

## **CHAPTER 3**

### **EXPERIMENTAL PROCEDURES AND TECHNIQUES**

#### **3.1 CHAPTER OVERVIEW**

Detailed information about samples preparation for the present research are given in this chapter. The prepared materials for this study are MnO<sub>2</sub>, reduced graphene oxide, carbon nanoparticles and reduced graphene oxide/MnO<sub>2</sub> nanocomposite. In addition, this chapter shows a background about chemical and physical characterization techniques, in order to study the properties of the prepared materials such as XRD, FTIR, TGA/DTA, FESEM, TEM, Raman, UV–Vis and N<sub>2</sub> adsorption–desorption techniques. Finally, the electrodes preparation and cells setup used for supercapacitive testing are mentioned in details.

#### **3.2 SAMPLES PREPARATION PROCEDURES**

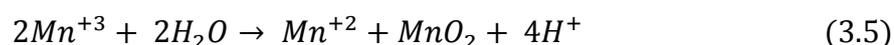
##### **3.2.1 Preparation of MnO<sub>2</sub> from Recycling of Spent Batteries**

A spent Zn–C battery (EVEREADY® D cell) was disassembled and the cathode black paste was taken and used for the subsequent process. The cathode black paste was dried at 130 °C for 24 hours, ground well in a mortar, and then was sieved using 200 μm

mesh. The sieved powder was later washed with deionized water (solid to liquid ratio 1:10) in order to remove  $\text{NH}_4\text{Cl}$  electrolyte from the cathode past in the battery and finally dried at  $105\text{ }^\circ\text{C}$  for 24 hours. The dried powder (20 g) was subsequently dissolved in  $\text{H}_2\text{SO}_4$  (200 mL, 2 M, Friendemann Schmidt), followed by addition of  $\text{H}_2\text{C}_2\text{O}_4$  (14.5 g, Aldrich) which act as reducing agent. The leaching process was continued with continuous stirring for 5 hours at  $80\text{ }^\circ\text{C}$  (Rácz and Ilea, 2013, Ferella et al., 2008). The reactions which were involved in this preparation are summarized as shown below:



The leached solution was filtered prior to electrowinning. For electrowinning, two stainless steel plates were set up as electrodes and the distance between electrodes was kept at 20 mm. Electrowinning was carried out in 50 mL of leached solution with current density of  $0.15\text{ A cm}^{-2}$  for 1 hour at room temperature. Electrowinning involves Mn(II) oxidation to Mn(III) and followed by disproportionation to Mn(II) and Mn(IV).  $\text{MnO}_2$  was then formed as dark precipitate at the bottom of the cell.  $\text{MnO}_2(\text{Bt})$  was used as a code for the prepared material. The reaction mechanism can be described as follows (Souza and Tenório, 2004):



### 3.2.2 Preparation of MnO<sub>2</sub> by Potentiostatic and Galvanostatic Electrodeposition

MnO<sub>2</sub> was electrodeposited from KMnO<sub>4</sub> solution (0.5 M, Aldrich) by potentiostatic and galvanostatic techniques by applying 10 V and 0.165 A cm<sup>-2</sup> for 30 minutes at room temperature, respectively. Two pre-treated stainless steel plates were used as electrodes. The distance between two electrodes was kept constant at 20 mm throughout the electrodeposition process. For both electrodeposition techniques, black films were obtained on the cathode and the mass was recorded after drying. MnO<sub>2</sub>(PS) and MnO<sub>2</sub>(GS) were used as codes for the prepared materials by potentiostatic and galvanostatic techniques, respectively.

### 3.2.3 Preparation of Reduced Graphene Oxide Nanosheets

Graphene oxide (GO) was prepared from graphite by Hummers' method (Hummers and Offeman, 1958). In order to prevent incomplete oxidation, graphite powder was pre-oxidized by slowly mixed and stirred with graphite (20 g, Merck), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (10 g, Aldrich) and P<sub>2</sub>O<sub>5</sub> (10 g, Aldrich) into concentrated H<sub>2</sub>SO<sub>4</sub> (30 mL). The reaction mixture was heated up to 80 °C using an oil bath and continuous stirring for 6 hours. The mixture was then diluted with distilled water, filtered and washed until the filtrate became neutral in pH condition. The washed powder was dried for 8 h in a vacuum oven at 60 °C. The pre-oxidized graphite powder was oxidized as follows: the pre-oxidized graphite powder was added to concentrated H<sub>2</sub>SO<sub>4</sub> (460 mL) cooling in an ice bath. KMnO<sub>4</sub> (60 g) was added to the pre-oxidized solution and continuously stirred over 30 minutes. The mixture was then heated up to 35 °C for 2 hours before distilled water (1 L) was added. The stirring was continued for 15 minutes and additional distilled water (3 L) and 30 % H<sub>2</sub>O<sub>2</sub> (50 mL, Merck) were added onto the mixture. The mixture was then filtered, washed with aqueous HCl (1:10, Merck) and dried in vacuum oven at 60 °C in order to obtain dry graphite oxide. Exfoliation of graphite oxide was done by sonicating graphite oxide dispersion (2 g L<sup>-1</sup>) at 200 W for 30 minutes. The dispersion was later centrifuged at 6000 rpm for 10 minutes to remove the