



CHAPTER III EXPERIMENT

3.1 Material

Bisphenol-A (Ba) was purchased from Aldrich, Germany. Formaldehyde (analytical grade) was purchased from Merck, Germany. Triethylenetetramine (TETA) was purchased from Fluka, Switzerland. Graphite ($< 20\mu\text{m}$) was purchased from Sigma-Aldrich, Thailand. Polybutadiene (PB) ($M_w=40,000$) was purchased from Dow Chemical, USA. Polyvinyl alcohol (PVA) ($M_w=30,000-70,000$) was purchased from Fluka, USA. Toluene (analytical grade), dimethylformamide (analytical grade), n-hexane and acetone (analytical grade) were purchased from Lab-scan, Thailand.

3.2 Equipment

The FT-IR spectrum of benzoxazine precursor was obtained using a Nicolet Nexus 670 FT-IR spectrometer. KBr pellet technique was applied in the preparation of powder samples. $^1\text{H-NMR}$ spectra were recorded on a Varian Mercury 300 (300 MHz) instrument, using deuterated dimethyl sulfoxide as solvent. DSC analyses were carried out using a Perkin-Elmer DSC 7 instrument. The samples were heated from 30° to 300°C at a heating rate of $10^\circ\text{C}/\text{min}$ under a N_2 atmosphere with a flow rate of 10 ml/min. TG-DTA curve was collected on a Perkin-Elmer Pyris Diamond TG/TGA instrument. The sample was loaded on the platinum pan and heated from 30° to 900°C at a heating rate of $20^\circ\text{C}/\text{min}$ under N_2 flow of 50 mL/min. HITACHI S-4800 scanning electron microscope was used to observe the surface morphology of polybenzoxazine-based aerogel and carbon aerogel. The specimens were coated with platinum under vacuum before observation. N_2 adsorption-desorption isotherms were obtained at -196°C on a Quantachrome Autosorb-1. Samples were degassed at 250°C for 15 hr in a vacuum furnace prior to analysis. Surface areas were calculated using the BET equation. The pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method, using the adsorption branch of the

nitrogen isotherm. Electrical resistance of conductive composite polymers membranes were measured using a digital multimeter (KEITHLEY 2700).

3.3 Methodology

3.3.1 Preparation of Carbon Aerogel

Carbon aerogel are obtained by three main stages. These three main stages can be distinguished in preparation of benzoxazine precursor, preparation of organic aerogel, and preparation of carbon aerogel from organic aerogel.

3.3.1.1 *Preparation of Benzoxazine Precursor*

Benzoxazine Precursor was prepared by mixing Bisphenol-A (2.31 g), triethylenediamine (1.74 g), and formaldehyde (3.28 g) in a 1:1:4 molar ratio. Dimethylformamide (15 g) was used as a solvent. The reaction was cooled in an ice bath and mix continuously for 1 hour until homogenous solution was perceived.

3.3.1.2 *Preparation of Organic Aerogel Derived from Benzoxazine Precursor*

The mixture was poured into vessels and sealed tightly. The vessels were kept at an ambient condition overnight and partially cured at 80°C for 3 days; consequently, highly cross-linked polymer was achieved. Then cross-linked wet gel was dried with supercritical carbon dioxide ($T_c=45$ °C; $P_c=7.5$ MPa). Finally that, dried gels were fully cured in an oven at temperature of 140 °C, 160 °C, 180 °C for 2 hours each and 200 °C for 3 hours, resulting in organic aerogel.

3.3.1.3 *Preparation of Carbon Aerogel Derived from Benzoxazine Precursor.*

CA was obtained by pyrolysis of organic aerogels in a quartz reactor using the following ramp cycle: 30 °C to 250 °C for 60 min, 250 °C to 600 °C for 300 min, 600 °C to 800 °C for 60 min and held at 800 °C for 60 min. The system was carried out in N₂ flow at 700 cm³/min. Finally, activation of CA was carried out in CO₂ at 900 °C, in order to have more surface area.

3.3.2 Characteristics of Polybenzoxazine and Carbon Aerogel Derived from Polybenzoxazine

The structural characteristics of polybenzoxazine-based aerogel were investigated using FTIR and ¹H-NMR. Thermal properties were measured using DSC and TG/DTA. Morphology was observed by SEM. Furthermore, surface area and pore distribution were measured using SAA.

3.3.3 Preparation of Composite Conductive Polymer Films for Gas Sensors

The CA and activated CA were triturated in a mortar; the average diameter of particle size was less than 180 μm. Then the CA and activated CA were dried at 100 °C in an oven overnight before use. The composite conductive polymer membranes were prepared by a four-step process. In the first step, the filler was introduced into 1 mL of solvent. Water and toluene were used as solvent for PVA and PB, respectively. The mixture was violently stirred for 3 hrs. and ultrasonically dispersed for 15 min. The second step involved the preparation of polymer solution by dissolving polymer in solvent. During the third step, 15 % of polymer solution was added into filler mixture which was then stirred overnight. Finally in the fourth step, the rest polymer solution was added into the filler mixture and stirred for 2 hrs. Then the films were fabricated by spin-coating technique on an interdigitated electrode. For comparison, the composite polymer films with graphite as a conductive filler were also manufactured by the same process.

The interdigitated electrode was fabricated by thermal evaporation of Al (100 nm) and Au (80 nm) on a glass slide (Figure 3.1) with a gap size between fingers of 200 μm.

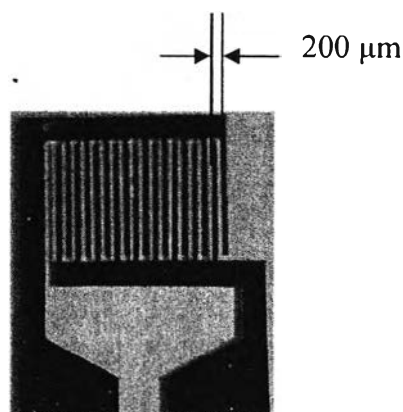


Figure 3.1 Interdigitated electrode.

3.3.4 Electrical Response Measurements of Conductive Composite Films for Gas Sensors

The testing steps started from obtaining a baseline resistance (R_b) by allowing only pure nitrogen gas to flow into the test chamber at a flow rate of 300 ml/min. Then an analyte gas vapor was carried by nitrogen gas through the test chamber in which a sensor was kept. Then the maximum of electrical resistance (R_m) of sensor was measured using a digital multimeter. Figure 3.1 shows the scheme of the electrical measurement.

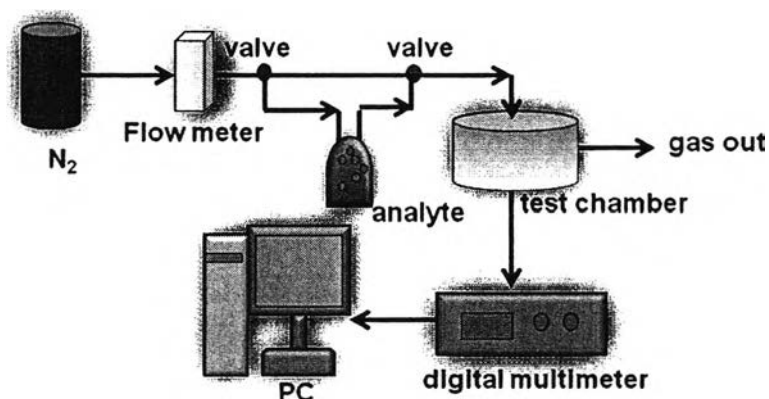


Figure 3.2 The scheme of the electrical measurement.