



## CHAPTER IV

### SULFONATED POLY(ETHER ETHER KETONE) AND SULFONATED POLY(1,4-PHENYLENE ETHER ETHER SULFONE) MEMBRANE FOR VANADIUM REDOX FLOW BATTERY

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#### Abstract

Nafion<sup>®</sup> is a currently used Proton Exchange Membrane (PEM) in Vanadium Redox Flow Batteries (VRB). It is an excellent proton conducting and fully hydrated membrane, but it has a very high cost. In order to reduce the cost of the membrane used in VRB and to reduce the vanadium permeability across the membrane during the operation, sulfonated poly(ether ether ketone) (PEEK), and poly(1,4-phenylene ether ether sulfone) (PPEES) membranes were fabricated and studied as a function of the sulfonation reaction time. The increase in the degree of sulfonation (DS) from 46 to 86% induces the increase in the water uptake, the ion exchange capacity (IEC), the proton conductivity, and the vanadium permeability. The vanadium permeability coefficients of S-PEEK and S-PPEES membranes are in the range of 0 to  $24.95 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ , which are significantly lower than that of Nafion<sup>®</sup> 117, which is  $30.84 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ .

**Keywords:** Sulfonated poly(ether ether ketone); Sulfonated poly(1,4-phenylene ether ether sulfone); Degree of sulfonation; Vanadium redox flow battery

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## Introduction

Vanadium Redox Battery, or VRB, is a type of a rechargeable flow battery used as an energy storage system. The VRB energy is stored chemically in different ionic forms of vanadium in a dilute sulfuric acid electrolyte. The function of a membrane is not only to prevent the cross mixing of the positive and negative electrolytes but also allowing the transport of ions to complete the circuit during the passage of current [1]. For a VRB system, the ideal membrane should possess low permeability of vanadium ions and a low water transport in order to obtain a higher Coulombic efficiency and a long circle life, and high proton conductivity to obtain a higher voltage efficiency [2].

Nafion<sup>®</sup> is a perfluorosulfonic polymer commonly used as a proton exchange membrane material in the VRB system because its high proton conductivity and good chemical stability; but its cost is very expensive compared to others [3]. The vanadium ions, however, are easy to penetrate through the Nafion membrane amidst the operation of the VRB because the selectivity of Nafion membrane is not sufficiently high. In addition, the preferential water transfer across the membrane can result in the precipitation of vanadium salt and cause the flooding of the solution tanks and ultimately causes the operational difficulties in commercial systems. A sulfonation is a well-known and alternative way in developing a new membrane for VRB system. Generally, the sulfonation is an electrophilic substitution reaction in which one of the hydrogen ions on the aromatic rings is substituted by the sulfonic acid group (-SO<sub>3</sub>H). The presence of the sulfonic acid group constitutes the S-Polymer to become highly hydrophilic and enable it to perform the high proton conductivity. The sulfonated aromatic poly(ether ether ketones) (S-PEEK) based membranes have been studied because of their good mechanical properties, thermal stability, and conductivity [4]. Furthermore, poly(1,4-phenylene ether ether sulfone) (PPEES) has been recently used as a backbone aromatic polymer. Thus, the aromatic rings can be sulfonated with electrophilic sulfonation agents.

In this work, PEEK and PPEES were selected as the potential membranes for the VRD system. The degree of sulfonation (DS) was controlled by the reaction

time and temperature. The effect of DS of S-PEEK and S-PPEES on membranes properties was investigated and shall be reported here.

## **Experimental**

### Materials

Poly(ether ether ketone) (PEEK) 150XF, (Victrex<sup>®</sup>), and Poly(1,4-phenylene ether ether sulfone) (PPEES), (Aldrich<sup>®</sup>) were used as the starting polymers. Concentrated sulfuric acid, H<sub>2</sub>SO<sub>4</sub> (Univar, 98 wt%) was used in the sulfonation of the polymers. Hydrochloric acid (RCI Labscan, 37%), sodium hydroxide 1 M (Fisher Scientific) and sodium chloride (RCI Labscan, A.R.) were used in the sulfonation and in the ion exchange capacity. Vanadyl sulfate hydrate (Aldrich<sup>®</sup>, 97%) and magnesium sulfate (Aldrich<sup>®</sup>, 99%) were used in the determination of the vanadium permeability. Dimethyl formamide (RCI Labscan, 99.9%), and n-methyl-2-pyrrolidone (Lab-Scan) were used as a solvent.

### Sulfonation of Poly(ether ether ketone) (S-PEEK)

The PEEK 150XF powder was dried in a vacuum oven at 100 °C for overnight. Then, 4.0 g of the polymer was dissolved in 100 ml of concentrated sulfuric acid (98%) and vigorously stirred at 25 ± 2 °C at different reaction times: 1, 2, 3, 7, and 9 days [5]. Subsequently, the polymer solution was accelerated into ice-cold water under continuous stirring. The polymer precipitate was filtered and washed by using distilled water and the process was repeated until the pH of polymer was neutral. The polymer was dried under vacuum at 100 °C for 24 h. The final product was the sulfonated poly(ether ether ketone) (S-PEEK). The scheme of the sulfonation of PEEK is shown in Figure 1.

### Sulfonation of Poly(1,4-phenylene ether ether sulfone) (S-PPEES)

The 4.0 g of PPEES powder was dissolved in 40 ml of concentrated sulfuric acid (98%) and stirred at 25 ± 2 °C at 12 h. Subsequently, the polymer solution was precipitated into ice-cold water under a continuous stirring. The polymer precipitate

was filtered and washed by using distilled water and repeated until the pH of polymer was neutral. The polymer was dried under vacuum at 100 °C for 24 h. Finally, the product was the sulfonated poly(1,4-phenylene ether ether sulfone) (S-PPEES). The scheme of the sulfonation of PPEES is shown in Figure 2.

#### Preparation of S-PEEK and S-PPEES membranes

The S-PEEK and S-PPEES were dissolved in dimethyl formamide (DMF). Then, the mixtures were cast onto a glass plate and dried for 24 h at 80 °C. Subsequently, the membranes were immersed for 24 h in a large volume of 2 M HCl aqueous solution to give the membranes in the acid form (H<sup>+</sup>) [6].

### **Characterizations and Testing**

#### FT-IR Spectrometer

The FT-IR spectra of sulfonated and non-sulfonated polymers were obtained using a Thermo Nicolet (Nexus 670) spectrometer to identify the presence of sulfonic acid group (-SO<sub>3</sub>H) in polymer samples. The spectrometer was operated in the absorption mode with 64 scans, a resolution of 4 cm<sup>-1</sup>, and wave numbers range of 4000-400 cm<sup>-1</sup>, using a deuterated triglycine sulfate as a detector. KBr and ZnSe disc were used as the background materials. Polymer samples were mixed with dried KBr. In contrast, each of the S-Polymer samples was prepared by casting as a thin film onto a ZnSe disc.

#### Thermogravimetric Analyzer (TGA)

The thermogravimetric analysis was used to determine the weight loss in the thermal degradations of S-PEEK and S-PPEES from 40 to 850 °C, with a scanning rate of 10 °C/min, under a nitrogen atmosphere, using a thermal analyzer (PerkinElmer, Pyris Diamond TG/DTA). The experiment was carried out by weighting a sample of 2-4 mg and placed it in an alumina pan. The samples were dried at 100 °C for 24 h to remove any moisture.

### Degree of Sulfonation (DS) by Titration

Degree of sulfonation (DS) is defined as the number of sulfonic acid groups divided by the number of repeating units in the polymer chain. First, the membranes were acidified with an excess 2 M HCl solution at room temperature for 24 h. Subsequently, the membranes in acid form ( $H^+$ ) were dried at 60 °C for 24 h and exchanged to sodium form by an immersion in 1 M NaCl solutions for 24 h. Then, the solution was titrated with 0.01 M NaOH by using phenolphthalein as an indicator. The titrations were repeated three times and the DS value was obtained.

### Ion-Exchange Capacity (IEC) by Titration

The titration technique was used to determine the IEC of the membranes which indicates number of milliequivalents of ions in 1 g of dry polymer (meq./g). Initially, the membranes were transformed to the sodium form by immersing the membranes in a 1 M NaCl solution for 24 h to exchange the  $H^+$  ions with  $Na^+$  ions. The exchanged  $H^+$  ions within the solutions were titrated with a 0.01 M NaOH solution. Phenolphthalein as the universal indicator was dropped in to help determine the neutral point [7]. The IEC of the cation exchange membrane was calculated from the following equation:

$$IEC \text{ (meq/g)} = \frac{\text{consumed ml NaOH} \times \text{molarity NaOH}}{\text{weight dried membrane}} \quad (1)$$

### Water Uptake Measurement

The membranes were dried in an oven at 100 °C for 24 h, weighed, soaked in deionized water overnight at room temperature. After equilibrated for 24 h, the membrane was taken out and the water adhering to the surface was quickly wiped using an absorbent paper [8]. The membrane was weighted again. Thus, water uptake was calculated from

$$\text{water uptake (\%)} = \left( \frac{G_{wet} - G_{dry}}{G_{dry}} \right) \times 100 \quad (2)$$

where  $G_{wet}$  and  $G_{dry}$  are the weights of the membrane in the wet and dry states, respectively.

### Proton Conductivity ( $\sigma$ )

The proton conductivity of the fully hydrated membranes was measured by using an Agilent E4980A LCR impedance analyzer at the potential of 1 V and the frequency range from 20 Hz to 2 MHz. The fully hydrated membranes were cut into 2×2 mm pieces and painted with a silver paint on both sides. The conductivity  $\sigma$  of the fully hydrated membranes was calculated from the impedance data by using the following equation:

$$\sigma = \frac{d}{RS} \quad (3)$$

where  $d$  and  $S$  are the thickness and the surface area of the membranes respectively, and  $R$  is the resistance of the membrane as derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the  $\text{Re}(Z)$  axis [9]. The impedance data was corrected for the contribution from the empty and short-circuited cell.

### Permeability of Vanadium ions

The vanadium permeability of the membranes was determined by using two connected reservoirs. The left reservoir was filled with the 50 ml of 1 M  $\text{VOSO}_4$  in 2 M  $\text{H}_2\text{SO}_4$ , and the right reservoir was filled with 50 ml of 1 M  $\text{MgSO}_4$  in 2 M  $\text{H}_2\text{SO}_4$ . The two reservoirs were separated by the membrane samples.  $\text{MgSO}_4$  was used to equalize the osmotic pressure. The two solutions were continuously stirred at a room temperature [9]. Samples of the  $\text{MgSO}_4$  solution were taken at a regular time interval in order to investigate the vanadium ions concentration by using a UV-VIS spectrometer at 760 nm [10]. Therefore, the vanadium ion concentration in the right reservoir as a function of time was calculated from following equation:

$$V_B \frac{dC_B(t)}{dt} = A \frac{P}{L} (C_A - C_B(t)) \quad (4)$$

where  $V_B$  represents the volume of the right reservoir,  $C_A$  is the vanadium ion concentration in the left reservoir, and  $C_B(t)$  is the vanadium ion concentration in the right reservoir as a function of time.  $P$  represents the permeability of vanadium ions.  $A$  and  $L$  are the area and thickness of the membrane.

### Mechanical Property

The mechanical properties of the membranes were measured by using a Universal Testing Machine (Lloyd, model SMT2-500N). Each membrane had a thickness between 110-280  $\mu\text{m}$  and the size of 1cm  $\times$  5cm. The membranes were immersed in de-ionized water for 24 h before testing using the gauge length of 30.0 mm and the speed of 10 mm/min at a room temperature. For each sample, at least five samples were measured and average value was calculated [11].

## **Results and discussion**

### FT-IR Spectrometer

In Figure 3 shows the FT-IR spectra of S-PEEK and PEEK. For S-PEEK, the peak at 708  $\text{cm}^{-1}$  can be assigned to the symmetric S-O stretching vibration. The peak at 1022  $\text{cm}^{-1}$  represents the symmetric S=O stretching. The symmetric and the asymmetric O=S=O stretching vibrations are confirmed by the strong characteristic peaks at 1078 and 1250  $\text{cm}^{-1}$  [12]. The peaks at 1650 and 1222  $\text{cm}^{-1}$  are assigned to the C=O and C-O-C stretching of the polymer backbone, respectively. The aromatic C-C peak at 1489  $\text{cm}^{-1}$  of PEEK is observed to split into two peaks at 1471 and 1491  $\text{cm}^{-1}$  for S-PEEK because of the new substitution of the sulfonation process [13]. For S-PPEES and PPEES, their spectra are shown in Figure 4. The peak at 709  $\text{cm}^{-1}$  can be assigned to the symmetric S-O stretching vibration. The peak at 1022  $\text{cm}^{-1}$  represents the symmetric S=O stretching. Lastly, the peaks at 1075 and 1252  $\text{cm}^{-1}$  represent the symmetric and the asymmetric O=S=O stretching vibrations, respectively. These data confirm the successful sulfonations of the PEEK and PPEES polymer backbones.

### Thermogravimetric Analyzer (TGA)

Figure 5 shows the thermal stability of S-PEEK and PEEK. The PEEK thermogram exhibits a single step degradation temperature of the polymer chain higher than 580  $^{\circ}\text{C}$ ; the S-PEEK thermogram exhibits three steps degradation. First, between 50 to 200  $^{\circ}\text{C}$  in the S-PEEK thermogram represents the weight loss of the physically and chemically bound water. The weight loss between 250 to 350  $^{\circ}\text{C}$  is

attributed to the decomposition of the sulfonic acid groups. Lastly, the weight loss above 510 °C is the S-PEEK backbone degradation. In Figure 6, the degradation of PPEES backbone is shown approximately at 550 °C. The weight loss between 250 to 350 °C is due to the sulfonic acid groups.

#### Degree of Sulfonation (DS) and Ion Exchange Capacity (IEC)

The sulfonations of PEEK and PPEES at different reaction times from 1 to 9 days versus IEC are shown in Table 1. S-PPEES can only be sulfonated at with DS value of about 80%. This is because the solubility of PPEES is very low. Due to the short reaction time of PPEES, it cannot be sulfonated to attain a lower DS value. The DS and IEC values of S-PEEK both increase with increasing sulfonation time due to the introduction of more SO<sub>3</sub>H groups. The lowest IEC of S-PEEK is  $1.25 \pm 0.01$  meq./g (DS ~ 46.21 ± 0.23%) and the highest IEC of S-PEEK is  $2.35 \pm 0.01$  meq./g (DS ~ 86.49 ± 0.49%). The IEC of S-PPEES is  $2.07 \pm 0.01$  meq./g (DS ~ 83.57 ± 0.43%). The IEC value of Nafion<sup>®</sup> 117 is 0.91 meq./g (DS ~ 100%) [14]. Therefore, the IEC value of Nafion<sup>®</sup> 117 is lower than those of S-PEEK and S-PPEES.

#### Water Uptake

Water uptake is a significant property of any ion exchange membranes. Furthermore, the water uptake can be related to the proton conductivity and the mechanical strength of the membrane. However, water uptake at a high percentage can lead to low mechanical strength [15]. In Table 1, the water uptake (%) increases with increasing DS because of the greater hydrophilicity. S-PPEES membrane has the highest water uptake value of  $121.93 \pm 0.13\%$  (DS ~ 83.57%). S-PEEK membranes show values between  $15.54 \pm 0.57$  to  $83.02 \pm 0.83\%$  (DS between 46.21 and 86.49%). These values are comparable to that of the Nafion<sup>®</sup> 117 which possesses the smallest the water uptake value of about  $20.52 \pm 0.03\%$ .

#### Proton Conductivity

The effect of the DS on the proton conductivity of S-PEEK and S-PPEES membranes at a room temperature is shown in Table 1. The proton conductivity of S-PEEK varies between  $2.72 \times 10^{-2}$  S/cm to  $1.51 \times 10^{-1}$  S/cm (DS 46.21 to 86.49%). For



S-PPEES, the proton conductivity is  $1.24 \times 10^{-1}$  S/cm which is higher than that of Nafion<sup>®</sup> 117 which is  $8.00 \times 10^{-2}$  S/cm [6]. In addition, with increasing DS, the membrane becomes more hydrophilic and absorbs more water which is responsible for the increase in the proton transfer through the membrane.

#### Vanadium Permeability

The permeability of the membrane was determined by the rate of permeability of  $\text{VO}^{2+}$  ions across the membrane at room temperature. Figure 7 shows the  $\text{VO}^{2+}$  ion concentrations across the S-PEEK, S-PPEES, and Nafion 117 membranes which were measured at a regular time interval using an UV-VIS spectrometer at 760 nm. S-PEEK with the DS values of 46.21, 57.99, 69.07, 76.49, and 86.49% membranes show  $\text{VO}^{2+}$  ion permeability values across the membranes of 0,  $24.18 \times 10^{-9}$ ,  $12.58 \times 10^{-7}$ ,  $14.13 \times 10^{-7}$ , and  $22.82 \times 10^{-7}$   $\text{cm}^2/\text{min}$ , respectively. For S-PPEES, it exhibits a lower vanadium permeability at  $24.95 \times 10^{-7}$   $\text{cm}^2/\text{min}$  than that of Nafion<sup>®</sup> 117 which is at  $30.84 \times 10^{-7}$   $\text{cm}^2/\text{min}$ . Thus, the reduction in  $\text{VO}^{2+}$  ion across the membranes could be achieved by using S-PEEK and S-PPEES membranes instead. Luo *et al.*, 2008 reported that the differing vanadium ions permeability of S-PEEK and Nafion membranes can be explained by the difference in their microstructures. In the Nafion membrane, the microstructures of polymers are composed of two parts: the extremely high hydrophobic fluorocarbon backbone and the extremely high hydrophilic sulfonic functional groups. It would give rise to some hydrophobic/hydrophilic nano-separation, especially in the presence of water. The hydrophilic sulfonic groups cluster to form hydrophilic domains, which are well interconnected because of the high flexibility of the fluorocarbon of Nafion membrane. Not only proton and water can transport through these domains, but vanadium ions can also permeate through these domains. In comparison with the Nafion membrane, the backbone of the S-PEEK membrane is less hydrophobic, and the sulfonic acid group is less acidic. This results in a smaller hydrophilic/hydrophobic separation corresponding to the highly dispersed sulfonic groups. Furthermore, the high rigidity of the S-PEEK backbone in which the  $-\text{SO}_3\text{H}$  groups are attached also prevents the neighboring dispersed sulfonic groups from aggregating to bigger clusters. Thus, the water filled channels in S-PEEK membrane

are narrower and branched with more dead end pockets compared with those in the Nafion membrane. This is perhaps the reasons for the reduction of vanadium permeability in the S-PEEK membranes [14].

### Tensile Strength

From Table 2, the mechanical properties of the wet S-PEEK and S-PPEES membranes were at room temperature are tabulated. S-PEEK membranes have the tensile strength, the young's modulus, and the elongation at break in the ranges of 12.57 to 40.85 MPa, 339.76 to 1136.60 MPa, and 33.82 to 204.05%, respectively. Tensile strength, young's modulus, and elongation at break of S-PPEES membrane are at 8.16 MPa, 194.27 MPa, and 53.03%, respectively. The tensile strength, young's modulus and elongation at break of the Nafion<sup>®</sup> 117 are 28.40 MPa, 1000.00 MPa, and 329.90%. S-PEEK DS 46.21% possesses much higher tensile strength and young's modulus than those of the Nafion<sup>®</sup> 117. On the other hand, Nafion<sup>®</sup> 117 has the highest elongation at break indicating it as a very flexible material.

### **Conclusions**

The sulfonated PEEK and PPEES were prepared from 98% sulfuric acid at different reaction times to fabricate S-PEEK and S-PPEES membranes at various degrees of sulfonation (DS). S-PPEES can only be sulfonated at the DS value of about 80% due to the poor solubility of PPEES and the short reaction time. According to the results obtained from the characterizations and the testing, the properties of S-PEEK and S-PPEES membranes depend critically on DS. An increase in DS induces the increases in the water uptake, IEC, the proton conductivity, and the vanadium ions permeability. On the other hand, an increase in DS also induces a decrease in the mechanical property of the membranes because an increase in the water uptake can lead to low mechanical strength. S-PEEK and S-PPEES show lower vanadium ions permeability values than that of the Nafion 117 membrane. This work thus demonstrates the potential fabrication and utilization of low-cost proton exchange membranes with reduced vanadium crossover for the vanadium redox flow battery.

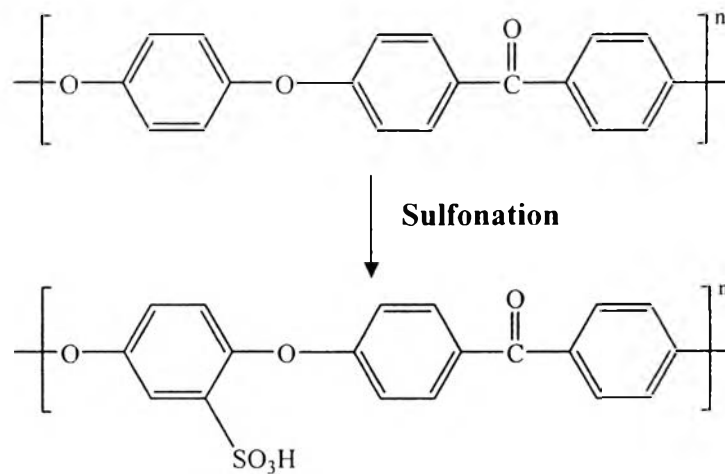
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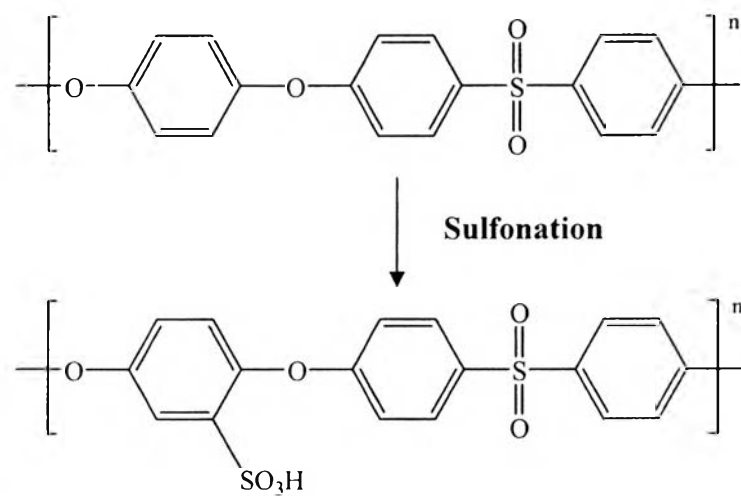
## References

- [1] Mohammadi, T., and Skyllas-Kazacos, M. (1995) *J. Membr. Sci.* 98, 77-87.
- [2] Teng, X., Zhao, Y., Xi, J., Wu, Z., Qiu, X., and Chen, L. (2009) *J. Membr. Sci.* 341, 149-154.
- [3] Luo, Q., Zhang, H., Chen, J., You, D., Sun, C., and Zhang, Y. (2008) *J. Membr. Sci.* 325, 553-558.
- [4] Li, X., Wang, Z., Lu, H., Zhao, C., Na, H., and Zhao, C. (2005) *J. Membr. Sci.* 254, 147-155.
- [5] Li, L., Zhang, J., and Wang, Y. (2003) *J. Membr. Sci.* 226, 159-167.
- [6] Zhao, C., Li, X., Wang, Z., Dou, Z., Zhong, S., and Na, H. (2006) *J. Membr. Sci.* 280, 643-650.
- [7] Gil, M., Ji, X., Li, X., Na, H., Hampsey, J.E., and Lu, Y. (2004) *J. Membr. Sci.* 234, 75-81.
- [8] Othman, M.H.D., Ismail, A.F., and Mustafa A. (2007) *J. Membr. Sci.* 299, 156-165.
- [9] Chen, D., Wang, S., Xiao, M., and Meng, Y. (2010) *J. Power Sources* 195, 2089-2095.
- [10] Wiedemann, E., Heintz, A., and Lichtenthaler, R.N. (1998) *J. Membr. Sci.* 141, 215-221.
- [11] Liu, B., Robertson, G.P., Kim, D.S., Guiver, M.D., Hu, W., and Jiang, Z. (2007) *Macromol.* 40, 1934-1944.
- [12] Zaidi, S.M.J. (2003) *Arabian J. Sci. Eng.* 28, 183-194.

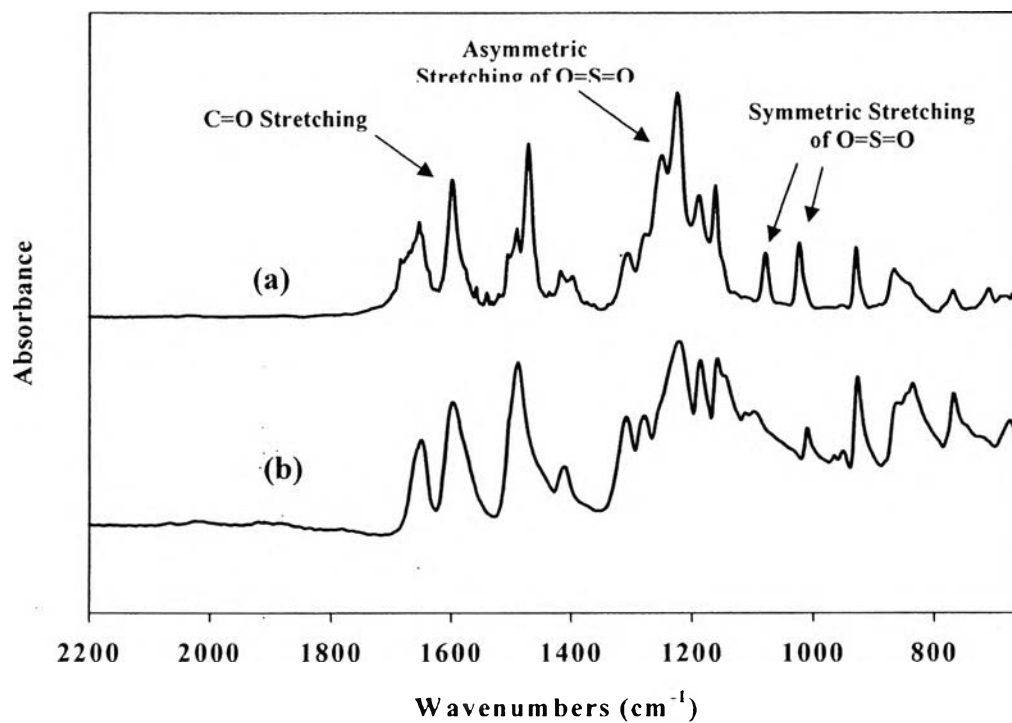
- [13] Jiang, R., Kunz, H.R., and Fenton, J.M. (2005) *J. Power Sources* 150, 120-128.
- [14] Luo, Q., Zhang, H., Chen, J., You, D., Sun, C., and Zhang, Y. (2008) *J. Membr. Sci.* 325, 553-558.
- [15] Li, H., Cui, Z., Zhao, C., Wu, J., Fu, T., Zhang, Y., Shao, K., Zhang, H., Na, H., and Xing, W. (2009) *J. Membr. Sci.* 343, 164-170.



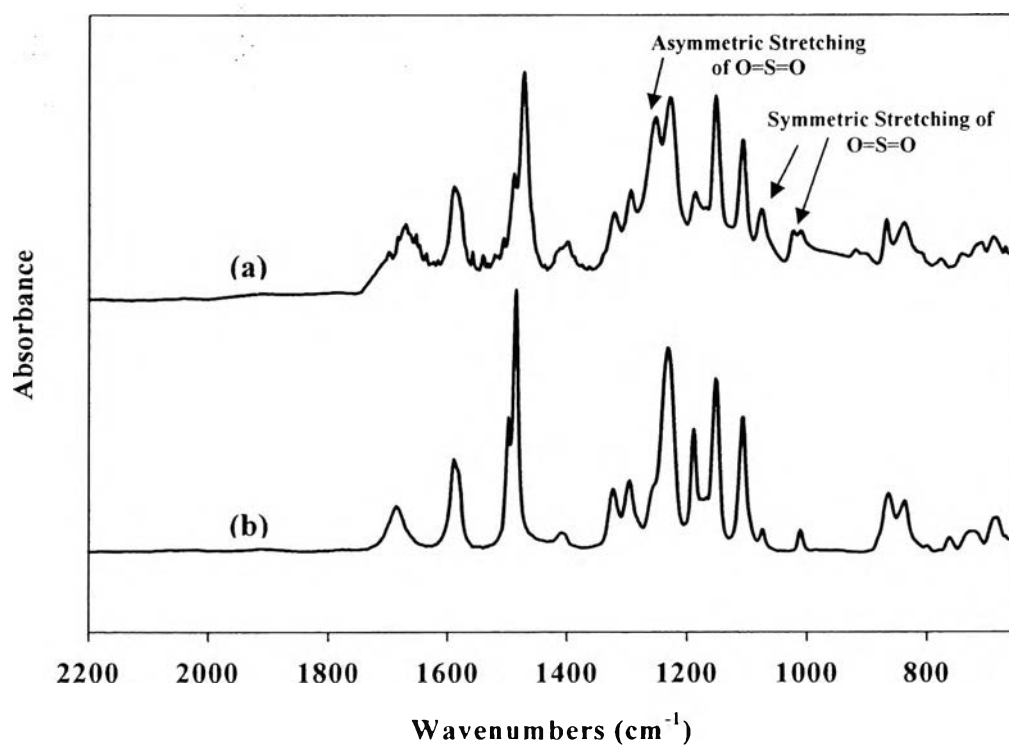
**Figure 1** The scheme of the sulfonation of PEEK.



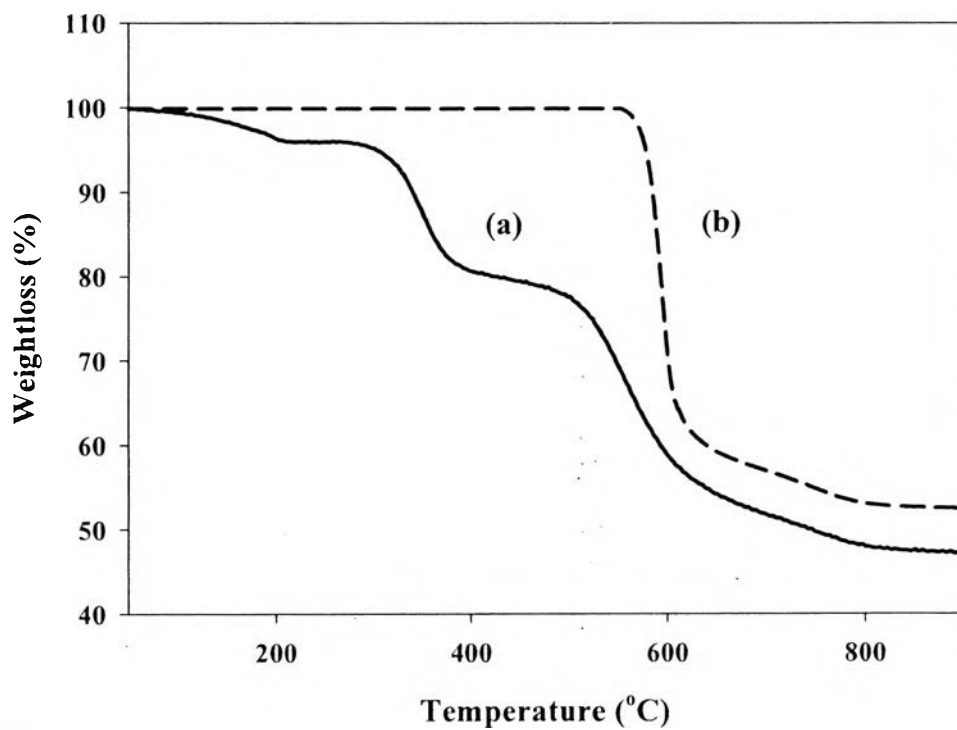
**Figure 2** The scheme of the sulfonation of PPEES.



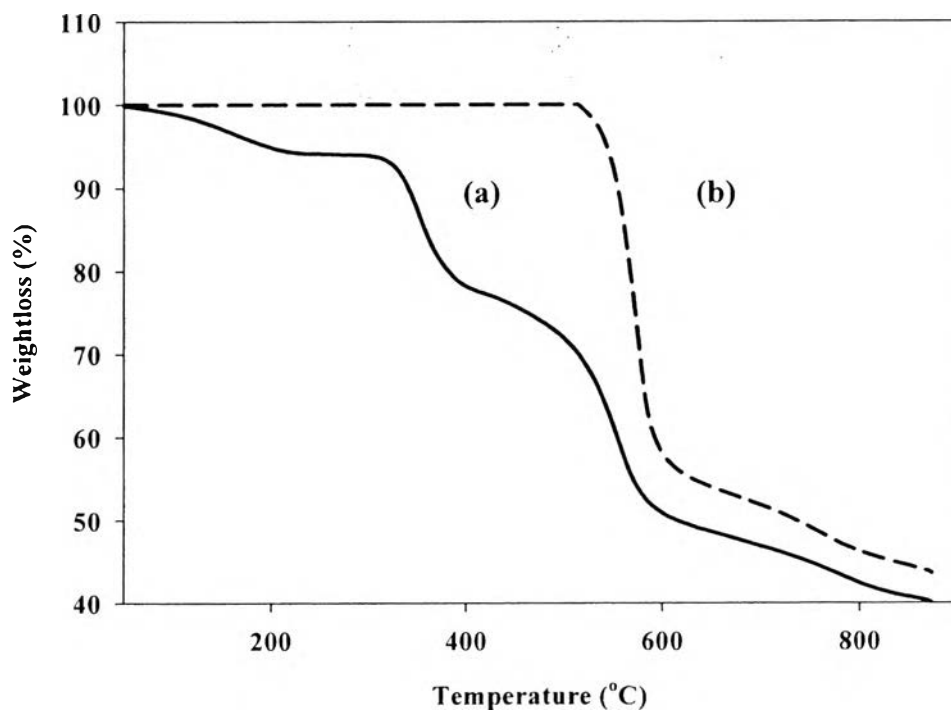
**Figure 3** The FT-IR spectra of: a) S-PEEK and b) PEEK.



**Figure 4** The FT-IR spectra of: a) S-PPEES and b) PPEES.



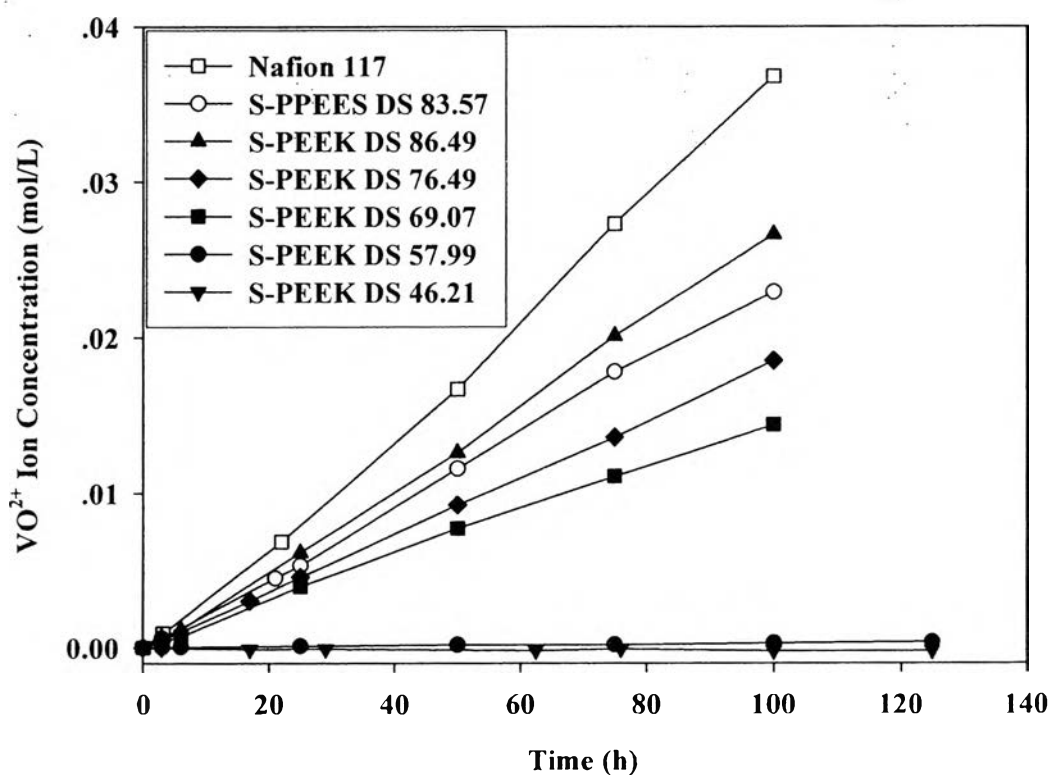
**Figure 5** TGA thermograms of: (a) S-PEEK; and (b) PEEK.



**Figure 6** TGA thermograms of: (a) S-PPEES; and (b) PPEES.

**Table 1** Characterization data of the S-PEEK, S-PPEES, and Nafion<sup>®</sup> 117 membranes

Polymer	Water Uptake (%)	IEC (meq./g)	Proton Conductivity, ( $\sigma$ ) (S/cm)	Vanadium Permeability, ( $P$ ) (cm <sup>2</sup> /min)
S-PEEK DS 46.21	15.54	1.25	0.0272	0
S-PEEK DS 57.99	30.57	1.58	0.0517	$24.18 \times 10^{-9}$
S-PEEK DS 69.07	27.16	1.87	0.0631	$12.58 \times 10^{-7}$
S-PEEK DS 76.49	67.65	2.08	0.0747	$14.13 \times 10^{-7}$
S-PEEK DS 86.49	83.02	2.35	0.1510	$22.82 \times 10^{-7}$
S-PPEES DS 83.57	121.93	2.07	0.1240	$24.95 \times 10^{-7}$
Nafion 117	20.52	0.91	0.0800	$30.84 \times 10^{-7}$



**Figure 7** The vanadium ions permeability across S-PEEK, S-PPEES, and Nafion<sup>®</sup> 117.



**Table 2** The mechanical properties of the membranes

<b>Polymer</b>	<b>Tensile strength (MPa)</b>	<b>Young's modulus (MPa)</b>	<b>Elongation at break (%)</b>
S-PEEK DS 46.21	40.85	1136.60	33.82
S-PEEK DS 57.99	34.56	881.68	99.08
S-PEEK DS 69.07	31.66	654.52	204.05
S-PEEK DS 76.49	25.58	512.90	134.44
S-PEEK DS 86.49	12.57	339.76	137.29
S-PPEES DS 83.57	8.16	194.27	53.03
Nafion 117 <sup>a</sup>	28.40	1000.00	329.20

<sup>a</sup> Ref. [11]