DEVELOPMENT OF MAGNESIUM COBALT OXIDE AND ITS COMPOSITE WITH REDUCED GRAPHENE OXIDE FOR ASYMMETRIC SUPERCAPACITOR APPLICATIONS

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I hereby declare that the work in this thesis is based on my original work except for quotations and citation which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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DEVELOPMENT OF MAGNESIUM COBALT OXIDE AND ITS COMPOSITE WITH REDUCED GRAPHENE OXIDE FOR ASYMMETRIC SUPERCAPACITOR APPLICATIONS

SYAM G. KRISHNAN

Thesis submitted in fulfilment of the requirements for the award of the degree
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DEDICATION

I dedicate this thesis to my parents, wife and my friends who constantly encouraged and supported me in this long research journey.

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LIST OF UNITS AND SYMBOLS

λ	wavelength
μ	micron (10^{-6})
τ	charge relaxation time
ν	scan rate
θ	angle
Å	angstrom (10^{-10})
A g^{-1}	ampere per gram
C'	real capacitance
C''	imaginary capacitance
C_d	double layer capacitance
C_S	specific capacitance
d	distance
D	diffusion coefficient
E	potential
f_0	charge relaxation frequency
F g^{-1}	farad per gram
g	grams
h	hours
j	current density
m^2 g^{-1}	meter square per gram
M	molar (mol/litre)
mL	milliliter
mV s^{-1}	millivolt per second
ms	millisecond
nm	nanometer
p/p_o	relative pressure
ppm	parts per million
q_i	inner charge
q_0	outer charge
q_T	total charge
R_{CT}	charge transfer resistance

R_D	diffusion resistance
R_S	series resistance
S cm^{-1}	Siemen per centimeter
t	time
t_c	charging time
t_d	discharging time
V	voltage
W	Warburg impedance
wt %	weight percentage
W kg^{-1}	watt per kilogram
Wh kg^{-1}	watt hour per kilogram
Z'	real impedance
Z''	imaginary impedance
Z_{CPE}	constant phase element impedance

LIST OF ABBREVIATIONS

AC	activated carbon
ASC	asymmetric supercapacitor
CD	charge discharge
CP	conducting polymer
CV	cyclic voltammetry
EC	electrolytic capacitor
EIS	electrochemical impedance spectroscopy
FESEM	field emission scanning electron microscope
HC	hybrid supercapacitor
HT	hydrothermal method
HTAB	hexadecyl trimethyl ammonium bromide
IHP	inner Helmholtz plane
MSM	molten salt method
NR	Not reported
OHP	outer Helmholtz plane
LIB	lithium ion batteries
PANI	polyaniline
PC	pseudocapacitance
SC	supercapacitor
SSC	symmetric supercapacitor
TGA	thermogravimetric analysis
TMC	ternary metal cobaltite
XRD	X-ray diffraction

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ABSTRAK

Tesis ini menyasarkan penilaian kesesuaian magnesium kobalt oksida ($MgCo_2O_4$) sebagai elektrod pseudokapasitor dalam superkapasitor simetri (ASC) yang mempunyai kepadatan tenaga (E_D) dan ketumpatan kuasa (P_D) yang lebih baik. $MgCo_2O_4$ tergolong dalam logam kobaltit ternari yang mempunyai sifat-sifat elektrokimia bersesuaian untuk peranti penyimpanan tenaga seperti bateri dan superkapasitor. Dalam mekanisma pseudokapasitor, cas disimpan di permukaan elektrod oleh tindak balas pantas faradic dan memberikan E_D dan P_D yang tinggi berbanding superkapasitor konvensional di mana penyimpanan cas adalah terhad oleh pengumpulan pada permukaan elektrod elektrolit. Dalam kajian ini, tiga morfologi tipikal $MgCo_2O_4$ disintesis menggunakan kaedah leburan garam (MSM) dan hidroterma (HT). Proses-proses sintetik menawarkan pengawalan hasil sifat-sifat dan skala pengeluaran bahan. Logam kobaltit ternari yang berprestasi tinggi, iaitu kobalt oksida mangan digunakan sebagai bahan kawalan kerana kapasiti teori yang lebih tinggi (~3620 $F \cdot g^{-1}$) berbanding dengan $MgCo_2O_4$ (~ 3120 $F \cdot g^{-1}$). Selain daripada sebatian tulen, sintesis analog grafin juga dilakukan. Pencirian bahan-bahan dijalankan dengan menggunakan analisis gravimetri haba (TGA), pembelauan sinar-X (XRD), spektroskopi fotoelektron sinar-X (XPS), mikroskop imbasan elektron pancaran medan (FESEM), dan teknik penjerapan gas permukaan. Sifat elektrokimia $MgCo_2O_4$ dan $MnCo_2O_4$ dinilai menggunakan voltammetri berkitar (CV), galvanostatic cas-discas (CD) dan spektroskopi elektrokimia impedan (EIS) dalam sistem tiga elektrod menggunakan 3 M LiOH sebagai elektrolit. Analisis terperinci terhadap prestasi pseudokapasitif pelbagai elektrod termasuk grafin yang telah diubahsuai pada kapasitan spesifik (C_S) telah dijalankan. Pencirian ini menunjukkan prestasi elektrod $MgCo_2O_4$ lebih baik berbanding elektrod $MnCo_2O_4$. Di samping itu, prestasi $MgCo_2O_4$ dan $MnCo_2O_4$ terubahsuai grafin menunjukkan C_S yang lebih tinggi iaitu ~570 dan ~440 $F \cdot g^{-1}$, dengan pengekalan kapasiti 104 dan 102% masing-masing pada akhir 3000 kitaran. ASC dibina menggunakan grapfin yang telah diubahsuai $MgCo_2O_4$ (HS-G-$MgCo_2O_4$) dan $MnCo_2O_4$ (HS-G-$MnCo_2O_4$) sebagai anod dan karbon teraktif (AC) sebagai katod. Kaedah cuba jaya digunakan untuk menentukan nisbah jisim yang sesuai daripada bahan-bahan dalam elektrod masing-masing untuk mencapai E_D dan P_D terbaik. E_D dan P_D terbaik diperolehi dengan 1:1 nisbah jisim pada anod dan katod. HS-G-$MgCo_2O_4$ / AC memberikan E_D maksimum 31.05 $Wh \cdot kg^{-1}$ di P_D 1.8 $kW \cdot kg^{-1}$, yang merupakan salah satu prestasi ASC yang terbaik dilaporkan berasaskan logam kobaltit ternari. Oleh itu, kajian ini telah berjaya mengenal pasti bahan elektrod pseudokapasitor yang baik untuk kegunaan komersial.

ABSTRACT

This thesis aims to evaluate the suitability of magnesium cobalt oxide ($MgCo_2O_4$) as a pseudocapacitor electrode in asymmetric supercapacitors (ASCs) with improved energy density (E_D) and power density (P_D). $MgCo_2O_4$ belongs to ternary metal cobaltites having desirable electrochemical properties for energy storage devices such as batteries and supercapacitors. In pseudocapacitors, charges are stored at the surface of an electrode by fast faradic reaction and offer improved E_D and P_D compared to conventional supercapacitors in which charge storage is limited by accumulation at the electrode–electrolyte interface. In this research, three typical morphologies of $MgCo_2O_4$ are synthesized using molten salt method (MSM) and hydrothermal method (HT). These synthetic processes offer controllability of properties of the materials thereby produced and scalability of materials production. A high performing ternary metal cobaltite, viz. manganese cobalt oxide ($MnCo_2O_4$) is used as a control material owing to its higher theoretical capacitance (~3620 $F \cdot g^{-1}$) compared to that of $MgCo_2O_4$ (~3120 $F \cdot g^{-1}$) in all the above synthesis. In addition to the pure compounds, their graphene modified analogues are also synthesized. The materials are characterized using thermogravimetric analysis (TGA), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), and gas surface adsorption techniques. Electrochemical properties of $MgCo_2O_4$ and $MnCo_2O_4$ are evaluated using cyclic voltammetry (CV), galvanostatic charge-discharge (CD) and electrochemical impedance spectroscopy (EIS) in a three-electrode system using 3 M LiOH as electrolyte. A detailed investigation of the pseudocapacitive performance of the various electrode including the graphene modified ones on the specific capacitance (C_S) has been undertaken in three-electrode configuration. These characterizations revealed the superiority of $MgCo_2O_4$ over $MnCo_2O_4$ electrodes. Furthermore, performance of graphene modified $MgCo_2O_4$ and $MnCo_2O_4$ showed superior capacitance of ~570 and ~440 $F \cdot g^{-1}$, with capacitance retention of 104 and 102%, respectively at the end of 3000 cycles. ASCs are fabricated using graphene modified $MgCo_2O_4$ (HS-G-$MgCo_2O_4$) and $MnCo_2O_4$ (HS-G-$MnCo_2O_4$) as anodes and activated carbon (AC) as cathode. A trial and error method is adopted to determine suitable mass loading of the materials in respective electrodes for high E_D and P_D. Highest E_D and P_D are obtained for 1:1 wt.% mass loading in anode and cathode. The HS-G-$MgCo_2O_4$/AC delivered a maximum E_D of ~31.05 $Wh \cdot kg^{-1}$ at P_D of 1.8 $kW \cdot kg^{-1}$, which is one of the best performances reported for ternary metal cobaltite based ASCs. This research, therefore, identifies a promising pseudocapacitor electrode material for commercial deployment.

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