CHAPTER IV

Processing of Proton Exchange Membrane for Direct Methanol Fuel cell

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Abstract

Proton exchange membrane (PEM) is a polymeric electrolyte for in direct methanol fuel cells (DMFC). The membrane supports proton transport and separates the cathode from the anode. Nafion is widely used as the membrane in DMFC because of its high proton conductivity and mechanical strength. Nevertheless, it is of high methanol permeability and very expensive. The high methanol permeability leads to a decrease in DMFC performance. Therefore, alternate polymer membranes were developed. Polysulfone and polyvinylidene fluoride were fabricated as PEMs in this work. The polymer membranes were characterized for the degree of sulfonation, ion exchange capacity, proton conductivity, water uptake, and mechanical strength. The degree of sulfonation was improved with increasing ratio of acid per polymer and affected both proton conductivity and water uptake. The properties of membranes were directly compared with a commercial membrane Nafion.

Keywords: Fuel cell, Proton exchange membranes, Polysulfone, Polyvinylidene fluoride, Sulfonated polymer

4.1 Introduction

A direct methanol fuel cell (DMFC) is the one type of the alternative energy source which utilizes methanol as a fuel to generate electricity (Carrette *et al.*, 2001). Methanol is oxidized to generate proton, electron, and carbon dioxide at the anode position in DMFC system. The proton is transported through the polymeric electrolyte membrane from the anode to the cathode and then combined with oxygen and electron to generate electricity (Wootthikanokkhan *et al.*, 2006). Proton exchange membrane (PEM) is an important component of DMFC because it is responsible for proton transport from the anode to the cathode and the entire fuel cell performance (Higashihara *et al.*, 2009; El-Araby *et al.*, 2012). The requirements of PEM are reasonable proton conductivity, high stability and durability in

fuel cell environment, good mechanical toughness, high thermal stability, and impermeability to fuel gas or liquid (Higashihara *et al.*, 2009).

Presently, the most commonly-used perfluorinated polymer is known its trade name, Nafion developed by DuPont as PEM because of its high proton conductivity (~0.1 S/cm) at ambient temperature (Qiao *et al.*, 2005), high chemical, electrochemical, and mechanical stability, a good thermal resistance (Wootthikanokkhan *et al.*, 2006; Boroglu *et al.*, 2011; Higashihara *et al.*, 2009). However, these are many disadvantages as limited operation temperature (0-80 °C) (Higashihara *et al.*, 2009), high cost, high methanol permeability (~10^{-6} cm^2/s) (Boroglu *et al.*, 2011), and difficulty in synthesis and processing (Chang *et al.*, 2007; Rhim *et al.*, 2004). Due to these shortcomings of Nafion, several researches have been reported sulfonated polymers used as a PEM. The sulfonation process enhances the hydrophilic pathway for proton transfer within a polymer matrix by attaching sulfonic groups (SO$_3$H) on its polymer backbone. There are many sulfonated polymers such as poly(ether ether ketone) (Macksasitorn *et al.*, 2012; Zaidi *et al.*, 2000; Liu *et al.*, 2007), poly(phenylene) (Ghassemi *et al.*, 2004; Kobayashi *et al.*, 1998), poly(arylene ether) (Gao *et al.*, 2005; Wang *et al.*, 2001), polyimides (Chen *et al.*, 2007; Miyatake *et al.*, 2007), polysulfone (Unnikrishnan *et al.*, 2012), and polyvinylidene (Macksasitorn *et al.*, 2012).

Kreuer et al. (2001) studied the sulfonated aromatic polymer as S-PEEK for PEM in DMFC application. The methanol permeability of S-PEEK was lower than that of Nafion membrane, which might help to reduce the high methanol crossover of Nafion in DMFC. Polysulfone (PSF) was modified by sulfonation process to prepare sulfonated polysulfone (SPSF) used as PEM in DMFC (Chen *et al.*, 2005; Fu *et al.*, 2006). The SPSF exhibited better performances comparable to those of Nafion115 due to its lower methanol crossover and high current density. Wootthikanokkhan et al. (2006) fabricated sulfonated polyvinylidene (SPVDF) used as PEM. The methanol permeability of SPVDF was lower than that of Nafion because of the hydrophobic nature of PVDF.

In this work, polymers, PSF and PVDF, were fabricated membranes and sulfonated at various sulfuric acids to polymer mole ratio. The water uptake, ion exchange capacity, proton conductivity, methanol permeability, and mechanical properties were investigated under the effect of degree of sulfonation and compared with those of a commercial membrane Nafion117.

4.2 Experimental

4.2.1 Materials

Polysulfone (PSF; Aldrich) and polyvinylidene fluoride (PVDF; Aldrich) were used as polymer based membranes. Concentration sulfuric acid (H_2SO_4; Univar, Ar grade) was used as a sulfonating agent. Methanol (Univar, Ar grade) was used in the methanol permeation study. Dichloromethane (DCM; RCI Labscan, AR grade), N-methyl-2-pyrrolidinone (NMP; RCI Labscan, HPLC grade), dimethylacetamide (DMAc; RCI Labscan, AR grade), and deionized water were used as solvents. Sodium hydroxide (NaOH; Ar Grade) was used in the titration processes find the degree of sulfonation and ion exchange capacities. Sodium chloride (NaCl; Analytical Grade) was used as an electrolyte for exchanging H^+ in the sulfonic groups of the sulfonated polymers.

4.2.2 Preparation of sulfonated polysulfone (S-PSF)and sulfonated poly(vinylidene fluoride) (S-PVDF)

S-PSF was prepared by dissolving 2 g of polysulfone (PSF) in a 10 ml of DCM. S-PVDF was prepared by dissolving PVDF (2 g) in NMP (60 ml). The concentrate H_2SO_4 was added into the polymer solution (PSF or PVDF solution) at various acid per polymer ratios and at various reaction temperatures between 25 and 50 °C. The sulfonated solution was continuously stirred for 4 h, then the solution was precipitated by methanol in an ice bath. The precipitate was washed using DI water until pH of precipitate reached neutral. The sulfonated polymer as S-PSF and S-PVDF was dried at 100 °C for 24 h (Macksasitorn *et al.*, 2012; Saxena *et al.*, 2009).

4.2.3 Fabricating polymer membrane (S-PSF and S-PVDF)

Either S-PSF or S-PVDF (1.5g of S-PSF and 1.5 g of S-PVDF was put in a round bottom flask and dissolved in a DMAc solvent (20ml) to form a polymer solution. The polymer solution was continuously stirred 25 °C until homogenous. The film was formed by a casting method and heated in a vacuum oven at 80 °C for 24 h.

4.2.4 Characterizations

The sulfonated polymers functional groups were determined using a FT-IR spectrometer (Nicolet, Nexus 670). The sulfonated polymers, used in a powder form, were

grinded and mixed with potassium bromide (dried at 100 °C for 24 h) as background, and compressed into pellets (Macksasitorn *et al.*, 2012). The measurements were carried out in the in the wave number range of 400-1600 cm^{-1} with 64 scans.

The structures of sulfonated PEEK and PPEES were determined by a NMR spectrometer (Bruker Biospin Avance 500 MHz NMR spectrometer) using deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent. For each analysis, 3 wt% polymer solution was prepared in DMSO and the experiment was conducted at room temperature.

The thermal property of sulfonated membrane was investigated using a Thermo-Gravimetric/Differential Thermal Analyzer (TG/DTA; Perkin Elmer, Pyris Diamond). The samples were weighed in the range of 4-10 mg and inserted into alumina pans. The measurements were carried out under nitrogen flow between 25 °C to 700 °C at a heating rate of 10 °C. min^{-1} (Zhang *et al.*, 2011).

The crystalline structure of polymer and sulfonated polymer was examined by a wide angle X-ray diffraction (Bruker AXS, D8 Advance). The CuK-alpha radiation source was operated at 40 kv/30 mA. The interference peak was eliminated by a K-beta filter. Divergence silt and scattering silt of 0.5° together with 0.3 mm of receiving silt were used. The samples were mounted on a sample holder and a measurement was continuously run. The experiment was recorded by monitoring the diffraction pattern appearing in the 2θ range from 5 to 50, with a scan speed of 1°/min, and a scan step of 0.02°.

4.2.5 Degree of Sulfonation (DS)

The degree of sulfonation was determined a using a titration method. The polymer membranes were acidified by 0.1 M of hydrochloric solution at room temperature for 24 h. Then the membranes were washed with deionization water and dried at 80 °C for 24 h. After that the membranes were placed in a sodium chloride solution for 24 h. The degree of sulfonation of polymer solution was determined by the titration with 0.01 M of sodium hydroxide using phenolphthalein as an indicator. The degree of sulfonation was calculated as in the following Eq. (1):

$$DS(\%) = \frac{(V_{NaOH} \times C_{NaOH})/1000}{Mole\ of\ polymer\ membrane} \times 100\% \qquad (1)$$

where V_{NaOH} refers to the volume of sodium hydroxide solution, and C_{NaOH} refers to the concentration of sodium hydroxide solution.

4.2.6 Water Uptake

In the Water uptake measurement, the membranes were immersed into DI water for 24 h at room temperature. Excess water was removed from the membrane surface with a paper and the membrane was weighed (noted as W_s). The membranes were dried at 100 °C for 24 h in a vacuum oven and weighed (noted as W_d). The percentage of water uptake was then calculated as in the following Eq. (3):

$$\text{Water uptake} = \frac{(W_s - W_d)\times 100}{W_d} \qquad (2)$$

where W_d refers to the weight of dried polymer, and W_s is the weight of swollen polymer

4.2.7 Proton Conductivity

Proton conductivity of membrane was measured by an impedance phase analyzer (HP, 4194) for measuring under dry state and using an impedance phase analyser HP 4194 for measuring under wet state at various frequencies from 100 Hz to 2 MHz and at room temperature. The membranes were cut into a 5×5 cm^2 specimen for the measurement with and without immersed in deionized water at room temperature for 24 h. Proton conductivity was calculated as in the following Eq. (4):

$$\sigma\,(Scm^{-1}) = \frac{d}{R \times A} \qquad (3)$$

where σ is the proton conductivity(Scm^{-1}), d is the thickness of the membrane (cm), A is the area of the interface of membrane in contact with the electrodes (cm^2), and R refers to the measured resistance of the membrane derived from the high frequency semi-circle on the complex impedance plane with the Z axis (ohm).

4.2.8 Ion Exchange Capacity (IEC)

Ion exchange capacity of membrane was determined by a titration method. Ion exchange capacity is a method to determine the number of milliequivalent of ions in 1 g of dry polymer (meq./g). The membranes were soaked in 0.1 M NaCl solution for 24 h to

exchange H^+ with Na^+. H^+ were titrated with 0.01 M NaOH solution with using phenolphthalein as an indicator. Ion exchange capacity of membrane was calculated using following Eq. (2) (Macksasitorn *et al.*, 2012):

$$IEC \ (mmol \ g-1) = \frac{Consumed \ ml(NaOH)xmolarityNaOH}{weight \ driedmembrane} \tag{4}$$

where consumed ml (NaOH) is the consumed volume of NaOH solution, molarity NaOH is the molar of NaOH solution, and weight dried membrane is the weight of membrane in a dry state.

4.2.9 Methanol Permeability

The methanol permeability refers the amount of methanol that permeates through the membrane. The permeation cell for methanol permeability measurement consisted of chamber A and chamber B as separated by the sulfonated polymer membrane. Chamber A was filled with 250 ml of methanol solution (2.0 M). Chamber B was filled with 250 ml of DI water. The membrane was placed between chamber A and chamber B. The methanol permeability was calculated as in the following Eq. (5):

$$P \ (cm^2/s) \ = \frac{k_B \times V_B \times L}{A \times (C_A - C_B)} \tag{5}$$

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

4.2.10 Mechanical Properties

The mechanical properties namely the tensile strength, yield strain, and Young's modulus were measured using a universal testing machine (Lloyd, model SMT2-500N) at room temperature with a 25 mm.min^{-1} speed. The membranes with 200 µm thick

were cut into 1×5 cm^2 specimens. Each sample was measured from 5 specimens and the average value was taken.

4.3 Results and Discussion

4.3.1 Characterization of sulfonated polymer

4.3.1.1 Fourier transform infrared spectroscopy

Figure 4.1 shows the FTIR spectra of PSF and SPSF. The peaks at 1485 cm^{-1}, 1412 cm^{-1}, 1365 cm^{-1}, and 1244 cm^{-1} refer to the aromatic C=C stretching, the asymmetric C-H bending deformation of methyl group, the symmetric C-H bending deformation of methyl group, and the asymmetric C-O-C stretching of aryl ether group, respectively (Naim et al.; Ficai et al., 2010). The peaks at 1107 and 1092 cm^{-1} can be assigned to the aromatic ring vibration. The peaks at 1325 and 1298 cm^{-1}, and 1550 cm^{-1} can be identified with the doublet resulting from the asymmetric O=S=O stretching of sulfone group and the symmetric O=S=O stretching of sulfone group, respectively (Naim et al; Karlsson et al., 2004). However, SPSF exhibits the peaks at 1170 and 1027 cm^{-1} corresponding to the asymmetric O=S=O stretching of sulfonate group and the symmetric O=S=O stretching of sulfonate group, respectively (Naim et al). The FT-IR peaks of PVDF and SPVDF appear at 1403 and 1185 cm^{-1} due to the CH$_2$ wagging vibration and the C-C bond, respectively. The peaks at 878 and 840 cm^{-1} refer to the C-C-C asymmetrical stretching vibration and the CF stretching vibration (Bai et al., 2012). However, the peak at 1400 cm^{-1} can be refered to the sulfonate group which only appears from SPVDF (CH$_2$ scissoring).

4.3.1.2 Nuclear Magnetic Resonance (NMR)

Furthermore, the sulfonated polymers namely SPSF and SPVDF were identified by NMR spectra. The NMR spectrum of sulfonated PSF showed the proton resonance at 7.25 ppm which can be assigned to the proton adjacent to the new pendent sulfonic acid on the PSF structure (Deurim et al., 2009). While sulfonated PVDF spectrum showed the proton resonance at 2.00 ppm identifying the sulfonic acid on the PVDF backbone. Thus the results of FTIR and NMR showed that the sulfonate group was successfully attached to the polymer backbones.

4.3.1.3 X-ray Diffraction (XRD)

The sulfonated polymers namely both SPSF and SPVDF showed broad amorphous scattering XRD patterns for both polymers after sulfonation. The increase in DS produced more amorphous PSF and PVDF structures because more sulfonic acid pendant groups present on the polymer backbones affecting the chain conformation and orientation of the amorphous structures (Reyna-Valencia et al., 2005; Zaidi, 2003). Figure 4.2 shows the XRD pattern of SPSF is broader than SPVDF because the SPSF has a benzene ring in the polymer backbone resulting in a lower chain packing than SPVDF (Rui *et al.*, 2013).

4.3.1.3 Thermogravimatric Analysis (TGA)

The PSF thermogram exhibited a single-step degradation temperature of the polymer backbone at higher than 450 °C. The SPSF thermogram exhibited three steps of degradation. The weight loss between 50 and 180 °C represented the evaporation of water. The weight loss between 180 and 400 °C can be attributed to the decomposition of the sulfonic acid group on the polymer backbone. Finally, the weight loss of SPSF backbone degradation occurred at 450 °C. The PVDF thermogram showed the polymer backbone degradation at around 430 °C. The SPVDF thermogram displayed three steps degradation. First, the weight loss between 100 and 200 °C represented the split of water. Secondly, the decomposition of the sulfonic acid group occurred between 200 and 400 °C. Lastly, the weight loss of SPVDF backbone degradation occurred at 440 °C (Devrim *et al.*, 2009).

4.3.2 Degree of Sulfonation (DS)

The DS was investigated based on the effect of mole ratios of acid per polymer and temperature of sulfonation process. The increment of mole ratio of acid per polymer induced increasing of DS (Figure 4.3) because the acid per polymer ratio enhanced the opportunity of sulfonic group attachment on the polymer backbones (Fu *et al.*, 2006). The DS of SPSF at 25 °C were 12.7% to 71.55% at various mole ratios of acid per polymer of 17 to 80. Furthermore, the DS increased with increasing sulfonation temperature from 25 to 50 °C. The DS was promoted to 50% DS at 50 °C in the sulfonation process at the same mole ratios of acid per polymer. From this result, it appears that the sulfonic group was accelerated in attaching onto the polymer backbones at a higher temperature due to increasing reaction rate (Duarte *et al.*, 2011).

4.3.3 Water Uptake

The water uptake in a membrane generally dictates the hydrophilic nature of polymer (Unnikrishnan *et al.*, 2012). The water uptake values of SPSF and SPVDF are shown in Figure 4.3. The water uptake increases with increasing DS because of more hydrophilic of polymer via sulfonic group (Seung *et al.*, 2006). The water uptake of SPSF membranes are between 2.16 and 9.01% (DS 12.75–71.55%). The water uptake of SPVDF is 2.78 at DS as 12.34%. However, the Nafion 117 provides the highest water uptake as 16.30% because the Nafion membrane has been grafted chemically into backbone with hydrophilic sulfonic acid groups (HSO_3). These ionic groups have caused the absorption of the large amount of water by polymer and therefore, led to hydration of polymer. Furthermore, the Nafion has a higher free volume between polymeric chains which induces more water absorption. (Peighambardoust *et al.*, 2010).

4.3.4 Proton Conductivity

The proton conductivity of SPSF and SPVDF was measured in a dry state and wet state at 25 °C. The proton conductivity increases with increasing the DS as shown in Figure 4.4 because the sulfonic group protonated the (SO_3H) site provided more hydrophilic pathways for proton transport. The protons transported by hopping between one hydrolyzed ionic site ($SO_3^-H_3O^+$) to another thoroughly the membrane (Macksasitorn *et al.*, 2012). Moreover, the proton conductivity of SPSF and SPVDF under wet state is higher than that of dry state because more water inside the membrane promotes the proton transfer (Macksasitorn *et al.*, 2012). The SPSF membranes were shown to possess the proton conductivity between 2.43×10^{-4} and 5.42×10^{-4} S/cm under dry state and between 4.60×10^{-4} and 9.77×10^{-4} S/cm under wet state at 25 °C. The proton conductivity of SPVDF was 2.08×10^{-4} S/cm under dry state and 2.09×10^{-4} S/cm under wet state. The proton conductivity of SPSF is higher than SPVDF at 12% of DS because the aromatic hydrocarbon polymer SPSF consists of polar group supporting proton transport (Rikukawa *et al.*, 2000). Moreover, a more amorphous structure of SPSF with higher free volume allows more for water absorption resulting in enhanced proton transport (Rikukawa *et al.*, 2000). The proton conductivity of Nafion117 is 3.17×10^{-4} S/cm under dry state and 2.88×10^{-3} S/cm under wet state. The proton conductivity of Nafion117 is higher than the sulfonated polymers, SPSF and SPVDF, under both dry and wet states because Nafion117 allow more water absorption as identified by the highest water uptake for proton transport (Baschek *et al.*, 1999). The proton conductivity of all S-PVDF and S-PSF membranes are relatively lower than the literatures as

tabulated in Table 4.1 because our impedance measurement condition was set at 25 °C and with 50%RH, the membranes were immersed in water for 24 h before measurement. Whereas in the previous work reported, SPSF and SPVDF proton conductivity was measured under fully hydrated state, so the proton conductivities of currently S-PVDF and S-PSF ($\sim$10^{-4}) were obviously lower than those of the previous work ($\sim$10^{-3} – 10^{-1}) (Yuanqin *et al.*, 2011; Ho Bum *et al.*, 2004; Nedal *et al.*, 2010; Lufrano *et al.*, 2009; Sheng-Li *et al.*, 2005; Yilser *et al.*, 2009; Lufrano *et al.*, 2011; Yongzhu *et al.*, 2007; Changkhamchom *et al.*, 2013).

4.3.5 Ion Exchange Capacity (IEC)

The increase DS induces increasing IEC as shown in Figure 4.6. The IEC is related to the concentration of sulfonic acid group within polymer membranes because the sulfonic groups provide more H$^+$ to exchange with cation (Na$^+$ from NaOH solution) (Peighambardoust *et al.*, 2010). The IEC values of SPSF are 0.121, 0.166, 0.187, 0.522, and 0.530 meq/g at various DSs. At the same DS, the IEC value of SPVDF is closed to SPSF because of nearly the same amount of sulfonic groups present for promoting H$^+$ to exchange. However, the IEC value of Nafion117 (0.750 meq/g) is the highest because of higher water uptake and proton conductivity.

4.3.6 Methanol Permeability

The methanol permeability is the cause of the loss of fuel and diminished efficiency (Baldauf *et al.*, 1999). A proton can move into the membrane with associated water content. The methanol molecule can be transported with the electro-osmotic drag and due to methanol properties (Carrette *et al.*, 2001). The increment of DS induced an increase in methanol permeability (as shown in Figure 4.5) because the hydrophilic nature of the polymers was improved by the sulfonation process. In Figure 4.5, the methanol permeability of SPSF varies from 0 to 9.59×10^{-08} cm^2/s at various DSs. The methanol permeability of SPVDF is 5.23×10^{-10} cm^2/s which is lower than that of SPVDF at the same DS. SPSF has a more amorphous structure than SPVDF as confirmed by the XRD pattern in Figure 4.2 with resulting in promoting methanol transfer. When compared with Nafion, the proton conductivity of Nafion is the highest (3.08×10^{-05} cm^2/s) because of greater water uptake and proton conductivity. The methanol permeability of all S-PVDF and S-PSF are extremely lower than Nafion and om previous work. The methanol permeability values of S-PVDF and S-PSF are in the range of $\sim$10^{-10} – 10^{-8} cm^2/s, whereas the Nafion and previous membranes shows the methanol permeabilities in the range of $\sim$10^{-5} -10^{-7} cm^2/s corresponding to a higher

proton conductivity (Yuanqin *et al.*, 2011; Ho Bum *et al.*, 2004; Nedal *et al.*, 2010; Changkhamchom *et al.*, 2013).

4.3.6 Mechanical Properties

The mechanical properties namely tensile strength, yield strain, and young's modulus of sulfonated polymer are tabulated in Table 4.2. The tensile strength, yield strain, and young's modulus of SPSF are in the ranges 42.0-28.4 MPa, 6.34-6.11 %, and 920.6-843.87 MPa, respectively when DS was varied from 12.74% to 71.55%. The tensile strength, yield strain, and young's modulus of SPVDF are 33.5 MPa, 16.53 %, and 884.45 MPa, respectively at DS equal to 12.34%. The tensile strength and young's modulus of the sulfonated SPSF decreased with increasing DS. On the other hand, the yield strain increased with increasing DS. The sulfonic groups obstruct the packing and decrease the crystallinity between the nearby chains due to the bulk sulfonic groups present (Changkhamchom *et al.*, 2013).

4.4 Conclusions

The SPSF and SPVDF were sulfonated with the concentrated sulfuric acid (98%). The DS of sulfonated polymers increased with increasing the ratio of mol (acid/polymer) and sulfonation reaction temperature. The increase in DS induced increasing water uptake, IEC, proton conductivity, and methanol permeability because of more hydrophilic pathways created by the sulfonic acid group. At the highest DSs of SPSF and SPVDF, they possessed proton conductivity values of 5.42×10^{-4} and 2.08×10^{-4} S/cm, respectively. The proton conductivity of the sulfonated polymers is, however, still lower than Nafion (7.49×10^{-04} S/cm). However, the methanol permeability values of SPSF at the highest DS and SPVDF were lower than Nafion by about 100 times (SPSF DS= 71%, 9.59×10^{-08}; SPVDF DS 12.34%, $5.23 \times 10^{-10} cm^2/s$; Nafion117 DS = 100%, $3.08 \times 10^{-05} cm^2/s$). The tensile strength of the sulfonated polymers decreased with increasing DS due the reduction in crystallinity via the sulfonation process. Thus, SPSF and SPVDF are potential PEM candidates in direct methanol fuel cell application because they possess better overall properties relative to Nafion.

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Wootthikanokkhan, J. and Seeponkai, N. Methanol permeability and properties of DMFC membranes based on sulfonated PEEK/PVDF blends. Journal of Applied Polymer Science, 2006, 102, 5941-5947.

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List of table and figure

Table 4.1 Comparison of proton exchange membranes used in DMFC

Polymer	25 °C RH 50% Wet membrane Proton Conductivity (S/cm)	25 °C RH100% Proton Conductivity (S/cm)	80 °C RH100% Proton Conductivity (S/cm)	25 °C Methanol (cm^2/s)	70 °C Methanol (cm^2/s)
PSf-sph-63[a]	-	8.00E-03	2.20E-02	2.92E-07	-
PSf-sph-82[a]	-	1.90E-02	4.50E-02	7.41E-07	-
PSf-sph-100[a]	-	4.40E-02	8.90E-02	1.15E-06	-
PSf-sph-122[a]	-	6.50E-02	1.43E-01	1.49E-06	-
PSf-sna-32[a]	-	1.10E-02	2.50E-02	3.60E-08	-
PSf-sna-39[a]	-	2.20E-02	5.10E-02	1.79E-07	-
PSf-sna-49[a]	-	4.10E-02	7.50E-02	3.01E-07	-
PSf-sna-58[a]	-	5.70E-02	1.17E-01	5.23E-07	-
Nafion[a]	-	9.00E-02	1.51E-01	1.68E-06	-
					-
SPSU-3[b]	-	5.50E-03	-	1.50E-07	-
SPSU-4[b]	-	1.50E-02	-	2.50E-07	-
SPSU-5[b]	-	2.20E-02	-	3.30E-07	-
SPSU-6[b]	-	5.00E-02	-	6.00E-07	-
SPSU-7[b]	-	7.00E-02	-	7.50E-07	-
SPSU-3-t[b]	-	1.30E-03	-	5.00E-08	-
SPSU-4-t[b]	-	5.50E-03	-	1.00E-07	-
SPSU-5-t[b]	-	2.20E-02	-	1.25E-07	-
SPSU-6-t[b]	-	5.00E+02	-	2.25E-07	-
SPSU-7-t[b]	-	6.00E-02	-	4.55E-07	-
					-
PPSU-A-0.75[c]	-	2.00E-04	1.40E-03	$3.98 \times 10{-}08$	-
PPSU-A-1.5[c]	-	5.00E-05	6.00E-03	$9.12 \times 10{-}08$	-
Nafion[c]	-	5.00E-02	8.00E-02	$6.80 \times 10{-}06$	-

| Polymer	25 °C RH 50% Wet membrane Proton Conductivity (S/cm)	25 °C RH100% Proton Conductivity (S/cm)	80 °C RH100% Proton Conductivity (S/cm)	25 °C Methanol (cm²/s)	70 °C Methanol (cm²/s)
SPSf57[d]	-	8.30E-03	-	-	-
SPSF66[d]	-	2.80E-02	-	-	-
SPSU 87[e]	-	-	9.00E-02	-	-
SPSU 127[e]	-	-	1.40E-01	-	-
sPS-15[f]	-	4.00E-03	2.10E-02	-	-
sPS-25[f]	-	7.00E-03	4.60E-02	-	-
sPS-40[f]	-	1.40E-02	1.20E-01	-	-
SPSf90[g]	-	0.5	-	-	-
					-
SPSf[h]	-	2.4E-04	-	-	-
Nafion 115[i]	-	0.144	-	-	-
Nafion 117[i]	-	0.143	-	-	-
Nafion 117[j]	-	8.56E-07	-	1.41E-06	1.17E-05
S-PEEK 150XF-0.25[j]	-	1.81E-08	-	4.57E-07	4.57E-07
S-PEEK 150XF-0.38[j]	-	8.45E-08	-	7.35E-07	7.35E-07
S-PEEK 150XF-0.52[j]	-	3.36E-07	-	1.06E-06	1.06E-06

*Remark

[a]Yuanqin et al., 2011

[b]Ho Bum et al., 2004

[c]Nedal et al., 2010

[d]Lufrano et al., 2009

[e]Sheng-Li et al., 2005

[f]Yilser et al., 2009

[g]Lufrano et al., 2011

[h]Yongzhu et al., 2007

[i]Acácio et al., 2012

[j]Changkhamchom et al., 2013

**Table 4.2** Mechanical properties of pristine and sulfonated membranes at 70 °C

| Sample	Tensile strength (MPa)	Yield strain (%)	Young modulus (MPa)
PSF	39.9 ± 1.7	7.7 ± 0.9	921 ± 85
SPSF 12.74%	42.0 ± 5.7	6.3 ± 0.7	1162 ± 145
SPSF 15.65%	30.6 ± 3.1	5.2 ± 0.3	1030 ± 171
SPSF 19.90%	31.6 ± 1.6	5.3 ± 0.5	1034 ± 83
SPSF 27.99%	29.55 ± 0.9	5.3 ± 0.5	992 ± 73
SPSF 44.66%	29.32 ± 0.8	5.3 ± 0.3	987 ± 64
SPSF 61.44%	29.0 ± 2.0	5.3 ± 0.9	987 ± 171
SPSF 71.55%	28.4 ± 5.4	6.1 ± 0.6	844 ± 156
PVDF	25.7 ± 2.9	30.9 ± 1.9	349 ± 114
SPVDF 12.34%	33.5 ± 1.0	16.5 ± 1.3	884 ± 28
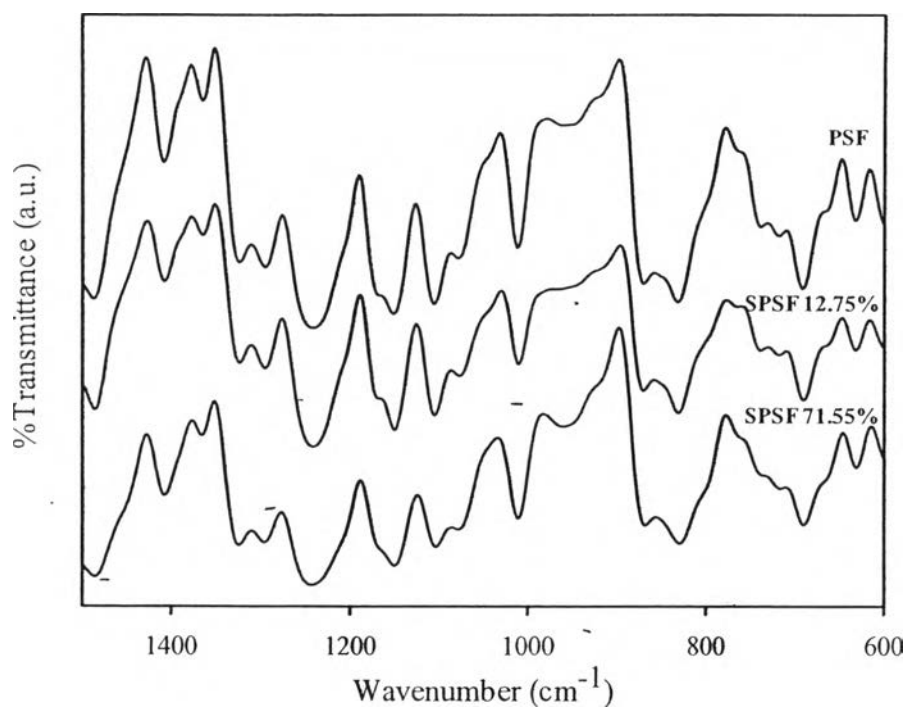
Figure 4.1 The FT-IR spectra of polysulfone (PSF) and sulfonated polysulfone (SPSF) at various degrees of sulfonation.
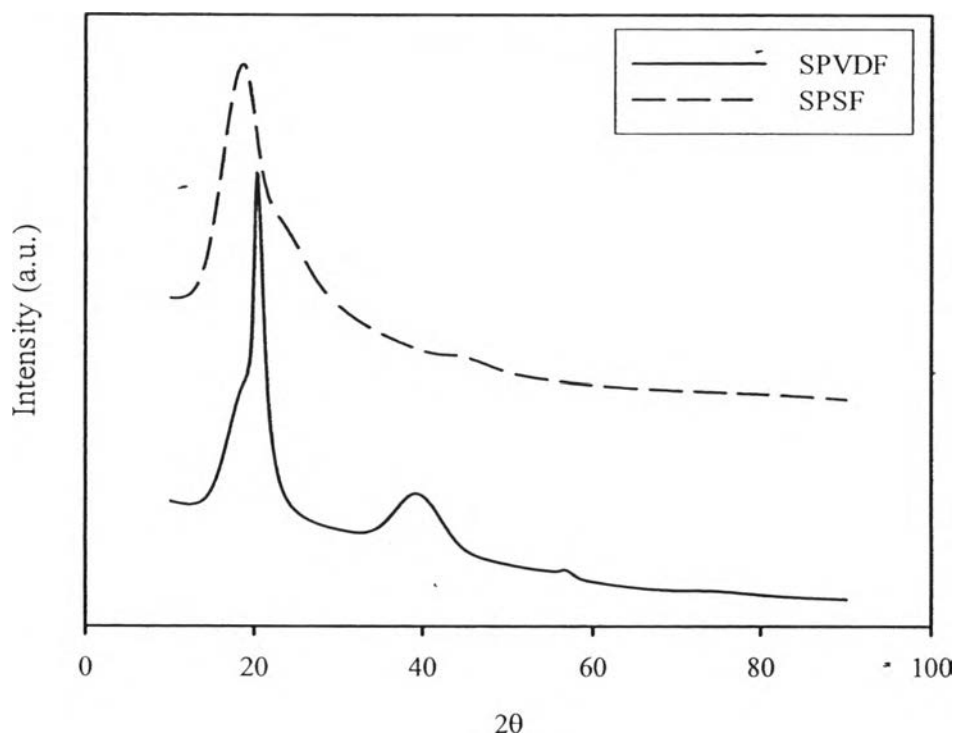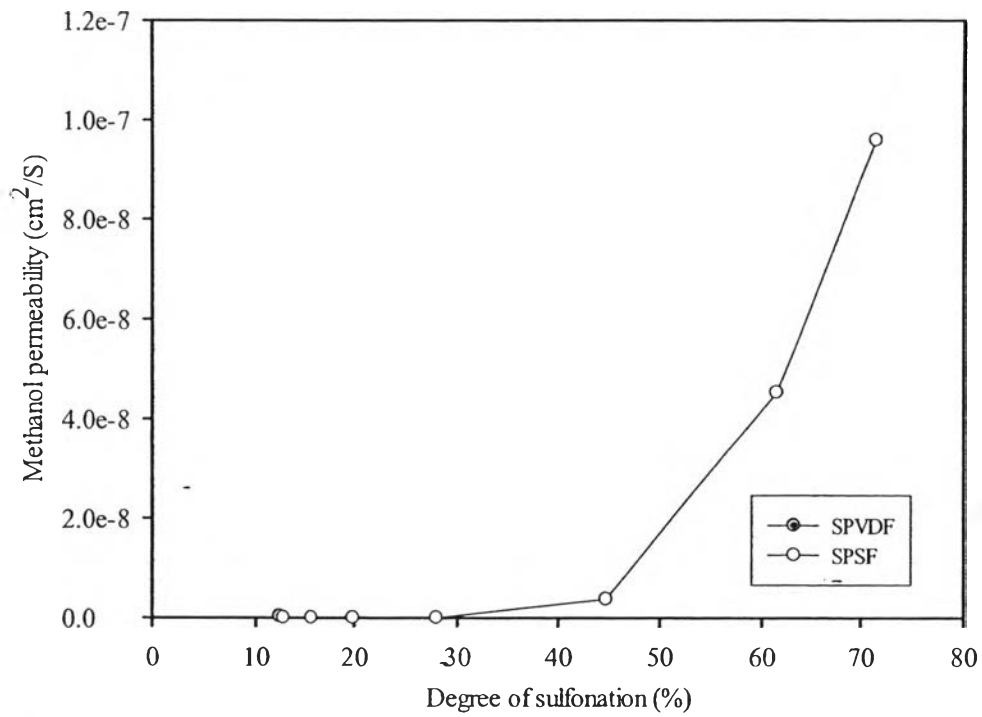

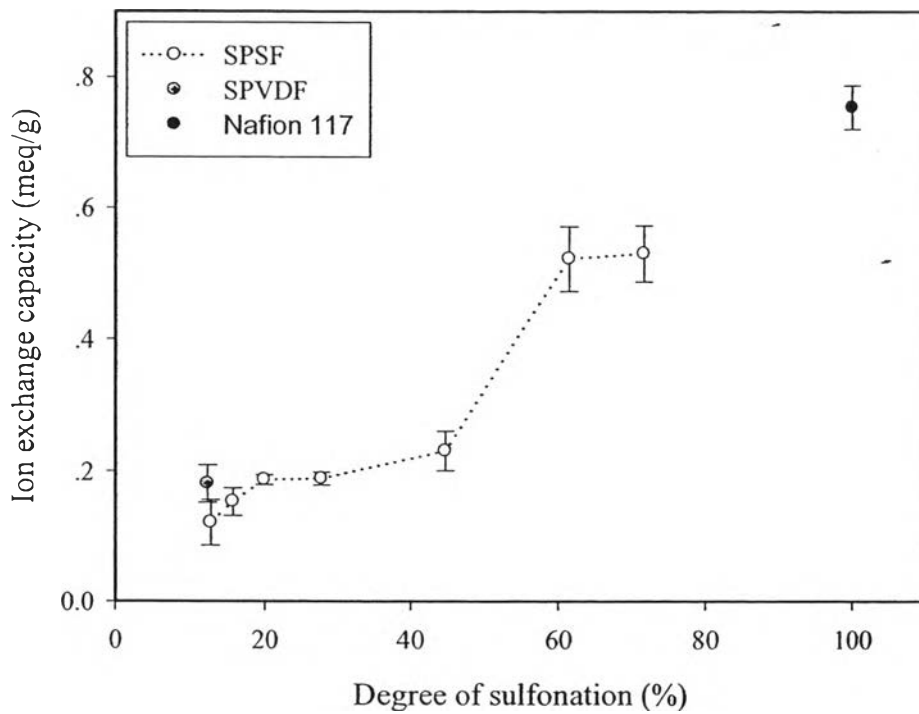**Figure 4.2** XRD pattern of sulfonated SPSF and SPVDF.
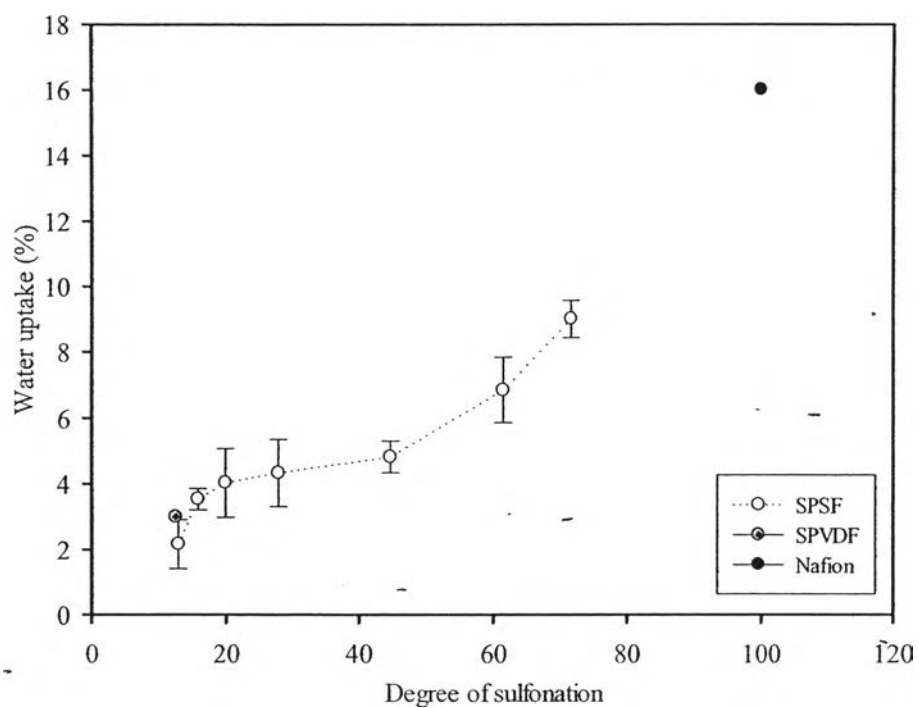
Figure 4.3 Water uptake of SPSF, SPVDF, and Nafion 117.
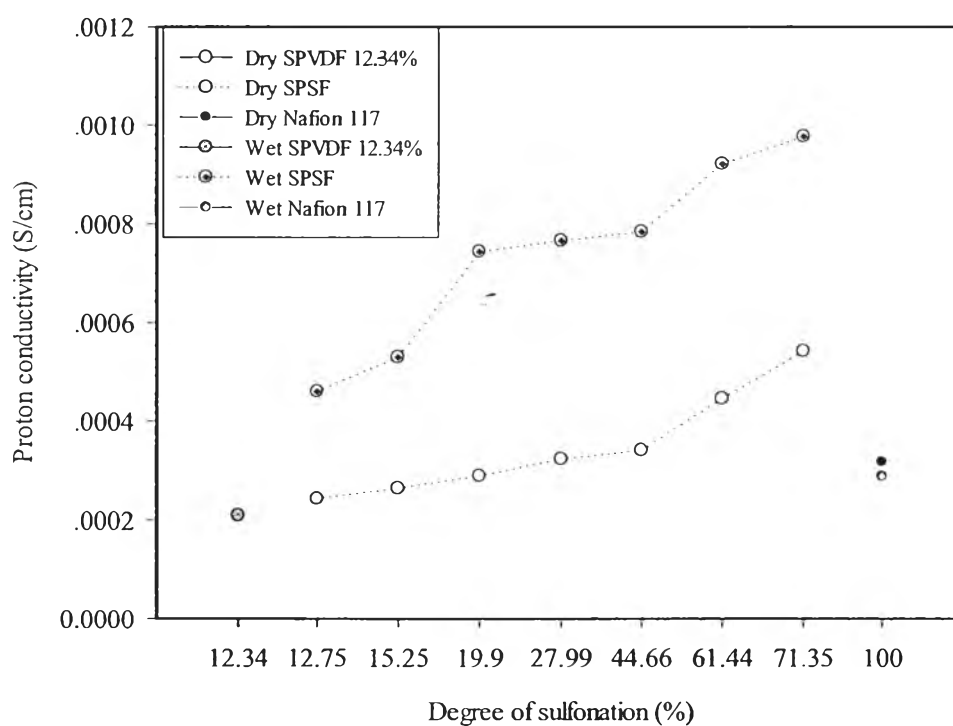
Figure 4.4 Proton conductivity of SPSF, SPVDF, and Nafion 117 under dry and wet state at 25 °C.

Figure 4.5 Methanol permeability of SPSF, SPVDF, and Nafion 117 .

Figure 4.6 Ion exchange capacity of SPSF, SPVDF, and Nafion 117.