

## CHAPTER III EXPERIMENTAL



### 3.1 Materials

In the polymerization process of polypyrrole, these chemicals were used: distilled pyrrole (ACROS) as a monomer, ammonium persulfate (MERCK) as an oxidant, naphthalene-2-sulfonic acid( $\beta$ ) sodium salt (90%, Fluka) as a dopant, methyl alcohol (AR grade, CARLO ERBA) as a washing solution. 1-methyl-2-pyrrolidone (98% Fluka) was used as a solvent in the UV Vis characterization.

Molecular sieve 13X was used as the minor component of our composites. Lithium chloride (99%, UNILAB), potassium chloride (99%, Fluka), and cesium chloride (99%, Fluka) were used in the cation exchanged processes.

Nitrogen gas (99%, TIG), carbon monoxide (1000ppm, TIG), sulfur dioxide (1000ppm, TIG), methane (97%, TIG), carbon dioxide (99.8%, TIG) and nitrogen dioxide (1000ppm, TIG) were used to study electrical conductivity responses of our composites. Carbon dioxide and methane were mixed with nitrogen to obtain 10% of methane before further use.

### 3.2 Methodology

#### 3.2.1 Preparation of Polypyrrole

Pyrrole monomer was purified by distilling pyrrole under the reduced pressure. The doped PPy with various dopant anions was chemically synthesized by the *in situ*-doped, oxidative coupling polymerization according to the method of Ruangchuay *et al.* (2003). The solution of 0.6846g (3 millimole) APS in 10.0 ml deionized water was slowly added to the mixture of 1.2 millimole of dopant anion and 1.0 ml (14.5 millimole) pyrrole in 20.0 ml deionized water. The reaction was carefully maintained at 0°C for 2 hours. The obtained PPy was precipitated by pouring the reaction mixture into a large excess amount of deionized water. The PPy

powder was then washed several times with deionized water and methanol before drying in a vacuum at room temperature for 2 days. The PPy powder was sieved through a mesh (53 $\mu$ m) and dried at room temperature before future use. In order to study effect of the molar ratio of dopant anion to pyrrole monomer ( $N_d/N_m$  ratio) on the properties of PPy, PPy was synthesized with various amounts of  $\beta$ -naphthalene sulphonic acid. The  $N_d/N_m$  ratios were chosen to be 1:96, 1:48, 1:24, 1:12, 1:6, and undoped.

### 3.2.2 Preparation of Molecular Sieve 13X

The cation-exchanged process was carried out by emerging molecular sieve 13X in 0.5 M LiCl, KCl, and CsCl solution (1 g of 13X /25 ml solution) at 80  $^{\circ}$ C for 1 hour and then centrifuging the emulsion to separate the liquid phase from the solid phase. The molecular sieve 13X was dried over night. The concentration of cation in 13X was increased by repeating the above steps. 13X was calcined at 200  $^{\circ}$ C under nitrogen flow for 2 hours to eliminate some volatile organics from their structures. The calcined sample was further grounded and sieved with a mesh (53 $\mu$ m) before further use.

### 3.2.3 Composite Preparation

The molecular sieve 13X and Ppy was ground and mixed. Then samples were pressed into discs by a hydraulic press machine at pressure of 6 tons. In order to study effect of zeolite content, various zeolite weights used were 5, 10, 20, and 40% by volume.

### 3.2.4 Characterization

#### 3.2.4.1 *UV-VIS Spectrophotometer*

To investigate the electronic structure of undoped PPy, and doped PPy, samples were dissolved in NMP at a concentration 0.05 g/l. The

solutions were contained in quartz cells, and UV absorption spectra were measured by using a UV-VIS spectrophotometer (PERKIN ELMER, Lambda 10).

#### *3.2.4.2 FTIR Spectrophotometer*

FTIR (Bruker, FRA 106/S) was used to identify the functional groups of synthesized undoped PPy, and doped PPy. In addition, the interaction between CO, SO<sub>2</sub>, and NO<sub>2</sub> and PPy samples were investigated. Samples were ground with KBr and FTIR spectrum was taken before and after the gas exposure.

#### *3.2.4.3 Thermogravimetric Analyzer(TGA)*

The amount of moisture and degradation temperature of PPy were measured by a TGA equipment (Dupont, TGA 2950) at a heating rate of 10°C/min to determine the water content and the degradation temperature, confirming that we obtained PPy.

#### *3.2.4.4 Scanning Electron Microscope (SEM)*

Surface morphology of PPy was investigated by using a scanning electron microscope or SEM (JEOL, model JSM-5200). PPy was fixed on the holder with an adhesive tape and coated with a layer of gold before measurements were taken.

#### *3.2.4.5 X-ray Diffraction Spectroscopy(XRD)*

An XRD (Phillips PW 1830/00 No. DY1241 Diffractometer, model Rigaku) was used to investigate arrangements of atoms or molecules and to determine the crystal structures of undoped PPy, doped PPy, and molecular sieve 13X. Each XRD sample was measured in a pellet form in an aluminium specimen holder and diffraction angle was varied from 5-50 degree.

#### *3.2.4.6 Elemental Analyzer*

The elemental analyzer, Perkin-Elmer, 2400 Series II CHS/O Analyzer, was used to determine doping level of polypyrrole. The samples were weighed at 1.5-2.5 mg and sealed in the tin capsules and place into the sample cells.

The sample was dropped in the combustion zone at a temperature between 975-1100 °C with helium as the carrier gas. The amounts of carbon (C), hydrogen (H) and nitrogen (N) were determined.

#### *3.2.4.7 Particle Size Analyzer*

The particle sizes of 13X and polypyrrole were determined by using a particle size analyzer (Malvern Instruments Ltd., Masterizer X). This instrument measured the average particle size and the size distribution.

#### *3.2.4.8 Surface Area Analyzer*

Thermo Finnigan, SORPTOMATIC1990 SIRES was used to measure the pore size and the surface area of each 13X. 13X powder was weighted at 300 mg and outgassed at 300 °C before each measurement.

#### *3.2.4.9 Atomic Absorption Spectrophotometer(AAS)*

13X has been digested by concentrated HNO<sub>3</sub> for 1 hour to obtain stock solutions. The stock solutions were diluted with DI water to obtain optimal range of concentration that could be measured by an atomic absorption spectrophotometer. The amount of cation in 13X was determined by an atomic absorption spectrophotometer (Varian, SpectrAA-300).

#### *3.2.4.10 X-ray Fluorescence (XRF)*

X-ray fluorescence technique (BUKER, SRS 3400 ) was used to determine the elemental composition of 13X. The powder of 13X and boric acid were weighted at 0.5 grams and 4.5 grams respectively, grounded and mixed together with mechanical mixing for 2-3 min. Powder mixture was then placed in a sample holder and pressed by a hydraulic press (150 lb/2 min) to make samples into a pellet form.

### 3.2.4.10 Four-point Probe Meter

This meter consisted of four probes. The inner two probes were connected to a voltmeter for measuring the voltage drop. The outer two probes were connected to a constant current source. The voltage drop was converted to the electrical conductivity of sample by using the following equation:

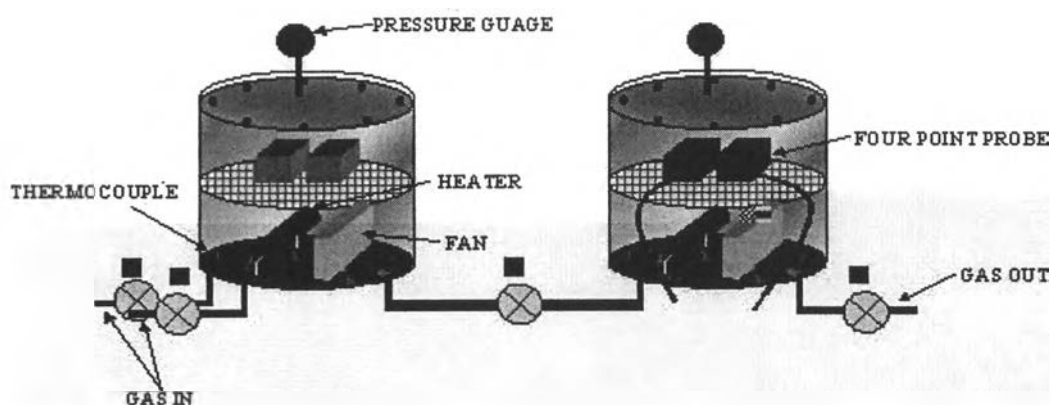
$$\sigma = (1/\rho) = (1/RtK) \quad (3.1)$$

where  $R$  is resistivity ( $\Omega$ ),  $t$  is the pellet thickness(cm), and  $K$  is the geometric correction factor. The geometric correction factor  $K$  takes into account of the geometric effect, depending on the configuration and probe tip spacing and  $K$  was determined by using standard materials whose specific resistivity values are known. In our case, the sheet resistivity was measured with a custom built four-point probe and the geometric correction factor was computed from the equation:

$$K = \rho_{ref}/(R_{st}) \quad (3.2)$$

where  $\rho_{ref}$  is known specific resistivity ( $\Omega.cm$ ) and  $t$  is film thickness(cm).

Two specially constructed gas chambers were used to study the electrical conductivity response of PPy and PPy/13X. They were connected in series. Each of them contained a fan and a temperature controller. The second chamber contained the two four point probe meters to measure the specific conductivity. We followed the procedure of Densakulprasert *et al.*(2003).



**Figure 3.1** Conductivity detectors with gas chamber.

Step 1 A current was applied to PPy 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<sub>2</sub> gas was fed into the first chamber until the pressure reached 2 atm as observed from the pressure gauge.

Step 5 Valve No. 3 was opened; the conductivity response of N<sub>2</sub> gas was recorded.

Step 6 Repeat step 2-6 until the conductivity response of N<sub>2</sub> was constant (this refers to preexposed  $\sigma_{N_2,preex}$ ).

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

Step 8 Carbon monoxide gas was fed into the first chamber until the pressure reached 2 atm as observed from the pressure gauge.

Step 9 Valve No. 3 was opened; the conductivity response of CO, NO<sub>2</sub>, and SO<sub>2</sub> gas at 1000 ppm 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 12 N<sub>2</sub> gas was fed into the first chamber until the pressure reached 2 atm as observed from the pressure gauge.

Step 13 Valve No. 3 was opened then the conductivity response of N<sub>2</sub> gas was recorded as it reached equilibrium, the  $\sigma_{recovery}$ .

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

$$\Delta\sigma = \sigma_g - \sigma_{N_2\text{preex}} \quad (3.3)$$

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

$\sigma_{N_2\text{preex}}$  = the specific conductivity of  $N_2$  (S/cm) before exposing the target gas

$\sigma_g$  = the specific conductivity of gas(S/cm)