

Synthesis and Characterization of Sulfonated Poly(phthalazinone ether sulfone)(sPPES)/Silica Membrane for Proton Exchange Membrane Materials

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Abstract: Organic-inorganic composite membranes based on sulfonated poly(phthalazinone ether sulfone) (sPPES)/silica hybrid were prepared using the sol-gel process under acidic conditions. The sulfonation of PPES with concentrated sulfuric acid as sulfonation agent was carried out to prepare proton exchange membrane material. The behaviors of the proton conductivity and methanol permeability are depended on the sulfonation time (5-100 hr). The hybrid membranes composed of highly sulfonated PPES (IEC value : 1.42 meq./g) and silica were fabricated from different silica content (5-20 wt%) in order to achieve desirable proton conductivity and methanol permeability demanded for fuel cell applications. The silica particles within membranes were used for the purpose of blocking excessive methanol cross-over and for forming the path way to transport of the proton due to absorbing water molecules with $\equiv\text{SiOH}$ on silica. The presence of silica particles in the organic polymer matrix results in hybrid membranes with reduced methanol permeability and improved proton conductivity.

Keywords: sulfonated poly(phthalazinone ether sulfone), silica, proton conductivity, methanol permeability, hybrid membrane

1. Introduction

A direct methanol fuel cells (DMFCs) using polymer electrolyte membranes are one of the most attractive power sources for a wide range of application from vehicles to portable utilities due to the stable operation at a rarely low temperature, the high energy generation yield and energy density, the simplicity of system[1,2]. Most DMFC research has concentrated on polymer electrolyte membrane fuel cells (PEMFC) fed directly with methanol[3]. Methanol itself is a fuel that possesses significant electroactivity and can be oxidized directly to carbon dioxide and water in so called direct methanol fuel cells[4,5]. The proton diffusion across

the membrane is associated with water transport in the membrane and methanol is also transported to the cathode by electro-osmotic drag, that is, methanol cross-over, due to the similar properties of methanol (such as its dipole moment), and consequently, a decrease in cell performance[6,7].

Sulfonation is commonly applied to modify polymers to increase hydrophilicity and ionic character[8-11]. For example, sulfonated polysulfones and polyetherketones have been reported to be useful in desalination, ion exchange and fuel cell membrane applications[12-14]. The poly(phthalazinone ether sulfone ketone)(PPESK) family of polymers has high glass transition temperatures and excellent physical properties and thermostability. Membranes made from PPESK have shown good separation and permeation properties for gas and liquid separation. Sulfonated PPESK has been prepared

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Table 1. Comparison of $[\eta]$ Before and After Sulfonation of PPES

Sample	$[\eta]$ before sulfonation	$[\eta]$ after sulfonation	% Increase in $[\eta]$
PPES	1.16	-	-
SP 5	1.16	1.214	4.64
SP 10	1.16	1.221	5.21
SP 20	1.16	1.304	12.4
SP 40	1.16	1.323	14.0
SP 60	1.16	1.425	22.8
SP 100	1.16	1.515	30.6

from previously synthesized polymers to improve the polymers' hydrophilicity and thereby utilize this type of polymer for membranes for application in ion exchange membrane[15]. Yan et al[16]. reported that sulfonated poly(phthalazinone ether sulfone)s were prepared to improve the hydrophilicity and thereby to use as polymer electrolyte membrane. Recently, the sulfonation and synthesis methods of poly(phthalazinone arylene ether)s have been reported for proton exchange membrane materials and these membrane shows high proton conductivity of up to $\sim 10^{-2}$ S/cm[17,18]. However, the methanol transport behavior of these membranes was not reported.

The preparation of hybrid organic-inorganic composites has attracted much attention because such hybrids may show controllable properties such as optical, electrical and mechanical behaviors by combining the properties of both organic polymer and inorganic compound[19, 20]. In the organic-inorganic hybrid, inorganic minerals precipitate in situ regularly in the organic polymer matrix, and the strong interaction between the organic polymer and inorganic mineral may result in a hybrid of markedly improved mechanical properties.

Considerable effort has been developed in order to reduce methanol crossover as well as to reach high proton conductivity ($\sim 10^{-2}$ S/cm). Membranes containing metallic blocking layers were proposed[21]. Organic-inorganic composite membranes containing Zr-phosphonates[22], zeolites[23] or silica[24] were investigated.

In this study, the proton exchange membranes were prepared using PPES as the base materials. The introduction of sulfonic acid group into polymer matrix was

achieved by the sulfonation with concentrated sulfuric acid under a variety of conditions. To reduce methanol permeability, silica domain was introduced into the polymer matrix using sol-gel process. Here, we might expect that the introduction of sulfonic group and silica domain might lead to both high proton conductivity and low methanol permeability. Their water swelling, proton conductivity and methanol permeability were investigated in an attempt to characterize membranes for DMFC application.

2. Experimental

2.1. Materials

Polymer used in this study was PPES (Mw = 86000; Polymer New Material Co., Ltd. China). N-methyl-2-pyrrolidinone (NMP), concentrated (98%) sulfuric acid, fuming sulfuric acid and other chemicals were obtained commercially and used without further purification. The tetraethyl orthosilicate (TEOS) and methanol (MeOH) used were also purchased from Aldrich, and were of analytical grade. The water used was distilled and deionized water.

2.2. Preparation of Membranes

PPES was dried in a vacuum oven at 120°C for 24 h. PPES and concentrated sulfuric acid were placed in a three-neck reaction vessel equipped with a mechanical stirrer. The sPPES with different degrees of sulfonation was obtained at certain reaction temperatures (60°C) and times (5~100 hr), as shown in Table 1. The polymers were precipitated in ethanol and then filtered.

The polymers were washed with ethanol/water to remove acid until pH was neutral, then swelled and washed with water. All the polymers were filtered and then dried in a vacuum oven at 120°C for 24 hr. The nomenclature used for the membrane described in this article is as follows. We use SP-xx symbolism, where xx refers to the sulfonation time.

Inorganic-organic hybrids were prepared by dissolving sulfonated PPES (sPPES) in NMP, and followed by the addition of TEOS solution. The TEOS solution was prepared in advance using a H₂O/TEOS/HCl (mole ratio of 4/1/0.1) solution, which were stirred at room temperature. The amount of TEOS was 5, 10, 15, and 20% by weight to sPPES weight. After hydrolysis, the mixture becomes a clear silica sol. The solution containing silica sols were mixed together with sPPES solution and stirred for 12 h at room temperature under N₂ gas. This solution was poured into a glass plat and cast using the doctor blade process. Freshly cast films were initially heated at 80°C for 24 h, then 100°C for 24 h. The nomenclature used for the membrane described in this article is as follows. We use SP-Si-xx symbolism, where xx refers to weight percentage of TEOS.

2.3. Characterization

2.3.1. IR Spectroscopy

The films with various amount of silica were analyzed by Fourier transform infrared (FT-IR, Nicolet Model Magna IR 550, Madison, WI, USA). All the films were dried in a vacuum oven for at least 2 day to remove water and kept under the nitrogen atmosphere before the analysis.

2.3.2. Scanning Electron Microscope

To investigate the morphology of films, fracture surfaces were investigated by field emission scanning electron microscope (FE-SEM, Jeol Model JSF 6340F, Tokyo, Japan). All the films were gold coated and mounted on aluminum mounts with carbon paste. The silica distribution was analyzed using an Energy dispersive spectrometer (EDS) attachment of the FE-SEM.

2.3.3. Thermal Analysis

The process of degradation and thermal stability of dry membranes were monitored by thermogravimetric analysis (TGA, Perkin-Elmer TGA7). The TGA measurements were carried out under the nitrogen atmosphere at a heating rate of 10°C/min from 50 to 700°C. All the films were dried in a vacuum oven to remove water and kept under the nitrogen atmosphere before the analysis.

2.3.4. Dynamic Vapor Sorption (DVS) and Measurement of Water Swelling Ration

Water vapor sorption experiments were carried out using a dynamic vapor sorption apparatus (DVS-1000, Surface Measurement Systems Ltd., London, UK).

The water content was measured by following.

After soaking the samples in distilled water for more than 24 hr, they were wiped filter paper and weighed immediately. The samples were then dried under a vacuum condition until a constant weight was obtained. Water swelling ration was determined by the following equation:

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

where, W_{wet} and W_{dry} are wet and dried membrane weight, respectively.

2.3.5. Ion-exchange capacity (IEC meq./g)

After immersing the samples in distilled water, they were soaked in a large volume of 0.1 mol/L HCl solution to change them into H⁺-form. They were washed with distilled water to remove excess HCl and then equilibrated with exact 100 mL of 0.1 mol/L NaOH solutions for 24 h. IEC was determined from the reduction in alkalinity measured by back titration.

2.3.6. Proton Conductivity and Methanol Permeability

The impedance of the membranes was determined by using an electrode system, which contained a four-probe cell depicted in Figure 1, connected with an im-

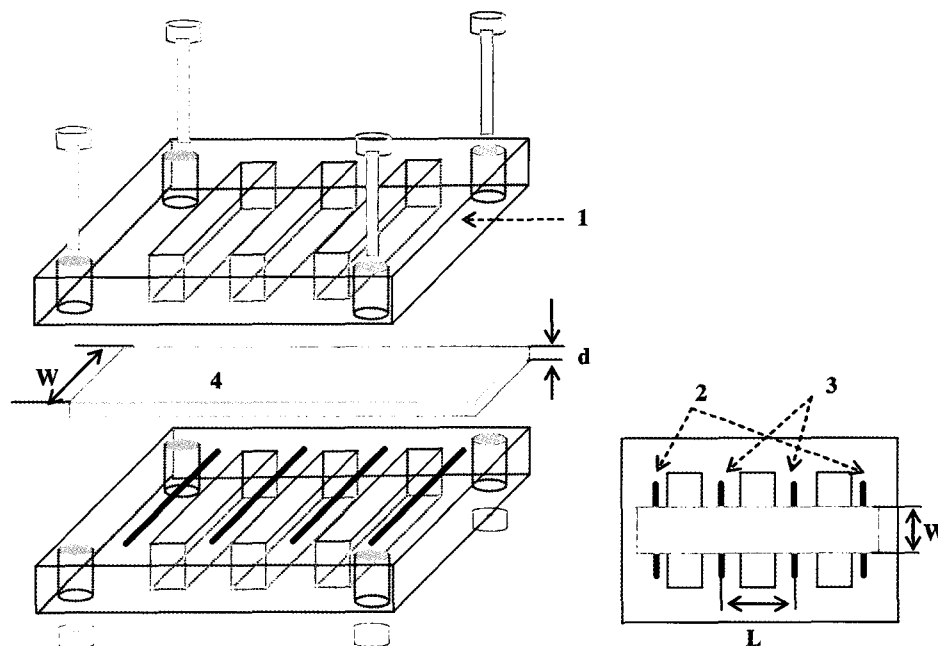


Fig. 1. Four-point probe conductivity cell for measuring proton conductivity (1) Teflon block; (2) Pt wire outer current-carry electrode, (3) Pt wire inner potential-sensing electrode (4) membrane specimen (4 cm × 1 cm).

pedance/gain-phase analyzer (Solatron 1260, Solatron Analytical, UK) in combination with an electrochemical interface (Solatron 1287). The hydrated membrane with deionized water during 24 hr was cut in (4 × 1) cm² prior to mounting on the cell. The cell was placed in a thermo-humidity controlled chamber to measure both the temperature and the humidity dependence of proton conductivity. Here, a fixed AC current was passed through two outer electrodes, and the conductance of the sample was obtained from an AC potential difference between the two inner electrodes. This method is relatively insensitive to the contact impedance and interfacial resistance at the current-carry electrode and is therefore well suited for measuring the proton conductivity. All measurements were carried out in the sealed cell to keep a suitable hydrated condition at a given temperature and the proton conductivity was obtained from

$$\sigma = \frac{L}{R \cdot S} \quad (2)$$

where σ is proton conductivity (in S/cm). L is the

distance between the counter electrodes and the working electrode used to measure the potential (1 cm). R is the impedance of membrane (in Ω). S is the surface area required for proton to penetrate the membrane (in cm²).

Methanol permeability of the membranes was determined using a diaphragm diffusion cell. This cell consisted of two reservoirs, each with a capacity of approximately 80 mL, separated by a vertical membrane. Prior to the test, the membranes were equilibrated in deionized water for at least 12 h. Initially, one reservoir (V_A) was filled with a 2 M methanol-water solutions, and the other reservoir (V_B) was filled with only pure ionized water. The concentration of methanol diffused from reservoir V_A to V_B across the membrane was measured with time using gas chromatography equipped with a thermal conductivity detector (Shimadzu, GC-14B, Tokyo, Japan). Under pseudosteady-state conditions and for $C_B \gg C_A$, the methanol concentration in the receiving chamber as a function of time is given by

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0) \quad (3)$$

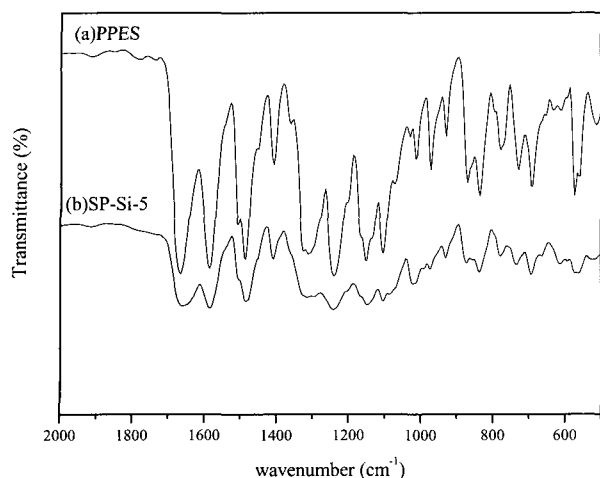


Fig. 2. FT-IR spectra of the membranes. (a) Pure PPES (b) SP-Si-5 hybrid membrane.

$$P = DK = \frac{1}{A} \frac{C_B(t)}{C_A(t - t_0)} V_B L \quad (4)$$

where C_B and C_A are the methanol concentration of permeated and feed side through the membrane, respectively. A and L the membrane area and thickness; D and K are the methanol diffusivity and partition coefficient between the membrane and the adjacent solution, respectively. The product, DK , denotes the membrane permeability ($P(\text{cm}^2/\text{s})$). The value of C_B was measured several times during the experiments, and the permeability was calculated from the gradient of the straight lines obtained from plots of the data.

3. Results

3.1. Structural Characterization of the sPPES Membranes

The FT-IR spectra obtained are shown in Figure 2 for PPES and SP-Si-5 membranes. In the spectra of sPPES, two new absorption peak appear at 1018 and 1079 cm^{-1} , which are absent in PPES. These are characteristic of the aromatic SO_3H symmetric and asymmetric stretching vibration, respectively. The IR spectra have an absorption band at 1666 cm^{-1} , due to the Ar-C=O stretching, an absorption band of aromatic C=C stretching at 1591 cm^{-1} and C-O-C stretching vibration

peak at 1240 cm^{-1} [25]. The broad band at around 1500 cm^{-1} , which can be observed in the spectrum of PPES, related to the aromatic ring 1, 4-substitution are seen in the spectra of sPPES, due to the sulfonic acid group. In addition, the new absorption peaks appear at 1085 cm^{-1} (characteristic of the Si-O-Si asymmetric stretching) in sulfonated hybrid membrane, which are absent in the PPES membrane. This indicates that the sol-gel reaction was successfully carried out.

The $^1\text{H-NMR}$ spectrum of PPES shown in Figure 3 (a) is broadly divided into four groups of multiplets: 8.68-8.53, 8.04-7.74, 7.72-7.6, and 7.26-7.06. The starting point for the peak assignment of $^1\text{H-NMR}$ of PPES was the absorptions resulting from atoms surrounding the electron rich ether moiety. As reported earlier[17], in a PPES repeat unit, the hydrogen atoms at the ortho position to the ether linkage were more shielded than any other hydrogen atoms because of a resonance effect of the oxygen's lone pair of electrons. As shown Figure 3, the furthest upfield signals (7.26-7.06 ppm) arose from the ortho to the ether linkage. It is most likely that it corresponds to H1/H4 of PPES phthalazionone units and/or H14/H15 of PPES phenyl ether group. Guiver et al[15] reported that H1/H4, meta to phthalazionone and ortho to the phenyl ether group, is the site where sulfonation is likely to occur most readily. The product of the sulfonation reaction is expected to occur at H1/H4 and H14/H15 on sPPES, as shown in Figure 3. A higher chemical shift upfield would indicate that protons on this site would be most susceptible to sulfonation by electrophilic substitution[15].

As shown in Figure 3(b), the ^1H spectrum of sPPES shows on d diminished upfield doublet, suggesting that sulfonation occurs at H1/H4. Other characteristic of spectrum is the appearance of series of downfield signals at 8.46 as well as the disappearance of the multiplet at 8.67-8.53. These obvious changes in chemical shift suggest that the presence of SO_3H groups perturbs the downfield protons in the same aromatic ring[15].

3.2. Viscosity of the Sulfonated PPES (sPPES)

The inherent viscosities of sPPES were determined

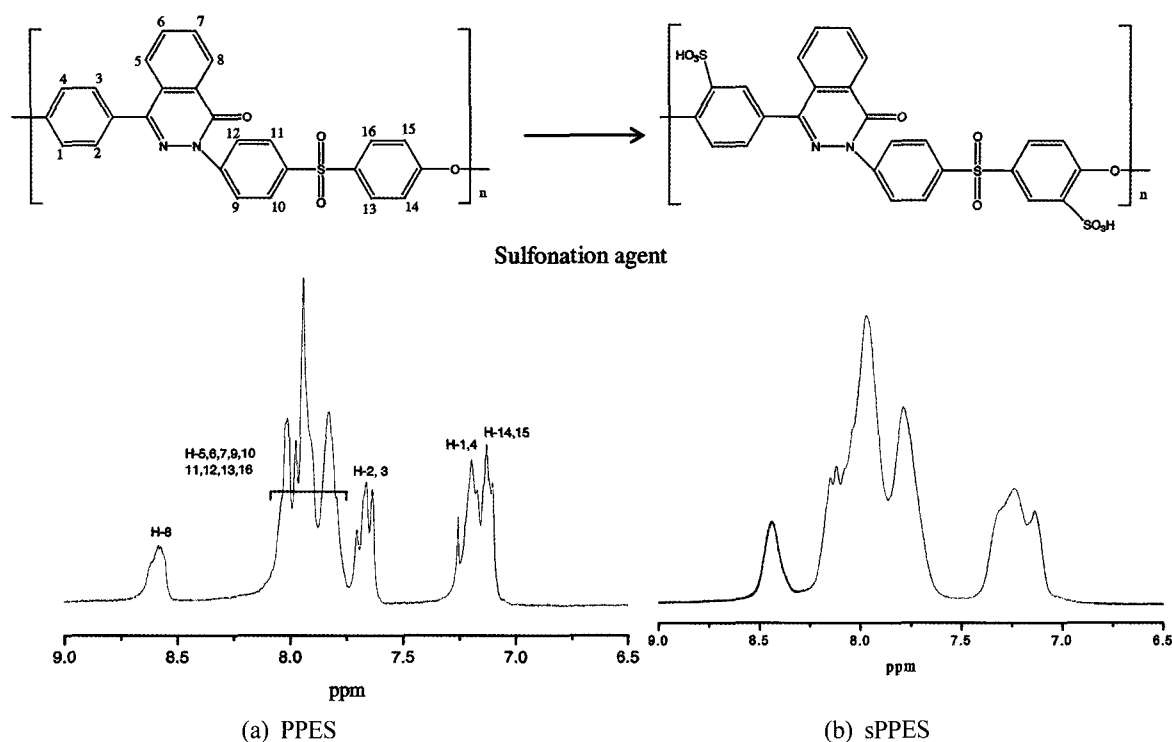


Fig. 3. ^1H NMR spectrum of (a) PPES (b) sPPES.

Table 2. Characteristics of the Membranes

Sample	IEC (meq./g)	Water content (%)	Proton conductivity (S/cm)	Methanol permeability (cm^2/s)
Nafion 117	0.9	26.5	2.54×10^{-2}	2.11×10^{-6}
SP 5	0.26	7.1	1.45×10^{-4}	4.36×10^{-9}
SP 10	0.41	9.6	5.68×10^{-4}	8.57×10^{-9}
SP 20	0.64	12.4	2.54×10^{-3}	1.40×10^{-8}
SP 40	0.8	15.6	5.74×10^{-3}	2.46×10^{-8}
SP 60	1.0	30.5	2.6×10^{-2}	1.37×10^{-7}
SP 100	1.42	42.7	4.7×10^{-2}	3.39×10^{-7}
SP-Si 5	1.41	46.5	6.4×10^{-2}	2.90×10^{-7}
SP-Si 10	1.39	50.4	7.2×10^{-2}	2.81×10^{-7}
SP-Si 15	1.4	46.5	5.6×10^{-2}	2.50×10^{-7}
SP-Si 20	1.4	40.5	4.1×10^{-2}	2.40×10^{-7}

using an Ubbelohde viscometer at a polymer concentration of 0.1 wt% in N,N-dimethylacetamide at 25°C. The inherent viscosity of sPPES with respect to IEC is shown in Tables. 1, 2. It was found that the inherent viscosity increased with the sulfonation degree. There is a significant increase in viscosity by the presence of a SO_3H group on the PPES polymer chain. All the sulfonated membranes have higher inherent viscosity

than the PPES, probably because the introduction of SO_3H groups leads to enhancement of interchain interactions with a consequent higher resistance to the stretching of the main chains.

3.3. Scanning Electron Microscope

Figure 4 shows SEM images of the hybrid membranes. Silica microparticles are observable. The average

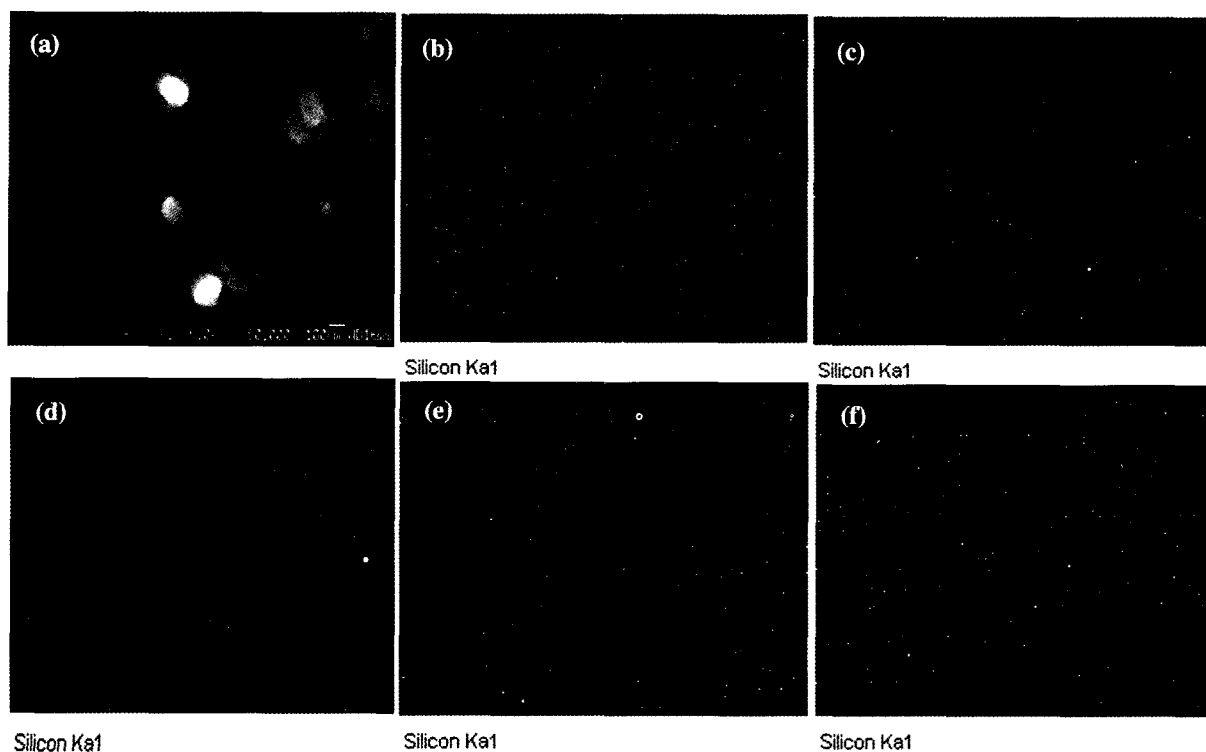


Fig. 4. SEM image (a) surface of SP-Si-5, EDS data surface: $60 \times 60 \mu\text{m}$ ((b)SP-Si-5) and cross-section ((c) SP-Si-5, (d) SP-Si-10, (e) SP-Si-15, (f) SP-Si-20).

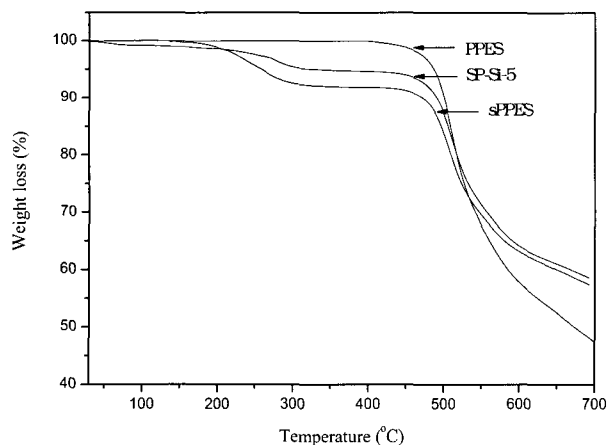


Fig. 5. TGA curves.

size of the silica microparticles is about $<100 \text{ nm}$. The silica microparticles were confirmed by energy-dispersive X-ray analysis (EDXA).

The silica particles were well-dispersed in the polymer matrix from the surface to the bulk state. The silica added to the polymer solution led to the formation of a common network providing a good adhesion between

organic and inorganic phases.

To determine the presence and distribution of silica in the hybrid membrane, EDS analysis was made on the cross-section of the membrane. Figure 4 shows the result of the EDS analysis for the hybrid membranes. The hybrid membranes reveal the silica as shown the bright dots. The silica particles were well-dispersed in the polymer matrix with silica contents.

3.4. Thermal Analysis

The TGA curves of membranes under nitrogen are shown in Figure 5. The pure PPES is stable until $450\text{--}500^\circ\text{C}$, when decomposition of the main chain occurs, whereas sulfonated PPES membranes show several steps of weight loss. They are due to the process of thermal salvation, thermal desulfonation and thermooxidation of a polymer matrix, respectively. The process of thermal salvation of the sPPES was not shown because the membranes were dried before the analysis. However, the SP-Si-5 hybrid membrane shows

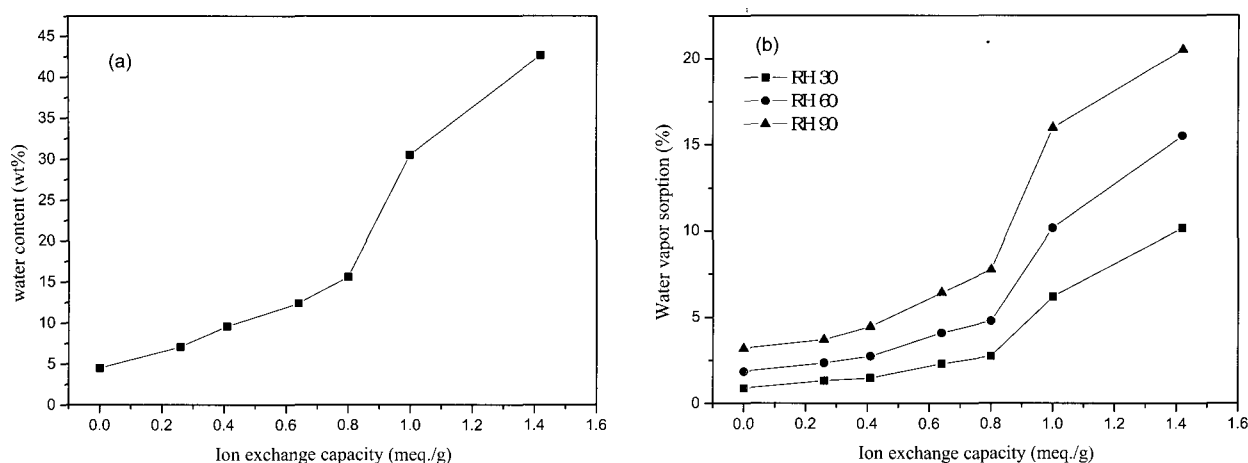


Fig. 6. (a) Water content and (b) water vapor sorption (%).

the thermal salvation step as shown in Figure 5. From the results of Figure 5, the water molecules were not evaporated from the hybrid membrane due to the strong hydrogen bond between water molecule and $\equiv\text{SiOH}$.

Two main degradation steps were shown by TGA curve of prepared membranes. They are due to the process of thermal desulfonation and thermooxidation of a polymer matrix. The first weight loss process (between 200 and 350°C) corresponded to a loss of sulfonic acid by the desulfonation. In the second weight loss process (after 450°C), the polymer residues were further degraded, corresponding to the decomposition of main chain of polymer.

3.5. Ion Exchange Capacity (IEC) and Water Contents

The water molecules and IEC as it is confined in the membrane play a significant role in determining the membrane transport properties such as proton conductivity and methanol permeability.

As shown in Table 2, IEC value (meq./g) linearly increased with the sulfonation time. The membranes prepared for each condition possessed IEC values in the range 0.26~1.42 meq./g for the dry membrane. The gradual increase of the sulfonation time yields higher IEC values in the membranes which leads to an increase in both the proton conductivity and the water

content of the membranes.

The total water content (%) and water vapor sorption (%) are shown in Figure 6. The total water content (%) linearly increased up to 40 hr of the sulfonation time, and then dramatically increased above 40 hr. This behavior was also observed in the water vapor sorption (%) results. The percolation threshold for water content occurred with the 40 h of the sulfonation time. The morphological development with the sulfonation time explained the water content behavior; the hydrophilic domain structure significantly increased with the sulfonation time, resulting in an abrupt increase in water contents. The percolation threshold for water content and morphology essentially occurred with the sulfonation times. This behavior was shown in the methanol permeability test, and this behavior will be discussed in the following section.

As listed in Table 2, the total water content of the hybrid membranes increase up to silica content of 10 wt%, and above this silica content, the water content in the hybrid membranes is not enhanced. The inserting silica enhanced the hydrophilicity in membrane due to the presence of numerous $\equiv\text{SiOH}$ groups. These $\equiv\text{SiOH}$ groups, which can hydrogen bond, have stronger bonding with H_2O molecules than $\text{SO}_3\text{H}-\text{H}_2\text{O}$ groups can. However, the limit of enhancement of the hydrophilicity could be existed due to the number of $\equiv\text{SiOH}$ group, implying that the membranes with a higher content of

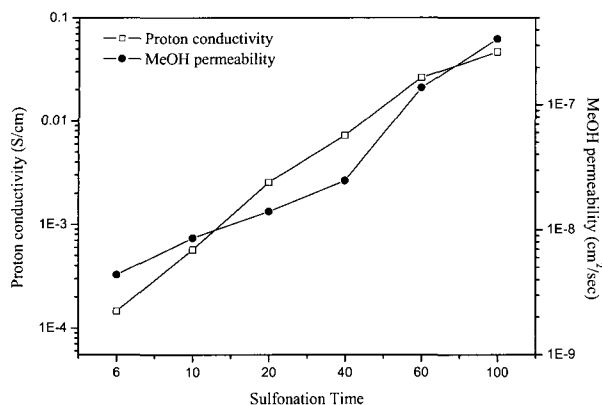


Fig. 7. Proton conductivity and methanol permeability (at 30°C) via sulfonation time.

SiO₂ do not always show higher water content.

3.6. Proton Conductivity and Methanol Permeability

Figure 7 shows a plot of the proton conductivity and methanol permeability of the membranes as a function of the sulfonation time. The proton conductivity increases with the sulfonation level. As sulfonation level increases, the number of hydrophilic domain gradually increases and finally water cluster begins to be closed so as to give rise to increase the proton conductivity.

The proton conductivity of the sulfonated polymers depends on charge carriers and on their mobility which is mainly ensured by water molecules and their clusters. Therefore, the hydrophilic pathway through which protons can pass easily may be broader with sulfonated monomer content by increasing water molecules-accessible space around charged group such as sulfonic acid group.

The proton conductivity mechanism through the proton exchange membrane was well-known to occur via two routes[26]. One is a hopping or jumping (Grotthuss) mechanism that a proton is passed down a chain of water molecules. The other is a vehicle mechanism that a proton combines with vehicles such as H₃O⁺ or CH₃OH₂⁺ and unprotonated vehicles (H₂O) allow the net transport of protons.

The methanol permeability of all SP membranes is

dependent on the content of sulfonation time and also lower than that of Nafion 117 (2.11×10^{-6} cm²/s). The methanol permeability linearly increased up to 40 hr of the sulfonation time, but a sudden leap is observed, referred as "percolation threshold" above 40 hr. Generally, the introduction of a hydrophilic moiety such as sulfonic acid group of polymer chains enhances the water content, and also methanol molecules can pass through the hydrophilic domains. As reported before[27,28], it seems that the proton conduction and the methanol permeation mostly take place through the same pathway in the membranes, such as hydrophilic cluster channels.

In the case of the SP membranes, the behavior of percolation was observed in the water content and methanol permeabilities, but is not observed in the proton conductivities of the SP membranes. A possible explanation for this behavior is related to the proton and methanol transport mechanism. The proton transports through the proton exchange membrane *via* water molecules due to Grotthuss and Vehicle mechanism. Therefore, the proton conductivity of the SP membranes linearly increases with the sulfonation level. However, the methanol permeability of the membranes shows a non-linear behavior; an abrupt increase in permeability was observed from 40 hr of the sulfonation time. We reported that[29,30] the methanol permeability can be reduced by reducing the free water content of the membrane, maintaining the high proton conductivity.

The proton conductivity increased up to an silica content of 10 wt% as listed in Table 2. This result suggests that the silica doped in membrane effect on forming the path way to transport proton due to absorbing water molecules. Therefore, the proton conductivity increased due to the synergy effect between the hydrated sulfonic group and the hydrated silica particles absorbed water molecules. However, this effect was not shown the SP-Si 15 hybrid membrane. We supposed that the SP-Si 15 hybrid membrane has the excess water molecules that may be preferentially distributed into the silica phase, and this water available for proton conduction may be lower. The methanol permeability de-

creased with silica content. It is known that methanol permeates through hydrophilic ionic channels. Therefore, it is expected that the methanol permeability should be decreased by blocking the ionic channels. The silica particles in membrane were used as materials for methanol transport blocking and for forming the path way to transport proton due to absorbing water molecules.

4. Conclusion

We reported experimental finding that the proton and methanol transport behavior of the sulfonated PPES and sPPES/silica hybrid membrane is related to the sulfonation time and silica contents. The silica was well-dispersed in the polymer matrix from the surface to the bulk state. The silica particles within membranes were used for the purpose of blocking excessive methanol cross-over and for forming the path way to transport proton due to absorbing water molecules with $\equiv\text{SiOH}$ on silica.

The hybrid membranes show higher proton conductivity and lower methanol permeability than that of Nafion 117 at low temperature. The presence of silica particles in the organic polymer matrix, which increase the water content due to the $\equiv\text{SiOH}$ on the surface of silica derived from sol-gel reaction, results in hybrid membrane with reduced methanol permeability and improved proton conductivity.

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