PREPARATION AND CHARACTERIZATION OF MANGANESE–BASED AND CARBON–BASED NANOMATERIALS FOR SUPERCAPACITORS APPLICATION

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ABSTRACT

In this study, electrochemical materials, namely MnO_2, reduced graphene oxide (rGO), porous carbon nanoparticles (PCNs), and rGO/MnO_2 nanocomposite, were prepared in diverse morphologies such as nanoflowers (MnO_2), nanosheets (rGO), and nanoparticles (carbon). Different physical and chemical characterizations have been conducted to study the structural and morphological properties of the materials under study. Electrochemical properties of the above materials have been studied comprehensively using cyclic voltammetry (CV), galvanostatic charge–discharge (CDC) and electrochemical impedance spectroscopy (EIS) in order to evaluate their suitability as an electrode for supercapacitive energy storage. MnO_2 nanoflowers was recovered from spent batteries by a combining leaching and electrowinning techniques. The recovered MnO_2 nanoflowers exhibited high specific capacitance (C_s) (303 F g^{-1} at 5 mV s^{-1}). Furthermore, MnO_2 was electrodeposited by potentiostatic and galvanostatic conditions. Under similar electrodeposition conditions, MnO_2 deposited by galvanostatic condition showed smaller particle size, less compact layered structure and wider band gap compared to potentiostatic deposition. The galvanostatic MnO_2 rendered facile ions diffusion, low resistances and showed superior capacitive behavior. The rGO nanosheets were prepared by hydrazine reduction of graphene oxide and their electrochemical properties were studied. The rGO showed high Cs of 191 and 168 F g^{-1} at 5 mV s^{-1}, in 5 M KOH and 1 M Na_2SO_4, respectively and high cycling stability > 96 % over 1000 cycles. In addition, PCNs with fine particles size of 35 nm were prepared from oil palm leaves using a catalyst free process. The C_s of PCNs is 245 and 213 F g^{-1} at 5 mV s^{-1} in 5 M KOH and 1 M Na_2SO_4, respectively. The PCNs showed high cycling stability of 95 %. Practical supercapacitors were developed using rGO and PCNs; the devices delivered energy densities ~18 and ~25 W h kg^{-1} at power densities 340 and 360 W kg^{-1}, respectively, under wider operating voltage window of 2 V in neutral electrolyte. rGO/MnO_2 nanocomposite has been prepared by simultaneous electrochemical conversion of GO and Mn_3O_4. The C_s of rGO/MnO_2 is 457 F g^{-1} at 5 mV s^{-1}, which are several folds higher compared to those for pure rGO and MnO_2. Furthermore, rGO/MnO_2 showed high stability of 95 % over 2000 CDC cycles. Therefore, the present study identifies electrochemical materials with improved energy storage capabilities.

ABSTRAK

Dalam kajian ini, bahan electrokimia iaitu MnO_2, graphene oksida terturun (rGO), karbon nanopartikel berongga (PCNs), dan rGO/MnO_2 nanokomposit telah disediakan in pelbagai morfologi, seperti nanobunga (MnO_2), nanolembaran (rGO), dan nanopartikel (karbon). Pelbagai ujian sifat fizikal dan sifat kimia yang berbeza telah dijalankan untuk memahami struktur dan morfologi bahan yang dikaji. Sifat electrokimia telah dikaji secara menyeluruh dengan menggunakan kaedah siklik voltammetrik (CV), galvanostatik cas-discas (CDC) dan electrokimia impedans spektroskopi (EIS) demi menilai kesesuaian sebagai elektrod dalam penyimpanan tenaga superkapasitif. MnO_2 nanobunga telah didapat kembali daripada bateri terpakai dengan kombinasi kaedah larut lesap dan *electrowinning*. MnO_2 nanobunga yang didapat kembali menunjukkan kapasitans spesifik (C_s) (303 F g^{-1} at 5 mV s^{-1}). Tambahan, MnO_2 juga dielektrodeposit dengan kaedah potentiostatik dan galvanostatik. Untuk keadaan proses electrodeposit yang sama, MnO_2 yang dideposit dengan kaedah galvanostatik menunjukkan partikel saiz yang lebih kecil, kepadatan struktur yang rendah dan jurang jalur yang lebih lebar berbading dengan kaedah potentiostatik. MnO_2 yang dihasilkan melalui kaedah galvanostatik membenarkan resapan ion yang mudah, rintangan yang rendah dan menunjukkan sifat kapasiti yang lebih baik. rGO nanolembaran telah disediakan melalui penurunan graphene oksida dengan hydrazine dan sifat electrokimia telah dikaji. rGO menunjukkan C_s yang tinggi iaitu 191 dan 168 F g^{-1} pada 5 mV s^{-1}, di dalam 5 M KOH dan 1 M Na_2SO_4, masing-masing dan kestabilan kitaran yang tinggi > 96 % untuk 1000 kitaran. Tambahan, PCNs dengan partikel saiz yang halus 35 nm turut disediakan dengan daun kelapa sawit tanpa menggunakan pemangkin. C_s untuk PCNs adalah 245 dan 213 F g^{-1} pada 5 mV s^{-1} di dalam 5 M KOH dan 1 M Na_2SO_4, masing-masing. PCNs menunjukkan kestabilan kitaran yang tinggi 95%. Superkapasitor praktikal telah disediakan dengan menggunakan rGO dan PCNs dan peranti tersebut menghasilkan tenaga ~18 dan ~25 W h kg^{-1} pada kuasa 340 and 360 W kg^{-1}, masing-masing, di bawah operasi voltan 2 V di dalam neutral elektrolit. rGO/MnO_2 nanokomposit telah disediakan dengan kaedah pertukaran electrokimia GO dan Mn_3O_4. C_s untuk rGO/MnO_2 adalah 457 F g^{-1} pada 5 mV s^{-1} dan nilai ini adalah beberapa kali ganda lebih tinggi berbanding dengan rGO dan MnO_2 tulen. Tambahan, rGO/MnO_2 menunjukkan kestabilan tinggi 95 % untuk 2000 kitaran CDC. Oleh demikian, kajian ini menunjukkan bahan electrokimia yang mempunyai keupayaan simpan tenaga yang ditambahbaikkan.

TABLE OF CONTENTS

CHAPTER 2 LITERATURE REVIEW

CHAPTER 3 EXPERIMENTAL PROCEDURES AND TECHNIQUES

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

α	Absorption coefficient
C	Capacitance
Q	Charge
Δt_c	Charging time
η	Coulombic efficiency
B	Constant relative to the material
I	Current
Ps_{XRD}	Crystalline size
θ	Diffraction angle (degree)
Δt_d	Discharging time
S_E	Electrochemical active specific surface area
E_g	Energy band gap
E	Energy density
F	Farad

f	Frequency
C''	Imaginary part of the cell capacitance
Z''	Imaginary part of the impedance
m	Mass of active material
M	Molar mass
n	Number of electrons
$h\upsilon$	Photon energy
ΔV	Potential window
P	Power density
C'	Real part of the cell capacitance
Z'	Real part of the impedance
τ	Relaxation time
υ	Scan rate
k	Scherrer constant

C_s	Specific capacitance
C_{theo}	Theoretical pseudocapacitance
V	Volt
λ	Wavelength

LIST OF ABBREVIATIONS

2D	Two Dimensional
3D	Three Dimensional
2ES	Two Electrode System
3ES	Three Electrode System
AC	Activated Carbon
ASSCs	Asymmetric Supercapacitors
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
CNTs	Carbon Nanotubes
CPE	Constant Phase Elements
CPs	Conducting Polymers
CV	Cyclic Voltammetry
DTA	Differential Thermal Analysis
DFT	Density Functional Theory

ECs	Electrochemical Capacitors
EDL	Electrochemical Double Layer
EDLCs	Electrochemical Double Layer Capacitors
EIS	Electrochemical Impedance Spectroscopy
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
GO	Graphene Oxide
HCs	Hybrid Capacitors
JCPDS	Joint Committee on Powder Diffraction Standards
MWCNTs	Multi–Walled Carbon Nanotubes
OCP	Open Circuit Potential
OPL	Oil Palm Leaves
PANI	Polyaniline
PCs	Pseudocapacitors

PCNs	Porous Carbon Nanoparticles
PBS	Phosphate Buffered Solution
PTFE	Polytetrafluoroethylene
rGO	Reduced Graphene Oxide
rGONS	Reduced Graphene Oxide Nanosheets
SSCs	Symmetric Supercapacitors
SWCNTs	Single–Walled Carbon Nanotubes
SWCNHs	Single–Walled Carbon Nanohorns
TEM	Transmission Electron Microscope
TGA	Thermogravimetric Analysis
UV–Vis	Ultraviolet–Visible Spectrophotometry
USEPA	United States Environmental Protection Agency
XRD	X–Ray Diffraction
Zn–C	Zinc–Carbon

CHAPTER 1

INTRODUCTION

1.1 CHAPTER OVERVIEW

This chapter introduces the basic aspects about the materials used in this study and background for the energy storage properties of the materials. Motivation of the research, problem statement, research objectives and scope of work are also presented in this chapter.

1.2 BACKGROUND AND MOTIVATIONS

Electrochemical capacitors (ECs) are also known as ultracapacitors or supercapacitors. It can be classified into two main categories based on energy storage mechanism, pseudocapacitors (PCs) and electrochemical double–layer capacitors (EDLCs). PCs store electrical energy faradically by electron charge transfer between electrode and electrolyte. Metal oxides and conducting polymers are used as electrode materials for PCs. In EDLCs, a double layer of electrolyte ions is formed on the surface of an electrode material, which arises from the potential–dependence of the surface density of charges stored electrostatically. The electrode materials for EDLCs include all carbon–based materials. Supercapacitors could be used in many applications because of

their higher energy output as compared to conventional capacitors and higher power than batteries, in addition to their miniature size. Various types of electrode materials can be used in supercapacitors, including carbon–based materials, conducting polymers and metal oxides. In addition, the electrolyte could be an aqueous, organic or an ionic liquid. In case of an aqueous electrolyte, the operating voltage is limited to 1 V (due to the electrochemical decomposition of water at 1.23 V), whereas an organic electrolyte can achieve a voltage range of 2.5 to 3.5 V (Syzdek et al., 2014). A higher voltage of up to 4.0 V can be achieved for the ionic liquid. Supercapacitors have many advantages, for example, long life cycles, fast charging time, low impedance and high energy and power density, environmental friendly, and also can be operated in a wide temperature range. This study aims to investigate different materials for supercapacitor applications with high power and long life criteria for better energy storage devices. The energy storage properties are directly depending on the structure and morphology of the electrode materials.

In recent years, manganese dioxide (MnO_2) has drawn increasing attention for supercapacitors application, mainly due to the high abundancy of manganese (Jang et al., 2012) that contributes to low material cost as compared to the expensive ruthenium metal. Pang et al. reported high specific capacitance (C_s) (700 F g^{-1}) for MnO_2 thin films in year 2000 and their findings had sparked strong interest among energy research community for its application in supercapacitor electrode (Pang and Anderson, 2000, Pang et al., 2000). Such high capacitance value arises from the ions insertion/desertion within MnO_2 structure and it depends crucially on the particle size, surface area and porosity. Since then, in achieving optimized condition for the aforementioned properties, MnO_2 with different morphologies have been developed, such as nanoflakes (Chou et al., 2006), nanorods (Yousefi et al., 2012a), nanowires (Yousefi et al., 2013), nanopetals (Yang et al., 2012) and nanosheets (Yan et al., 2012). The synthesis route plays a vital role in determining its morphology. The most common synthesis route for MnO_2 is chemical coprecipitation method (Deng et al., 2013, Jiang et al., 2009) involving dissolved Mn^{4+} precursor. However, instability of Mn^{4+} precursor in the aqueous solution as well as the contact resistance between synthesized MnO_2 and current collectors have hindered its wider use in electrochemical applications (Xu et al., 2008, Prasad and Miura, 2004).

Electrochemical deposition is proven to be an effective method to prepare MnO_2 nanostructures (Hu et al., 2014, Yousefi et al., 2013).

On the other hand, carbon–based materials possessing high surface area as the electrode material, and the capacitive originates from the charge accumulation at the interface between electrode and electrolyte (Portet et al., 2005). Pseudocapacitors employ transition metal oxides or conductive polymers (Patil et al., 2013, Song et al., 2013, Xie et al., 2012) as the electrode material. Though the energy densities in pseudocapacitors are higher than that of EDLCs, the faradic reactions within pseudocapacitors could lead to phase changes and limit their life time (Compton and Nguyen, 2010). Graphene with its high surface area and nanosheets morphology and carbon nanoparticles with porous structure are a promising materials from energy storage applications.

1.3 PROBLEM STATEMENT

The need for the development of efficient energy storage systems is paramount in meeting the world's future energy targets, especially when the energy costs are on the increase in addition to the escalating demand. Energy storage technologies can improve efficiencies in supply systems by storing the energy when it is in excess, and then release it timely. Nowadays, batteries are slowly becoming obsolete due to their poor cycleability (limited to a few thousands) and long charge time (tens of minutes) in comparison to supercapacitors. On the other hand, supercapacitors have long life time and fast charging times (Vangari et al., 2013). Nowadays the research focus on developed suitable electrode materials which directly reflect in supercapacitor technology enhancement.

MnO_2 has been identified as a promising pseudocapacitive material to replace toxic and costly materials especially ruthenium oxide. Though manganese source can be found abundantly in nature, it is imperative to stop exploiting nature for the advancement of technology. Instead, recovery of manganese from waste sources could be an alternative to obtain MnO_2. According to United States Environmental Protection Agency (USEPA) analysis, an average of 8 disposable batteries are consumed by an individual annually.

Annually, around 160 000 tonnes of batteries are placed on the market and around 20 000 tonnes per year of manganese could be recovered (Gallegos et al., 2013). Thus figures raise an alarm on the disposal issue where the common practice in handling spent batteries is landfill which could potentially harm the environment. Furthermore, high percentage of manganese in spent batteries could be a motivation in manganese recovery from batteries to be used as supercapacitor electrode (Sayilgan et al., 2009).

Carbon–based materials are the most widely used materials in commercial supercapacitor. However, activated carbon possesses the problem of achieving high C_s and thus limiting its wide application in supercapacitor. Graphene possesses high surface area, stable structure and exhibits many interesting electronic, optical and mechanical properties due to its 2D crystal structure. Graphene could be the solution for this problem. On the other hand, as a move to preserve the environment as well as maintain low cost material, waste precursors could be the potential source for the production of carbon–based materials. This include with oil palm biomass residues (leaves, fronds, trunks, empty fruit bunches, shells and fibers) constitute biomass waste produced from oil palm industries which is in abundance in south–east Asia (Chavalparit et al., 2006) (around 73.74 million tonnes per year in Malaysia (Rafatullah et al., 2013). A common practice in managing oil palm residues is burning which give rise to environmental issues. Furthermore, it is composed of high carbon content (about 18 wt %) (Rafatullah et al., 2013), and could be the potential source for the production of carbon–based material for supercapacitor electrode construction.

EDLCs materials possess good stability but provide with the limited specific capacitance. On the other hand, PCs materials possess good capacitive storage but at a cost of low stability. It is timely to develop a hybrid energy system comprising of both materials and investigating their synergetic effect towards capacitive storage.

1.4 OBJECTIVES OF RESEARCH

The objectives of this research are:

1. To determine the physical and chemical characteristics of supercapacitor electrode materials such as MnO_2, reduced graphene oxide, carbon nanoparticles and reduced graphene oxide/MnO_2 nanocomposite.
2. To evaluate the electrochemical characteristics of MnO_2 recovered from spent batteries as supercapacitor electrode.
3. To evaluate the electrochemical characteristics of reduced graphene oxide from graphite source and porous carbon nanoparticles from biowaste (oil palm leaves) as supercapacitor electrodes.
4. To investigate the synergetic effect of carbon–based nanomaterials and MnO_2 towards enhanced energy storage properties.

1.5 SCOPE OF THE THESIS

The following research activities are required to achieve the mentioned objectives:

1. Recover MnO_2 from spent batteries through electrochemical method and produce MnO_2 with different electrochemical approaches.
2. Synthesize reduced graphene oxide nanosheets via modified Hummers' method and produce carbon nanoparticles from oil palm leaves via thermal annealing.
3. Synthesize reduced graphene oxide/MnO_2 nanocomposite through electrochemical method.
4. Study the structural properties of the synthesized materials with X–ray diffraction, UV spectroscopy, infrared spectroscopy, electron microscopy, N_2 adsorption–desorption and Raman spectroscopy.
5. Study the electrochemical properties of the synthesized materials with cyclic voltammetry, galvanostatic charge discharge and electrochemical impedance spectroscopy.
6. Fabricate the supercapacitor device with the synthesized materials and evaluate its long term stability.

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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_2, reduced graphene oxide, carbon nanoparticles and reduced graphene oxide/MnO_2 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_2 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_2 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 NH_4Cl electrolyte from the cathode past in the battery and finally dried at 105 °C for 24 hours. The dried powder (20 g) was subsequently dissolved in H_2SO_4 (200 mL, 2 M, Friendemann Schmidt), followed by addition of $H_2C_2O_4$ (14.5 g, Aldrich) which act as reducing agent. The leaching process was continued with continuous stirring for 5 hours at 80 °C (Rácz and Ilea, 2013, Ferella et al., 2008). The reactions which were involved in this preparation are summarized as shown below:

$$Mn_2O_3 + H_2SO_4 \rightarrow MnO_2 + MnSO_4 + H_2O \tag{3.1}$$

$$Mn_3O_4 + 2H_2SO_4 \rightarrow MnO_2 + 2MnSO_4 + 2H_2O \tag{3.2}$$

$$MnO_2 + H_2C_2O_4 + H_2SO_4 \rightarrow MnSO_4 + 2CO_2 + 2H_2O \tag{3.3}$$

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 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). MnO_2 was then formed as dark precipitate at the bottom of the cell. MnO_2(Bt) was used as a code for the prepared material. The reaction mechanism can be described as follows (Souza and Tenório, 2004):

$$2Mn^{+2} \rightarrow 2Mn^{+3} + 2e^- \tag{3.4}$$

$$2Mn^{+3} + 2H_2O \rightarrow Mn^{+2} + MnO_2 + 4H^+ \tag{3.5}$$

3.2.2 Preparation of MnO_2 by Potentiostatic and Galvanostatic Electrodeposition

MnO_2 was electrodeposited from $KMnO_4$ solution (0.5 M, Aldrich) by potentiostatic and galvanostatic techniques by applying 10 V and 0.165 A cm^{-2} 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_2(PS) and MnO_2(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), $K_2S_2O_8$ (10 g, Aldrich) and P_2O_5 (10 g, Aldrich) into concentrated H_2SO_4 (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_2SO_4 (460 mL) cooling in an ice bath. $KMnO_4$ (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_2O_2 (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^{-1}) at 200 W for 30 minutes. The dispersion was later centrifuged at 6000 rpm for 10 minutes to remove the