



CHAPTER III EXPERIMENTAL

3.1 Materials and Instruments

3.1.1 Materials

Poly(ether ether ketone) (PEEK) 150XF, (Victrex[®]), and Poly(1,4-phenylene ether ether sulfone) (PPEES), (Aldrich[®]) were used as the starting polymers. Concentrated sulfuric acid, H₂SO₄ (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[®], 97%) and magnesium sulfate (Aldrich[®], 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.

3.1.2 Instruments

A fourier transform infrared spectrometer (Thermo Nicolet, Nexus 670), with the number of scans of 64 was used for identifying functional groups of S-PEEK. A thermogravimetric analyzer (PerkinElmer, Pyris Diamond TG/DTA), with the temperature scan from 40 to 850 °C with a heating rate of 10 °C/min under nitrogen flow was used to study thermal property of S-PEEK and S-PPEES. A universal testing machine (Lloyd, model SMT2-500N) was used to determine the mechanical properties of the membranes. UV-VIS spectrometer (Nanoquant, model infinite M200) was used to measure vanadium concentration through the membranes. LCR meter (Agilent E4980A) was used to determine the proton conductivity of the membranes.

3.2 Experimental Methods

3.2.1 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. Subsequently, the polymer solution was accelerated into ice-cold water under continuous stirring (Li *et al.*, 2003). 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).

3.2.2 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).

3.2.3 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^+) (Zhao *et al.*, 2006).

3.3 Characterizations and Testing

3.3.1 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 ($-\text{SO}_3\text{H}$) in polymer samples. Then, the spectrometer was operated in the absorption mode with 64 scans, a resolution of 4 cm^{-1} , and wave numbers range of $4000\text{--}400\text{ cm}^{-1}$ as well as 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 S-Polymer sample was prepared by casting a thin film of S-Polymer onto ZnSe disc.

3.3.2 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 $850\text{ }^\circ\text{C}$ with a scanning rate of $10\text{ }^\circ\text{C}/\text{min}$ under a nitrogen atmosphere by using a thermal analyzer (PerkinElmer, Pyris Diamond TG/DTA). The experiment was carried out by weighting a sample of $2\text{--}4\text{ mg}$ and placed it in an alumina pan. The samples were dried at $100\text{ }^\circ\text{C}$ for 24 h to remove any moisture.

3.3.3 Degree of Sulfonation (DS) by Titration

Degree of sulfonation (DS) is defined as the number of sulfonic acid groups per repeating unit 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 $60\text{ }^\circ\text{C}$ 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.

3.3.4 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 (Gil *et al.*, 2004). The IEC of the cation exchange membrane was calculated from the following equation:

$$IEC \text{ (meq/g)} = \frac{\text{consumed ml NaOH} \times \text{molarity NaOH}}{\text{weight dried membrane}} \quad (3.1)$$

3.3.5 Water Uptake Measurement

Water uptake is additionally a significant property of any ion exchange membranes. 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. The membrane was weighted again. Thus, water uptake was calculated from

$$\text{water uptake (\%)} = \left(\frac{G_{wet} - G_{dry}}{G_{dry}} \right) \times 100 \quad (3.2)$$

where G_{wet} and G_{dry} are the weights of the membrane in wet and dry state respectively (Othman *et al.*, 2007).

3.3.6 Proton Conductivity (σ)

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 σ of the fully hydrated membranes was calculated from the impedance data by using the following equation:

$$\sigma = \frac{d}{RS} \quad (3.3)$$

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 (Chen *et al.*, 2010). The impedance data was corrected for the contribution from the empty and short-circuited cell.

3.3.7 Permeability of Vanadium Ions

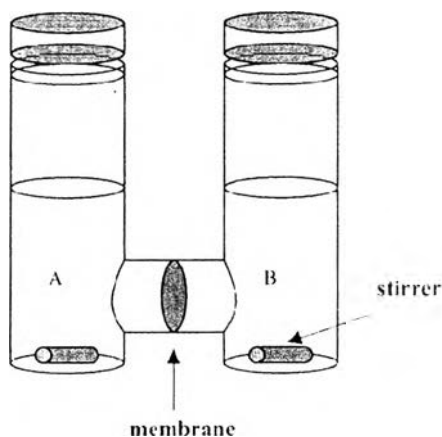


Figure 3.1 Device for the measurements of vanadium permeability.

The vanadium permeability of the membranes was determined by using the two reservoirs. The left reservoir was filled with the 50 ml of 1 M VO_2SO_4 in 2 M H_2SO_4 , and the right reservoir was filled with 50 ml of 1 M MgSO_4 in 2 M H_2SO_4 . The two reservoirs were separated by the membrane samples. MgSO_4 was used to equalize the osmotic pressure. The two solutions were continuously stirred at room temperatures (Chen *et al.*, 2010). Samples of the MgSO_4 solution were taken at a regular time interval in order to investigate the vanadium ions concentration by using an UV-VIS spectrometer at 760 nm (Wiedemann *et al.*, 1998). Therefore, the vanadium ion concentration in the right reservoir as a function of time was calculated from following equation:

$$V_B \frac{dC_B(t)}{dt} = A \frac{P}{L} (C_A - C_B(t)) \quad (3.4)$$

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.

3.3.8 Mechanical Property

The tensile strength of the membranes was measured by using a Universal Testing Machine (Lloyd, model SMT2-500N) for characterization of the mechanical properties of the membrane at thickness 110-280 μm and size 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 10mm/min at room temperature. For each sample, at least five samples were measured and average value was calculated (Liu *et al.*, 2007).