



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 sulphuric acid (95-97% H₂SO₄ analytical grade) were purchased from Merck, Germany. *N,N*-Dimethylformamide (DMF) was purchased from Labscan Asia Co., Ltd., Thailand.

3.2 Measurements

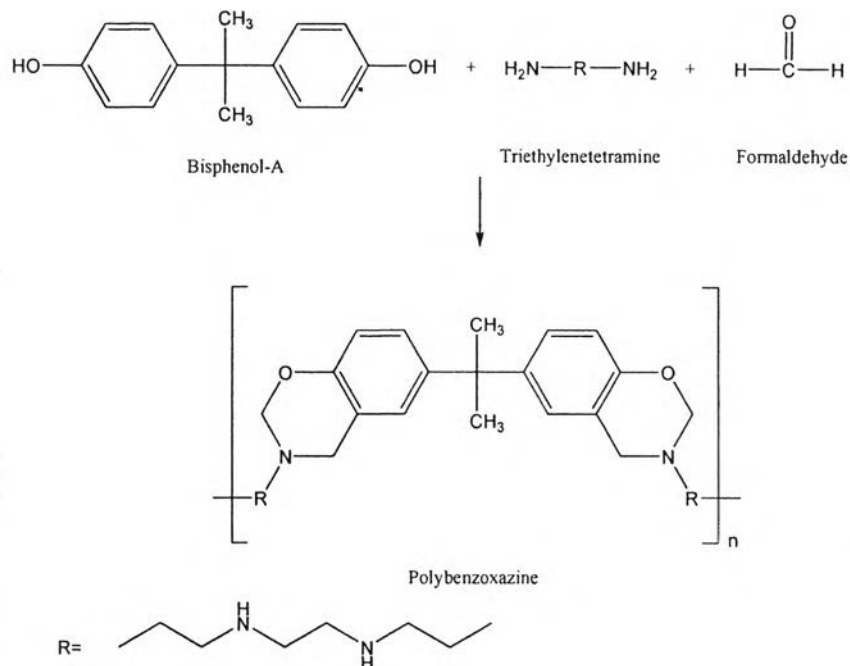
Thermal behaviors of polybenzoxazine aerogel were determined with differential scanning calorimetry (DSC), Perkin Elmer DSC7; The sample was heated from ambient temperature to 300 °C at a heating rate of 10 °C/min under nitrogen flow rate of 10 ml/min. Thermogravimetric analysis was also conducted with 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 aerogel 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 aerogel; the samples were coated with platinum under vacuum prior to investigation. BET surface area and pore size distribution of all carbon aerogels 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. For all electrochemical measurements, the electrochemical test cell consisted of graphite sheets as current collectors and two carbon aerogel electrodes separated by microporous polyethylene membrane. The carbon aerogel electrodes were soaked in 3M H₂SO₄ 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 mAcm⁻² up to 1 V and discharged with 5 mAcm⁻² 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

The synthesis of polybenzoxazine precursor was started by dissolving Bisphenol-A (2.3075 g) in *N,N*-dimethylformamide (DMF) (15.00 g) and stirring continuously. Formaldehyde solution (3.2824 g) was then added into the bisphenol A solution. The solution was kept under low temperature by using ice bath. TETA (1.7388 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 Scheme 3.1. Next, the precursor was filled in a vial with seal and placed in an oven at 80°C for 72 hr in a close system to generate benzoxazine aerogels. The benzoxazine aerogels were cut into disc shape and then dried at ambient temperature followed by placing in an oven at 160° and 180°C for 3 hr at each temperature and 200°C for 2 hr in order to polymerize benzoxazine aerogel.



Scheme 3.1 Preparation of polybenzoxazine precursor.

3.3.2 Preparation of Carbon Aerogel Electrodes

The benzoxazine aerogels were cut into a disc shape electrode and then pyrolyzed under a nitrogen flow rate of 600 cm³/min. The heating profile was 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 60 min and finally cooling down to room temperature. The carbon aerogel electrodes were heat treated at 300°C in air for 120 min to modify the electrode surface and to improve affinity with the electrolyte (Kim S. J. *et al.*, 2005).

Activated carbon aerogel (ACA) was prepared by carbonization of carbon aerogel with carbon dioxide at 900°C for 180 min.

3.3.3 Characterization of Polybenzoxazine Precursor and Carbon Aerogel Electrodes

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

The surface area of carbon aerogels and activated carbon aerogels

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 was characterized using scanning electron microscope (SEM).

For 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.