

UNIVERSITI PUTRA MALAYSIA

PREPARATION OF GRAPHENE-POLYPYRROLE AND GRAPHENE-POLYPYRROLE-MANGANESE OXIDE NANOCOMPOSITES AS ELECTROCHEMICAL SUPERCAPACITOR ELECTRODE

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By

LIM YEE SENG

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy December 2013

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

PREPARATION OF GRAPHENE-POLYPYRROLE AND GRAPHENE-POLYPYRROLE-MANGANESE OXIDE NANOCOMPOSITES AS ELECTROCHEMICAL SUPERCAPACITOR ELECTRODE

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December 2013

Chair: Tan Yen Ping, PhD Faculty: Science

Electrode material with high capacity performance is indispensable for realizing high performance supercapacitors. Hence, the key aspect for improving the performance of supercapacitors is to improve the capacity performance of the active materials. The work present herein focuses on the synthesis, electrochemical capacity performance of the graphene-based nanocomposite materials for supercapacitors, and elucidation of the physical factors which contribute towards the observed capacity performance. This research work was divided into four parts. An initial study was focuses on synthesis of polypyrrole/graphene (PPy/GR) hybrid materials. A one-step electrochemical deposition has been employed to synthesize binary nanocomposite films of PPy/GR. The bulbous surface of polypyrrole (PPy) and the almost transparent tissue-like GO nanosheets were replaced by new appearance of the nanocomposite where the surface was flat but creased. The electrical conductivity of the PPy/GR nanocomposite was higher than that of the pure PPy film, based on the electrical conductivity study measured with a four point probe. The high electrical conductivity of PPy/GR nanocomposite film demonstrated its potential application as supercapacitor electrode. The second part of the work was to evaluate the capacitive performance of synthesize PPy/GR nanocomposite films. Studies showed that PPy/GR electrode displayed better capacitive performance than that of pure PPy, reflecting a synergistic effect between PPy and GR, as analysed by a three electrode electrochemical experiment. The electrochemical results revealed that the capacitive performance of PPy/GR nanocomposites depended on deposition parameters such as concentration of pyrrole and GO, deposition time and deposition potential. The third part of the work was investigated the integration of additional nanostructure metal oxide, specifically manganese oxide into PPy/GR nanocomposite to maximise the electro-active surface area accessible to electrolyte ions. An increase of capacity performance (up to 320.6 F/g) was observed through the integration of manganese oxide, which is attributed to the morphology of polypyrrole/graphene/manganese (PPy/GR/MnO_x) ternary composite maximize the pseudocapacitive oxide contribution from redox-active MnOx and PPy and EDLC contribution from

individual GR sheets. The final studies sought to focuses on control of size, morphology, quantity and distribution of PPy particles in the nanocomposite matrix, aimed at fully harness the capacitive performance of functional components and improving the pore accessibility of graphene. In this study, FeCl₃ catalyst was used to control the particle size of polypyrrole coated on GR aimed to avoid polymeric agglomeration. The improved capacitive performance (797.6 F/g) was attributed to the controlled particle size of polypyrrole growth on individual GR sheets and overlap of GR sheets forming a highly open structure provides easier access of electrolyte into composite film maximize the pseudocapacitive contribution from redox-active polypyrrole and EDLC contribution from individual GR sheets.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENYEDIAAN GRAPHEN-POLYPYRROLE DAN GRAPHEN-POLYPYRROLE-MANGAN OKSIDA NANOKOMPOSIT SEBAGAI ELEKTROD ELEKTROKIMIA SUPERKAPASITOR

Oleh

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Elektrod dengan keupayaan kapasitan yang tinggi adalah diperlukan untuk membina superkapasitor yang berpretasi tinggi. Oleh itu, faktor utama untuk meningkatkan prestasi superkapasitor adalah dengan meningkatkan prestasi keupayaan kapasitan elektrod. Kajian ini memberi tumpuan kepada sintesis, penilaian prestasi keupayaan kapasitas nanokomposit berasaskan graphen untuk superkapasitor, dan penerangan tentang faktor-faktor fizikal yang menyumbang kepada kapasitan yang diperhatikan sepanjang pengajian. Kajian ini dibahagikan kepada empat bahagian. Kajian pertama akan memberi tumpuan kepada sintesis bahan hybrid polypyrrole/graphen (PPy/GR). Proses eletrokimia telah digunakan untuk mensintesis filem binari nanokomposit PPy/GR. Permukaan PPy yang bulat dan nanokepingan GO yang telus seperti tisu telah tukar penampilan baru kepada permukaan adalah rata dan berkedutan. PPy/GR nanokomposit menunjukkan kekonduksian elektrik yang lebih tinggi daripada filem PPy melalui kajian kekonduksian elektrik. Dengan mempunyai kekonduksian elektrik yang tinggin, filem PPy/GR berpotensi digunakan sebagai elektrod superkapasitor. Bahagian kedua dalam kajian ini adalah menilai prestasi keupayaan kapasitan filem PPy/GR. Kajian ini menunjukkan bahawa PPy/GR elektrod mempaparkan prestasi kapasitan yang lebih baik daripada PPy tulen. Ini adalah disebabkan kesan sinergi antara PPy dan graphen. Di samping itu, penilaian elektrokimia menunjukkan bahawa keupayaan kapasitan PPy/GR juga bergantung kepada faktor seperti kepekatan pyrrole dan GO, masa pemendapan dan potensi yang digunakan. Bahagian ketiga kajian ini adalah mensiasat kesan tambahan nanostruktur logam oksida, khususnya mangan oksida ke dalam komposit PPy/GR untuk meningkatkan kawasan permukaan elektroaktif yang diakses oleh ion electrolit. Peningkatan prestasi kapasitan (sehingga 320.6 F/g) yang diperhatikan melalui kesan tambahan mangan oksida boleh dikaitkan dengan morfologi ternary nanokomposit polypyrrole/graphen/mangan oksida (PPy/GR/MnOx) yang akan meningkatkan sumbangan pseudokapasitan dari redox-aktif MnOx, PPy dan sumbangan EDLC daripada kepingan graphen. Bahagian akhir dalam kajian ini memberi tumpuan kepada kawalan saiz, morfologi, kuantiti dan pengedaran komponen berfungsi (zarah PPy) dalam matrik nanokomposit. Ini bertujuan memanfaatkan prestasi kapasitan komponen berfungsi dengan sepenuhnya dan meningkatkan liang akses graphen. Dalam kajian ini, FeCl₃ telah digunakan sebagai pemangkin untuk mengawal saiz zarah polypyrrole bersalut pada graphen supaya mengelakkan penumpuan polimer. Akhirnya, prestasi kapasitan telah dipertingkatkan (797.6 F/g). Ini adalah disebabkan zarah polypyrrole terkawal pada permukaan kepingan graphen dan perbentukan struktur yang terbuka akibat pertindihan kepingan graphen. Fenomena ini akan menyenangkan akses elektrolit ke dalam filem komposit lantaran itu menpertingkatkan sumbangan pseudokapasitif dari redok-aktif polypyrrole dan sumbangan EDLC daripada kepingan graphen.

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LIST OF ABBREVIATIONS

AC	Activated carbon
ac	Alternating current
aMEGO	Activated microwave expanded graphite oxide
av	Alternating voltage
CNTs	Carbon nanotubes
С	Capacitance
C-PPy/GR	Catalyst assisted polypyrrole/graphene
R _{ct}	Charge transfer resistance
CVD	Chemical vapor deposition
CV	Cyclic voltammetry
C _{diff}	Diffuse region double layer capacitance
C_{dl}	Double layer capacitance
EDLC	Electrical double layer capacitor
EIS	Electrochemical impedance spectroscopy
ESR	Equivalent series resistance
FESEM	Field emission scanning electron microscopy
FT-IR	Fourier transform infrared spectroscopy
GR	Graphene
GO	Graphene oxide
C _H	Helmholtz type compact double layer
	capacitance
HRTEM	High resolution transmission electron
	microscopy
ITO	Indium tin oxide
MWCNTs	Multiwall carbon nanotubes
OCP	Open circuit potential
PA	Polyacetylene
PANI	Polyaniline
PEDOT	Poly(3,4-etylenedioxythiophene)
PMeT	Poly(3-methyl thiophene)
PPy	Polypyrrole
PPy/GR	Polypyrrole/graphene
PPy/GR/MnO _x	Polypyrrole/graphene/manganese oxide
PS	Polystyrene
PTh	Polythiophene
SCE	Saturated calomel electrode
Ag/AgCl	Silver/silver chloride
Cm	Specific capacitance
TGA	Thermal gravimetric analysis
3D	Three-dimensional
2D	Two-dimensional
XRD	x-ray diffraction
XPS	x-ray photoelectron spectroscopy

CHAPTER I

INTRODUCTION

The energy sector has changed drastically over the few decades since the era of industrialization. Since then, abundant and economical energy and developing a modern civilization is inseparable. Moreover, the steady growth of human population, as well as the significant improvement in the living quality, leads to an increase energy consumption that will soon exceed the production capacity; the world energy is facing unprecedented uncertainty.

From the reference scenario of World International Energy, the world primary energy is expected to increase 40 % from the year of 2007-2030 (World Energy Outlook, 2009), another main drivers of the growth is due to developing Asian countries. Malaysia, being a fast developing country among Asian countries, it is expected that its economic growth will affect on the increase in the growing of energy consumption demand in the nation. However, heavily relying on the combustion of fossil fuels and coal will lead to diminishing reserves of energy supply since it is in the form of non-renewable energy and bring severe impact on the environment such as global warming.

Recently, transforming natural energy, such as wind, hydro and solar energies is under serious consideration as alternative energy and power source since it can generate large amounts of clean and sustainable energy. In unison, the development of energy storage devices is particularly vital to store the harvested energy for a wide range of applications. Thus, the energy challenge is apparent; economic and environmental reasons are driving a transition from the actual energy sources and cleaner and sustainable energy future. The development of energy sources and energy storage system with lower environmental impact, with attention focusing on renewable energies is indispensable.

1.1 Energy Storage System

A technological advance society extensively relies on large and small energy storage system in the major scale to satisfy all purposes. From a hydroelectric system that stored energy in the form of potential energy through the use of the gravitational force of falling water to potential energy that stored in fuel and oil becomes available through combustion. However, the hydroelectric system required large reservoir of land for operation, this will result in significant physical, chemical and biological transformation for local ecosystem (Gleick, 1992). In the case of a fuel combustion system that require energy transduction devices such as steam-turbine, steam-piston and internal combustion engines, will suffer from poor efficiency which are limited by thermodynamic Carnot cycle.

A cleaner energy conversion and storage system is important to ensure the energy sustainability and to reduce the environmental impact. Recently, electrochemical energy storage system is under serious consideration as an alternative energy and power source, as long as this energy consumption is designed to be more sustainable and more environmentally friendly. Moreover, electrochemical energy storage system is not thermal machines, so their performance is not limited by Carnot cycle, being able to approach 100% efficiency theoretically. Devices that rely on electrochemical energy storage and conversion system include batteries, fuel cells, and supercapacitors (also known as electrochemical supercapacitor or ultracapacitor).



Fig. 1.1 Ragone plot of various energy devices (Winter and Brodd, 2004)

Supercapacitors appear to be devices that had received considerable attention due to its superior characteristic, these include large power density than batteries (Portet *et al.*, 2005), longer life cycle (Ruiz *et al.*, 2008), and their higher energy density (Hu *et al.*, 2009) compared to conventional electric double layer capacitor (Yang *et al.*, 2008). Supercapacitors function mainly as backup energy sources for the memories, system boards, and clocks. In case of power outages of primary power sources, supercapacitors will supply the critical power. Recently, the application of supercapacitors has expanded into portable electronics due to the development of advanced supercapacitors device with increase in energy and power density. On the other hand, supercapacitors also becoming attractive energy storage system particular involving high power requirements due to its high specific power especially with the emerging technologies of hybrid vehicles or hybrid electric vehicle to suit the varied energy demand (Bentley *et al.*, 2005; Yu *et al.*, 2011).

The performance of energy storage devices based on the power and energy density can be expressed by Ragone plot as shown in Fig. 1.1. It can be noted that no single energy device can match all power and energy region. From the Ragone plot, batteries and fuel cells can deliver high-energy, whereas supercapacitors are considered to be a high power system. However, supercapacitors, being the device that fills up the gap between the conventional capacitors and batteries, are ideal electrochemical energy storage system. Although the mechanism involves for these systems is different, there are "electrochemical similarities" of these three systems. The common features are that batteries, fuel cells and supercapacitors all comprises two electrodes in contact with an electrolyte solution and the energy converting process take place at the phase boundary of electrode/electrolyte interface and the electron and ion transport are separated (Winter and Brodd, 2004).

Electrical energy is generated by conversion of chemical energy via Faradaic reactions at the electrodes (anode and cathode) in batteries and fuel cells. The difference between batteries and fuel cells is related to the location of energy storage and conversion. Batteries rely on Faradaic reactions taking place in the electrode material itself, being as "active mass", for the charge storage mechanism, the conversion occur in the same compartment (closed system). Thus, the generation of electrical energy is via electrochemical reactions of electrode materials with ions in an electrolyte (Winter and Brodd, 2004). The discharge rates of batteries are solely determined by the reaction kinetics as well as mass transport of active materials, therefore, generally yield high energy densities, but rather low power densities and suffer from low cycle life.





Fuel cells are open systems where the electrodes are just charge transfer media and supply of "active mass" (hydrogen, methanol etc.) and an oxidant (oxygen or air) are delivered from outside the cell, either from the environment, for example oxygen from the air, or from a tank, for example, fuel such as hydrogen and methanol. Energy storage and energy conversion are thus locally separated (Winter and Brodd, 2004). Although the fuel cell can be considered as a power source with nearly unlimited energy with almost zero impact on environment, there are obstacles such as to meet the cost performance barrier and it poor transient performance.



Fig. 1.3 Representation of a fuel cell showing the continuous supply of reactants and redox reactions in the cell (Winter and Brodd, 2004)

There is a general difference between the charge storage mechanisms of supercapacitors than that of batteries and fuel cells. In supercapacitors, energy is stored physically via non-Faradaic process through an electrostatic charging by the orientation of electrolyte ions at the electrode/electrolyte interface, forming electrical double layers (namely electrical double layer capacitors). This rendered supercapacitor the ability to store/release energy in a short time scale (few seconds) and the process is highly reversible. As a result, supercapacitors have higher power density compare with batteries and higher energy density than that of conventional capacitors. Furthermore, the electrode of supercapacitors does not undergo any chemical phase and composition change during the charge/discharge processes, thus, it shows higher cycle life when compared to batteries and fuel cells.



Fig. 1.4 Representation of a supercapacitor, illustrating the energy storage in the electric double layers at the electrode-electrolyte interfaces (Winter and Brodd, 2004)

In another type of system, an intermediate situation arises where Faradaic charge transfer occurs, but there is some continuous dependence of charge, q, passed Faradaically in oxidation or reduction, upon the electrode potential, V. Thus, a derivative dq/dv can arise that corresponds to a pseudocapacitance that is measurable, and utilizable as capacitance and designated as pseudocapacitance (Conway, 1999). Hence, the materials for supercapacitors can be divided into two different types: double layer capacitive materials and pseudocapacitive materials.

The key factor that restricts the supercapacitors to be used in market is its limited energy density, meanwhile the rapid growth of clean and sustainable energy require energy storage devices that able to offer high energy density, high power density and long life cycle. The increase demand for energy devices greatly promoted the searching for novel electrode materials and development of next generation supercapacitors. The recent discovery of novel electrode materials, such as graphene is breaking new ground for researchers to design and fabricate novel and advance electrode materials for high performance supercapacitors.

1.2 Problem Statements

Fundamental issues such as low energy density of current supercapacitor must be addressed to develop high performance supercapacitors as a new generation of energy storage system. The energy density of activated carbon currently dominates the market as an electrode material is generally less than 10 Wh/kg (Simon and Gogotsi, 2010), which much lower than that of batteries. Metal oxide or conducting polymer electrodes may construct high energy density supercapacitors, but they

suffer from poor cycling stability (Park et al., 2002). Thus, the improvement of cycling stability of metal oxides and conducting polymers is crucial.

For supercapacitor to be utilizable in practical application, the choice of electrolyte also is a decisive factor. The used of organic electrolytes and ionic liquids offer broad operating potential windows thus, higher energy density. However, organic electrolyte suffers from poor electrical conductivity resulting in increased diffusion resistance of electrolyte while ionic liquids are cost ineffective. Hence, both types of electrolytes are undesirable in practical applications (Zhang *et al.*, 2011). Considering the environmental and cost, aqueous electrolytes are attractive electrolytes if configured with appropriate electrode materials. Thus, novel and advanced electrode materials are the key to develop high performance supercapacitors (Zhang *et al.*, 2011).

The progress in the development of novel material is continuing at a steady rate. Since the isolation of graphene in 2004 (Brownson *et al.*, 2011), it has received attention among scientist due to its exceptional physical attribute. The graphene holds considerable promise as a new electrode material in supercapacitor due to its unique physical and chemical properties (high electrical conductivity and large surface area). Hence, utilizing graphene as supercapacitor based on the existing wealth of knowledge and current techniques available, ground breaking performance is expected to surpass current supercapacitor devices at the same time proving to be more energy efficient alternative. However, one of the intractable issues for the use of graphene as supercapacitor electrode is that graphene suffers from serious agglomeration and restacking after removal of dispersed solutions and drying due to van der Waals interaction between graphene sheets, consequently crippling the electrochemical performance of graphene (Liu *et al.*, 2010).

To fully utilize the potential advantages of graphene, novel conducting nanocomposites are the best way to achieve breakthrough. Fabrication of graphene/conducting polymer or metal oxides nanocomposites is expected to maximize the practical use of the combined advantages for both graphene and pseudocapacitive materials as functional components for improving the electrochemical energy storage, and solve the current electrode problems of the individual components.

In this work, graphene-based nanocomposite is developed with the aim of having several benefits to the performance of the electrode:

(1) The synergistic effect of functional pseudocapacitive component (conducting polymer or metal oxide) and graphene. Graphene provides chemical functionality and compatibility to allow easy processing of nanocomposite. Pseudocapacitive materials provide high capacitive performance depending on its size and structure. The resultant nanocomposite is thus regarded as material with new functionalities and properties.

- (2) Structural modification of nanocomposite. Functional component that disperse on graphene suppress the agglomeration and restacking of graphene and increase the available surface area of graphene alone, leading to improved electrochemical capacitive performance. On the other hand, graphene acts as a support or template induce the nucleation, growth and formation of nano-microstructures with uniform dispersion and controlled morphology on the surface of graphene.
- (3) The nanocomposite will form the integrated conductive structure and shorten the diffusion length of ions.

Therefore, it is well worth investigating how the functional components and graphene influence the electrochemical capacitive performance of the potential supercapacitor electrode material. Due to increasing interest in developing energy storage devices for portable electronics, it is important to synthesize potential supercapacitors electrode that is small, lightweight and flexible. Hence, in this aspect, a flexible nanocomposite film is favorable. Furthermore, the rational design and control of the morphology of the nanocomposite film is essential. This will ensure reproducibility and better understanding of the relationship between morphology of nanocomposite to its electrochemical performance.

1.3 Scope of Research

This thesis aims to design and prepare novel graphene-based nanocomposite with enhanced electrochemical capacitive performance as well as good cycling stability. The driving question behind this doctoral work is identifying green approaches to produce graphene from graphene oxide. Moreover, keeping graphene from restacking also plays a key role in improving the electrochemical performance of graphene-based materials in supercapacitors.

Therefore the overall scope of this doctoral work is to synthesize graphene-based nanocomposite, since the restacking and agglomeration of graphene can inhibit or decrease through incorporating of conducting polymer/metal oxide. Studies also include innovative approaches to fabricate graphene-based nanocomposite to involve a combined focus on new chemistry, controlled synthesis and device performance of novel nanocomposite materials with optimized properties and functionalities, which is essential to improve the performance of graphene-based nanocomposite as electrode for supercapacitors.

1.4 Research Objectives

- (1) To develope nanocomposite materials consisting of graphene and conducting polymer/metal oxide as supercapacitor electrode.
- (2) To measure the intrinsic electrical and capacitive properties of the nanocomposite by preparing graphene-based nanocomposite using the electrochemical deposition method.
- (3) To optimize the capacitive properties of graphene-based nanocomposite by varying the synthesis parameters.
- (4) To improve the electrochemical performance of the graphene-based nanocomposite with new approaches with controllable morphology and structure.

1.5 Outline of Thesis

Chapter II presented a comprehensive literature review on the background and working principles of supercapacitors. This chapter also discussed a thorough literature review on the current state-of-art electrode supercapacitors technologies, especially with the materials used and possible technologies utilized to synthesize a variety of composites.

Chapter III presented the chemicals, reagents, characterization techniques and experimental method used in this thesis.

Chapter IV presented the method of preparation of polypyrrole/graphene nanocomposite (PPy/GR)via electrodeposition techniques and its characterization. Instrumental analysis including X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Field-emission scanning electron microscopy (FESEM), Raman spectroscopy, Thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and four point probe conductivity measurement. A plausible mechanism for the formation of PPy/GR nanocomposite was postulated schematically.

Chapter V discussed the application of synthesized nanocomposite as electrode materials for use in supercapacitors via cyclic voltammetry (CV), galvanostatic charge/discharge and also electrochemical impedance spectroscopy (EIS).

Chapter VI discusses the preparation, characterization and electrochemical capacitive performance of polypyrrole/graphene/manganese oxide (PPy/GR/MnO_x) nanocomposite with an emphasis on the relationship between morphology and electrochemical performance.

Chapter VII presented the experimental setup of preparation and characterization of catalyst assisted polypyrrole/graphene (C-PPy/GR). The formation of nano-particles PPy with respect to the catalyst amount was investigated and the plausible mechanism for the formation of nano-particles PPy was postulated.

Chapter VIII summarizes the whole work and suggestion on further research work.

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