

CHAPTER III EXPERIMENTAL

3.1 Materials and Instruments

3.1.1 Materials

3,3',4,4'-benzophenonetetracarboxylic dianhydride (Aldrich, purity 96%), 4,4'-diaminodiphenylmethane (Aldrich, purity 97%), and adipic acid dihydrazide (Fluka, purity 97%) were used as the starting monomers. Fuming sulfuric acid (Merck, 65%), concentration sulfuric acid (Univar, 98%), and sodium hydroxide (Univar, pellet purity 97%) were used in the sulfonation. Hydrochloric acid (Univar, 37%), sodium chloride (Lab-Scan, 99.0%), and 1M sodium hydroxide (Fisher Scientific) were used to determine the sulfonation degree and the ion exchange capacity. Methanol (Lab-Scan, 99.9%) and ethanol (Lab-Scan, 99.9%) were used in the determination of the methanol permeability. Dimethylsulfoxide (RCI Labscan, 99.9%) and Dimethylformamide (RCI Labscan, 99.8%) were used as a solvent. Benzoic acid (Univar, purity 99.9 %) and Triethylamine (Fluka, purity 98%) were used in the synthesis. Acetone (Burdick & Jackson, purity 99.9%) was used to precipitate the polymer.

3.1.2 Instruments

A Fourier transform infrared spectrometer (Thermo Nicolet, Nexus 670) was used for identifying functional groups of S-coPI. A nuclear magnetic resonance (NMR) spectrometer was used to determine the position of the sulfonated group in the monomer. A thermogravimetric analyzer (PerkinElmer, Pyris Diamond TG/DTA) was used to study the thermal property of the S-coPI membranes. A universal testing machine (Lloyd, model SMT2-500N) was used to determine the mechanical properties of the membranes. Gas chromatography (GC) (Pr2100) was used to determine the methanol concentration through the membrane. X-Ray Diffractometer (Bruker AXS, model D8 Advance) was used to study the crystallinity of the polymer. LCR meter (Agilent E4980A) was used to determine the proton conductivity of the membranes.

3.2 Experimental Methods

3.2.1 Synthesis of 4,4'-Diaminodiphenylmethane-2,2'-Disulfonic Acid Disodium Salt (S-DDM)

4,4'-diaminodiphenylmethane was dissolved in 98% sulfuric acid (50% w/v) in a round bottom flask with a mechanical stirring device. The solution was submerged in an ice bath until completely dissolved, then 65% fuming sulfuric acid was added and stirring was continued for 2 h, after which it was heated to 80 °C and stirred for 2 h. The solution was slowly poured into a crush ice and the product was precipitated by adding a sodium hydroxide solution until obtaining a basic solution. The precipitate was filtered, washed with deionized water, and dried at room temperature in vacuum for 24 h (Somboonsub *et al.*, 2010).

3.2.2 Preparation of Sulfonated Poly(Aromatic Imide-co-Aliphatic Imide)

S-DDM, DDM, and ADH at various mole ratios were dissolved first in dimethylsulfoxide; the degree of sulfonation was controlled by changing the molar ratio of S-DDM and DDM. For example, to synthesis of S-coPI-1 with molar ratio of 1:3:6, it was proceeded as follow; 0.374 g (0.931 mmol) of S-DDM and 0.554 g (2.793 mmol) of DDM were dissolved in DMSO and then 0.26ml (1.86 mmol) of triethylamine was added, after that 0.973g (5.586 mmol) of ADH was added to the solution, 3.00 g (9.31 mmol) of BPTDA in dimethylsulfoxide solution was added later, and lastly 0.25 g (2.05 mmol) of benzoic acid was added. The reactions were carried under a nitrogen atmosphere for 24 h to get a sulfonated polyamic acid. After that, the solution was heated to 90 °C for 4 h. After the solution was cooled, the precipitate in acetone was vigorously stirred to get a yellow powder. The precipitate was dried at room temperature under vacuum for 24 h.

3.2.3 Films Preparation

The polymer powder was dissolved in DMF and casted onto a glass plate, then dried at 80 °C under vacuum for 24 h and 160 °C, and under vacuum for 24 h (Woo *et al.*, 2003) to get sulfonated poly(aromatic imide-co-aliphatic imide) membrane. Washed with deionized water several times, and kept in water at room temperature.

3.3 Characterizations and Testing

3.3.1 Fourier Transform Infrared (FT-IR)

S-DDM and S-coPI powders were first characterized for the functional groups on a FT-IR spectrometer (Thermo Nicolet, Nexus 670) in absorption mode with 64 scans and a resolution of 4 cm^{-1} , with a wavenumber range of $4000 - 400\text{ cm}^{-1}$. Optical grade KBr was used as the background material and the powders were mixed with the dried KBr before measurements.

3.3.2 ^1H -Nuclear Magnetic Resonance (^1H -NMR)

^1H -NMR spectra of S-DDM in deuterated dimethyl sulfoxide (DMSO- d_6) was recorded on a Varian mercury 400 MHz instrument.

3.3.3 Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (PerkinElmer, Pyris Diamond TG/DTA) was performed to determine the thermal stability of the polymer membrane (Kausar *et al.*, 2010). The experiment was carried out by weighting a film sample of 2 - 4 mg and placed in an alumina pan, and then heated it under nitrogen atmosphere with the heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in the temperature range of $50 - 800^\circ\text{C}$. All the samples were dried at $100\text{ }^\circ\text{C}$ for 24 h before measurement.

3.3.4 Tensile Test

The mechanical properties of the polymer films were measured using a universal testing machine (Lloyd, model SMT2-500N) at the gauge length 30.0 mm, at the speed of $10\text{ mm}/\text{min}$, and at room temperature. At least five measurements were taken for each polymer sample. The membranes about $160 - 200\text{ }\mu\text{m}$ in thickness were cut in to $1\text{ cm} \times 5\text{ cm}$ pieces and soaked in a deionized water for 2 days before testing.

3.3.5 X-Ray Diffraction (XRD)

The Wide angle X-ray diffraction microscope (Bruker AXS, model D8 Advance) was used to study crystallinity of Non S-coPI and S-coPI. The S-coPI-3 was used as a sample of S-coPI. The Cu K-alpha radiation source was operated at $40\text{ kV} / 30\text{ mA}$. K-beta filter was used to eliminate the interference peak. A divergence slit and scattering slit 0.5 deg together with 0.3 mm of receiving slit are set on the instrument. The film was placed into a sample holder and the measurement

was continuously run. The data were recorded by monitoring the diffraction appeared in the 2θ range from 5 to 90 with a scan speed of 5 deg/min and a scan step of 0.02 deg.

3.3.6 Water Uptake and Moisture Absorption

The polymer membranes were dried in an oven at 100 °C for 24 h. The dried membranes were weighed (W_d). Then the polymers were soaked in de-ionized water at a room temperature for 2 days. They were removed from the water, quickly dry-wiped with an absorbent paper to remove any surface moisture, and then weighed immediately to determine their wet masses (W_w). The measurements were repeated three times to obtain the average water uptake value. The water uptake (Xue *et al.*, 2007) was calculated with the following formula (3.1):

$$\text{Water uptake(\%)} = \frac{(W_w - W_d) \times 100}{W_d} \quad (3.1)$$

The moisture absorption was determined in the same method of the water uptake but after the membranes were dried, the membranes were placed at a room temperature for 2 days before weighted (W_m) again. The moisture absorption was calculated with the following formula (3.2):

$$\text{Moisture absorption(\%)} = \frac{(W_m - W_d) \times 100}{W_d} \quad (3.2)$$

3.3.7 Degree of Sulfonation (DS)

Polymer membranes were acidified with an excess 0.1 M HCl solution at room temperature for 24 h. Then, they were washed and dried at 80 °C for 24 h. The membranes were immersed in 50 ml of 1 M NaCl for 24h. The solution was titrated by 0.01 M NaOH using phenolphthalein as an indicator. The titrations were repeated two times and the DS value was obtained with formula (3.3):

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

V_{NaOH} is the volume of sodium hydroxide solution, M_{NaOH} is the concentration of sodium hydroxide solution.

3.3.8 Ion Exchange Capacity (IEC)

The IEC indicates the number of milliequivalents of ions in 1 g of dry polymer (meq./g). The membrane samples (0.25-0.30 g) in acid form were immersed in 50 ml of 1 M NaCl solution at room temperature for 24 h to allow the H^+ ions to

be replaced by Na^+ ions. Then, the H^+ ions were titrated with 0.01 M NaOH solution using phenolphthalein as an indicator. The titrations were repeated two times for the average IEC value. The IEC was calculated from the titration result as equation (3.4):

$$\text{IEC (meq./g)} = \frac{V_{\text{NaOH}} \times M_{\text{NaOH}}}{W_d} \quad (3.4)$$

where V_{NaOH} is the volume of sodium hydroxide solution, M_{NaOH} is the concentration of sodium hydroxide solution, and W_d is the weight of dried membrane.

3.3.9 Proton Conductivity Measurement

Proton conductivity of the films was measured by an Agilent E4980A LCR meter in terms of the impedance data. The fully hydrated films (Ahmad *et al.*, 2006) were cut into 0.5×0.5 cm and painted with silver paints on both side of the films. The films were measured at a potential of 1 V and an alternating current in the frequency range of 20 Hz - 2 MHz. Then, graph was plotted between the radian and the impedance. The conductivity σ of the samples was calculated from the impedance data by the following equation (3.5):

$$\sigma (S \text{ cm}^{-1}) = \frac{d}{SR} \quad (3.5)$$

where σ = the proton conductivity

d = the thickness of the membrane

S = the area of the interface between the membrane and the electrode

R = the measured resistance of the membrane — derived from the intersection of the low frequency semi-circle on the complex impedance plane with the Z' axis.

3.3.10 Methanol Permeability

The methanol permeability of the membranes was determined by using the two compartments diffusion cell technique. One compartment ($V_A = 250$ ml) was filled with a solution of 2.5 M methanol. The other compartment ($V_B = 250$ ml) was filled with deionized water. The membrane was clamped between the two compartments. The solutions in the two compartments were magnetically stirred during the permeation experiments. Methanol will flow across the membrane due to the methanol concentration difference between the compartment A and the

compartment B. The methanol permeation (Feng *et al.*, 2010) in the compartment B as a function of time is given by equation (3.6):

$$P \text{ (cm}^2/\text{s)} = \frac{k_B \times V_B \times L}{A \times (C_A - C_B)} \quad (3.6)$$

Where P = the methanol permeability

C_A = the methanol concentration in the compartment A

C_B = the methanol concentration in the compartment B

A = the area of a membrane

L = the thickness of a membrane

V_B = the volume of the solution in the compartment B

k_B = the slope of methanol concentration profile in the compartment B

The methanol concentrations were measured by using a PR2100 gas chromatography fitted with a Thermal Conductivity Detector (TCD); 2.5M ethanol was used as an internal standard. The selectivity (Φ) was also calculated by the equation (3.7):

$$\Phi = \sigma/P \quad (3.7)$$

The selectivity is an effective parameter evaluating the membrane performance in DMFC system. The higher selectivity is the better performance the membrane (Li *et al.*, 2008).

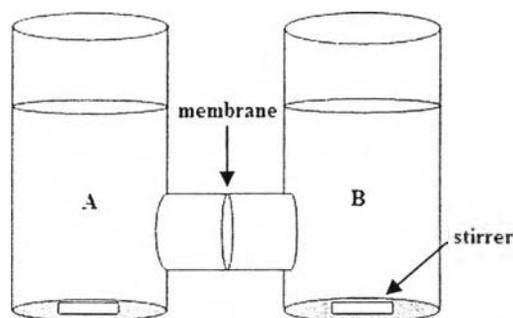


Figure 3.1 Schematic diagram for methanol permeability measurement.