

## CHAPTER III EXPERIMENTAL

### 3.1 Materials and Instruments

#### 3.1.1 Materials

Poly(ether ether ketone) (PEEK; Victrex, 150XF) and poly(phenylene ether ether sulfone) (PPEES; Aldrich) were used as polymer membranes. Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ; Univar, 98%) was used as a sulfonating agent in the sulfonation process to introduce sulfonic groups onto the polymer backbones. Magnesium sulfate ( $\text{MgSO}_4$ ; Aldrich, 99%) and vanadium (IV) oxide sulfate ( $\text{VOSO}_4$ ; Aldrich, 97%) were used in a solution in the vanadium permeability study. Sodium hydroxide ( $\text{NaOH}$ ; LobaChemie, 98%) was used in the titration method where phenolphthalein acted as an indicator. Dimethyl sulfoxide (RCI Labscan, 99.9%) and deionized water were used as solvents. Sodium chloride (Fluka, 26%) was used in the ion exchange capacity titration.

#### 3.1.2 Instruments

Fourier transform infrared spectrometer (FT-IR; Thermo Nicolet, Nexus 670) was used to identify the chemical structure of the polymers and sulfonated polymers. The polymer membrane properties such as proton conductivity, thermal property, and mechanical property were investigated using an impedance gain/phase analyzer (Hewlett Packard, 4194A), a thermogravimetric analyzer (TGA; PerkinElmer, Pyris Diamond), a NMR spectrometer (Bruker Biospin Avance 500 MHz NMR spectrometer), a wide angle X-ray diffraction (Bruker AXS, D8 Advance), and a universal testing machine (Lloyd, SMT2-500N), respectively. A UV-VIS spectrometer (Nanoquant, Infinite M200) was used to determine the amount of vanadium permeation.

## 3.2 Methodology

### 3.2.1 Preparation of Sulfonated Poly(ether ether ketone) (S-PEEK) and Sulfonated Poly(phenylene ether ether sulfone) (S-PPEES)

#### 3.2.1.1 *Sulfonation of Poly(Ether Ether Ketone) (S-PEEK)*

The poly(ether ether ketone), PEEK, powder was dried at 100 °C for 24 h. For an excess molar ratio (mole of sulfuric acid : mole of repeating unit of polymer) of 200 as shown in Table 3.1, 2.592 g of PEEK powder was added in 100 mL of sulfuric acid (98%) and vigorously stirred at  $50 \pm 2$  °C at various reaction times. Subsequently, the polymer solution was precipitated in deionized water. Then, it was filtered and washed with deionized water, and the process was repeated until the pH was neutral. The sulfonated poly(ether ether ketone), S-PEEK, was dried at 100 °C for 24 h.

**Table 3.1** Relation between excess molar ratio and volume fraction for poly(ether ether ketone) sulfonation

Excess molar ratio	Weighed polymer (g)	Sulfuric acid (cm <sup>3</sup> )	Volume fraction (%)
50	10.368	100	91.74
100	5.184	100	95.69
150	3.456	100	97.09
200	2.592	100	97.80
300	1.728	100	98.52
400	1.296	100	98.89

#### 3.2.1.2 *Sulfonation of Poly(Phenylene Ether Ether Sulfone) (S-PPEES)*

The poly(phenylene ether ether sulfone), PPEES, pellet was dried at 100 °C for 24 h. For an excess molar ratio (mole of sulfuric acid : mole of repeating unit of polymer) of 100 as shown in Table 3.2, 5.832 g of PPEES pellet was added in 100 mL of sulfuric acid (98%) and vigorously stirred at  $25 \pm 2$  °C at various reaction times. Subsequently, the polymer solution was precipitated in

deionized water. Then, it was filtered and washed with deionized water, and the process was repeated until the pH was neutral. The sulfonated poly(phenylene ether ether sulfone), S-PPEES, was dried at 100 °C for 24 h.

**Table 3.2** Relation between excess molar ratio and volume fraction for poly(phenylene ether ether sulfone) sulfonation

Excess molar ratio	Weighed polymer (g)	Sulfuric acid (cm <sup>3</sup> )	Volume fraction (%)
50	11.664	100	91.86
100	5.832	100	95.76
150	3.888	100	97.13
200	2.916	100	97.83
300	1.944	100	98.54
400	1.458	100	98.91

### 3.2.2 Preparation of Sulfonated Polymer Membrane

#### 3.2.2.1 Sulfonated Poly(Ether Ether Ketone) Membrane

The 1.4 g of S-PEEK was dissolved in 20 mL of dimethyl sulfoxide at 80 °C for 8 h. Then, the solution was cast on a petri dish in a dust-free environment and dried at 80 °C for 48 h.

#### 3.2.2.2 Sulfonated Poly(Phenylene Ether Ether Sulfone) Membrane

The 1.4 g of S-PPEES was dissolved in 20 mL of dimethyl sulfoxide at 80 °C for 8 h. Then, the solution was cast on a petri dish in a dust-free environment and dried at 80 °C for 48 h.

**Table 3.3** The list of polymer membranes and degrees of sulfonation

DS (%)	20	40	50	60	80
S-PEEK	S-PEEK20	S-PEEK40	S-PEEK50	S-PEEK60	S-PEEK80
S-PPEES	S-PPEES20	S-PPEES40	S-PPEES50	S-PPEES60	S-PPEES80

The samples are cited as S-PEEK-XX and S-PPEES-XX (XX denotes the different degree of sulfonation as shown in Table 3.3). The properties of sulfonated membrane as the proton conductivity, vanadium permeability, ion exchange capacity, and water uptake were studied based on the effect of degree of sulfonation.

### 3.3 Characterization and Testing

#### 3.3.1 Proton Conductivity

Proton conductivity under dry state and wet state of the membrane was determined by an impedance gain/phase analyzer (Hewlett Packard, 4194A) and an impedance phase analyser HP 4194, respectively. The 5 cm × 5 cm film with and without immersed in deionized water at room temperature for 24 h was measured at 1 V potential using the alternating current in the frequency range of 100 Hz – 2 MHz. A plot of  $Z'$  vs  $Z''$  showed the relationship between the real impedance ( $Z\cos\theta$ ) and the imaginary impedance ( $-Z\sin\theta$ ). The proton conductivity ( $\sigma$ ) was calculated from the impedance plot with a computer curve-fitting technique to determine the resistance ( $R$ ) as following Eq. (3.1) (Ahmad *et al.*, 2006; Chen *et al.*, 2010):

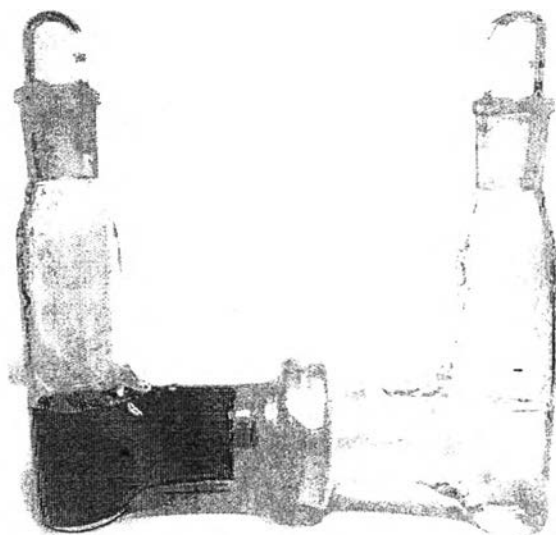
$$\sigma = \frac{d}{R \times A} \quad (\text{S/cm}) \quad (3.1)$$

where  $\sigma$  is the proton conductivity (S/cm),  $d$  is the membrane thickness (cm),  $A$  is the surface area of membrane in contact with the electrode (cm<sup>2</sup>), and  $R$  refers to the membrane resistance ( $\Omega$ ) ( $R$  is derived from the intersect of the high frequency semicircle on a complex impedance plane with the Re ( $Z$ ) axis).

#### 3.3.2 Vanadium Permeability

The vanadium permeability was measured by the method according to the literature (Chen *et al.*, 2010; Jia *et al.*, 2010). The left reservoir was filled with 50 mL of 1M VOSO<sub>4</sub> in 2M H<sub>2</sub>SO<sub>4</sub> solution, while the right reservoir was filled with 50 mL of 1M MgSO<sub>4</sub> in 2M H<sub>2</sub>SO<sub>4</sub> solution as shown in Figure 3.1. MgSO<sub>4</sub> was used to

equalize the osmotic pressure. The two reservoirs were separated by the membrane which its area was equal  $5 \text{ cm}^2$ .



**Figure 3.1** Vanadium permeability device.

Both solutions were continuously magnetic stirred at room temperature. Vanadium ions in left reservoir penetrated through the membrane to the right reservoir. Samples of the solution from the right reservoir was taken at a regular time interval, then vanadium ions were analyzed by a UV-VIS spectrometer (Nanoquant, Infinite M200) at the wavenumber of 760 nm.

The vanadium permeability was calculated with the following Eq. (3.2):

$$V_R \frac{d C_R(t)}{dt} = A \frac{P}{L} (C_L - C_R(t)) \quad (3.2)$$

where  $V_R$  = the volume of the right-hand reservoir ( $\text{cm}^3$ )  
 $C_L$  = the vanadium ion concentration in the left-handreservoir (M)  
 $C_R(t)$  = the vanadium ion concentration in the right-hand reservoir as a function of time (M)

- P = the permeability of vanadium ions (cm<sup>2</sup>/min)  
 A = the area of the membrane (cm<sup>2</sup>)  
 L = the thickness of the membrane (cm)

### 3.3.3 Degree of Sulfonation (DS)

The polymer membrane was washed with deionization water and dried at 100 °C for 24 h. The degree of sulfonation of solution was determined by the titration with 0.01 M of sodium hydroxide until pH was neutral using phenolphthalein as an indicator. The DS was defined as the number of sulfonic acid groups divided by the number of repeating units in a polymer chain that was calculated as in Eq. (3.3):

$$DS (\%) = \frac{(V_{NaOH} \times C_{NaOH}) / 1000}{\text{Mole of polymer membrane}} \times 100 \quad (3.3)$$

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

### 3.3.4 Ion Exchange Capacity (IEC)

The IEC is defined as mmol of sulfonic acid groups for 1 g of dry polymer determined through the acid–base titration. The membranes were dried at 100 °C for 24 h, weighed and then immersed 24 h in a known volume 0.1 M of NaCl solution to exchange the H<sup>+</sup> to Na<sup>+</sup> ions. The H<sup>+</sup> containing solution was determined by back titration with a 0.01 M of NaOH solution until pH was neutral with phenolphthalein as indicator. IEC was calculated according to Eq. (3.4) (Sukkar *et al.*, 2004; Zhai *et al.*, 2007):

$$\text{IEC (mmol} \cdot \text{g}^{-1}) = \frac{V_{eq} \cdot C_{NaOH}}{W_d} \quad (3.4)$$

where  $V_{eq}$  is the equivalent volume of NaOH solution (mL),  $W_d$  refers to the weight of the dry membrane (g).

### 3.3.5 Mechanical Properties

The tensile properties of thin film was investigated on a universal testing machine (Lloyd, SMT2-500N) under ASTM D882 with 500 N capacity 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 with a gauge length of 30 mm, a width of 10 mm, and nominal thickness was not greater than 0.250 mm (Laxmeshwar *et al.*, 2012). The parameters consisting of the Young's modulus, tensile strength, and elongation at break were reported. All these tests were conducted at ambient temperature and an average value of five repeated tests was taken for each material.

### 3.3.6 Water Uptake

Water uptake determines the amount of water absorbed under specified conditions following by ASTM D570. 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  $23 \pm 1$  °C for 24 h. Then, the membrane was taken out and the water adhering to the surface was quickly wiped off using absorbent paper. The membrane was weighed again. Then, the water uptake was calculated as in Eq. (3.5) (Macksasitorn *et al.*, 2012):

$$\text{water uptake (\%)} = \left( \frac{W_w - W_d}{W_d} \right) \times 100 \quad (3.5)$$

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

### 3.3.7 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of pristine polymer as PEEK and PPEES and sulfonated polymer as S-PEEK and S-PPEES were obtained employing a spectrometer (Thermo Nicolet, Nexus 670) to examine the presence of sulfonic acid group ( $-\text{SO}_3\text{H}$ ) in polymer samples. Then, the spectrometer was operated in the absorption mode with a resolution of  $4\text{ cm}^{-1}$  and wave numbers range of  $4000\text{-}400\text{ cm}^{-1}$ . KBr was employed as the background materials for sample powder and sample of sulfonated polymer membrane, respectively.

### 3.3.8 Thermogravimetric Analysis (TGA)

The thermal property of pristine polymer as PEEK and PPEES and sulfonated polymer as S-PEEK and S-PPEES was investigated using a Thermogravimetric/differential thermal analyzer (TG/DTA) (Zhang *et al.*, 2011). The measurement was carried out under nitrogen flow at  $25\text{ }^\circ\text{C}$  for 15 min and then heated to  $900\text{ }^\circ\text{C}$  with a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ .

### 3.3.9 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 ( $\text{DMSO-}d_6$ ) as the solvent. For each analysis, 3 wt% polymer solution was prepared in DMSO and the experiment was conducted at room temperature.

### 3.3.10 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  $\text{CuK-}\alpha$  radiation source was operated at  $40\text{ kv}/30\text{ mA}$ . The interference peak was eliminated by a K-beta filter. Divergence slit and scattering slit of  $0.5^\circ$  together with  $0.3\text{ mm}$  of receiving slit 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  $2\theta$  range from 5 to 50, with a scan speed of  $1^\circ/\text{min}$ , and a scan step of  $0.02^\circ$ .