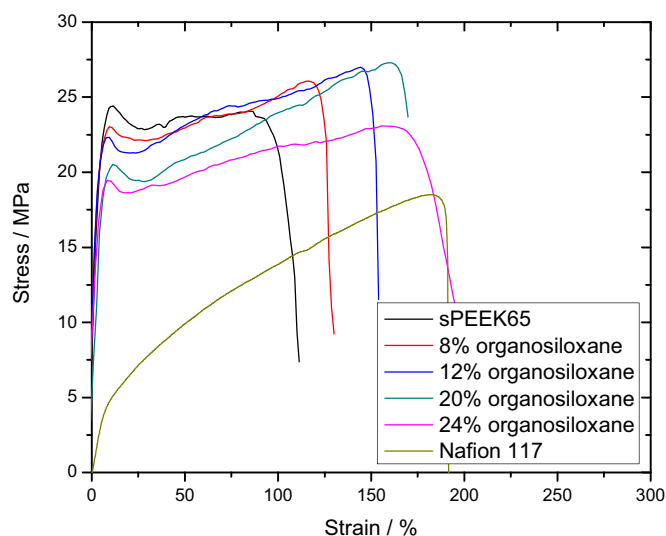


Fig. 7. Stress–strain curves of semi IPN membranes with different organosiloxane content.

membranes reduces with increasing organosiloxane content, as the bare organosiloxane network is mechanically poorer than the bare sPEEK65 in terms of tensile strength. However, all the semi IPN samples prepared in this study show much higher strength than Nafion® (18.1 MPa). Also, addition of organosiloxane component renders the membranes more flexible. The elongation at break increases with increasing organosiloxane content. The elongations at break for 0, 8, 12, 20, 24% semi-IPN and Nafion membranes are 90, 120, 145, 162, 170 and 188%, respectively. The increase in the flexibility reduces the surface energy of the membrane, presumably leading to enhancement of adhesion strength between membrane and catalyst-embedding layers in MEA fabrication.

3.8. DMFC performance

Fig. 8a and b show the single cell DMFC performance of semi-IPN membranes operated at 80 °C. Methanol aqueous solution (2.0 M) was introduced in the anode side as a fuel, and the oxygen in the cathode at 0.2 MPa. The cell performance of the semi-IPN membranes is superior to that of pristine one, showing a slight increase in the open circuit voltages (OCV) from 0.65 to 0.69 V with increasing organosiloxane content up to 24 wt% in Fig. 8a. At the fixed current density of 320 mA cm⁻², the cell voltages of pristine sPEEK65, 16 wt%, 24 wt% organosiloxane semi IPN, and Nafion® 117 membrane are 0.27, 0.335, 0.378 and 0.38 V, respectively in Fig. 8a. In Fig. 8b, the power density of the semi-IPN membranes increases with increasing organosiloxane content. While the pristine sPEEK65 membrane shows a maximum power density of 85 mW cm⁻², the semi-IPN membranes with 12 and 24 wt% organosiloxane, showed 121 and 135 mW cm⁻², respectively. This enhancement of cell performance for the semi-IPN systems is attributed to the increased proton conductivity (reduced ohmic resistance) with low methanol permeability maintained by addition of the organosiloxane component into sPEEK65 membrane. Moreover, the organosiloxane composite membranes are so flexible that the interfacial resistance could be reduced due to the good adhesion between catalyst layer and membrane.

4. Conclusions

The semi-IPN membranes composed of the sPEEK65 and organosiloxane-based hybrid network are prepared. The proton

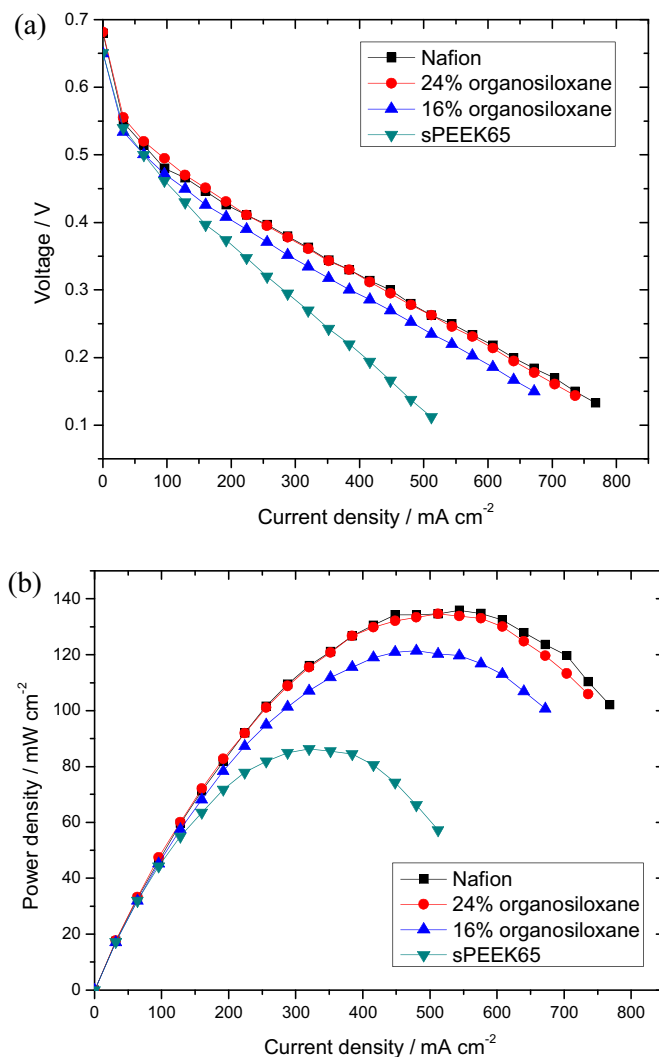


Fig. 8. (a) Polarization curves, (b) power density of semi IPN and Nafion® 117 membranes.

conducting property of the semi-IPN membranes is provided not only by the sulfonic acid groups in the sPEEK, but the phosphoric acid groups in the organosiloxane component. The proton conductivity incrementally increases with the organosiloxane concentration, and reaches that of Nafion® at 20 wt%. The semi-IPN membranes prepared show very low methanol permeability, about one third of Nafion®, but no noticeable increase of methanol permeability is observed upon addition of the organosiloxane component. Addition of organosiloxane also increases water uptake. The membrane containing 24% organosiloxane is, however, still stable in water at 80 °C, where the proton conductivity is even higher than Nafion® 117. The pristine sPEEK80 membrane also shows proton conductivity comparable to Nafion®, but this membrane is not useful in a fuel cell due to tremendous swelling and dissolution in 80 °C water. From the SAXS patterns, the enhanced proton conductivity of semi IPN systems is attributed to the increase in ionic cluster size. The semi-IPN membranes possess a high thermal stability up to 300 °C and a higher tensile strength than Nafion® 117. The maximum power density of the MEA fabricated with the semi-IPN membrane with 24% organosiloxane is 135 mW cm⁻²; its excellent cell performance is attributed to the increased proton conductivity with low methanol permeability provided by the semi IPN membrane structure.

Acknowledgments

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