CHAPTER IV

PROCESSING OF PROTON EXCHANGE MEMBRANE FOR VANADIUM REDOX FLOW BATTERY

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Abstract

Vanadium redox flow battery (VRFB) is a rechargeable energy storage device that converts chemical energy into electrical energy. Commercially, VRFB uses perfluorosulfonic acid, Nafion, as a proton exchange membrane (PEM) due to its high proton conductivity. However, Nafion is an expensive and possesses high vanadium permeability. In order to reduce this shortcoming, two new modified aromatic membranes, namely poly(ether ether ketone), PEEK, and poly(phenylene ether ether sulfone), PPEES, were developed to be used as proton exchange membrane through a sulfonation process. The effect of degree of sulfonation (DS) on membrane properties namely water uptake, proton conductivity, and vanadium permeability were investigated. Increasing DS induced increase in water uptake, and proton conductivity. The proton conductivity of sulfonated polymer was higher than Nafion due to their difference in the hydrophilic/hydrophobic structures. Furthermore, the vanadium permeabilities of the sulfonated polymers depended on DS and the vanadium permeabilities of DS lower than 73.32% for S-PEEK and 62.53% for PPEES was lower than Nafion. Thus, the sulfonated polymer membranes fabricated for are potential membrane candidates for VBRF.

Keywords: vanadium redox flow battery, proton exchange membrane, poly(ether ether ketone), poly(phenylene ether ether sulfone)

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4.1 Introduction

At present, the energy consumption increases sharply against limited supply, alternative energy sources and storage technologies are attractive towards world's economy and industry [1]. Vanadium redox flow battery (VRFB), a rechargeable energy storage implementation, is one of most attractive choices due to large charge/discharge cycle, rapid response, and reasonable capital cost [2]. The VRFR consists of two electrolyte tanks which are VO_2^+/VO^{2+} and V^{3+}/V^{2+} electrolyte solutions, two pumps, and a battery cell. The important part of VRFB is the ion exchange membrane used to separate the positive and negative electrolyte and to complete the current circuit by transferring ions [3].

Many researches are focused on commercially suitable and stable membranes with good ion conductivity, low area resistance, and high chemical and mechanical stability for VRFB [3]. The Nafion commercial membrane provides a high performance in the proton conductivity; however, the Nafion membrane has a high vanadium permeability resulting in reducing the energy efficiency of redox flow battery. Aromatic containing membrane have been investigated to be used as a proton exchange membrane extensively due to their sufficient proton conductivity and higher mechanical property [4-8]. The department of energy (US DOE) expects that the membranes should have proton conductivity of at least 0.1 S/cm at 80 °C [9]. The proton conductivity of an aromatic polymer can be generally improved by a sulfonation process. The sulfonic groups are attracted on the polymer backbone or pendant group. The sulfonic attachement enhances proton transfer within the polymer matrix because it promotes the hydrophilic domains for proton transfer [9].

The objective of work was to fabricate sulfonated aromatic polymer membranes which possess the crucial properties such as the proton conductivity and vanadium permeability. The two polymers: poly(ether ether ketone) and poly(phenylene ether ether sulfone) were chosen and used as the aromatic polymer membranes because of their good thermal and mechanical stability, and ion conductivity [10-12]. The effect of the degree of sulfonation was investigated to determine the optimal membrane properties for VRFB application and compared with those of Nafion117.

4.2 Experimental

4.2.1 Materials

Poly(ether ether ketone) (PEEK; Victrex, 150XF) and poly(phenylene ether ether sulfone) (PPEES; Aldrich) were used as the starting polymers. Concentrated sulfuric acid (H_2SO_4; Univar, 98%) was used as a sulfonation agent. Magnesium sulfate ($MgSO_4$; Aldrich, 99%) and vanadium (IV) oxide sulfate ($VOSO_4$; Aldrich, 97%) were used as in a solution in the vanadium permeability measurement. Sodium hydroxide (NaOH; LobaChemie, 98%) and phenolphthalein as an indicator were used in the titration. Dimethyl sulfoxide (RCI Labscan, 99.9%) and deionized water were used as solvents for casting and precipitation.

4.2.2 Preparation of Sulfonated Poly(Ether Ether Ketone) (S-PEEK) and Sulfonated Poly(Phenylene Ether Ether Sulfone) (S-PPEES)

The poly(ether ether ketone), PEEK, or poly(phenylene ether ether sulfone), PPEES was dried at 100 °C for 24 h. Then, 2.592 g of PEEK powder or 5.832 g of PPEES pellet was dissolved in 100 ml of sulfuric acid (98%) and vigorously stirred (at 50 °C for PEEK and 25 °C for PPEES) at various sulfonation times. Subsequently, the polymer solution was precipitated in deionized water. Then, sulfonated polymers as S-PEEK and S-PPEES were then filtered and washed with deionized water until the pH was neutral. S-PEEK and S-PPEES were dried at 100 °C for 24 h in a vacuum oven.

4.2.3 Preparation of Sulfonated Polymer Membrane

1.5 g of S-PEEK or S-PPEES was dissolved in 20 mL of dimethyl sulfoxide at 80 °C for 8 h. Then, the solution was cast onto a petri dish in a dust-free environment and dried at 80 °C for 48 h in a vacuum oven.

4.2.4 Characterizations

4.2.4.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of PEEK, PPEES, S-PEEK, and S-PPEES were obtained employing a spectrometer (Thermo Nicolet, Nexus 670) to examine the presence of sulfonic acid group ($-SO_3H$) in polymer backbones. The spectrometer was operated in the absorption mode with a resolution of 4 cm^{-1} and in wave numbers range of 400-4000 cm^{-1}.

4.2.4.2 Nuclear Magnetic Resonance (NMR)

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.

4.2.4.3 Thermogravimatric Analysis (TGA)

The thermal property of the pristine polymers as PEEK and PPEES and sulfonated polymers as S-PEEK and S-PPEES was investigated using a Thermo-gravimetric/differential thermal analyzer (TG/DTA) [13]. The measurement was carried out under nitrogen flow at 25 °C for 15 min and then heated to 900 °C with a heating rate of 10 °C/min.

4.2.4.4 X-ray Diffraction (XRD)

The crystalline structures of polymer and sulfonated polymer were 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. Each sample was mounted on a sample holder and the 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°.

4.2.4.5 Degree of Sulfonation (DS)

The dried membranes (4 cm^2) were dissolved in dimethyl sulfoxide (30 mL). The DS of solution was determined by the titration with 0.01 M of NaOH until pH was neutral using phenolphthalein as an indicator. The DS is defined as the number of sulfonic acid groups divided by the number of repeating units in a polymer chain that was calculated as in the following equation (4.1):

$$DS\ (\%) = \frac{(V_{NaOH} \times C_{NaOH})/1000}{Mole\ of\ polymer\ membrane} \times 100 \tag{4.1}$$

where V_{NaOH} refers to the volume of sodium hydroxide solution (cm^3), and C_{NaOH} refers to the concentration of sodium hydroxide solution (M).

4.2.4.6 Water Uptake

Water uptake was used to determine the amount of water absorbed under specified conditions following the ASTM D570 standard. The membrane sheet (76.2 mm long, 25.4 mm wide) was dried at 110 °C for 24 h, weighed, and soaked in deionized water at 23 °C for 24 h. Then, the membrane was taken out and the water adhering to the surface was quickly wiped off using an absorbent paper. The membrane was weighed again. Then, the water uptake was calculated as in equation (4.2):

$$water\ uptake\ (\%) = \left(\frac{W_w - W_d}{W_d}\right) \times 100 \tag{4.2}$$

where W_w and W_d refer to the weights of the wet and dry samples (g), respectively.

4.2.4.7 Proton Conductivity

Proton conductivity under dry state and wet state of the membranes was determined by an impedance gain/phase analyzer (Hewlett Packard, 4194A) and an impedance phase analyser HP 4194, respectively. A 5 cm × 5 cm film sample with and without immersed in deionized water at room temperature for 24 h was measured using an alternating volatage at 1 V in the frequency range of 100 Hz – 2 MHz. The data showed the relationship between the real impedance (Zcosθ) and the imaginary impedance (-Zsinθ). The resistance (R) was calculated

from the x-intercept of the high frequency impedance plot with a computer curve-fitting technique [14].

$$\sigma = \frac{d}{R \times A} \tag{4.3}$$

where σ is the proton conductivity (S/cm), d is the thickness of the membrane (cm), the surface area of membrane in contact with the electrodes (cm^2), and R refers to the measured resistance of the membrane (Ω).

4.2.4.8 Vanadium Permeability

The vanadium permeability was measured by the method according to the literature [15]. The left reservoir was filled with 50 mL of 1 M VOSO$_4$ in 2 M H$_2$SO$_4$ solution, while the right reservoir was filled with 50 mL of 1 M MgSO$_4$ in 2 M H$_2$SO$_4$ solution. The two reservoirs were separated by the membrane which its surface area equal to 5 cm^2. Both solutions were continuously magnetic stirred at room temperature. Samples of the solution from the right reservoir were taken at a regular time interval, and then vanadium ions were analyzed by a UV-VIS spectrometer (Nanoquant, Infinite M200). The vanadium permeability was calculated by the following equation (4.4):

$$V_R \frac{d\,C_R(t)}{dt} = A \frac{P}{L} (C_L - C_R(t)) \tag{4.4}$$

where V_R is the volume of the right-hand reservoir (cm^3), C_L is the vanadium ion concentration in the left-hand reservoir (M), $C_R(t)$ is the vanadium ion concentration in the right-hand reservoir as a function of time (M), P is the permeability of vanadium ions (cm^2/min) , A is the area of the membrane (cm^2). L is the membrane thickness (cm).

4.2.4.9 Mechanical Properties

The tensile properties of thin film was investigated on a universal testing machine (Lloyd, SMT2-500N) under ASTM D882 with 500 N at 23 $\pm$ 2 °C and 50 $\pm$ 5% RH. The initial gauge separation and crossspeed was set to 50 mm with 25 mm/min, respectively. A specimen was of a guage length of 30 mm, a

width of 10 mm, and a nominal thickness not greater than 0.250 mm [16]. The property parameters consist of the Young's modulus, stress at yield, and elongation at yield were reported from repeated measurements of 5 times.

4.3. Results and discussion

4.3.1 Characterization of Sulfonated Polymer

4.3.1.1 Fourier Transform Infrared Spectroscopy

The FT-IR spectra of PPEES and S-PPEES as shown in Figure 4.1 exhibit the peaks at 1226 and 1485 cm^{-1} which are assigned to the C-O-C [17] and C-C aromatic [18], respectively. The peaks at 1328, 1291, 1016 and 1070 cm^{-1} are identified as the asymmetric S=O stretching, asymmetric O=S=O stretching, symmetric S=O stretching, and symmetric O=S=O stretching on the polymer backbone, respectively ; [17-20]. However, the S-PPEES spectrum shows the peaks at 654 and 720 cm^{-1} which can be referred as the symmetric S-O stretching. PEEK and S-PEEK spectra display the peak at 1650 cm^{-1} for the C=O stretching [17]. The presence of sulfonic group in S-PEEK induced the peaks at 1020 and 1080 cm^{-1} for the symmetric O=S=O stretching and asymmetric O=S=O stretching, respectively [19, 21]. The data thus confirm the successful sulfonation of PEEK and PPEES polymer backbones [17, 21].

4.3.1.2 Nuclear Magnetic Resonance (NMR)

NMR spectra can be used to confirm the sulfonated polymer. Sulfonations of PEEK and PPEES are an electrophilic substitution reaction, in which the SO_3H groups are introduced into the hydroquinone segment of the polymer chains by the ether linkage and the sulfone linkage of PEEK and PPEES, respectively. The presence of the SO_3H groups on S-PEEK and S-PPEES causes a down-field shift of the hydrogen (H_E) to 7.55 ppm and 7.45 ppm for S-PEEK and S-PPEES, respectively. The doublets at 7.15 and 7.25 can be assigned to the hydrogen (H_C and H_D) on hydroquinone ring [22, 23].

4.3.1.3 Thermogravimatric Analysis (TGA)

The thermal stability curves of PPEES and PEEK exhibit the single step degradation temperatures at 550 and 580 °C, respectively which are attributed polymer backbone degradation. However, the S-PPEES and S-PEEK show two steps degration temperatures. S-PPEES displays the degradation temperature from 350 to 450 °C and 500 to 750 °C. S-PEEK thermogram shows the degradations occuring from 300 to 450 °C and from 500 to 700 °C. For both S-PPEES and S-PEEK, the first degradation temperature refers to the characteristic of sulfonic acid group degradation, and the second degradation temperature is the degradation temperature of polymer backbone. The degradation temperature of sulfonated polymer backbone is lower than that of pristine polymer because the catalytic degradation of polymers backbone caused by sulfonic acid groups [17, 21].

4.3.1.4 X-ray Diffraction (XRD)

The XRD patterns of the polymers after the sulfonation process as S-PEEK and S-PPEES exhibit a more amorphous structure with increasing DS. The increasing DS induces more SO_3H groups on the polymer backbone with resulting in changing the chain conformation and decreasing the chain free volume, and thus facilitates orientation of the amorphous structure [19, 24]. Furthermore, the XRD pattern of S-PPEES is broader than S-PEEK as shown in Figure 4.2. This result indicates that the S-PPEES is a more amorphous structure than S-PEEK due to steric hindrance. The chain packing of S-PPEES is lower than S-PEEK because S-PPEES is composed of the sulfone groups (O=S=O) which provide more steric hindrance than the ketone groups (C=O) of S-PEEK, resulting in a more amorphous structure [25].

4.3.2 Degree of Sulfonation (DS)

The DS of S-PEEK and S-PPEES increase with increasing sulfonation time as shown in Figure 4.3. The lowest DS of S-PEEK is 48.05 ± 2.51 % and the highest DS of S-PEEK is 89.04 ± 5.51 % for 1 and 9 h sulfonation times, repectively. For S-PPEES, the lowest DS is 52.81 ± 1.00 % and the highest DS is 83.99 ± 4.47 % for 12 and 48 h sulfonation times, respectively. The time-dependent degree of

sulfonation increases significantly due to the introduction of more SO_3H groups from the sulfonation agent onto the polymer backbones [26].

4.3.3 Water Uptake

A higher DS leads to an increase in water uptake (Figure 4.4) because the SO_3H moiety has a high affinity for water of salvation [8]. As the SO_3H group number is higher, the membrane can absorb more water because of its high hydrophilicity. For S-PEEK, the lowest water uptake is 30.38% and the highest water uptake is 55.61 for the DS of 39.02% and 77.43%, respectively. Comparing with S-PPEES, the lowest water uptake is 73.02% and the highest water uptake is 107.89% for the DS of 52.81% and 83.99%, respectively. At the same DS, the water uptake of S-PEEK is lower than that of S-PPEES because S-PPEES is of an amorphous structure that can accommodate more water absorption. Futhermore, S-PPEES has a polar group as a sulphone group that can attach a water molecule via sulphone group on PPEES structure [25].

4.3.4 Proton Conductivity

The sulfonation process promotes the proton conductivity significantly as shown in Figure 4.5. The proton conductivity increases with increasing DS because a higher sulfonated aromatic polymer has more hydrophilic domains for protons to transport and like to absorb more water or moister, which are well known for proton transport enhancement in solid electrolytes [27]. The proton transport is provided by the protonated sites of sulfonic acid (SO_3H) promoting proton hopping between one hydrolyzed ionic site to another site. Moreover, the proton conductivity under wet state is higher that of dry state because the water absorption in membrane promotes the proton mobility [25, 28]. For S-PEEK, the proton conductivity raises up from 0.068 to 1.023 mS/cm under dry state and from 0.715 to 4.897 mS/cm under wet state with DS ranging from 39.02% to 77.43%. Especially, the proton conductivity of S-PPEES increases from 0.685 to 1.902 mS/cm under dry state and from 3.556 to 25.470 mS/cm under wet state within the DS range of 52.81% and 83.99%. Thus, S-PPEES has higher proton conductivity than S-PEEK with nearly the same DS because of its amorphous structure as shown by XRD

pattern in Figure 4.2 and a higher water uptake. The higher water uptake facilitates the dissociation of SO_3H groups and the proton migration within the membrane [25, 28].

In Figure 4.5, both of S-PEEK and S-PPEES display higher proton conductivity than Nafion 117 (0.317 mS/cm and 2.894 mS/cm under dry state wet state, respectively) due to their difference in the hydrophilic/hydrophobic structures. Generally, the Nafion structure combines 1: high hydrophobicity of fluorine-containing backbone and 2: high hydrophilicity of the sulfonic acid pedant groups which aggregate to form a hydrophilic cluster. The neighboring hydrophilic clusters facilitate the transport of protons and water. For the S-PEEK and S-PPEES morphologies, they possess smaller flexible backbones and lesser separations between hydrophilic/hydrophobic domains (the backbone is less hydrophobic and the sulfonic acid functional group is less acidic). Thus, they can provide higher proton and water transports when compared with Nafion [29].

4.3.5 Vanadium Permeability

Figure 4.6 shows that the vanadium permeability increases with increasing DS because the enrichment and increment of SO_3H groups in the membrane provide larger and more continuous transport channel for the cation to transfer [30]. For S-PEEK, the vanadium permeability increases from 1.512×10^{-6} to 1.038×10^{-5} cm^2/min with the DS range of 39.02% to 77.43%. While vanadium permeability of S-PPEES increases from 5.720×10^{-6} to 1.280×10^{-5} cm^2/min with the DS range of 52.81% to 83.99%. At the same DS, S-PPEES has a higher the vanadium permeability than that of S-PEEK because of its higher proton conductivity and water uptake via its amorphous structure. The vanadium permeability of Nafion (6.76×10^{-6} cm^2/min) is higher than that of S-PEEK (at the DS lower than 73.32%) and S-PPEES (at the DS lower than 62.53%). Normally, the sulfonated aromatic polymer provides a narrow channel for ion transport when comparing with Nafion due to its hydrophilic/hydrophobic structures [31]. The vanadium permeability of sulfonated aromatic polymer is lower than Nafion at lower DS. However, the vanadium permeability of sulfonated polymer is higher than that

of Nafion at higher DS because the greater amount of SO_3H creates a larger channel for ion transport by aggregated SO_3H groups forming hydrophilic clustera [29].

The selectivity is defined the ratio of proton conductivity to vanadium permeability. The selectivity of S-PPEES is higher than that of S-PEEK due to its higher proton conductivity. The optimum selecticity of S-PPEES was 158 S.min /cm^3 at DS equal 77.88% and the optimum selecticity of S-PEEK was 122.93 S.min /cm^3 at DS equal to 73.32%. Moreover, the selectivity values of S-PPEES and S-PEEK are higher than that of Nafion (46.95 S.min /cm^3), with the exceptions of the selectivity values of S-PEEK at DS equal to 39.02%, 44.14%, and 59.60% that are lower than Nafion. Therefore, a balance between ion conductivity and vanadium permeability can be optimally achieved in VBRF with the fabricated S-PEEK and S-PPEES membranes, relative to Nafion 117.

4.3.6 Mechanical Properties

The mechaical property reported as Young's modulus, stress at yield, and percentage strain at yield of S-PEEK, S-PPEES, and Nafion are tabulated in Table 4.1. The three mechanical properties of S-PEEK and S-PPEES initially increase with increasing DS because the sulfonation reaction created a more rigid and tough material [31]. The three mechanical properties show peaks at DS equal to 59.8 for S-PEEK and DS equal to 77.88 S-PPEES, beyond those DS the three mechanical properties decrease because of the reduction in the glass transition temperatures at higher degree of sulfonation [23]. S-PEEK provides a better mechanical property than S-PPEES due to its more crystallinity [32]. Moreover, the mechanical property of S-PEEK and S-PPEES are higher than those of Nafion 117. Thus, S-PEEK and S-PPEES membranes are sufficietly strong and tough for usages as the proton excahnge membrane in VRFB.

Table 4.2 shows the comparison of proton exchange membrane properties used inVRFB of vaious polymer types. The aromatic polymers sulfonated were S-PPEES and S-PEEK at various DSs using H_2SO_4 as the sulfonation agent [17]. The proton contivity and vanadium permeabilty depended on DS. However, the proton conductivity of S-PPEES and S-PEEK obtained from this previous work were higher than this work. The sulfonated poly(fluorenyl ether ketone) (S-PFEK) was

fabricated and investigated membrane for using in VRFB application [7]. S-PFEK provided a lower vanadium permeability than that S-PEEK and S-PPEES because the fluorenyl group of S-PFEK provided a lower proton conductivity than those of the ketone group of S-PEEK and the sulfone group of S-PPEES [7]. Diels Alder poly(phenylene) (S-DAAP) was developed for using as PEM in VRFB by sulfonating at various DSs using $ClSO_3H$ as a sulfonatio agent [8]. The increase DS induced increasing both the proton conductivity and vanadium permeability. The vanadium permeability of S-DAAP was lower than S-PEEK, SPEES, and S-PFEK because of a lower acid stength of the sulfonation pendant group. Sulfonated poly(fluorenyl ether ketone) (SPFEK) was improved as the polyaromatic membrane for using in VRFB via direct fluorinatation [6]. The vanadium permeability was the lowest when compared with those of S-PPEES, S-PEEK, S-PFEK, and S-DAPP because the introduction of fluorine is an efficient strategy to improve the oxidative stability of sulfonated polymer.

Therefore, the properties of membrane depend on the types of aromatic polymer, DS. modification methode, and sulfonation or fluorination agent.

4.4 Conclusions

The sulfonated PPEES and PEEK were prepared at various DSs using 98% sulfuric acid as a sulfonation agent. The membrane properties depended on the DS and the type of aromatic polymers. The water uptake, proton conductivity, and vanadium permeability increased with increasing DS. S-PPEES provided greater properties than S-PEEK because its structure was an amorphous and higher polarity of sulfon group promoting higher water uptake and proton conductivity. Futhermore, the properties of sulfonated polymers were greater than those of Nafion 117. The vanadium permeability of S-PPEES was higher than that of S-PEEK for the same DS. Comparing with Nafion, the vanadium permeability values of S-PEEK at DS lower than 73.32% and of S-PPEES at DS lower than 63.53% were lower than the vanadium permeability of Nafion 117. The selectivity of S-PPEES was higher than that of S-PEEK due to the proton conductivity. The optimum selecticity of S-PPEES was 158 S.cm/min at DS equal to 77.88% and the optimum selecticity of S-PEEK

was 123 S.cm/min at DS equal to 73.32%. However, the selectivity values of S-PPEES and S-PEEK membranes were higher than Nafion 117, except the selectivity values of S-PEEK at DS equal to 39.02%, 44.14%, and 59.60% that are lower than that of Nafion. Therefore, the sulfonated polymer membranes fabricated here, S-PEEK and S-PPEES, for VBRF are potetial membrane candidates for VBRF.

Acknowledgements

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Table 4.1 Mechanical properties of S-PEEK, S-PPEES, and Nafion117

Polymer	Young's modulus (Mpa)	Stress at yield (Mpa)	Percentage strain at yield (%)
S-PEEK	-		
DS39.02	720.3 ± 78.3	19.40 ± 2.21	4.317 ± 0.632
DS44.14	742.6 ± 36.1	27.46 ± 1.50	5.916 ± 0.298
DS59.60	850.3 ± 29.7	36.33 ± 1.79	7.229 ± 0.174
DS73.32	642.9 ± 26.2	21.29 ± 1.42	5.925 ± 0.373
DS77.43	530.6 ± 24.9	16.52 ± 2.53	5.341 ± 0.188
S-PPEES			
DS52.81	437.1 ± 29.6	13.56 ± 2.16	6.115 ± 0.722
DS62.53	446.0 ± 37.7	16.94 ± 0.91	6.525 ± 0.827
DS68.73	519.2 ± 61.2	17.83 ± 2.00	7.014 ± 0.895
DS71.69	609.8 ± 125	23.06 ± 1.36	7.398 ± 2.477
DS77.88	669.9 ± 75.5	24.78 ± 0.59	8.589 ± 1.668
DS83.99	504.7 ± 90.4	15.32 ± 2.50	5.475 ± 0.274
Nafion 117	185.0 ± 10.2	10.99 ± 0.41	24.12 ± 1.91

Table 4.2 Comparison of proton exchange membranes used in VRFB

Membrane	Approach	Agent	T_s	DS	σ (mS/cm)	P (μm^2/min)
S-PPEES[17]	Sulfonation	H_2SO_4	25	0.83	124	250
S-PEEK [17]	Sulfonation	H_2SO_4	25	0.58	52	2.42
			-	0.76	75	141
				0.86	151	228
S-PFEK [7]	Sulfonation	SDFBP	175	1.20	17	98.5
S-DAPP [8]	Sulfonation	$ClSO_3H$	-50	1.20	49	44.0
				1.60	78	81.0
				2.00	87	430
F-SPFEK [6]	Fluorination	F_2	25	1.20	31	3.25
S-PEEK [26]	Blend	PVDF	50	0.73	9.2	1.14
S-PEEK [25]	Blend	PEI	25	N/A	72	4.78
S-PEEK [12]	Blend	S-PES	25	N/A	N/A	66

*T_s = Sulfonation temperature

μm^2/min = 10^{-8} cm^2/min
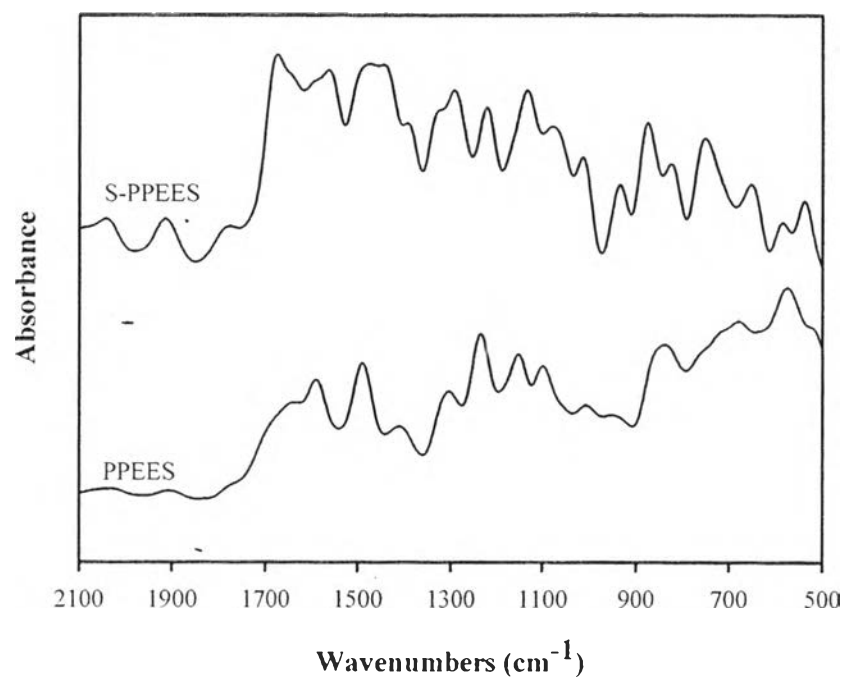
Figure 4.1 FTIR spectrum of PPEES and S-PPEES.
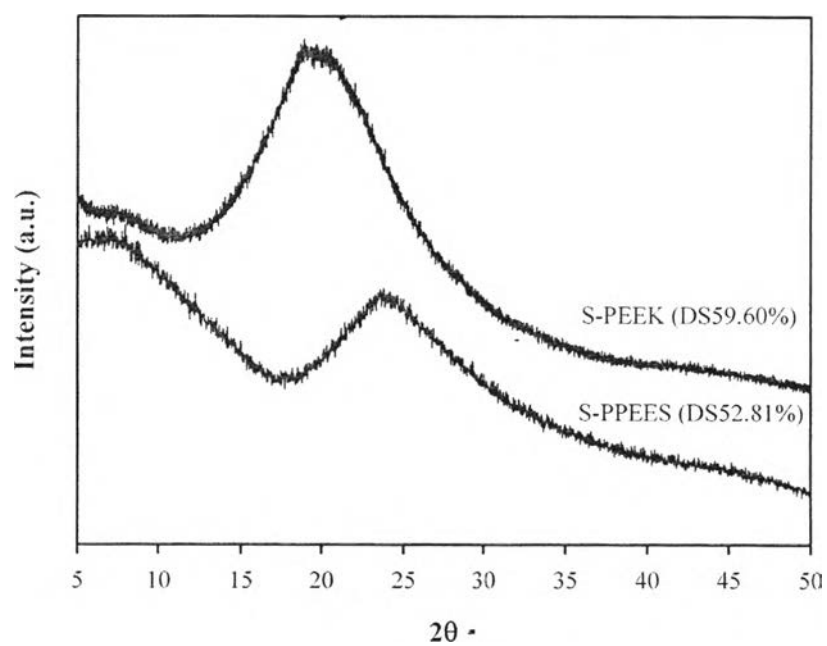
Figure 4.2 XRD pattern of sulfonated PPEES and S-PPEES.

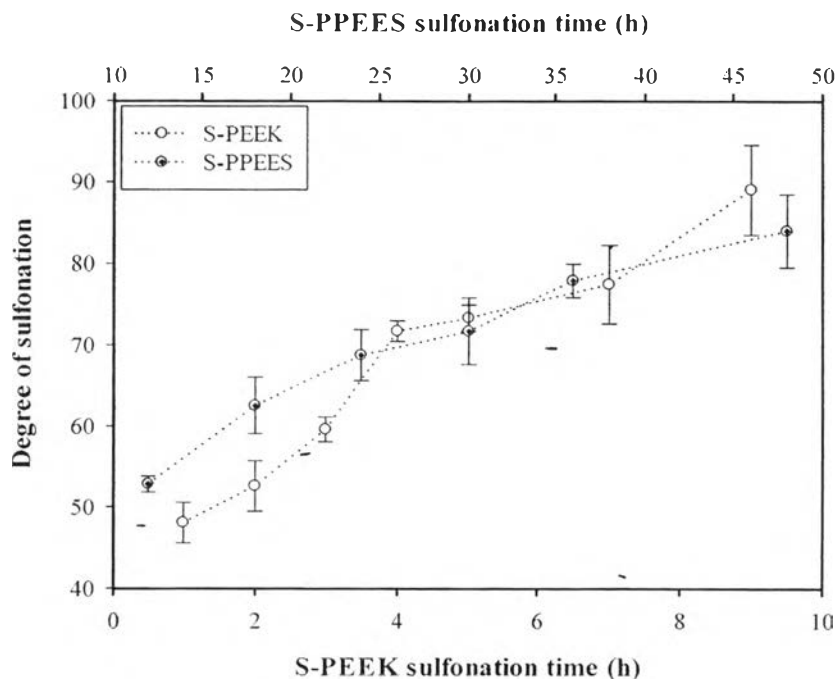**S-PPEES sulfonation time (h)**

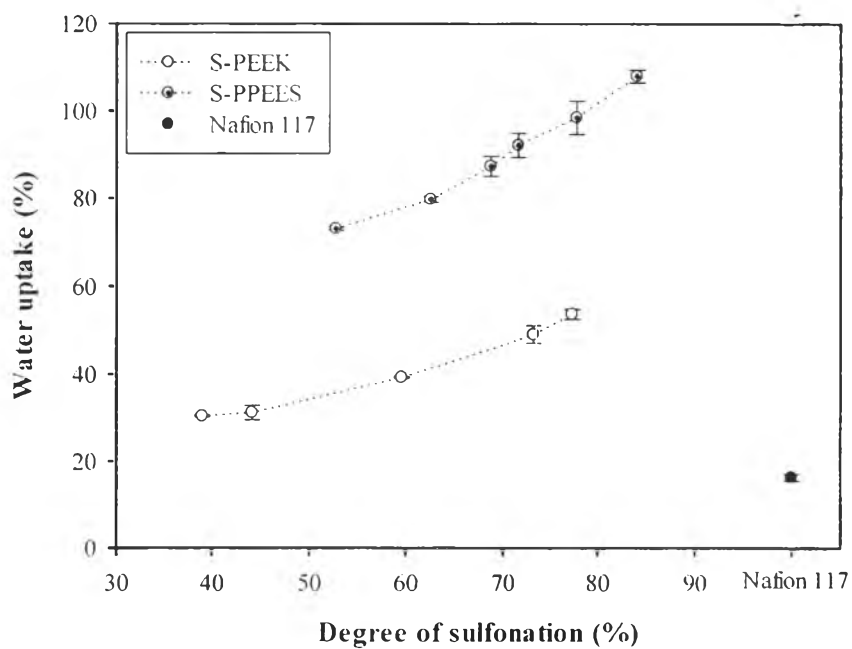**Figure 4.3** Degree of sulfonation of S-PPEES and PEEK at various sulfonation times.

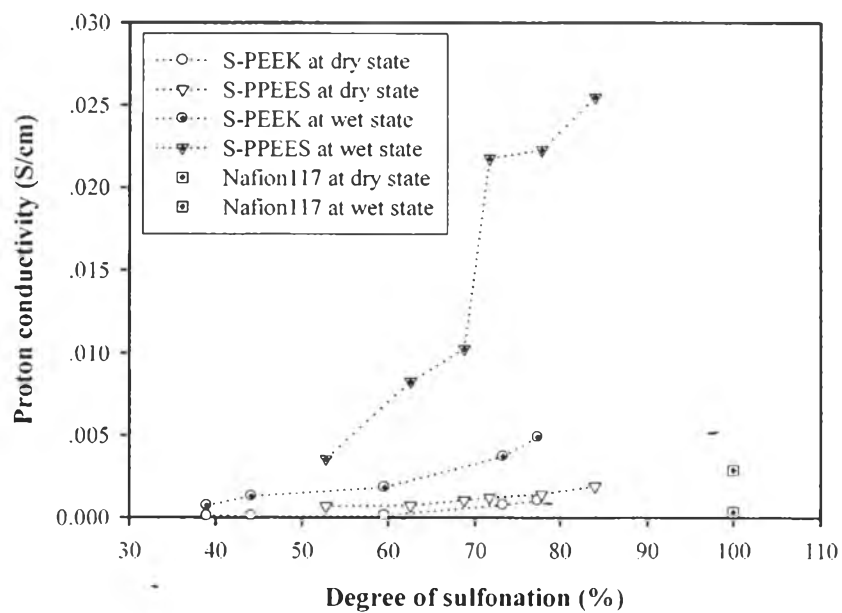**Figure 4.4** Water uptake of S-PEEK, S-PPEES, and Nafion117.

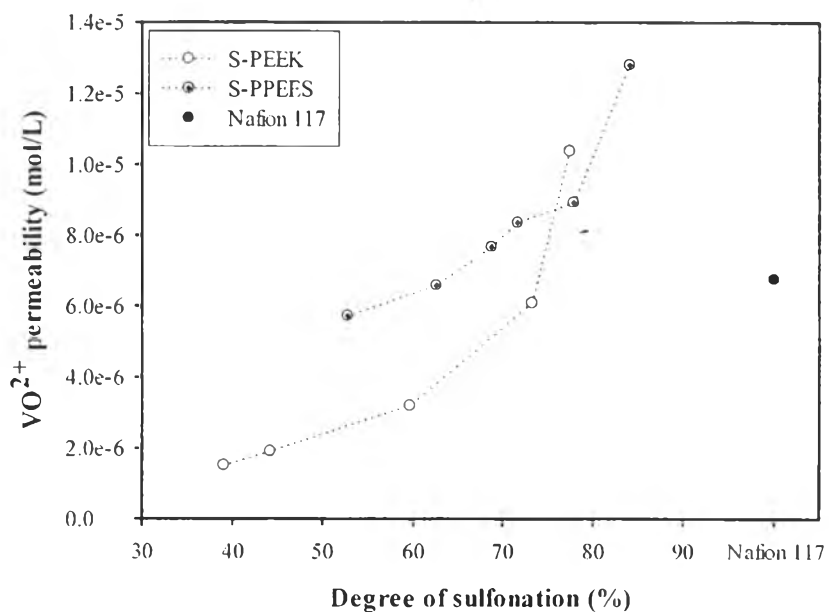**Figure 4.5** Proton conductivity of S-PEEK, S-PPEES, and Nafion117 under dry and wet state.

Figure 4.6 Vanadium permeability of S-PEEK, S-PPEES and Nafion 117 at 25 °C.