

CHAPTER III

EXPERIMENTAL

3.1 Materials

All chemicals were used without further purification. Bisphenol-A was purchased from Aldrich, Germany. Triethylenetetramine (TETA) was purchased from FACAI Group Limited, Thailand. Formaldehyde solution (37% by weight) and potassium hydroxide (KOH analytical grade) were purchased from Merck, Germany. *N,N*-Dimethylformamide (DMF) was purchased from Labscan Asia Co., Ltd., Thailand. Ferrous chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) were purchased from Fluka, Germany. Ammonium hydroxide (NH_4OH) was purchased Panreac Quimica Sau.

3.2 Measurements

Thermal behaviors of polybenzoxazine aerogel were determined with differential scanning calorimetry (DSC), Perkin Elmer DSC7; The sample was heated from ambient temperature to 300 °C at a heating rate of 10 °C/min under nitrogen flow rate of 10 ml/min. Thermogravimetric analysis was also conducted with Perkin Elmer Thermogravimetric/Differential Thermal Analyzer (TG-DTA) where the sample was heated from ambient temperature to 900 °C at a heating rate of 20 °C/min under nitrogen flow rate of 50 ml/min. FT-IR spectra of polybenzoxazine precursor and carbon xerogel were recorded on a Nicolet Nexus 670 FT-IR spectrometer using KBr pallet technique. The field emission scanning electron microscope (FE-SEM, HITACHI S4800) was used to study the microstructure of carbon xerogel, the samples were coated with platinum under vacuum prior to investigation. BET surface area and pore size distribution of all carbon xerogels were calculated from nitrogen adsorption isotherms at 77 K using a Quantachrome/Autosorb-1 Surface Area Analyzer based on the Brunauer–Emmett–Teller (BET) and Barret-Joyner-Halenda (BJH) methods, respectively. X-Ray Diffractometer (XRD) was used to characterize the crystalline structure of iron oxide (Fe_3O_4). For all electrochemical

measurements, the electrochemical test cell consisted of graphite sheets as current collectors and two carbon xerogel or two hybrid composite electrodes separated by microporous polyethylene membrane. The electrodes were soaked in 6M potassium hydroxide (KOH) electrolyte for 24 hr before measurement to ensure complete filling of the porous electrodes (Kim S. J. *et al.*, 2005; Hwang S. W. *et al.*, 2007). The electrochemical properties were measured by a computer-controlled potentiostat/galvanostat (Autolab PG-STAT 30 with GPES software). Cyclic voltammograms were performed in the potential range of -1.0 V to 1.0 V with various scan rates. For galvanostatic charge/discharge measurement, the testing cell was charged with current density of 5 mA/cm² up to 1 V and discharged with 5 mA/cm² down to 0 V (Kim et al, 2005). Electrochemical impedance spectroscopy measurements were carried out by Autolab PG-STAT 30 with FRA software in the frequency range of 10 kHz to 10 mHz with a sinusoidal signal of 10 mV. All of the electrochemical measurements were performed at room temperature.

3.3 Methodology

3.3.1 Synthesis of Polybenzoxazine Aerogels

Polybenzoxazine precursor was synthesized by dissolving bisphenol-A (2.30 g) in *N,N*-dimethylformamide (DMF) (15.00 g) and stirring continuously. Formaldehyde solution (3.28 g) was then added into bisphenol-A solution. The solution was kept under low temperature by using ice bath. TETA (1.74 g) was subsequently added dropwise into the mixture followed by continuous stirring for 1 hr until homogeneous yellow viscous liquid was obtained. The molar ratio of bisphenol-A: formaldehyde: TETA was 1:4:1. The synthetic reaction is shown in Figure 4.1. After that the precursor was filled in a vial with seal and placed in an oven at 80°C for 72 hr into a close system yielding benzoxazine aerogel. The benzoxazine aerogel was then dried by ambient method and placed in an oven by using the fully curing step at 140, 160, 180 °C for 2 hr at each temperature and 200°C for 15 minutes in order to polymerize benzoxazine aerogel.

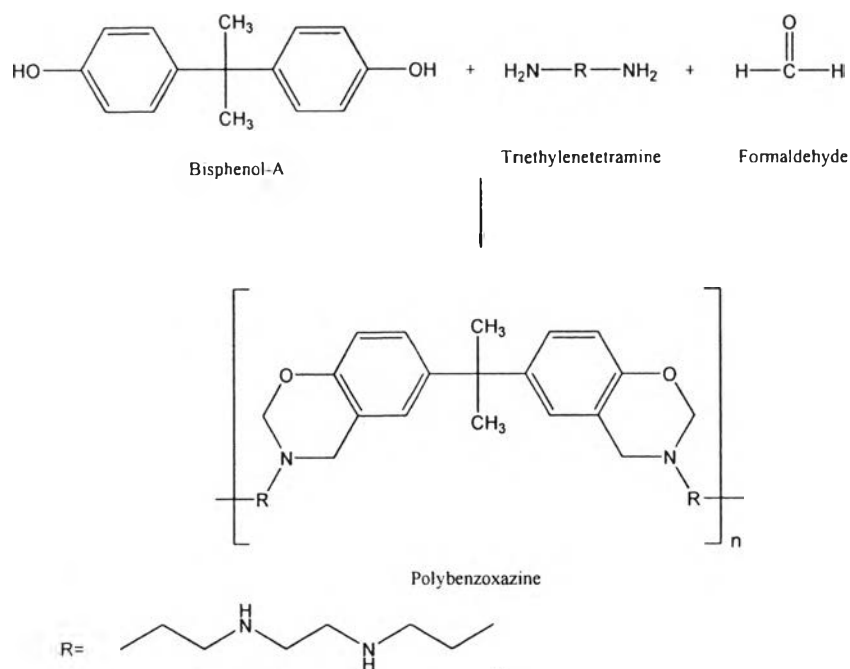


Figure 3.1 Preparation of polybenzoxazine precursor.

3.3.2 Preparation of Iron Oxide

The iron oxide (Fe_3O_4) was prepared by the following procedure: 4.80 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2.40 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 100 ml of deionized water under nitrogen gas. Next, 10 ml of NH_4OH (30%) was added at 80-90 °C and heated for 30 min. The black lump-like gel was separated by magnetic decantation and cooled to room temperature.

3.3.3 Preparation of Carbon Xerogel Electrodes

Benzoxazine aerogels were cut into the disc shape and pyrolyzed under a condition of nitrogen flow rate at $600 \text{ cm}^3/\text{min}$. The heating profile was used as follows: heating from room temperature to 250°C in 60 min, 250° to 600°C in 300 min, 600° to 800°C in 60 min and holding at 800°C for 120 min and finally cooling down to room temperature.

Heat-treated carbon xerogels (HCX) were prepared by using the heating profile at 300°C in air for 120 min to modify the electrode surface and to improve affinity with the electrolyte (Kim *et al.*, 2005).

3.3.4 Preparation of Carbon Xerogel Composite Electrodes

The heat-treated carbon xerogel electrode discs with a thickness of 1 mm were impregnated in an iron oxide solution by varying the iron oxide content (1, 3, 5 %wt) and were then dried in a vacuum oven at 200 °C for 6 hr to remove solvent.

3.3.5 Characterization of Iron Oxide (magnetite), Polybenzoxazine Precursor, and Carbon Xerogel Electrodes

X-ray diffraction (XRD) technique was used to characterize the crystallographic structure of iron oxide or magnetite (Fe_3O_4).

The chemical structure of benzoxazine precursor was characterized by Fourier Transform Infrared (FT-IR) spectroscopy. The thermal characteristics were measured using DSC and TG-DTA.

The surface area of carbon xerogels, heat-treated carbon xerogels were calculated from nitrogen adsorption isotherms at 77 K based on the Brunauer–Emmett–Teller (BET) method and the pore size distribution was calculated with the adsorption data based on the Barret-Joyner-Halenda method (BJH). The surface morphology, microstructure and EDX (energy dispersive X-ray) results were characterized using scanning electron microscope (SEM).

In case of electrochemical measurement, the galvanostatic charge/discharge, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were determined. All of the electrochemical measurements were performed at room temperature. The electrochemical test cell consisted of graphite sheets as current collectors, two carbon xerogels and/or carbon xerogel composite electrodes separated by microporous polyethylene membrane and 6M KOH solution. Moreover, in any measurement, the carbon xerogels and/or carbon xerogel composite electrodes were immersed in 6M KOH electrolyte for 24 hr to ensure complete filling of the porous electrodes (Kim *et al.*, 2005; Hwang *et al.*, 2007).