LAYER-BY-LAYER ASSEMBLED CONDUCTIVE FILMS BASED ON POLY(3,4-ETHYLENEDIOXYTHIOPHENE) AND POLYPYRROLE COMPOSITES FOR HYBRID SUPERCAPACITORS

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By

SHALINI KULANDAIVALU

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in fulfilment of the requirement for the Degree of Doctor of Philosophy

August 2019

DEDICATION

To my beloved parents, Mr. Kulandaivalu Kuppusamy & Mrs. Sashikala Chandrasakir who had given me dreams to look forward to…

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

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Chairman: Assoc. Prof. Yusran Sulaiman, PhD
Faculty: Science

Electrochemical supercapacitors are highly potential and environment-friendly storage system that widely used in electronic devices considered as a good solution to reduce the global environmental issues. A good electrochemical supercapacitor should possess remarkable specific energy, long shelf life, fast charge-discharge capacity and good specific power which can be improved by designing the electrode materials. In this study, the layer-by-layer (LBL) approach has been shown to be a viable option in the fabrication of electrode materials for supercapacitors. Two different preparation methods, electrodeposition (chronoamperometry) and vacuum filtration have been chosen to design the electrode materials. The focus was placed on multi-layered composition as electrode materials for a symmetrical supercapacitor device, where each layer was made of composites containing two or more materials. By carefully controlling the number of layers and the order of the layers, high-performance LBL assembled composite films have been obtained. X-ray diffractometry, Raman spectroscopy, Fourier transform infrared spectroscopy, field emission scanning electron microscopy, Brunauer–Emmett–Teller analysis and X-ray photoelectron spectroscopy have been used to characterize the as-formed layered composites. In this work, different composition of materials consisting of conducting polymers, i.e. poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyrrole (PPy), carbon-based materials, i.e. graphene oxide (GO), reduced graphene oxide (rGO), nanocrystalline cellulose (NCC) and multi-walled carbon nanotubes (MWCNTs) and nickel-cobalt layered double hydroxides (Ni-Co LDHs) were incorporated to form multilayered composites. The electrochemically deposited PEDOT/GO with PEDOT/NCC bilayer composite showed good performance with high specific capacitance (129.03 F g^{-1} at 25 mV s^{-1}), good capacity retention (85% of initial value after 2000 cycles), remarkably low charge transfer resistance (4.02 Ω) and good specific power and specific energy compared to its individual binary hybrid nanocomposites. After replacing the PEDOT with PPy to form composite film via vacuum filtration method, the as-formed bilayer composite film showed good improvement in the supercapacitive performances. This bilayer film had a surface area

of 42.88 m^2 g^{-1}, a mesoporosity system, and delivered a high specific capacitance of 562.9 F g^{-1} at 3 mV s^{-1} with a maximum specific energy of 19.3 Wh kg^{-1} and maximum specific power of 884.6 W kg^{-1}. Subsequently, by substituting the second layer with MWCNTs/rGO/NCC, the film with mesopores (0.558 cm^3 g^{-1}) and specific surface area of 106.02 m^2 g^{-1} exhibits a high specific capacitance of 882.2 F g^{-1} at 10 mV s^{-1}, remarkable cycling stability of ~90% over 10000 cycles and a high specific energy of 44.6 Wh kg^{-1} with a high specific power of 2889.9 W kg^{-1}. Another separate study has been carried out by layering Ni-Co LDHs hexagonal flakes on PPy/rGO to investigate the electrochemical performances of this electrode material. The as-obtained composite film endowed Ni^{2+} and combination of Co^{2+}/Co^{3+} valence states. Interestingly, outstanding specific capacitance of 1018 F g^{-1} at 10 mV s^{-1} and specific energy of 46.5 Wh kg^{-1} at 464.9 W kg^{-1} were obtained in a symmetrical device. The works carried out in this study have shown that the LBL approach is an inspiring and promising way to produce high-performance electrode materials for supercapacitors. Moreover, the presence of composite in each layer via this approach has increased the surface area of the material and synergy contribution of each material for the overall performances.

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

PENYEDIAAN LAPISAN-DEMI-LAPISAN FILEM KONDUKTIF BERASASKAN KOMPOSIT POLI(3,4-ETILDIOKSITIOFENA) DAN POLIPIROL UNTUK HIBRID SUPERKAPASITOR

Oleh

SHALINI KULANDAIVALU

Ogos 2019

Pengerusi: Profesor Madya Yusran Sulaiman, PhD
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Superkapasitor elektrokimia adalah sistem penyimpanan yang sangat berpotensi dan mesra alam yang digunakan secara meluas dalam peranti elektronik dianggap sebagai penyelesaian yang baik untuk mengurangkan isu-isu alam sekitar sejagat. Superkapasitor elektrokimia yang baik sepatutnya mempunyai tenaga spesifik yang luar biasa, jangka hayat yang panjang, kapasiti cas-discas yang cepat dan kuasa spesifik yang baik yang boleh diperbaiki dengan mereka-bentuk bahan elektrod. Dalam kajian ini, pendekatan lapisan-demi-lapisan (LBL) telah terbukti menjadi pilihan yang berdaya maju dalam fabrikasi bahan elektrod untuk superkapasitor. Dua kaedah penyediaan, elektropemendapan (kronoamperometri) dan penapisan vakum telah dipilih untuk merekabentuk bahan elektrod. Kajian ini tertumpu kepada komposisi pelbagai lapisan sebagai bahan elektrod untuk peranti superkapasitor simetri, di mana setiap lapisan diperbuat daripada komposit yang mengandungi dua atau lebih bahan. Dengan mengawal bilangan lapisan dan aturan lapisan, komposit pelbagai lapisan yang prestasi tinggi telah diperolehi. Pembelauan sinar-X, spektroskopi Raman, spektroskopi transformasi Fourier inframerah, mikroskopi elektron pengimbasan pancaran medan, analisis Brunauer-Emmett-Teller dan spektroskopi fotoelektron X-ray telah digunakan untuk mencirikan komposit lapisan yang terbentuk. Dalam kajian ini, komposisi bahan yang berbeza yang terdiri daripada konduktif polimer, iaitu poli(3,4-etildioksitiofena) (PEDOT) dan polipirol (PPy), bahan berasaskan karbon, iaitu grafen oksida (GO), grafen oksida terturun (rGO) nano selulosa berhablur (NCC) dan tiub nano karbon berbilang berdinding (MWCNTs) dan hidroksida berlapis nikel-kobalt (Ni-Co LDHs) telah digabungkan untuk membentuk komposit perbagai lapisan. Pemendapan secara elektrokimia bagi PEDOT/GO dengan PEDOT/NCC untuk manghasilkan komposit dwilapisan menunjukkan prestasi yang baik dengan kapasitan spesifik yang tinggi (129.03 F g^{-1} pada 25 mV s^{-1}), pengekalan kapasiti yang baik (85% daripada nilai permulaan selepas 2000 kitaran), rintangan pemindahan cas yang rendah (4.02 Ω) dan tenaga spesifik dan kuasa spesifik yang tinggi berbanding nanokomposit hibrid binari individunya. Selepas menggantikan PEDOT dengan PPy untuk membentuk komposit

filem melalui kaedah penapisan vakum, filem komposit dwilapisan yang terbentuk menunjukkan peningkatan prestasi superkapasitor yang baik. Filem dwilapisan ini mempunyai luas permukaan 42.88 m^2 g^{-1}, sistem keliangan meso, dan kapasitan spesifik yang tinggi 562.9 F g^{-1} pada 3 mV s^{-1} dengan tenaga spesifik maksimum 19.3 Wh kg^{-1} dan kuasa spesifik maksimum 884.6 W kg^{-1}. Selanjutnya, dengan menggantikan lapisan kedua dengan MWCNTs/rGO/NCC, filem dengan liang meso (0.558 cm^3 g^{-1}) dan luas permukaan spesifik 106.02 m^2 g^{-1} menunjukan kapasitan spesifik yang tinggi 882.2 F g^{-1} pada 10 mV s^{-1}, kestabilan kitaran luar biasa (~90% lebih daripada 10000 kitaran) dan tenaga spesifik yang tinggi 44.6 Wh kg^{-1} dengan kuasa spesifik yang tinggi 2889.9 W kg^{-1}. Satu lagi kajian berasingan berasaskan heksagonal Ni-Co LDH dilapiskan diatas PPy/rGO untuk mengkaji prestasi elektrokimia bahan elektrod ini. Filem komposit yang diperolehi mempunyai valensi Ni^{2+} dan gabungan valensi Co^{2+}/Co^{3+}. Menariknya, kapasitan spesifik 1018 F g^{-1} pada 10 mV s^{-1} dan tenaga spesifik 46.5 Wh kg^{-1} pada 464.9 W kg^{-1} diperolehi untuk komposit ini dalam peranti simetri. Kerja-kerja yang dijalankan dalam kajian ini menunjukkan bahawa pendekatan LBL adalah kaedah yang memberi inspirasi dan menjanjikan untuk menghasilkan bahan elektrod berprestasi tinggi untuk superkapasitor. Selain itu, kehadiran komposit di setiap lapisan melalui pendekatan ini telah meningkatkan luas permukaan spesifik dan turut menyumbangkan kesan sinergi daripada setiap bahan.

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Many thanks to all whose work, guidance and support helped me to complete this Ph.D. journey.

None of us got to where we are alone. Whether the assistance we received was obvious or subtle, acknowledging someone's help is a big part of understanding the importance of saying thank you.

-Harvey Mackay-

I certify that a Thesis Examination Committee has met on 26 August 2019 to conduct the final examination of Shalini Kulandaivalu on her thesis entitled "Layer-by-layer assembled conductive films based on poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyrrole (PPy) composites for hybrid supercapacitors" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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Supervisory Committee : Adila Mohamad Jaafar

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

Symbols	Meaning	Unit
Δt	Time	s
ΔV	Potential window	V
CPE	Constant phase element	F
C_{sp}	Specific capacitance	F g^{-1}
E	Specific energy	Wh kg^{-1}
ESR	Electrical series resistance	Ω
I	Current	A
m	Mass of electrode	g
P	Specific power	W kg^{-1}
R_{ct}	Charge transfer resistance	Ω
S	Enclosed area in the CV curve	AV
Z'	Real impedance	Ω
Z''	Imaginary impedance	Ω
W	Warburg impedance	Ω
ΔU	Potential window	V
υ	Scan rate	V s^{-1}
χ^2	Chi squared	-

LIST OF ABBREVIATIONS

0D	Zero dimensional
1D	One dimensional
2D	Two dimensional
3D	Three dimensional
A	Ampere
AC	Activated carbon
Ag/AgCl	Silver/silver chloride
b-Co_3O_4	Ball-like Co_3O_4 nanoparticles
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
b-PEI	Branched polyethyleneimine
CBD	Chemical bath deposition
$Co(OH)_2$	Cobalt hydroxides
Co_3O_4	Cobalt oxides
CPs	Conducting polymers
CTAB	Hexadecyltrimethylammonium bromide
CTAB	Cetyltrimethylammonium bromide
CV	Cyclic voltammetry
CVD	Chemical vapour deposition
DTAB	Dodecyltrimethylammonium bromide
EDLC	Electrochemical double layer capacitor
EDOT	3,4-ethylenedioxythiophene
EDX	Energy dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
ErGO	Electrochemically reduced graphene oxide
f-Co_3O_4	Flower-like Co_3O_4 nanoparticles
FeO_2	Iron oxides
FESEM	Field emission scanning electron microscope
FLG	Few-layered graphene
FTIR	Fourier transform infrared spectroscopy
GCD	Galvanostatic charge-discharge
GFN	Graphene-family nanomaterials
GO	Graphene oxide
H_2SO_4	Sulfuric acid
HS	Hollow spheres
ICPs	Intrinsically conducting polymers
ITO	Indium tin oxide
KCl	Potassium chloride
$KMnO_4$	Potassium permanganate
KOH	Potassium hydroxide
LBL	Layer-by-layer
LDHs	Layered double hydroxides
LVO/PEDOT/LMO	Layered vanadium oxide/poly(3,4ethylenedioxythiophene)/layered manganese oxide
$Mg(OH)_2$	Brucite
MnO_2	Manganese dioxide
MWCNTs	Multi-walled carbon nanotubes

n	Number of bilayer
NCC	Nanocrystalline cellulose
$Ni(OH)_2$	Nickel hydroxides
Ni-Co LDHs	Nickel-cobalt layered double hydroxides
PANI	Polyaniline
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEDOT/GO|PEDOT/NCC	Poly(3,4-ethylenedioxythiophene)/graphene oxide layered with Poly(3,4-ethylenedioxythiophene) /nanocrystalline cellulose
PET	Polyethylene terephthalate
PGMGN	Polypyrrole/graphene oxide layered with multiwalled carbon nanotubes/graphene oxide/nanocrystalline cellulose
PNMPy	Poly(N-methylpyrrole)
PPy	Polypyrrole
PPy/GO|PPy/NCC	Polypyrrole/graphene oxide layered with polypyrrole/nanocrystalline cellulose
PPy/rGO|Ni-Co LDHs	Polypyrrole/reduced graphene oxide layered with nickel-cobalt layered double hydroxides
PPy/rGO|PPy/NCC	Polypyrrole/reduced graphene oxide layered with polypyrrole/nanocrystalline cellulose
PS	Polystyrene
Py	Pyrrole
rGO	Reduced graphene oxide
r-PGMGN	Polypyrrole/reduced graphene oxide layered with multiwalled carbon nanotubes/reduced graphene oxide/nanocrystalline cellulose
RuO_2	Ruthenium oxides
SCs	Supercapacitors
SDS	Sodium dodecylsulfate
SILAR	Successive ionic layer adsorption and reaction
SS	Stainless steel
TMOs	Transition metal oxides
UV-vis	Ultraviolet-visible
V_2O_5	Vanadium oxide
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background

Abundant fossil fuels in the earth converted agricultural society to an industrial society, known as the industrial revolution. Since then, due to the growing needs for energy to support economic growth and sustainable society, the non-renewable fossil fuels are limited in supply. Based on the report provided in the British Petroleum (BP) Statistical Review of World Energy 2018 by the BP Company PLC, the growth of global primary energy consumption was estimated to increase in the rate of 2.2% as of 2017 and, the world set the highest fuel consumption record for natural gas (BP, 2018). Throughout industrialization, an alarming level of fossil fuel consumption is associated with environmental issues. The massive carbon dioxide emission from fossil fuels consumption has caused major climate change faced by today's world and also responsible for global warming and pollutions. This has triggered the quest for effective usage of renewable energy sources to replace fossil fuels. However, despite cost and efficiency, energy storage is the main hurdle in keeping up with renewable energies. Therefore, the electrochemical energy storage systems are usually integrated with renewable energy sources to store and to deliver the energies efficiently.

In that context, development of nanotechnology, exploration for nano-sized materials, devices and systems have shed light on producing energy conversion and storage systems. Notably, in recent years, many significant efforts have been devoted to developing next generation high performance energy storage devices, particularly electrochemical supercapacitors. In 1957, General Electric has introduced the first double layer capacitor and patented the work. However, the outbreak of the era of supercapacitors is from Standard Oil of Ohio (SOHIO) when they commercialized the double layer supercapacitors as an official energy storage device in 1966 (Pandolfo and Hollenkamp, 2006). Since then, it continues to tempt the attention of scientific communities as pointed by the number of articles published in supercapacitors (Figure 1.1a and b). To date, this device exemplified as state-of-the-art for its impressive performances and also regarded as a highly promising electrochemical energy storage system among the available energy storage devices. It has unearthed profound impacts on today's world.

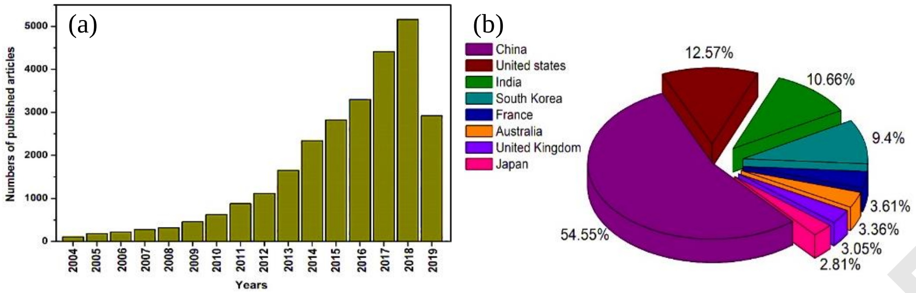

Figure 1.1: (a) Trends in the number of articles published on supercapacitor and (b) proportions of overall publications by countries from 2004 to 2019 using the keyword "supercapacitor". (Data is collected from Scopus on June 1, 2019)**.**

1.2 Problem statement

Regardless of the extraordinary properties of the supercapacitors and their potential applications in a wide variety of fields, the electrochemical performances of commercially available supercapacitors are still disappointing. Thus, new electrode materials with improved electrochemical properties i.e. high specific capacitance, high specific energy with high specific power and good cycling stability are highly desirable to meet the demand. Conducting polymers, carbon materials and layered double hydroxides are the materials that attracted immense interest for supercapacitor applications. Each material has its own unique properties that differentiate them from one to another. The conducting polymers (eg, poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyrrole (PPy)) are known for their high specific capacitance, while, the carbon-based materials (eg., graphene oxide (GO), reduced graphene oxide (rGO), multiwalled carbon nanotubes (MWCNTs) and nanocrystalline cellulose (NCC)) recognized for their remarkable cycling stability. Whereas, the layered double hydroxides (eg., nickel-cobalt layered double hydroxides (Ni-Co LDHs)) have multiple oxidation states which greatly can enhance the electrochemical activity. Nevertheless, the poor cycle lifetime of conducting polymers and layered double hydroxides and low specific capacitances of carbon-based materials are the clear drawbacks of these materials. Yet, the combination of these materials can help to fill in each other's advantages and disadvantages. Indeed, the major scope of this study is to combine the as-mentioned materials to produce composites for high-performance supercapacitors.

It is worth to note that the preparation methods used to synthesize these composites are mostly complicated and need the aid of surfactants or additives to combine the materials together. Simple and straightforward preparation method without surfactant or additives is another focus of the current study. Thus, in this study, a layer-by-layer (LBL) assembly approach has been utilized to prepare the composites for supercapacitors. This approach is an ideal technique to fabricate composites with fine control over architecture and composition. Most importantly, this approach is suitable for tailoring the internal structure of the composite to improve the properties as well as the electrochemical performances. In addition to this, as mentioned earlier, the use of surfactants or additives is avoided and also the fabrication process is conducted in aqueous solution concerning the environmental safety and economic issue. Indeed, LBL assembly is a wellestablished approach and has been applied widely in the fabrication of electrode materials for supercapacitor such as manganese oxide nanosheets (Zhang *et al.*, 2008), GO multilayered films (Liu *et al.*, 2015a) and multilayered films in alternative order of PEDOT and poly(N-methylpyrrole) (Aradilla *et al.*, 2010). All these studies consist of a single type of material in each layer. Even though these reported studies were able to give comparable electrochemical performances, search for a better supercapacitive performance for a real application is still needed. As an attempt towards it, in this dissertation, the LBL assembly approach was utilized to produce multilayers in which each layer is made up of a composite. The composite in each layer could be a combination of conducting polymer with carbon-based material or combination of different type of carbon materials or layered double hydroxides.

1.3 Research objectives

This study emphasis on the development of electrode materials for supercapacitors consisting of conducting polymers (PEDOT and PPy), carbon-based materials (GO, rGO, MWCNTs and NCC) and Ni-Co LDHs utilizing LBL assembly approach. The objectives of this study are:

1. To prepare LBL assembled conducting polymers/carbon materials-based composites via electrodeposition and vacuum assisted approach.
2. To layer nickel-cobalt layered double hydroxides on the PPy/rGO composite via vacuum-assisted approach.
3. To study the physicochemical properties of the prepared LBL assembled composites.
4. To evaluate the electrochemical performances (specific capacitance, specific energy, specific power and stability) of the formed LBL assembled composites in a symmetrical supercapacitor.

1.4 Thesis outline

- Chapter 1 describes an introduction on the progression of energy consumption in modern society and the requirement of the new generation energy storage devices. This chapter also includes the problem statement, objectives of the study and organization of chapters in the thesis.
- Chapter 2 provides a detailed explanation on electrochemical supercapacitor, information on LBL assembly including the techniques, specification of the electrode materials comprising conducting polymers, carbon materials and layered double hydroxides. The literature on LBL assembled conducting polymer-based composites and a combination of layered double hydroxides with carbon-based materials for supercapacitors are provided.
- Chapter 3 focusses the electrodeposition of PEDOT/NCC composite on PEDOT/GO composite, (PEDOT/GO|PEDOT/NCC) and its electrochemical performances.
- Chapter 4 describes the LBL assembled of PPy/NCC composite on PPy/rGO composite, (PPy/rGO|PPy/NCC) through vacuum-assisted approach. This chapter also discusses the effect on specific capacitance upon the increment of a number of layers

and compares the electrochemical performance of the prepared bilayer film before and after the reduction process.

- Chapter 5 deals with the symmetrical electrode material for supercapacitor composed of the LBL assembled of MWCNTs/rGO/NCC composite on PPy/rGO composite, (PPy/rGO|MWCNT/rGO/NCC) through the vacuum-assisted approach. The electrochemical performances of the assembled bilayer electrode are discussed in detail in this chapter.
- Chapter 6 comprises the study on electrochemical performances of symmetrical electrode material made from Ni-Co LDHs on PPy/rGO composite, (PPy/rGO|Ni-Co LDH) via vacuum filtration.
- Chapter 7 gives the overall summary of the findings and conclusions of the works. This chapter also highlighting the future scope based on the present work.

1.5 Scope and limitation

This dissertation was focused mainly on fabricating electrode materials for supercapacitor. The specification of a good supercapacitor is determined based on its electrochemical performance which relies on the type of materials used as electrodes. Understanding the nature of materials will aid in developing a high performance supercapacitor. The four important factors of a supercapacitor are specific power, specific energy, specific capacitance and cycling stability. These factors are used as indicators to evaluate the supercapacitor by measuring against either current density or scan rate through a potential window. However, extensive current density, scan rate, potential window and number of cycles (in the study of stability) degrade the electrode material. Mainly, the values are varied based on the type of materials used as electrode materials.

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