

CHAPTER III EXPERIMENTAL

3.1 Materials and Instruments

3.1.1 Materials

Using 3-thiopheneacetic acid, 3TAA (AR grade, Fluka) as the monomer and anhydrous ferric chloride, FeCl_3 (AR grade, Riedel-delHean) as the oxidant that were used as received. Chloroform, CHCl_3 (AR grade, Lab-Scan), methanol, CH_3OH (AR grade, Lab-Scan) and dimethyl sulfoxide (DMSO) were dried over CaH_2 for 24 hours under the nitrogen atmosphere and then distilled and used as solvents. Hydrochloric acid, HCl (AR grade, Lab-Scan) was used to neutralize and to precipitate the polymer synthesized. Sulfuric acid, H_2SO_4 , was used to protect the oxidative decomposition of monomer. Diethyl ether and deionized water were used to extract and wash materials. Sodium hydroxide, NaOH , was used as the hydrolyzing agent. Perchloric acid dopant, HClO_4 (AR grade, Panreac Quimica) was used as received.

Zeolite L, Modenite and Beta, having K, Na and H as the cations respectively, were purchased from Tosoh Corp. They were used to mix with PTAA for altering gas adsorption properties.

Gases were supplied by TIG. Nitrogen gas was used as the carrier gas. Hydrogen (99.999%) was used as the target gases.

3.1.2 Instruments

A Fourier transform infrared spectrometer (Thermo Nicolet, Nexus 670), with the number of scans of 32, was used for identifying functional groups of side chain of polythiophene. A UV-Visible absorption spectrometer (Perkin Elmer, Lambda 10) was used to investigate the doping level of polythiophene. A thermalgravimetric analyzer (DuPont, model TGA 2950), with the temperature scan from 30 to 800 °C with a heating rate of 10°C/min under air flow was used to study thermal property of undoped

and doped polythiophenes. A scanning electron microscope (JOEL, model JSM-5200-2AE) was used to determine the morphological structure of polythiophene and composites. A custom-built two-point probe electrometer (Keithley, Model 6517A) was used to measure electrical conductivity of the polythiophene and polythiophene/zeolite composites. BET (Sorptomatic 1990, Thermc Finnigan) was used to determine the surface area and the pore volume of zeolites. Crystallinity was investigated by XRD (Phillips, Rigaku). Contents of ions were indentified by the atomic absorption (AAS, Varian, spectr AA. 300).

3.2 Experimental Methods

3.2.1 Polymerization Procedure

3.2.1.1 *Preparation of 3-Thiophene Methyl Acetate (TMA)*

Poly(3-thiopheneacetic acid) was synthesized by the oxidative coupling polymerization according to the method of Kim *et al*, 1999. 10.0 g of 3-thiopheneacetic acid (3TAA) was refluxed for 24 h in 50 ml of dry methanol with 1 drop of concentrated H₂SO₄, to protect the oxidative reaction of the monomer at the carboxylic acid group during polymerization. Then, the methanol was evaporated and the residue was extracted with diethyl ether. The extract was washed with deionized water, dried with anhydrous MgSO₄, and filtered. The 3-thiophene methyl acetate (3TMA) was recovered after evaporation of diethyl ether by a rotating evaporator.

3.2.1.2 *Synthesis of Poly(3-Thiophene Methyl Acetate) (P3TMA)*

The prepared monomer, 3TMA, of 10 mmol was dissolved in 20 ml chloroform and then added dropwise to a solution of 40 mmol ferric chloride in 30 ml chloroform under nitrogen atmosphere. The reaction was carefully maintained at 0°C (± 0.5 °C) for 24 h. The mixture was precipitated by pouring into an excess amount of methanol. Then the precipitate was washed with methanol and deionized water to remove the residual oxidant and the oligomers after filtering. Finally P3TMA was obtained.

3.2.1.3 Synthesis of Poly(3-Thiopheneacetic acid) (P3TAA)

P3TMA was hydrolyzed by heating 0.5 g precipitate in 50 ml of 2.0 M NaOH solution for 24 h at 100°C. Poly(3-thiopheneacetic acid) (PTAA) was obtained by neutralization and precipitation with a dilute HCl solution. The P3TAA was repeatedly washed with deionized water before vacuum drying at room temperature for 2 days.

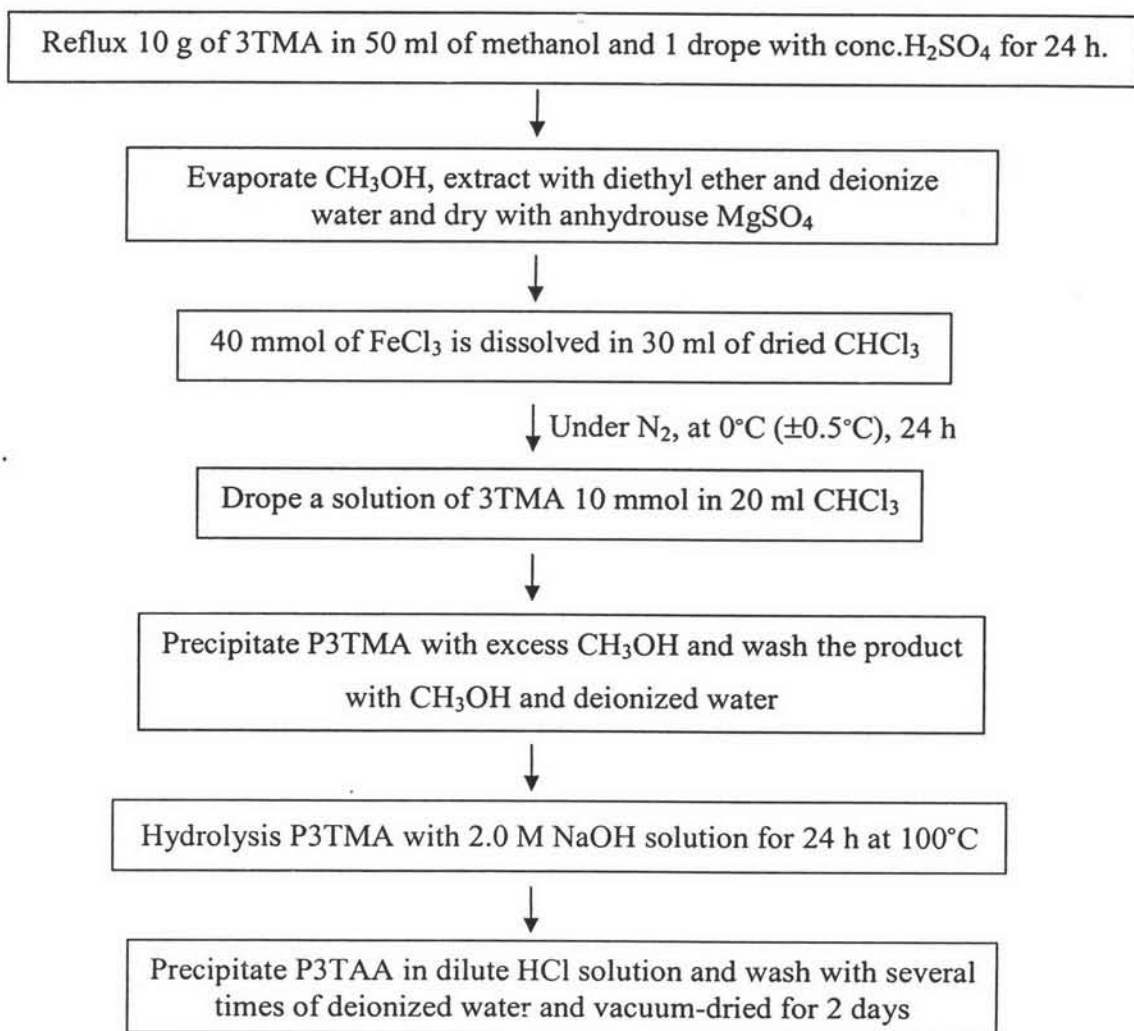


Figure 3.1 Synthesis route of poly(3-thiophene acetic acid).

3.2.2 Doping of Polythiophene

Polythiophene was doped by perchloric acid (HClO_4) as dopant following the method of Kim *et al.*, 2000. Grinded polythiophene was stirred in 2.0 M HClO_4 at room temperature for 3 days. The ratio of $\text{HClO}_4/3\text{TAA}$ for doping was 200:1. Doped polythiophene was obtained after been filtered and vacuum-dried. After the doping process, their electrical conductivity was measured by using a custom-built two-point probe electrometer (Keithley, Model 6517A).

3.2.3 Ion Exchanged Zeolites

Zeolite L and Modenite were exchanged with different cations in order to investigate the effect of zeolite concentration and cation types. Zeolite L was stirred in 1 M of an NaCl at 80 °C for 2 hours, using 70 ml per gram zeolite and zeolite mordenite was stirred in 1M of an LiCl and KCl in similar procedure. This process was repeated many times until zeolite contained the required amount of cation. After filtering and washing with distillation water for several times, the ion exchanged zeolite was dried and calcined at 500 °C for 5 hours.

3.2.4 Preparation of Composites

Polythiophene/zeolite composites were prepared by mechanical mixing of polythiophene and zeolite powder. Before mixing, polythiophene was grinded and sieved with a mesh size of 38 μm . Composites were pressed into a pellet form by a hydraulic press machine. Polythiophene was used as the matrix and the dispersed phase was zeolite. Sample with different volume ratios of zeolite to polymer were prepared to investigate the effect of zeolite content on electrical conductivity when exposed with H_2 gas.

3.2.5 Characterization

3.2.5.1 *Fourier-Transform Infrared Spectrometer (FT-IR)*

Undoped and doped poly(3-thiophene acetic acid) powder was identified for their functional groups by a FT-IR spectrometer (Thermo Nicolet, Nexus 670) operated in the absorption mode with 32 scans and a resolution of $\pm 4 \text{ cm}^{-1}$, covering a wavenumber range of $4000\text{-}400 \text{ cm}^{-1}$. Optical grade KBr (Carlo Erba Reagent) was used as the background material. The synthesized P3TAA was mixed with dried KBr at a ratio of P3TAA:KBr = 1:20 and molded into pellets under the pressure of 6 tons. In order to investigate the spectrum of Pth_200:1 and zeolite L, mordenite and beta, before exposure, under exposure and after exposure with H_2 gas, a gas cell with ZnSe window were used.

3.2.5.2 *UV-Visible Spectroscopy*

UV-Vis absorption spectrophotometer (Shimadzu, UV-2550) was used to identify the successfully doped of polythiophene. Measurements were taken in the absorbance mode in the wavelength range of 200-800 nm. Synthesized P3TAA and doped P3TAA were grinded into a fine powder and dissolved in DMSO at the concentration of $2.8134 \times 10^{-6} \text{ M}$.

3.2.5.3 *Thermogravimetric Analysis (TGA)*

A thermal gravimetric analyzer (DuPont, model TGA 2950) was used to investigate thermal property of undoped and doped poly(3-thiophene acetic acid) (P3TAA). Polymer powder was loaded into an aluminium pan and heated at temperature scan from 30 to 800°C with a heating rate of $10^\circ\text{C}/\text{min}$ under air condition..

3.2.5.4 *Scanning Electron Microscope (SEM)*

Scanning electron micrographs were taken with a scanning electron microscope (JEOL, JSM-5200) to determine the morphology of poly(3-thiophene acetic acid), zeolites and polythiophene/zeolite composites in powder forms. Sample powder was placed and adhered on a stub with a carbon tape. Before measuring, sample surface was coated with gold by using JFC-1100E ion-sputtering device for 4 seconds.

3.2.5.5 Particle Size Analyzer

The average particle size and the standard size distribution of poly(3-thiophene acetic acid) and zeolite were determined by using a particle size analyzer (Malvern, Masterizer X), using 45 mm lenses in order to measure the particle size in microns level. Consequently, the specific surface area was calculated from the particle diameter with the assumption of being a spherical particle.

3.2.5.6 X-ray Diffraction Spectroscopy (XRD)

Crystallinity and structure of poly(3-thiophene acetic acid) and zeolite powders were identified by an x-ray diffractometer (Phillips, Rigaku). Sample powder was packed onto a glass plate and measured with $2\theta = 2-90^\circ$, $2-50^\circ$ for polythiophene and the zeolites, respectively. Undoped and doped poly(3-thiophene acetic acid), with ion exchanged zeolite were also examined.

3.2.5.7 Electron Dispersive Spectroscopy (EDS)

Electron Dispersive Spectroscopy (EDS) (Oxford, PentafetLink) was used to investigate doping level of poly(3-thiophene acetic acid). An amount of each element, such as C, S and Cl, was calculated. Sample preparation is the same as that of SEM.

3.2.5.8 Nuclear Magnetic Resonance (NMR)

Proton Nuclear Magnetic Resonance was used to identify the successfully synthesized of poly(3-thiopheneacetic acid). Undoped and doped of poly(3-thiophene acetic acid) were dissolved in chloroform and DMSO respectively before testing.

3.2.5.9 Atomic Absorption Spectrophotometer (AAS)

Atomic Absorption Spectrophotometer (Varian, Spectr AA.300) was used to determine the amount of cations which were ion exchanged into zeolites. Standard, blank and sample solutions were prepared before testing the cation type in the zeolites. Each cation type in zeolite was identified by using the different lamp sources.

3.2.5.10 BET

The surface area and the pore size of each zeolite were identified by BET (Sorptomatic1990, Thermo Finnigan). Zeolite powder was out gassed at 300 °C over night before adsorption and desorption with He and N₂ gases. During operation zeolite powder was cooling by liquid N₂.

3.2.5.11 Conductivity Measurement: Two-Point Probe Meter

Electrical conductivity is the inversion of specific resistivity (ρ) which indicates the ability of material to transport electrical charge. The meter consists of two probes, making contact on the surface of a film sample. These probes were connected to a source meter (Keithley, 6517A) for a constant voltage source and for reading current. The applied voltage was plotted versus the resultant current to determine the linear ohmic regime of each sample. The applied voltage and the resultant current in the linear ohmic regime were converted to the electrical conductivity of polymer using equation (3.1) as follow:

$$\sigma = \frac{1}{\rho} = \frac{1}{R_s \times t} = \frac{I}{K \times V \times t} \quad (3.1)$$

where σ is specific conductivity (S/cm), ρ is specific resistivity ($\Omega \cdot \text{cm}$), R_s is sheet resistivity (Ω), I is measured current (A), K is geometric correction factor, V is applied voltage (voltage drop) (V), and t is pellet thickness (cm).

The geometrical correction factor was taken into account of geometric effects, depending on the configuration and probe tip spacing and was determined by using standard materials where specific resistivity values were known; we used silicon wafer chips (SiO₂). In our case, the sheet resistivity was measured by using the two-point probe and then the geometric correction factor was calculated by equation (3.2) as follow:

$$K = \frac{\rho}{R \times t} = \frac{I \times \rho}{V \times t} \quad (3.2)$$

where K is geometric correction factor, ρ is known resistivity of standard silicon wafer ($\Omega \cdot \text{cm}$), t is film thickness (cm), R is film resistance (Ω), and I is measure current (A).

3.2.5.12 *Temperture Program Desorption (TPD)*

H_2 adsorption property of sample powder, Pth_200:1, Pth_200:1/MOR, L, MOR and BEA was investigated by TPD. Sample powder was weighted about 0.1-0.2 g to pretreat under N_2 and adsorb with H_2 . Then sample powder was desorbed H_2 and the data was analyze. The step of pretreatment and analysis was operated by setting temperature program.

3.2.6 Electrical Conductivity Measurement

Electrical conductivity of doped poly(3-thiopheneacetic acid) and composites of this polymer with zeolites was carried out by using a special constructed gas cell that show in the figure 3.2. It consisted of two chambers connected in series. The chambers were made from stainless steel. The first chamber was used for mixing gas of nitrogen and the target gas (H_2) into homogeneous gas and conductivity response was measured in the second chamber. The first chamber and the second chamber were called mixing and measurement chamber, respectively. The temperature controllers, connecting to both chambers, were used to monitor and control the temperature within the gas chamber. The second chamber contained two four point probe meters for conductivity measurement. The procedures for measuring the electrical conductivity in the presence of hydrogen (H_2) gas were as follows.

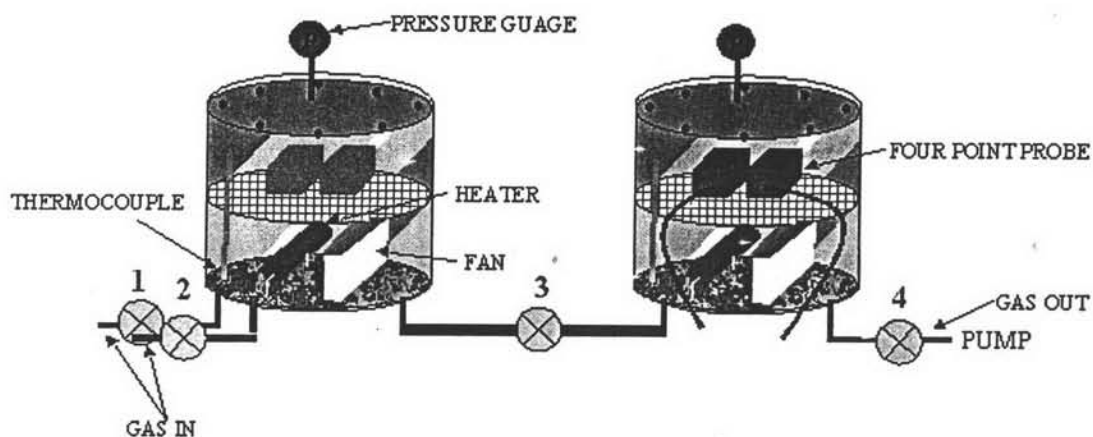


Figure 3.2 Conductivity detectors with gas chamber.

Step 1 A current was applied to sample pellets in order to measure conductivity before exposing to gas.

Step 2 Both chambers were closed and evacuated by using a vacuum pump in order to remove gases (valve No.1 and 2 were closed; valve No. 3 and 4 were opened).

Step 3 Valve between the two chambers (No. 3) and valve between the second chamber and the vacuum pump (No.4) were closed.

Step 4 N_2 gas was fed into the first chamber until the pressure reached 1 atm as observed from the pressure gauge.

Step 5 Valve No. 3 was opened; the conductivity response of N_2 gas was recorded.

Step 6 Step 2-6 were repeated until the conductivity response of N_2 was constant (this refers to preexposed $\sigma_{\text{initial } N_2}$).

Step 7 Both chambers were closed and evacuated by using a vacuum pump in order to remove gases.

Step 8 Hydrogen gas was fed into the first chamber until the pressure reached 1 atm as observed from the pressure gauge.

Step 9 Valve No.3 was opened; the conductivity response of H₂ gas was recorded until it reached an equilibrium value.

Step 10 Both chambers were closed and evacuated by using a vacuum pump in order to remove gas.

Step 11 Valve between the two chambers (No. 3) and valve between the second chamber and the vacuum pump (No.4) were closed.

Step 13 N₂ gas was fed into the first chamber until the pressure reached 1 atm as observed from the pressure gauge.

Step 14 Valve No. 3 was opened then the conductivity response of N₂ gas was recorded as the final $\sigma_{N_2, final}$.

The differences in the change of electrical conductivity ($\Delta\sigma$) were calculated by Equation (3.3) following;

$$\Delta\sigma = \sigma_{H_2} - \sigma_{initial N_2} \quad (3.3)$$

where $\Delta\sigma$ = the difference in specific conductivity (S/cm)

$\sigma_{initial N_2}$ = the specific conductivity of N₂ at final (S/cm)

σ_{H_2} = the specific conductivity of H₂ (S/cm)