

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

- Poly(2,6-dimethyl-1,4-phenylene oxide) (Aldrich)
- Zeolite Y (Zeolyst, CBV400, Si/Al = 5.1, H⁺)
- Concentration sulfuric acid (Univar, 98%)
- Hydrochloric acid (Univar, 37%)
- Sodium chloride (Lab-Scan, 99.0%)
- Sodium hydroxide (Univar, 97%)
- Methanol (Lab-Scan, 99.9%)
- Ethanol (Lab-Scan, 99.9%)

3.1.2 Solvents

- Dimethylacetamide (RCI Labscan, 99.9%)
- Chloroform (RCI Labscan, 99.8%)

3.2 Equipments

- Fourier Transform Infrared spectrometer (FTIR, Thermo Nicolet, Nexus 670)
- Thermogravimetric Analyzer (TGA, Thermo, TGA 50)
- Gas chromatography (GC, Pr2100)
- LCR meter (Agilent E4980A)
- Universal Testing Machine (Lloyd, model SMT2-500N)

3.3 Methodology

3.3.1 Preparation of sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO)

The PPO 5 g was dissolved in 50 ml of chloroform and vigorously stirred at room temperature for 30 min. In the next step, concentrated sulfuric acid was added dropwise to the previous solution under vigorous stirring at room temperature. The polymer solution was poured into the ice-cold water bath. Then, the precipitated polymer was filtered and washed by using distilled water until the pH became neutral. The polymer was dried at 100 °C for 24 h. The obtained product was the sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) powder (Sadrabadi *et al.*, 2008).

3.3.2 Preparation of sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) membranes

The SPPO was dissolved in dimethylacetamide (DMA) at 80 °C. The viscous solution was casted on a clean glass plate, dried at room temperature for 24 h, and at 70 °C for 8 h, and then dried at 120 °C overnight (Sadrabadi *et al.*, 2008).

3.3.3 Preparation of composite membranes

The SPPO was dissolved in dimethylacetamide (DMA) and stirred at 80 °C. Zeolite Y at various concentrations was suspended in SPPO solution at 80 °C and ultra-sonicated for 30 min. The mixture was stirred at 80 °C for 8 h. The viscous solution was casted on a clean glass plate, dried at room temperature for 24 h, and at 70 °C for 8 h, and then at 120 °C overnight (Sadrabadi *et al.*, 2008).

3.4 Characterizations and Measurements

3.4.1 Fourier Transform Infrared (FTIR)

FTIR spectrometer (Thermo Nicolet, Nexus 670) was used to study the chemical structures of PPO and SPPO. The spectrometer was operated in the transmittance mode in the wave number range 400-4000 cm^{-1} . Optical grade KBr

was used as the background material. PPO and SPPO are mixed with KBr before the measurement (Jung *et al.*, 2004).

3.4.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA, Thermo, TGA 50) was used to determine the thermal stability of PPO and SPPO. The membranes were dried in vacuum for 24 h to remove any moisture in the membranes. The experiment was carried out by weighting a membrane sample of 4-20 mg and placed it in an platinum pan. The sample pan was heated under nitrogen atmosphere from 30 to 800 °C with a heating rate 10 °C/min (Li *et al.*, 2007).

3.4.3 Degree of Sulfonation (DS)

Degree of sulfonation is defined as the number of sulfonic groups per repeating units in polymer chain. The polymer membranes were acidified by 2 M HCl solution at room temperature for 24 h. Then the membranes were dried at 60 °C for 24 h. After that the membranes were placed in a 1 NaCl solution for 24 h. And then, the solution was titrated with 0.01 M NaOH by using phenolphthalein as an indicator. Degree of sulfonation was calculated by the following equation:

$$DS = \frac{(V_{\text{NaOH}} \times M_{\text{NaOH}})/1000}{\text{Mole of polymer membrane}} \times 100 \quad (3.1)$$

where DS is the degree of sulfonation (%), V_{NaOH} is the volume of NaOH consumed (ml), and M_{NaOH} is the molarity of NaOH (Macksasitorn *et al.*, 2012).

3.4.4 Ion Exchange Capacity (IEC)

Ion exchange capacity (IEC) of the SPPO membranes was measured by a titration. The membranes were cut into small pieces. Then the membranes were immersed into 1 M NaCl solution for 24 h. The solution was titrated with 0.01 M NaOH solution. Phenolphthalein was used as an indicator. Ion exchange capacity was calculated from following equation:

$$\text{IEC} = \frac{\text{Consumed NaOH} \times \text{molarity NaOH}}{W_{\text{dry}}} \quad (3.2)$$

where IEC is the ion exchange capacity (meq/g), V_{NaOH} refers to the volume of sodium hydroxide solution, C_{NaOH} refers to the concentration of sodium hydroxide solution (Deligoz *et al.*, 2008).

3.4.5 Water Uptake

The SPPO membranes were dried in an oven at 100 °C for 24 h, weighed, and placed into distilled water overnight at room temperature. After that, the membranes were taken out, quickly wiped with a tissue paper. The membranes were weighed again. The water uptake of SPPO membrane was calculated from the following equation:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (3.3)$$

where W_{wet} and W_{dry} refer to the weights of the wet and dry samples, respectively (Deligoz *et al.*, 2008).

3.4.6 Proton Conductivity

The proton conductivity of the SPPO and the composite membranes was measured by using an Agilent E4980A LCR meter. The fully hydrated membrane was cut into 0.5 × 0.5 cm pieces and coated with silver. The coated membrane was measured at a 1 V, and using the alternating current in the frequency range of 20 Hz – 2 MHz. The conductivity was calculated from the impedance as follows:

$$\sigma = \frac{d}{R \times A} \quad (3.4)$$

where σ is the proton conductivity (S/cm), d is the thickness of the membrane, S is the area of the interface of membrane in contact with the electrodes, and R refers to the measured resistance of the membrane – derived from the low frequency semicircle on the complex impedance plane with the Z axis (Park *et al.*, 2006).

3.4.7 Methanol Permeability

The methanol permeability of SPPO and the composite membranes was determined by a liquid permeation cell where the concentration of methanol that permeated the cell at 60 °C was measured. The liquid permeation cell is composed of two components. The two components were separated by a membrane sample. Compartment A was filled methanol at 2.5 M 250 ml and a compartment B was filled DI water 250 ml. The two solutions were continuously stirred during measurement. The methanol concentration was determined by using the gas chromatography. The methanol permeability coefficient was calculated from the following equation:

$$P = \frac{k_B V_B L}{A(C_A - C_B)} \quad (3.5)$$

where

- P = the methanol permeability (cm²/s)
- C_A = the methanol concentrations in the compartment A
- C_B = the methanol concentrations in the compartment B
- k_B = the methanol concentration permeate per time of permeate (the slope of methanol concentration profile in the compartment B)
- V_B = the solution volume of the permeate
- L = the thickness of the membrane
- A = the effective area of membrane

The methanol concentration profile was obtained by using a PR2100 gas chromatography fitted with a Thermal Conductivity Detector (TCD). The internal standard was 0.1 M of ethanol (Zhai *et al.*, 2007).

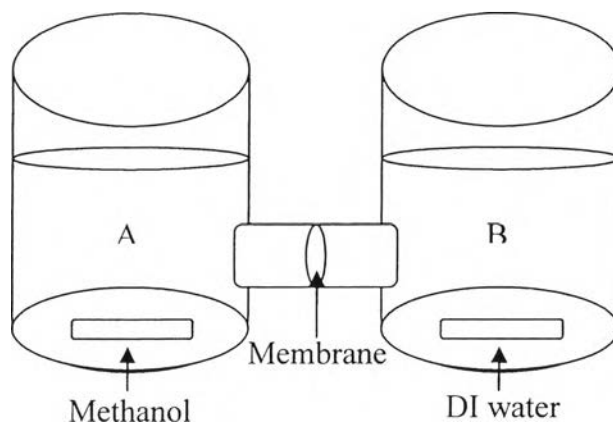


Figure 3.1 Schematic diagram of methanol permeability measurement.

3.4.8 Membrane selectivity

The membrane selectivity, which is defined as the ratio of proton conductivity to methanol permeability, is used to determine the potential performance of DMFC membranes. Membrane which has higher selectivity parameter is high performance for DMFC application. The membrane selectivity values of SPPO and the composite membranes were compared with those of Nafion 117 (Sadrabadi *et al.*, 2009).

3.4.9 Mechanical property

The tensile strength of SPPO and the composite membranes was determined by using a Universal Testing Machine (Lloyd, model SMT2-500N) for characterization of the mechanical property. The samples were cut into size 1cm × 5cm. The samples were immersed in de-ionized water for 24 h before testing and using the speed of 10 mm/min (Macksasitorn *et al.*, 2012).