CHAPTER VI

HIGH PROTON CONDUCTIVITY ZSM-5/SULFONATED POLY(ETHER KETONE ETHER SULFONE) (S-PEKES) COMPOSITE PROTON EXCHANGE MEMBRANE FOR USING IN DIRECT METHANOL FUEL CELL

6.1 Abstract

Composited proton exchange membranes consisting of ZSM-5 embeded in sulfonated(poly ether ketone ether sulfone) (S-PEKES) were fabricated by solvent casting technique in a dispensed zeolite polymer solution. Composite membranes with ZSM-5 content up to 10%v/v exhibit good mechanical properties. The influences of Si/Al and amount of the ZSM-5 on the proton conductivity, methanol permeability, physical properties, and thermal stability of the membranes are investigated. The composite membranes are characterized by FTIR, TGA, LCR meter, and GC techniques. The important properties of the composite membrane are compared with the pristine S-PEKES and Nafion 117 membranes.

Keywords: Sulfonatedpoly(ether ketone ether sulfone); ZSM-5; Proton Exchange Membrane (PEM); Proton conductivity

6.2 Introduction

Direct methanol fuel cell (DMFC) generally has more advantages than the proton exchange membrane fuel cell (PEMFC) due to its low cost, easy handling and storage. Moreover, it does not require the re-charging time, the methanol can be fed to the anode directly and the DMFC can produced electricity immediately. DMFC take advantage of a higher energy density per unit volume with respect to hydrogen-fed units (Antonucci et al., 1999). It has attracted substantial interest as an alternative energy source for applications in various portable devices such as mobile phone, laptop, and etc. A polymer electrolyte membrane (PEM) is a solid polymer

electrolyte membrane used in both PEMFC and DMFC. However, PEM requires some specific properties, it is an electrical insulator which allows protons to pass through and acts as a barrier to prevent the fuell crossover. Currently used PEM is Nafion produced by Dupont, it is sulfonated tetrafluoroethylene ionomer which has sulfonic scid group along the polymer backbone. Nafion has excellent proton conductivity in the fully hydrated state However, it still has high methanol permeability and cannot be used at high temperature above 80 to 100 °C. Furthermore, it is very expensive. The challenges for developing PEM (Carette *et al.*, 2001) are high proton conductivity and thermal stability, low cost, and methanol permeability.

In recent years, there are many types PEM developed: polybenzimidazoles, polyphenylquinozalines, poly(phenylene oxide), poly(phenylene sulfide), poly(aryl ether sulfone)s, poly(aryl ether ketone)s, polyphosphazenes, etc. There have been many routes to increase the proton conductivity such as grafting fuctional groups that can conduct protons, direct polymerization of sulfonated monomer, polermer blends, and composite membranes (Roziere *et al.*, 2003). Many research works focus on fabricate composite membrane with high proton conductivity, in order to improve the functioning of PEM, by modifying the membrane composition throug adding fillers. Adding an inorganic into the polymer matrix is for reducing methanol permeability, increasing proton conductivity, maintainng water at high temperatures, and increasing mechanical support (Ramirez-Salgado *et al.*, 2007). In this context, the incorporation of inorganic fillers such as zeolites, into the sulfonated polymer matrix, has been developed to form composite proton exchange membranes. The incorporation of a zeolite, within a suitable polymer matrix, can offer several utilities: proper mixing of fillers and polymer at a molecular level provides higher mechanical stability than a pristine polymer membrane; the proton conductor particles can provide pathway on the surface for proton transport. The higher surface area could also help to increase the proton conductivity (Smitha *et al.*, 2005).

In the previous work, the proton conductivity of the composite membranes based on zeolite fillers embedded in Nafion were fabricated. Two natural zeolites were selected as inorganic fillers: chabazite and clinoptilolite. The presence of these zeolites affected proton conductivity, methanol permeability, and selectivity of the

membranes (Tricoli *et al.*, 2003). The self-humidifying polymer electrolyte membrane was fabricated by incorporating zeolite HY-supported Pt particles into Nafion, therefore maintaining the water level inside the membrane due to the zeolite hygroscopic property (Son *et al.*, 2007). Furthermore, the series of zeolite A/Nafion 117 membranes were studied, for DMFC towards decreasing methanol permeability as much as 86% (Li *et al.*, 2007). The systems of zeolites 3A, 4A, 5A, 13X, modenite, and HZSM-5 incorated into chitosan matrix were also studied; they found that the hydrophobic zeolites could help to prevent the methanol diffusion, whereas the hydrophilic zeolites increase the methanol permeability of (Wang *et al.*, 2008). Sulfonated poly(ether ether ketone) is one of the candidates for PEM, the zeolite beta was shown to improve the proton conductivity of this system. The highest conductivity belonged to the zeolite beta/SPEEK composite membrane having a SiO_2/Al_2O_3 ratio of 50 at 10%wt loading (Sengul *et al.*, 2009).

In this work, the objective is to exploit the molecular sieving properties of the zeolite ZSM-5 to increase the proton conductivity. The effects of a SiO_2/Al_2O_3 ratio and zeolite content were investigated. The S-PEKES was used as the polymer matrix, where the synthesized process has been established elsewhere (Changkhamchom *et al.*, 2010). The S-PEKES with a sulfonation degree of 0.66 was chosen to prepare the composite membranes. The ZSM-5 zeolite with different Si/Al ratio were used as the inorganic fillers at various volume percentages. All composite membranes were fabricated by solvent casting. The influence of the molecular sieves on the water uptake (%), thermal and mechanical properties, proton conductivity, and methanol permeability of the membranes were characterized and compared with those of the pristine S-PEKES and Nafion 117 membranes.

6.3 Experimental

6.3.1 Materials

Nafion 117 was purchased from Electrochem, Inc. Bisphenol S or 4,4'-dichlorobenzophenone and 4,4'-sulfonyldiphenol (98–99%, Aldrich) were used as the monomers. Concentrated sulfuric acid (Univar, 98 wt%), sodium chloride

(Univar, 99.9%), , and sodium hydroxide (Univar, 97%) were used as received. Toluene (Fisher-Scientific 99.99%), potassium carbonate (Riedel-de-Haen, 98–100%) and dimethyl sulfoxide (Riedel-de-Haen, 99.5%), were used as received. Dimethyl sulfoxide was purchased from RCI Labscan Limited. Zeolite ZSM-5: CVB 2314, CVB 5524G, CVB 8014, and CVB 28014 which have Si/Al of 23, 50, 80, and 180, respectively, as the inorganic fillers were purchased from Zeolyst International.

6.3.2 Synthesis of poly (ether ketone ether sulfone) (PEKES) and sulfonated poly(ether ketone ether sulfone) (S-PEKES)

Both PEKES and S-PEKES at the degree of sulfonation of 0.66 were synthesized following our previous work (Changkhamchom *et al.*, 2010). S-PEKES was synthesized by using two starting monomers: 4,4'-dichlorobezophenone and bisphenol S via the nucleophilic aromatic substitution reaction.

The sulfonation process was applied to attach the sulfonic acid group into the PEKES backbone. 5 grams of the PEKES powder was vigorously stirred in 50 ml concentrated H_2SO_4 (98%), at 25 ± 2 °C for 84 h. Then, the polymer solution was precipitated on crushed ice. The white rubber-like solid was achieved. The suspension was left for 12 h at room temperature. Then, the precipitate was filtered and washed several times with de-ionized water until a neutral pH was obtained, The obtained S-PEKES was dried under vacuum at 60 °C for 24 h.

6.3.3 Membrane Preparation

One gram of mixture was dissolved in 30 mL dimethyl sulfoxide (DMSO) with vigorous stirring for 12–18 hours until the polymer solutions were homogeneous and the molecular sieve was dispersed evenly. Composite proton exchange membranes were prepared by solvent casting via the incorporation of 4% v/v of different Si/Al ZSM-5: CVB 2314, CVB 5524G, CVB 8014, and CVB 28014 which have Si/Al ratios of 23, 50, 80, and 180, respectively, into the solution of the sulfonated poly(ether ketone ether sulfone) (S-PEKES) at the sulfonation degree of 0.66. Each solution was cast on a petri dish and kept at room temperature for 12 h, followed by drying at 80 °C for 2 days under a vacuum. The composite membrane

which showed the most suitable properties was selected to further study the effect of zeolite content varying from 2–10%v/v.

6.3.4 Polymer Characterization

6.3.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the pristine S-PEKES, 4% v/v of CVB 2314, CVB 5524G, CVB 8014, and CVB 28014/S-PEKES composite membranes were taken, using a Thermo Nicolet/Nexus 670 FTIR spectrometer, and the background material was spectronic-grade KBr. The operation condition covered the wavenumber range of 4000–400 cm^{-1} under the absorption mode with 32 scans at a resolution of $\pm$ 4 cm^{-1} (Changkhamchom et al., 2010).

6.3.4.2 Thermal Behavior

A thermogravimetric analyzer (TGA) (PerkinElmer/TGA7) was used to investigate the degradation temperature of all composite proton exchange membranes: Nafion 117, pristine S-PEKES; 4% v/v of CVB 2314, CVB 5524G, CVB 8014, and CVB 28014/S-PEKES composite membranes. Between 5.0 and 10.0 mg samples were heated from 50–800 °C at a rate of 10 °C/min under N_2 atmosphere (Wang et al., 2006).

6.3.4.3 Water Uptake (%)

The 4%v/v of ZSM-5/S-PEKES composite membranes with various Si/Al ratios were dried in an oven at 80 °C for 24 h. Then, the membranes were soaked in de-ionized water at room temperature for 24 h, removed from the water, quickly dry-wiped by an absorbent paper to remove any surface moisture, and immediately weighed to determine their wet masses (M_{wet}). The polymer membranes were then dried at 100 °C for 24 h and weighed again to determine their dry masses (M_{dry}). The water uptakes were measured in triplicate and calculated by using the following equation (Vetter et al., 2005)

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

Then, the composite membrane with the highest water uptake (%) was selected to further study the effect of zeolite content (%v/v).

6.3.4.4 Proton Conductivity (σ)

The proton conductivity one of the most important properties of PEM, the proton conductivity values of the pristine S-PEKES, Nafion 117 and all composite proton exchange membranes were measured by an Agilent E4980A LCR meter at a AC potential of 1 V and in the frequency range between 20 Hz to 2 MHz, at 27 ± 1 °C and 50%RH. The composite membranes were immersed in de-ionized water for 24 h. The water uptake (%) of the membranes was calculated from the method previously reported (Unnikrishnan et al., 2010). The conductivity values (σ) of all samples were calculated from the impedance data, using this equation

$$\sigma = d/RS, \tag{2}$$

where σ is the proton conductivity (S/cm), d is the membrane thickness (cm), S is the membrane surface area (cm^2), and R is the resistance which can be derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Re(Z) or Z' axis (Mikhailenko et al., 2004). The impedance of each sample was measured for 3 times to ensure data reproducibility. The proton conductivities of the 4%v/v of ZSM-5/S-PEKES composite membranes with various Si/Al ratios were compared with the pristine S-PEKES and Nafion 117 membrane. And the composite membrane with the highest proton conductivity was selected to further study the effect of zeolite content (%v/v).

6.3.4.5 Methanol Permeability (P)

The composite membranes methanol permeabilities were determined by using the two compartments diffusion cell as previously reported

(Changkhamchom *et al.*, 2013). The compartment A (V_A = 250 ml) was filled with a solution of methanol (2.5 mol/L). The compartment B (V_B= 250 ml) was filled with de-ionized water. The membrane was clamped between the two compartments. The solutions in the two compartments were mechanically stirred during the permeation periods. The solutions in compartment A and B were sampling during these times where the methanol diffused pass through the membrane due to the methanol concentration difference between the compartment A and the compartment B (Mukoma *et al.*, 2004). The methanol permeation in the receiving compartment as a function of time was calculated by:

$$P \text{ (cm}^2\text{/s)} = \frac{k_B \times V_B \times L}{A \times (C_A - C_B)} \, , \tag{3}$$

where P is the methanol permeability, C_A and C_B are the methanol concentrations in the compartment A and B respectively, k_B is the slope of the methanol concentration gradient in the compartment B, V_B is the volume of the solution in the compartment B, L and A are the thickness and the area of a membrane respectively. The methanol concentrations were measured by using a gas chromatography (Pr2100) fitted with a thermal conductivity detector (TCD); ethanol solution (1 mol/L) was used as an internal standard.

6.4 Results and Discussion

6.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the composite proton exchange membranes, incorporated with 4%v/v different types of ZSM-5 based on the various Si/Al ratio (CBV 2314, CBV 5524G, CBV 8014, and CBV 28014 have Si/Al of 23, 50, 80, and 280, respectively), with the highest degree of sulfonation S-PEKES (DS 0.66), are shown in Figure 6.1 and compared with the pristine S-PEKES. The FTIR spectra confirmed the existence of the hydrogen bonds formed between the S-PEKES molecules and ZSM-5 zeolites. The broad band of all composite membranes appear in the wavenumber range 3700–3200 cm^{-1} due to the stretching of the hydroxyl

group. The other FTIR spectra, which appear in the wavenumber range of 1800-400 cm^{-1}, indicate various characteristic peaks of S-PEKES functional groups reported in our previous work (Changkhamchom *et al.*, 2010).

The intensity values of the hydroxyl characteristic peaks followed the order of CBV 2314/S-PEKES > CBV8014/S-PEKES > CBV 5524G/S-PEKES > pristine S-PEKES > CBV 28014/S-PEKES which possess the Si/Al ratio of 23, 80, 50, 0, and 280, respectively. The incorporation of ZSM-5 zeolite into the S-PEKES matrix increases the hydrogen-bonding interactions between the hydroxyl groups on the surface of zeolite and the sulfonic acid group of the S-PEKES. Thus, all the composite membranes possess higher intensity of hydroxyl stretching peak than the pristine S-PEKES except the CBV 28014/S-PEKES composite membrane.

The acid intensity of the zeolite surface is increased with the increment of Si/Al ratio, which leads to the strong hydrogen-bonding interaction (Wang *et al.*, 2008). Therefore, the hydroxyl group intensity of the composite membranes is higher than that of the S-PEKES membrane.

6.4.2 Thermogravimetric Analysis (TGA)

The thermograms of Nafion 117, S-PEKES, composite proton exchange membranes incorporated with 4%v/v different types of ZSM-5 based on various Si/Al ratios (CBV 2314, CBV 5524G, CBV 8014, and CBV 28014 have Si/Al of 23, 50, 80, and 280, respectively), with the highest degree of sulfonation S-PEKES (DS 0.66), are shown in Figure 6.2. The thermal stability of Nafion 117 membrane possesses the most inferior degradation temperature, its first degradation step occurs around 250–280 °C and the second step weight loss is at 400 °C. Whereas, the first step weight loss of the pristine S-PEKES membrane starts above 300 °C, representing the sulfonic acid group splitting-off. The second step weight loss occurs at 420–450 °C, representing the degradation temperatures of S-PEKES backbone which are related with our previous work (Changkhamchom *et al.*, 2013). All ZSM-5/S-PEKES composite membranes show higher thermal stability than both Nafion 117 and pristine S-PEKES, the major weight loss stage of all composite membranes start over 400 °C which corresponds to the S-PEKES main chain

degradation. Especially, the CBV 28014/S-PEKES composite membrane, with it is the highest Si/Al ratio, has the extremely high degradation temperature around 600 °C. In general, the thermal stability can be enhanced by the intermolecular and intramolecular hydrogen-bonding (Wan *et al.*, 2006). In summary, all ZSM-5/S-PEKES composite membranes have high thermal stability within the survice temperature range 25–120 °C, and thus are uasble for use in the DMFC application.

6.4.3 Water Uptake (%)

The water uptake (%) values of the pristine S-PEKES (DS = 0.66), and 4%v/v of composite membranes based on S-PEKES (DS = 0.66) with CBV 2314 (Si/Al =23), CBV 5524G (Si/Al = 50), CBV 8014 (Si/Al = 80), and CBV 28014 (Si/Al = 280) included at room temperature (27 °C) are shown in Figure 6.3. The effect of Si/Al ratio of the ZSM-5 on the water uptake is investigated here. The water uptake (%) values of the pristine S-PEKES membranes at 0.66 DS is 20.44 ± 1.90%. Whereas the ZSM-5/S-PEKES composite membranes possess the water uptake (%) values of 43.28 ± 2.31%, 36.80 ± 3.43%, 31.28 ± 2.91%, and 17.38 ± 1.62%, belonging to the system of CBV 2314, CBV 5524G, CBV 8014, and CBV 28014, respectively. First, the adding of ZSM-5 with a low Si/Al ratio (23) facilitates the membrane to adsorb more water than the pristine S-PEKES, the water cluster can be easily trapped in the zeolite pores. Secondly, the enhancement of Si/Al ratio in the composite membrane leads to a decrese of water uptake (%) because the membranes become more hydrophobic and do not preferentially adsorb water molecules.

Figure 6.4 shows the effect of zeolite content (%v/v) on the water uptake (%) of the composite membranes. The water uptake (%) of the composite membranes based on S-PEKES (DS = 0.66) with CBV 2314 (Si/Al =23) included was selected for further study due to its highest water uptake (%) among those composite membranes. At various ZSM-5 contents, the 2, 4, 6, 8, and 10 %v/v CBV 2314/S-PEKES composite membranes possess the water uptake (%) values of 49.77 ± 1.86%, 43.27 ± 2.31%, 34.54 ± 0.95%, 21.96 ±1.73%, and 17.45 ± 1.22%, respectively. Thus, the addition of ZSM-5 weakens the affinity toward water due to its hydrophobic properties.

6.4.5 Proton Conductivity (σ)

The proton conductivity (σ) is one of the most important properties of the polymer electrolyte membrane, indicating the performance of the PEMFC or DMFC. The effect of Si/Al ratio of ZSM-5 on the proton conductivity is investigated in the present work. Figure 6.5 represents the proton conductivities of the pristine S-PEKES (DS = 0.66), the 4%v/v of composite membranes based on S-PEKES (DS = 0.66) with CBV 2314 (Si/Al =23), CBV 5524G (Si/Al = 50), CBV 8014 (Si/Al = 80), and CBV 28014 (Si/Al = 280) included at room temperature, they possess the values of $8.45 \times 10^{-3} \pm 5.75 \times 10^{-4}$, $1.35 \times 10^{-2} \pm 1.53 \times 10^{-4}$, $1.31 \times 10^{-2} \pm 4.00 \times 10^{-4}$, $1.07 \times 10^{-2} \pm 4.73 \times 10^{-4}$, and $7.81 \times 10^{-3} \pm 2.93 \times 10^{-4}$ S.cm^{-1}, respectively. The CBV 2314/S-PEKES composite membrane possesses the highest proton conductivity values which are 1.24 and 1.60 times higher than those of Nafion 117 and S-PEKES, respectively. The low Si/Al ratio ZSM-5 facilitates to increase the proton conductivity, however at a higher the Si/Al ratio, the lower in proton conductivity is obtained corresponding to the increment of hydrophobicity. This phenomenon directly depends on the water uptake (%) of the composite membrane, the membrane that can hold much more water molecules provides the proton transport capability via the vehicle mechanism in the form of hydromium ion. Moreover, the proton can generally move via the hopping mechanism along the sulfonic group of S-PEKES.

The effect of ZSM-5 amount (v/v%) within the composite proton exchange membranes on the proton conductivity is investigated next. Figure 6.6 shows the proton conductivities of Nafion 117, pristine S-PEKES (DS = 0.66), which possess the values of $1.09 \times 10^{-2} \pm 1.39 \times 10^{-3}$, $8.45 \times 10^{-3} \pm 5.75 \times 10^{-4}$ S.cm^{-1}, respectively. For the composite membranes based on S-PEKES (DS = 0.66) with CBV 2314 (Si/Al =23) included at various ZSM-5 contents 2, 4, 6, 8, and 10 %v/v at room temperature, they possess the values of $1.76 \times 10^{-2} \pm 3.61 \times 10^{-4}$, $1.35 \times 10^{-2} \pm 1.52 \times 10^{-4}$, $1.10 \times 10^{-2} \pm 2.52 \times 10^{-4}$, $9.47 \times 10^{-3} \pm 3.06 \times 10^{-4}$, and $7.30 \times 10^{-3} \pm 5.15 \times 10^{-4}$, respectively. The CBV 2314/S-PEKES composite membrane with 2%v/v zeolite content possesses the highest proton conductivity which is 1.61 and 2.08 times higher than those Nafion 117 and S-PEKES, respectively.. The proton conductivity decreases with the enhancement of the ZSM-5 content. This is

consistent with the facta that the water uptake (%) of the composite membrane decreases with the increament of Si/Al ratio, as the mambranes could not hold much water due to their hydrophobicity. The proton transport mainly takes place within the S-PEKES bulk phase instead of the ZSM-5 phase and this phenomenon produces the reduction of the proton conductivity.

6.4.6 Methanol Permeability

Methanol crossover is the major problem in the DMFC applications; methanol permeates easily through the electrolyte membrane from the anode and passes through the polymer electrolyte membrane to the cathode side of the DMFC. As a consequence, excessive methanol crossover of any PEM not only wastes the methanol fuel but also decrease the efficiency in fuel cell performance (Carette *et al.*, 2001). Table 6.1 shows the methanol permeabilities (P) of all proton exchange membranes at the temperatures of 27 °C. The methanol permeabilities of Nafion 117, pristine S-PEKES (DS = 0.66), and 4%v/v of composite membranes based on S-PEKES (DS = 0.66) with CBV 2314 (Si/Al = 23), CBV 5524G (Si/Al = 50), CBV 8014 (Si/Al = 80), and CBV 28014 (Si/Al = 280) included at room temperature possess the values of 1.41×10^{-6}, 1.03×10^{-7}, 7.85×10^{-8}, 7.73×10^{-8}, 7.52×10^{-8}, 6.34×10^{-8} cm^2.s^{-1}, respectively. All composite membranes show lower methanol permeabilities than the pristine S-PEKES and extremely lower than that of Nafion 117 membrane. The lowest methanol permeability belongs to CBV 2314/S-PEKES composite membrane which its value is 1.32 time lower than S-PEKES and 18 times lower than Nafion 117.. The methanol permeability slightly decreases with increasing the Si/Al ratio.

The effect of zeolite content (v/v%) within the composite proton exchange membranes on the methanol permeability is investigated next . The CBV 2314/S-PEKES composite membrane was selected to fabricate the membranes at various zeolite contents of 2, 4, 6, 8, and 10%v/v. They possess the methanol permeability values of 8.32×10^{-8}, 7.86×10^{-8}, 7.27×10^{-8}, 6.45×10^{-8}, and 5.26×10^{-8} cm^2.s^{-1}, respectively. Therefore, the methanol permeability decreases with the addition of ZSM-5 zeolite. The transport process of methanol is mainly based the methanol diffusivity. The methanol molecules are preferentially adsorbed and

trapped within the zeolites during the diffusion through the membrane. Thus the penetrated molecules cause the delay in the methanol diffusion (Wang *et al.*, 2008).

The membrane selectivity is the ratio between the proton conductivity and the methanol permeability, as shown in table 6.1. The highest membrane selectivity belongs to the 2%v/v CBV 2314/S-PEKES composite membrane which has the value of 2.12×10^5 s.S.cm^{-3}. This composite membrane is thus the most suitable for using in the actual DMFC applications due to its optimized fuel efficiency.

6.5 Conclusions

The ZSM-5/S-PEKES composite membranes show high thermal stability, because the degradation temperature start at above 400 °C. The water uptake (%) of the composite membrane first increases and then decreases with the increment of Si/Al ratio and amount of zeolite due to its hydrophobicity. The ZSM-5 zeolite helps to increase the proton conductivity relative to the pristine S-PEKES and Nafion 117 membranes. For the effects of the Si/Al ratio and zeolite content on the proton conductivity, the same tendency occurs as with the water uptake (%). Moreover, the methanol permeabilities of all composite membranes investiagetd are much lower than the S-PEKES and Nafion 117 membrane, due to the hindered methanol diffusionThe 2%v/v CBV 2314/S-PEKES composite membrane isselected to be the proton exchange membrane candidate due to its membrane selectivity is the highest among all the composite membranes investigated.

Acknowledgements

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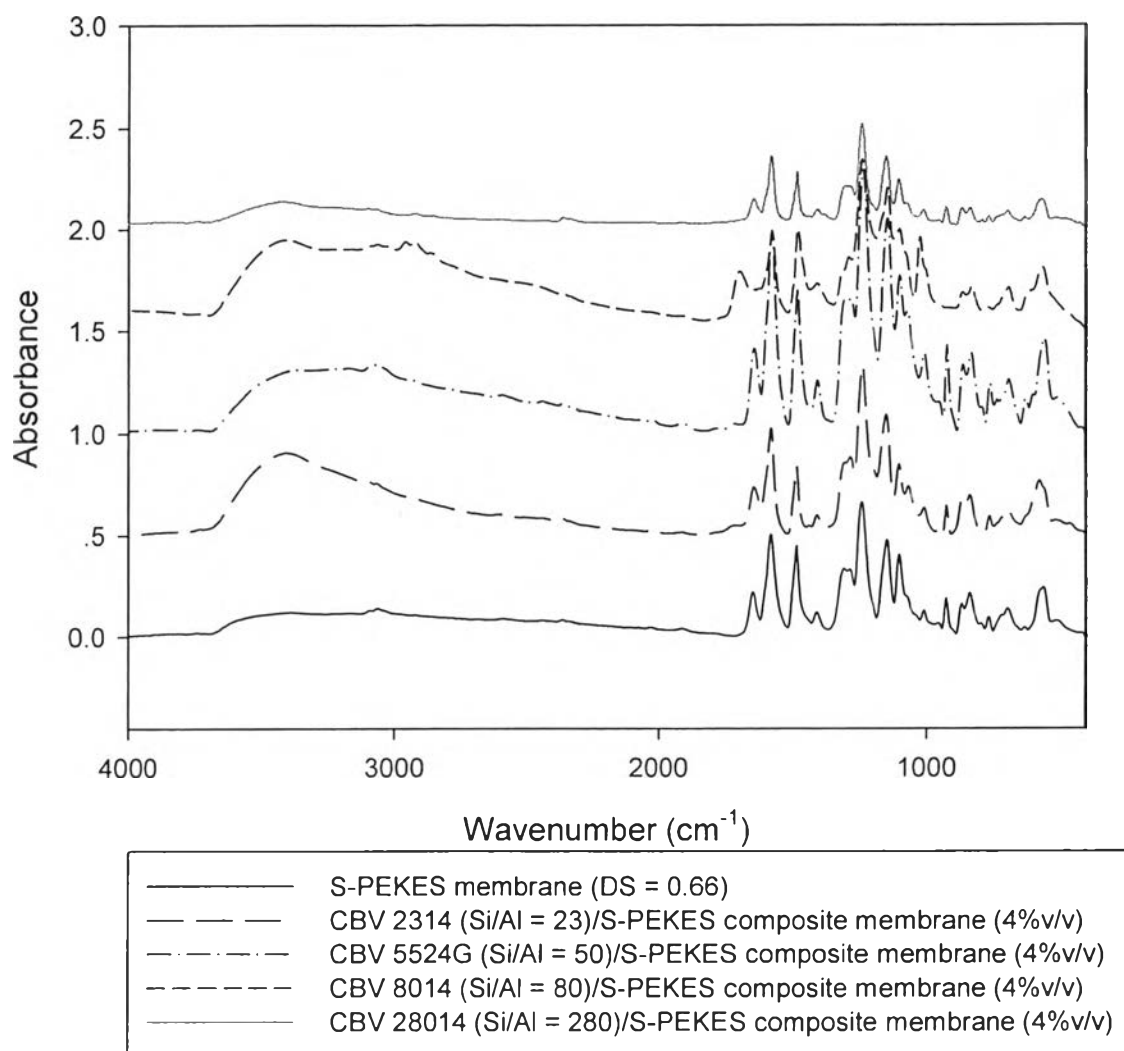
Figure 6.1 FTIR spectra of composite proton exchange membrane incorporated with 4%v/v ZSM-5 zeolites (various Si/Al ratios) with the highest degree of sulfonation S-PEKES (DS 0.66).
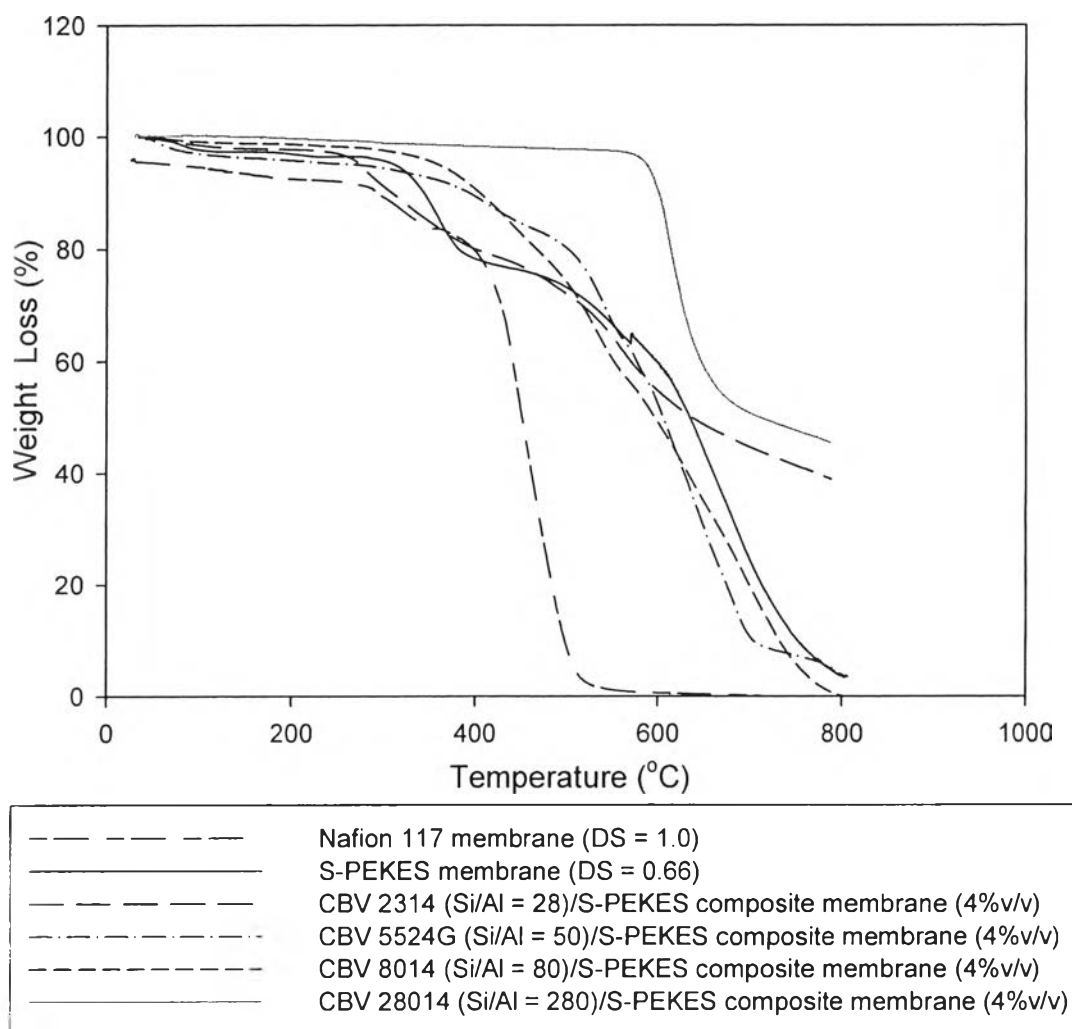
Figure 6.2 Thermograms of Nafion 117, pristine S-PEKES, 4%v/v ZSM-5/S-PEKES composite membranes (various Si/Al ratios).
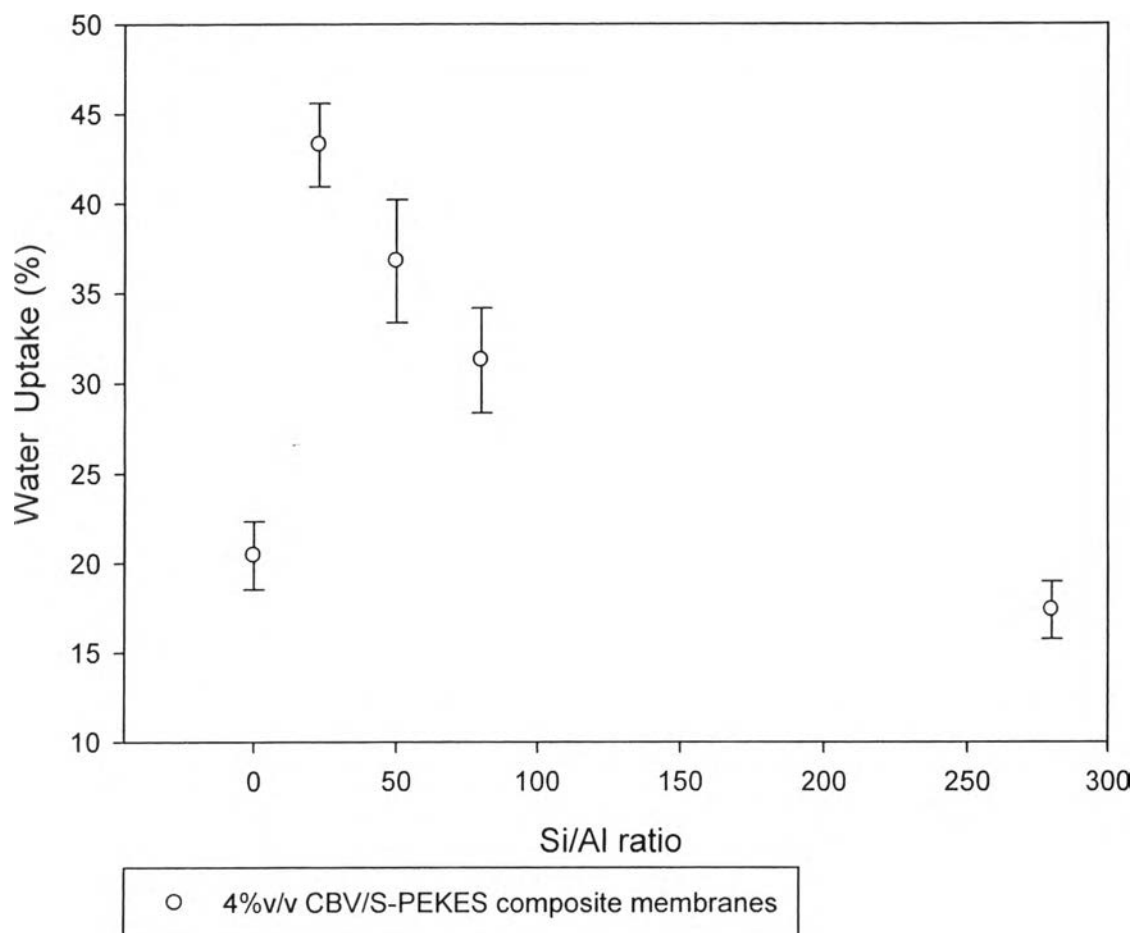
Figure 6.3 The water uptake (%) of the pristine S-PEKES (DS = 0.66), and 4%v/v of composite membranes based on S-PEKES (DS = 0.66) with CBV 2314 (Si/Al =23), CBV 5524G (Si/Al = 50), CBV 8014 (Si/Al = 80), and CBV 28014 (Si/Al = 280) at room temperature (27 °C).
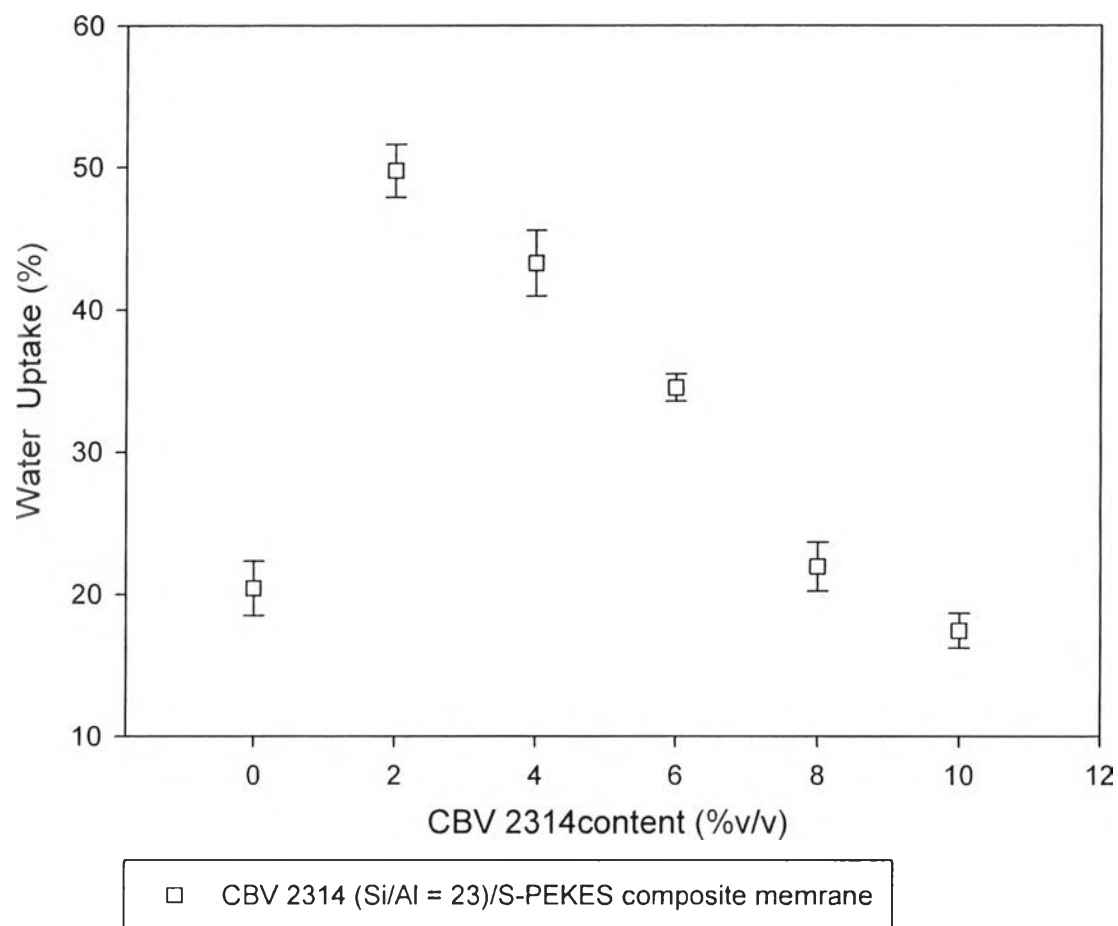
Figure 6.4 The water uptake (%) of the pristine S-PEKES (DS = 0.66), and composite membranes based on S-PEKES (DS = 0.66) with CBV 2314 (Si/Al =23) included at various zeolite contents: 2, 4, 6, 8, and 10 %v/v, respectively, at room temperature (27 °C) .
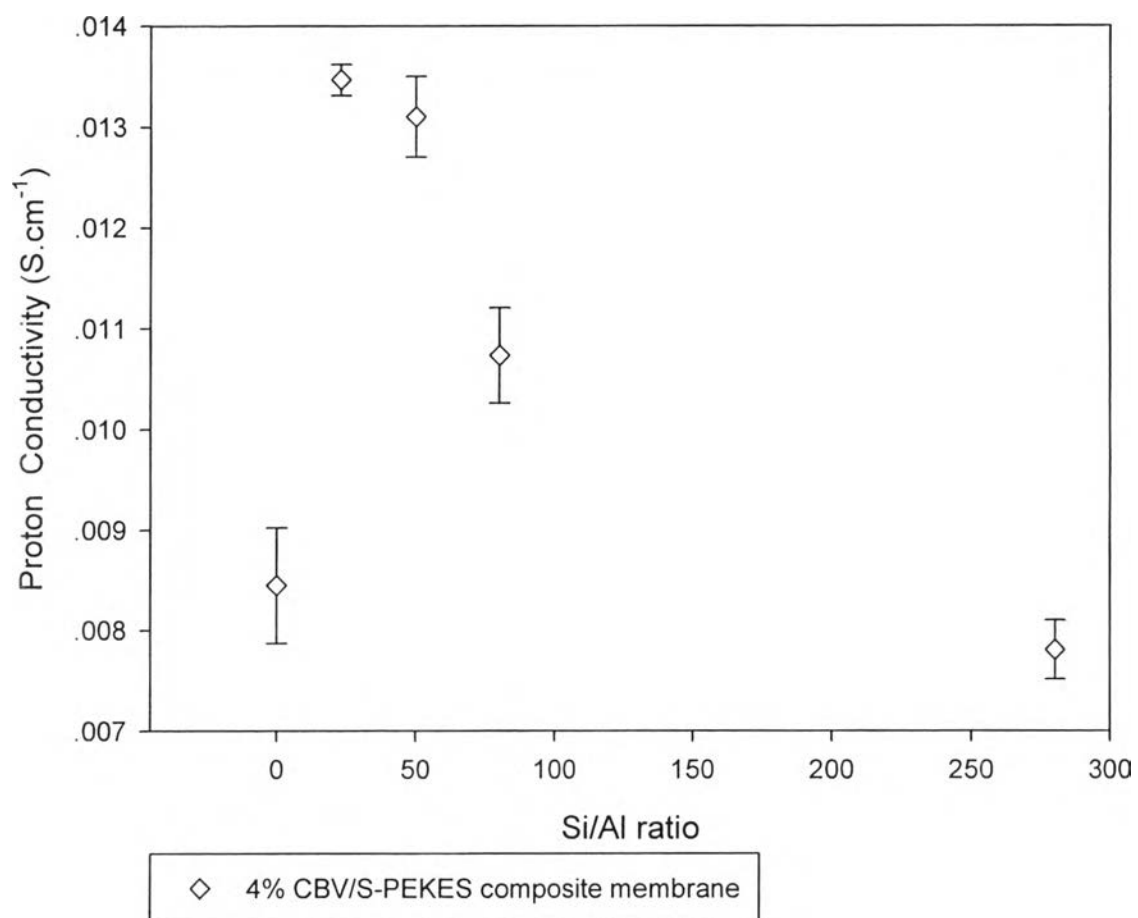
Figure 6.5 The proton conductivities of the pristine S-PEKES (DS = 0.66), and 4%v/v of composite membranes based on S-PEKES (DS = 0.66) with CBV 2314 (Si/Al =23), CBV 5524G (Si/Al = 50), CBV 8014 (Si/Al = 80), and CBV 28014 (Si/Al = 280) at room temperature (27 °C).
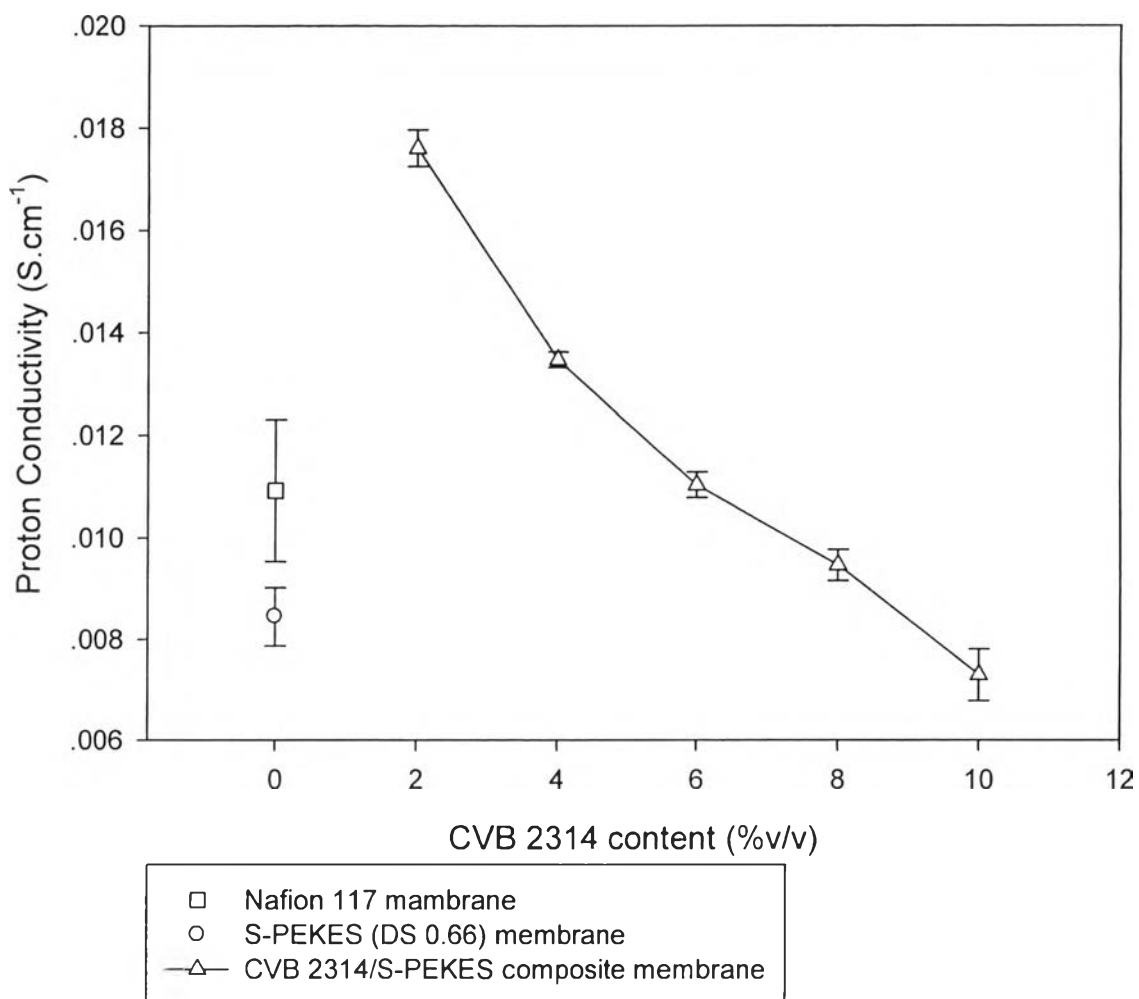
Figure 6.6 The proton conductivities of Nafion 117, pristine S-PEKES (DS = 0.66), and composite membranes based on S-PEKES (DS = 0.66) with CBV 2314 (Si/Al = 23) included at various zeolite content: 2, 4, 6, 8, and 10 %v/v, respectively, at room temperature.

Table 6.1 Methanol permeabilities (P) of all proton exchange membranes at the temperature of 27 °C

PEM Composite	Si/Al	Zeolite (%v/v)	Thickness (cm)	Methanol Permeability ($cm^2.s^{-1}$)	Proton Conductivity ($S.cm^{-1}$)	Membrane Selectivity ($s.S.cm^{-3}$)
Nafion 117 membrane (DS = 1.0)	0	0	0.0200	1.4147E-06	1.0917E-02	7.7166E+03
S-PEKES-B membrane (DS = 0.66)	0	0	0.0278	1.0347E-07	8.4467E-03	8.1634E+04
CBV 2314/S-PEKES composite membrane	23	2	0.0286	8.3153E-08	1.7600E-02	2.1160E+05
CBV 2314/S-PEKES composite membrane	23	4	0.0314	7.8575E-08	1.3467E-02	1.7139E+05
CBV 2314/S-PEKES composite membrane	23	6	0.0327	7.2668E-08	1.1033E-02	1.5183E+05
CBV 2314/S-PEKES composite membrane	23	8	0.0329	6.4521E-08	9.4667E-03	1.4672E+05
CBV 2314/S-PEKES composite membrane	23	10	0.0330	5.2683E-08	7.2967E-03	1.3850E+05
CBV 5524G/S-PEKES composite membrane	50	4	0.0327	7.7368E-08	1.3100E-02	1.6932E+05
CBV 8014/S-PEKES composite membrane	80	4	0.0328	7.5224E-08	1.0733E-02	1.4268E+05
CBV 28014/S-PEKES composite membrane	280	4	0.0347	6.3448E-08	7.8067E-03	1.2304E+05