SYNTHESIS AND CHARACTERIZATION OF LAYERED ALKALINE MANGANATES, TITANATES, AND MOLYBDATES FOR SUPERCAPACITOR APPLICATIONS

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n	Number of electron involved
F	Faraday's constant
ΔE	Redox potential of the material
MW	Molecular weight
C	Capacitance
V	Voltage window
η	Coulombic efficiency
ε_0	Space permittivity
ε_r	Relative permittivity
A	Surface area
d	Distance between the plate
Q	Charge stored
R	Resistance
C_{dl}	Double layer capacitance
C_H	Helmholtz double layer capacitance
C_{diff}	Diffuse double layer capacitance
θ	Theta
hv	X-ray photon energy
Ek	Kinetic energy of photo electron
Eb	Binding energy of photo electron
f	Work function induced by the analyzer
i_{pc}	Cathodic peak current
i_{pa}	Anodic peak current
i_p	Peak current

T	Temperature
R	Gas constant
D_{ions}	Diffusion coefficient of the electroactive species
C	Bulk concentration of the electroactive species
v	Scan rate of the voltammograms
I	Discharge current density in Ampere
Δt	Discharge time in second
m	Mass of active material in gram
ΔV	Potential range
C'	Real capacitance
C''	Imaginary capacitance
$Z'(\omega)$	Real part of complex impedance
$Z''(\omega)$	Imaginary part of complex impedance
ω	Angular frequency
f	Frequency
f_0	Maxima frequency of the peak
τ	Relaxation time constant
q_+	Charge stored at the anode
q_-	Charge stored at the cathode
m_+	Mass of anode material
m_-	Mass of cathode material
V_+	Voltage range of anode material
V_-	Voltage range of cathode material
V_a	Anodic redox peak
V_c	Cathodic redox peak

ΔV_{ac} Voltage difference between V_a and V_c

t_c Charging time

t_d Discharging time

R_{ct} Charge transfer resistance

R_{Ω} Bulk solution resistance

σ Warburg's coefficient

LIST OF ABBREVIATIONS

AAO	Anodic aluminum oxide
AC	Activated carbon
ASC	Asymmetric supercapacitor
BE	Binding energy
BET	Brunauer-Emmett-Teller
CE	Counter electrode
CNF	Carbon nanofiber
CNT	Carbon nanotube
CPs	Conducting polymers
C_S	Specific capacitance
CV	Cyclic voltammetry
CVD	Chemical vapor deposition
EC	Equivalent circuit model
ECs	Electrochemical capacitors
EDL	Electrochemical double layer
EDLCs	Electrochemical double layer capacitors
EIS	Electrochemical impedance spectroscopy
E_S	Energy density
ESR	Equivalent series resistance
FESEM	Field emission scanning electron microscope
GCD	Galvanostatic charge-discharge
GO	Graphite oxide
H	Helmholtz
HCs	Hybrid capacitors

HPC	Hydro porous carbon
HRTEM	High resolution transmission electron microscope
IHP	Inner Helmholtz plane
ILs	Ionic liquids
KE	Kinetic energy
LDHs	Layer double hydroxides
MWCNT	Multiwalled carbon nanotube
NT	Nanotube
NTA	Nanotube array
NB	Nanobelt
NP	Nanoparticle
NF	Nanofiber
NR	Nanorod
NMP	N-methyl-2-pyrrolidinone
OHP	Outer Helmholtz plane
PCs	Pseudocapacitors
PCNF	Porous carbon nanofiber
PECVD	Plasma enhanced chemical vapor deposition
PEDOT	Poly(3,4-ethylenedioxythiophene)
PFPT	poly(3-(4flurophenyl) thiophene)
PDTT	Poly(ditheno (3,4-b:3',4'd) thiophene)
PMT	Poly(3-methyl thiophene)
PVDF	Polyvinylidenefluoride
RE	Reference electrode
RGO	Reduced graphene oxide

SAED	Selected area electron diffraction
SCE	Saturated calomel electrode
SILAR	Successive ionic layer adsorption and reaction
ST	Sodium titanate
SFT	Sodium free titanate
TNT	Titania nanotube
TTIP	Titanium tetra isopropoxide
USA	United State of America
WE	Working electrode
XPS	X-ray photoelectron spectroscopy
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional

LIST OF CHEMICAL COMPOUNDS

RuO_2	Ruthenium oxide
TiO_2	Titanium dioxide
MnO_2	Manganese oxide
CuO	Copper (II) oxide
Co_3O_4	Cobalt oxide
$Ni(OH)_2$	Nickel hydroxide
$Co(OH)$	Cobalt hydroxide
MoS_2	Molybdenum disulfide
CoS_2	Cobalt disulfide
Mo_9Se_{11}	Molybdenum selenide
WSe_2	Tungsten diselenide
CO_2	Carbon dioxide
NH_3	Ammonia
O	Oxygen
N	Nitrogen
B	Boron
S	Sulfur
H	Hydrogen
Pt	Platinum
Ta	Tantalum
Al	Aluminum
Ag	Silver
$TEABF_4$	Tetraethyl ammonium tetrafluoroborate

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ABSTRACT

Development of pseudocapacitors, in which electrical charge is stored through a redox reaction when it is brought in contact with an electrolyte, is an active area of research to achieve high energy density (E_S) and power density (P_S) in supercapacitors. Many promising materials such as RuO_2, δ-MnO_2, Co_3O_4 are proposed as desirable pseudocapacitor electrodes; however, they are either poorly abundant and toxic or resistive and difficult to be synthesized. On the other hand, there are several highly abundant transition metal oxides exhibiting poor and/or non-capacitive behavior such as titanium dioxide (TiO_2) and some polymorphs of manganese oxide (α-MnO_2). It is hypothesized that making a layered structure of the above metal oxides could enhance their electrochemical performance because the lamellar space between the layers could easily intercalate/de-intercalate of ions. Consequently, this thesis aims to synthesize layered analogues of TiO_2, α-MnO_2 by incorporating hydrated alkaline ions and study their electrochemical properties. Effect of incorporating hydrated alkaline ions in an intrinsically layered material, i.e., Mo_9Se_{11}, on its electrochemical properties has also been undertaken to make a contrast. The physicochemical characterization was analyzed using X-ray diffraction (XRD), selected area electron diffraction (SAED), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscope (FESEM), transmission electron microscope (HRTEM) and Brunauer-Emmett-Teller (BET) surface analyzer. The electrochemical properties of the samples were studied by cyclic voltammetry (CV), galvanostatic charge-discharge cycling (GCD) and electrochemical impedance spectroscopy (EIS) in a three-electrode system configuration. A comprehensive investigation on the structure and properties of the materials before and after incorporation has been undertaken and the results are discussed deeply. It showed that alkaline layered structure of manganate and titanate material exhibits ~2.5 and ~16 times higher specific capacitance (C_S) than that of the non-layered ones in optimized electrolytes. However, alkaline layered molybdate material shows 6 times lower C_S value than non-alkaline layered structure. The capacitive performance was correlated with the characteristic resistance and time of the electrodes employing EIS. The energy storage capability of the layered structure materials is evaluated by assembling asymmetric supercapacitors (ASC) using the layered materials as anode and commercial activated carbon as cathode. The electrochemical performance of ASCs were compared with the symmetric device fabricated using the commercial activated carbon (AC). The best performing ASCs delivered E_S of ~63, ~17, and ~42 Wh/kg at P_S of ~962, ~600, and ~960 W/kg for Na-MnO_2//AC, $Na_2Ti_2O_4(OH)_2$//AC, and Mo_9Se_{11}//AC cells in the optimized electrolytes of 1M LiOH, 1M KOH and 3M LiOH, respectively, which are an order of magnitude higher than that achieved by the AC//AC device. Among them, Na-MnO_2//AC showed ~98% retention of charge storage, which is much superior to the other devices; therefore, this device is promising to further develop for commercial applications.

ABSTRAK

Pembangunan pseudokapasitor, di mana cas elektrik disimpan melalui tindak balas redoks apabila ia dihubungkan dengan elektrolit, adalah penyelidikan yang aktif untuk mencapai kepadatan tenaga yang tinggi (E_S) dan kepadatan kuasa (P_S) dalam superkapasitor. Banyak bahan berpotensi seperti RuO_2, δ-MnO_2, Co_3O_4 dicadangkan sebagai elektrod pseudokapasitor; Walau bagaimanapun, bahan tersebut sukar didapati dan bertoksik atau berintangan dan ia adalah sukar untuk disintesis. Sebaliknya, terdapat banyak oksida logam peralihan yang menunjukkan perilaku bukan kapasitif dan / atau kapasitif yang lemah seperti titanium dioksida (TiO_2) dan beberapa polimorf oksida mangan (α-MnO_2). Berdasarkan hipotesis, pembinaan struktur berlapis daripada oksida logam di atas boleh meningkatkan prestasi elektrokimia mereka kerana ruang lamela antara lapisan dengan mudah dapat menampung ion dengan proses interkalasi caj / de-interkalasi yang sangat mudah. Oleh yang demikian, tesis kajian ini bertujuan untuk mensintesis analog lapis TiO_2, α-MnO_2 dengan menggabungkan ion alkali terhidrat dan mengkaji sifat elektrokimia bahan. Kesan penggabungan ion alkali terhidrat ke dalam bahan asasnya berlapis, iaitu, Mo_9Se_{11}, ke atas sifat elektrokimia telah juga dikaji untuk dijadikan satu perbandingan. Pencirian secara fizikal dan kimia bahan dianalisis menggunakan pembelauan sinar-X (XRD) dan pembelauan elektron kawasan terpilih (SAED), X-ray fotoelektron spektroskopi (XPS), mikroskop elektron imbasan (SEM), mikroskop transmisi elektron (TEM) dan Brunauer-Emmett-Teller (BET) analisis permukaan. Sifat-sifat elektrokimia sampel telah dikaji menggunakan voltametri berkitar (CV), galvanostatik cas-nyahcas (GCD) dan spektroskopi elektrokimia impedans (EIS) dalam konfigurasi sistem tiga elektrod. Penyelidikan ke atas struktur dan sifat bahan sebelum dan selepas penggabungan telah dilaksanakan dan keputusan dibincangkan secara mendalam. Ia menunjukkan bahawa bahan berstruktur berlapis alkali manganat dan titanat mempamerkan nilai C_S yang 2.5 dan 16 kali lebih tinggi berbanding dengan bahan berstruktur tidak berlapis dalam elektrolit yang optimum. Akan tetapi, bahan berstruktur berlapis alkali molibdat menunjukkan nilai C_S yang 6 kali lebih rendah berbanding bahan berstruktur berlapis molibdat. Prestasi kapasitif telah dikaitkan dengan rintangan ciri dan masa elektrod menggunakan EIS. Keupayaan penyimpanan tenaga daripada bahan-bahan struktur berlapis dinilai dengan memasang supercapacitors simetri (ASC) menggunakan bahan berlapis sebagai anod dan karbon komersial diaktifkan sebagai katod. Prestasi elektrokimia ASC dibandingkan dengan peranti simetri direka menggunakan karbon komersial diaktifkan (AC). Prestasi terbaik ASC melaksanakan dihantar E_S ~ 63, ~ 17, dan ~ 42 Wh/kg pada P_S ~ 962, ~ 600, dan ~ 960 W/kg untuk Na-MnO_2//AC, $Na_2Ti_2O_4(OH)_2$//AC sel-sel, dan Mo_9Se_{11}//AC dalam elektrolit dioptimumkan iaitu 1M LiOH, 1M KOH and 3M LiOH, masing-masing, yang mempunyai magnitud lebih tinggi daripada yang dicapai oleh peranti AC//AC. Na-MnO_2//AC menunjukkan pengekalan ~ 98% penyimpanan caj, lebih baik daripada peranti yang satu lagi; oleh itu, peranti ini sesuai untuk aplikasi komersial.