DEVELOPMENT OF SUPERCAPACITORS WITH IN-SITU POLYMERIZED POLYANILINE ON MnO_2 AND Co_3O_4 ANODES AND ACTIVATED CARBON CATHODES

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Thesis submitted in fulfillment of the requirements for the
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LIST OF SYMBOLS/UNITS

~	approximately
%	percent
λ	wavelength
μ	micron (10^{-6})
η	coulombic efficiency
τ	dielectric relaxation time constant
2θ	Bragg angle
^{o}C	degree celcius
Å	angstrom (10^{-10})
A g^{-1}	ampere per gram
a.u.	arbitrary unit
C g^{-1}	charge per gram
C’	real capacitance
C’’	imaginary capacitance
Cu Kα	X-ray diffraction from copper K energy levels
cm^{-1}	per centimeter
C_S	specific capacitance
d	distance
D	diffusion coefficient
D_{K+}	potassium ion diffusion
e.g.	*exempli gratia* (example)
et al.	*et alii* (and others)
E	potential
E_D	energy density
F g^{-1}	farad per gram
g	grams
h	hour
i.e.	*id est* (that is)
i_p	peak current
j	current density
L	thickness of electrode film

$m^2 g^{-1}$	meter square per gram
M	molar (mol/L)
min	minute
mol	mol
mL	milliliter
mV s^{-1}	millivolt per second
n.a.	not available
NR	not reported
nm	nanometer (10^{-9})
P/P_o	relative pressure; obtained by forming the ratio of the equilibrium pressure and vapour pressure Po of the adsorbate at the temperature where the isotherm is measured
P_D	power density
ppm	part per million
q_i	inner charge
q_o	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	scan rate
V	voltage
viz.	*videlicet* (namely)
wt %	weight percentage
W kg^{-1}	watt per kilogram
Wh kg^{-1}	watt hour per kilogram
Z’	real impedance
Z’’	imaginary impedance

LIST OF ABBREVIATIONS

AC	activated carbon
AC-C	chemically modified activated carbon
AC-P	physically modified activated carbon
ASC	asymmetric supercapacitor
CDC	charge discharge
CoH	hydrothermal synthesized cobalt oxide
CoM	molten salt synthesized cobalt oxide
CP	conducting polymer
CV	cyclic voltammetry
EIS	electrochemical impedance spectrospcopy
EDLC	electrochemical double layer capacitance
FESEM	field emission scanning electron microscope
FTIR	Fourier transform infrared
IHP	inner Helmholtz plane
MnH	hydrothermal synthesized manganese oxide
MnM	molten salt synthesized manganese oxide
MSS	molten salt synthesis
OHP	outer Helmholtz plane
LIB	lithium ion batteries
PKS	palm kernel shell
PANI	polyaniline
PANI-CoH	polyaniline composite with hydrothermal synthesized cobalt oxide
PANI-CoM	polyaniline composite with molten salt synthesized cobalt oxide
PANI-MnH	polyaniline composite with hydrothermal synthesized manganese oxide
PANI-CoM	polyaniline composite with molten salt synthesized managenese oxide
PC	pseudocapacitance

SC	supercapacitor
SSC	symmetric supercapacitor
TEM	transmission electron microscope
TGA	thermogravimetric analysis
XRD	X-ray diffraction

DEVELOPMENT OF SUPERCAPACITORS WITH IN-SITU POLYMERIZED POLYANILINE ON MnO_2 AND Co_3O_4 ANODES AND ACTIVATED CARBON CATHODES

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ABSTRACT

Supercapacitors (SCs) store electrochemical energy at an electrode – electrolyte interface with high power density (P_D), fast recharge capability and long cycle life. The SCs are two types according to the charge storage mechanisms: electric double layer capacitors (EDLCs) and pseudocapacitors (PCs). Allotropes and polymorphs of carbon are choice to build EDLCs electrodes whereas PCs are built from nanostructured metal oxides, hydroxides, chalcogenides and conducting polymers. Broad objective of this doctoral research is to develop a SC device with PC as anode and EDLC as cathode – this type of devices are called asymmetric supercapacitors (ASCs). Popular PC electrodes such as MnO_2 and Co_3O_4 have poor electrical conductivity – making their composite with conducting polymers such as polyaniline (PANI) is proposed to be a superior PC electrode. In this research, MnO_2 and Co_3O_4 were synthesized by hydrothermal reaction and molten salt methods and their polymeric composite were developed by in situ polymerization. The materials were characterized by thermal analyses, X-ray and electron diffraction, FTIR spectroscopy, gas adsorption studies, scanning and transmission electron microscopy, and cyclic voltammetry. The electrochemical properties of the electrodes were evaluated systematically using cyclic voltammetry, galvanostatic charge–discharge cycling, and electrochemical impedance spectroscopy. The relationship between the pores in the electrodes and the size of the solvated ions in the electrolyte on the final capacitance in various aqueous electrolytes were investigated – the pores smaller than the size of the solvated ions do not contribute to the capacitance of the electrode. Aqueous KOH shown the best diffusion coefficient (6.8×10^{-10} cm^2 s^{-1}) and capacitive properties in this study; therefore, it was chosen as the electrolyte of choice. The PANI provided faster ion channeling to the surface of metal oxides and showed improved charge storage capacity than their bare analogues. Highest specific capacitance (C_S) obtained in this study was in a PANI composite of Co_3O_4 synthesized by the molten salt method (C_S ~985 F g^{-1} at 2 mV s^{-1}), recording an increase of ~253% compared to its bare analogue. Three choice of EDLC electrodes were considered in this study, viz. (i) activated carbon from palm kernel shells (PKS) as it form a local abundant natural resource, (ii) commercial activated carbon (AC), and (iii) ordered mesoporous carbon (OMC). The PKS were pyrolyzed and activated using physical and chemical activation methods whereas the other two were obtained from commercial sources. Structural, thermal, morphological, surface, and electrochemical properties of the carbon electrodes were also systematically studied as done for the PC electrodes. The PKS activated carbon showed high areal capacitance (~45 μF cm^{-2}), which is one of the highest reported so far in literature, besides showing high cycle stability (95–97%). The ASCs were fabricated using the PC electrodes as anodes and carbons as cathodes. For MnO_2 series, PANI-MnO_2 (hydrothermal)//OMC recorded the highest energy density (E_D) ~27 Wh kg^{-1} at P_D ~400 W kg^{-1} whereas for Co_3O_4 series, PANI-Co_3O_4 (hydrothermal)//OMC gives E_D of ~23 Wh kg^{-1} at similar P_D. Despite its nominally smaller E_D, the Co_3O_4 based device showed superior cycling stability than the other.

ABSTRAK

Superkapasitor (SCs) menyimpan tenaga elektrokimia pada antara muka elektrod – elektrolit dan mempunyai ketumpatan kuasa (P_D) yang tinggi, pantas untuk pengecasan semula dan jangka hayat yang panjang. Menurut mekanisma simpanan cas, SC terdiri dari dua jenis: superkapasitor elektrik dua lapisan (EDLCs) dan pseudokapasitor (PCs). Alotrop dan polimorf karbon adalah pilihan untuk membangunkan elektrod EDLCs sementara PCs dibangunkan dari logam oksida berstruktur nano, hidroksida, chalcogenida dan polimer berkonduksi. Objektif luas kajian kedoktoran ini ialah membangunkan peranti SC dengan PC sebagai anod dan EDLC sebagai katod – peranti jenis ini dikenali sebagai superkapasitor asimetrik (ASCs). Elektrod PC yang popular seperti MnO_2 dan Co_3O_4 mempunyai konduksi elektrik yang lemah – di mana komposit dengan polimer berkonduksi seperti polianilin (PANI) dicadangakan untuk penghasilan elektrod PC yang lebih baik. Dalam kajian ini, MnO_2 dan Co_3O_4 disintesis dengan tindakbalas hidroterma dan kaedah garam lebur dan komposit polimer pula dibangunkan menggunakan kaedah pempolimeran in-situ. Bahan-bahan yang telah disintesis dicirikan menggunakan analisis terma, pembelauan electron dan sinar-X, spektroskopi FTIR, kajian penjerapan gas, mikroskopi imbasan dan transmisi elektron, dan voltametri berkitar. Sifat elektrokimia elektrod dinilai secara sistematik menggunakan voltammetry berkitar, kitaran cas–discas galvanostatik, dan spektroskopi impedans elektrokimia. Hubungkait antara liang elektrod dan saiz ion tersolvat dalam elekrolit terhadap kapasitan akhir dalam pelbagai elektrolit telah dikaji – liang bersaiz lebih kecil dari saiz ion tersolvat tidak menyumbang kepada kapasitan elektrod. KOH akuas menunjukkan koeffisi difusi (6.8×10^{-10} cm^2 s^{-1}) dan sifat kapasitan terbaik dalam kajian ini; oleh itu, ia dipilih sebagi elektrolit. PANI menghasilkan penyaliran ion yang cepat kepada permukaan logam oksida dan menunjukkan peningkatan kapasiti storan cas berbanding analog asal. Kapasitan spesifik (C_S) tertinggi yang direkodkan dalam kajian ini ialah komposit PANI dengan Co_3O_4 yang disintesis mengan kaedah logam lebur (C_S ~985 F g^{-1} at 2 mV s^{-1}), peningkatan ~253% berbanding analog asal. Tiga jenis elektrod EDLC diperincikan dalam kajian ini, iaitu (i) karbon taraktif dari tempurung kelapa sawit (PKS) memndangkan ia merupakan sumber semulajadi yang banyak didapati, (ii) karbon teraktif (AC) komersil dan (iii) karbon berliang meso tersusun (OMC). PKS dipirolisis dan diaktifkan menggunakan kaedah pengaktifan kimia dan fizik sementara dua lagi karbon diperolehi dari sumber komersil. Sifat struktur, terma, morfologi, permukaan dan elektrokimia elektrod karbon dikaji secara sistematik seperti yang dilakukan kepada elektrod PC. Karbon teraktif PKS menunjukkan kapasitan area yang tinggi (45 μF cm^{-2}), merupakan salah satu nilai tertinggi berbanding literatur, selain menunjukkan stabiliti kitaran yang tinggi (95 – 97%). Peranti ASCs yang difabrikasi menggunakan elektrod PC sebagai anod dan karbon sebagai katod. Untuk siri MnO_2, PANI-MnO_2(hidroterma)//OMC mencatatkan ketumpatan tenaga (E_D) tertinggi ~27 Wh kg^{-1} pada P_D ~400 W kg^{-1} sementara untuk siri Co_3O_4, PANI-Co_3O_4(hidroterma)//OMC memberikan E_D ~23 Wh kg^{-1} pada P_D yang sama. Walaupun mempunyai E_D yang kecil, peranti berasaskan Co_3O_4 menunjukkan stabiliti kitaran yang lebih baik berbanding elektrod lain.