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Nano/composite materials for lithium-ion batteries and supercapacitors

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**NANO/COMPOSITE MATERIALS FOR
LITHIUM-ION BATTERIES AND
SUPERCAPACITORS**

**A thesis submitted in fulfillment of the requirements for the
award of the degree of**

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

SHULEI CHOU, B. Sc., M. Sc.

**INSTITUTE FOR SUPERCONDUCTING &
ELECTRONIC MATERIALS, FACULTY OF
ENGINEERING**

May 2010

CERTIFICATION

I, Shulei Chou, declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting & Electronic Materials, Faculty of Engineering, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Shulei Chou

29/May/2010

DEDICATION

For my parents, brother, and Bo.

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ABSTRACT

Lithium-ion batteries and supercapacitors are both important energy storage systems and can make energy storage and usage more efficiently than with previous solutions. Both systems would be excellent choices for Electrical Vehicles (EVs) or Hybrid Electrical Vehicles (HEVs), and also other portable devices requiring both high power and high energy density. The key aspect for improving the performance of both kinds of energy devices is to improve the performance of the active materials. The use of nanostructured materials and conductive composite materials is designed to enhance both ion transport and electron transport by shortening the diffusion lengths of ions (such as, Li^+ , Na^+ , K^+ , H^+ , and OH^-) and increasing the conductivity within the electrode materials, respectively. In this doctoral work, several nanostructured materials and conductive (carbon or conducting polymer) composites were examined and characterized for possible application as electrode materials for lithium-ion batteries or supercapacitors. For the Li-ion battery, tin dioxide (SnO_2) nanotubes, carbon-coated SnO_2 composite, hematite ($\alpha\text{-Fe}_2\text{O}_3$) carbon composite, lithium iron phosphate (LiFePO_4) polypyrrole composite, and vanadium pentoxide (V_2O_5) nanomaterials were investigated. Meanwhile, several flexible electrode materials for supercapacitors were also studied: manganese dioxide (MnO_2) nanowire-carbon nanotube composite, MnO_2 nanowires on stainless steel mesh (SSM), porous vanadium oxide (VO_x) on SSM, and cobalt hydroxide (Co(OH)_2) nanoflakes on SSM.

Anode materials for Lithium-ion battery

The SnO₂ nanotubes were synthesized by anodic electrochemical deposition under ambient conditions without using any additional template. Controlled self-bubbling O₂ acted as both the template and the oxidizing agent for obtaining SnO₂ tube structures at the interface of the gas (O₂) and the liquid (electrolyte). The length of the tube could be controlled by adjusting the electrochemical deposition time. Electrochemical results show that the nanotubes have higher discharge capacity and better high-rate capability than microtubes. The morphology of the hollow nanotube structures composed of ultra-fine nanoparticles could be responsible for the enhanced high-rate performance and improved cycling stability as an electrode material. Electrochemical impedance spectroscopy (EIS) measurements showed that the nanotubes had a much higher electrochemically active surface area than microtubes. From the Arrhenius plots, the apparent activation energies were calculated to be 61.9 and 85.7 kJ mol⁻¹ for the nanotubes and microtubes, respectively, indicating the enhanced kinetics. Carbon-coated SnO₂ nanoparticles were prepared by a novel facile route using commercial SnO₂ nanoparticles treated with concentrated sulfuric acid in the presence of sucrose at room temperature and ambient pressure. The key features of this method are the simple procedure, low energy consumption, and inexpensive and non-toxic source materials. The electrochemical measurements showed that the carbon-coated SnO₂ nanoparticles with 10 % carbon and using carboxymethyl cellulose (CMC) as a binder displayed the best electrochemical performance, with the highest specific capacity of 502 mAh g⁻¹ after 50 cycles at a current density of 100 mA g⁻¹. In addition, owing to the water solubility of CMC, the

usage of CMC as binder makes the whole electrode fabrication process cheaper and more environmentally friendly.

Hollow-structured α -Fe₂O₃/carbon (HIOC) composite with high surface area around 260 m² g⁻¹ was synthesized by one-step, in-situ, and industrially-oriented spray pyrolysis method using iron (II) lactate solution and sucrose as the precursor. The electrochemical tests show that the HIOC composite with 14.7% carbon using CMC as binder, without pressing of the electrode, shows the best electrochemical performance, in terms of the high capacity (1000 mAh g⁻¹ at 0.1 C), good rate capability (700 mAh g⁻¹ at 2 C), and good cycling stability (720 mAh g⁻¹ at 2 C up to 220 cycles). The high surface area, hollow structure, selected binder, and carbon content account for the high performance with respect to lithium storage properties.

Cathode materials for Lithium-ion battery

Highly flexible, paper-like, free-standing polypyrrole (PPy) and polypyrrole-LiFePO₄ composite films were prepared using the electropolymerization method. The films are soft, lightweight, mechanically robust, and highly electrically conductive. The electrochemical performance of the free-standing pure PPy electrode was improved by incorporating the most promising cathode material, LiFePO₄, into the PPy films. The cell with PPy-LiFePO₄ composite film had a higher discharge capacity beyond 50 cycles (80 mAh g⁻¹) than that of the cell with pure PPy (60mAh g⁻¹). The free-standing films can be used as electrode materials to satisfy the new market demand for flexible and bendable batteries that are suitable for the various types of design and power needs of soft portable electronic equipment.

V_2O_5 nanomaterials, including nanoribbons, nanowires, and microflakes, have been synthesized by an ultrasonic assisted hydrothermal method combined with a post annealing process. A room temperature ionic liquid (RTIL) was used as the electrolyte in rechargeable lithium metal batteries along with V_2O_5 nanomaterials as cathode materials. The electrochemical tests show near-theoretical specific capacity, improved cycling stability, good high-rate capability, and enhanced kinetics. The thermogravimetric analysis (TGA) results show that the RTIL can prevent the dissolution of V_2O_5 during charge and discharge. The rechargeable lithium battery using V_2O_5 nanoribbons as cathode material and RTIL as the electrolyte could be the next generation lithium battery with high capacity, excellent safety, and long cycle life.

Materials for Supercapacitor

MnO_2 nanowires were electrodeposited onto carbon nanotube (CNT) paper by a cyclic voltammetric (CV) technique. The as-prepared MnO_2 nanowire/CNT composite paper (MNCCP) can be used as a flexible electrode for electrochemical supercapacitors. Electrochemical measurements showed that the MNCCP electrode displayed specific capacitance as high as 167.5 F g^{-1} at a current density of 77 mA g^{-1} . After 3000 cycles, the composite paper can retain more than 88% of initial capacitance, showing good cyclability. The CNT paper in the composite acts as a good conductive and active substrate for flexible electrodes in supercapacitors, and the nanowire structure of the MnO_2 could facilitate the contact of the electrolyte with the active materials, and thus increase the capacitance.

Flexible porous Co(OH)_2 nanoflake, porous vanadium oxide, and MnO_2 nanowire films were synthesized by an electrochemical deposition method using stainless steel mesh as the substrate. The cyclic voltammetry (CV) results show that the MnO_2 nanowire film has a specific capacitance of 195, 170, 158, and 91 F g^{-1} at scan rates of 5, 10, 20, and 50 mV s^{-1} , respectively. The porous VO_x film displays specific capacitance of 152, 124, 99, and 76 F g^{-1} at scan rates of 5, 10, 20, and 50 mV s^{-1} , respectively. The capacitance losses for the MnO_2 nanowire film and the porous VO_x film are only 5 % and 10 % for 1000 cycles, respectively. The porous Co(OH)_2 nanoflake film shows the highest capacitance of 609.4 F g^{-1} . The electrochemically active specific surface area of the annealed porous Co(OH)_2 nanoflake film remained virtually unchanged after 3000 cycles, showing the stability of the microstructure.

NOMENCLATURE

List of Abbreviations

Abbreviation	Full name
LiNTf ₂	Lithium bis(trifluoromethanesulfonyl)imide N-methyl-N-propyl pyrrolidinium
[C ₃ mpyr][NTf ₂]	bis(trifluoromethanesulfonyl) imide
1D	One dimensional
2D	Two dimensional
3D	Three dimensional
a.u.	Arbitrary unit
AC	Activated carbon
ACF	Activated carbon fiber
BET	Brunauer Emmett Teller
BSE	Back-scattered electrons
CB	Carbon black
CCD	Charge-coupled detector
cm	Centimeter
CMC	Sodium carboxymethyl cellulose
CNT	Carbon nanotube
CS-1	Carbon-coated SnO ₂ nanoparticles sample 1
CS-2	Carbon-coated SnO ₂ nanoparticles sample 2
CV	Cyclic voltammetry
DMC	Dimethyl carbonate
DWCNT	Double-walled carbon nanotube
EC	Ethylene carbonate
ECs	Electrochemical capacitors
EDL	Electrical double layer
EDX	Energy dispersive x-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
EV	Electric vehicle
FE-SEM	Field-emission scanning electron microscopy
FT-IR	Fourier transform inferior red Spectroscopy

Abbreviation	Full name
FWHM	Full width at half maximum
HEV	Hybrid electric vehicle
HIO	Hollow-structured α -Fe ₂ O ₃
HIOC	Hollow-structured α -Fe ₂ O ₃ /carbon
HRTEM	High-resolution transmission electron microscopy
IHP	Inner Helmholtz plane
IPRI	Intelligent Polymer Research Institute
ISEM	Institute for Superconducting and Electronic Materials
JCPDS	Joint committee on powder diffraction standards
MNCCP	MnO ₂ nanowire/CNT composite paper
MWCNT	Multi-walled carbon nanotube
nm	Nanometer
NMP	1-methyl-2-pyrrolidinone
OCP	Open circuit potential
OHP	Outer Helmholtz plane
PC	Propylene carbonate
PPy	Polypyrrole
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
Py	Pyrrole
RBM	Radial breathing mode
RTIL	Room temperature ionic liquid
RTIL	Room temperature ionic electrolyte
SAED	Selected area electron diffraction
SCE	Saturated calomel electrode
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
SHE	Standard hydrogen electrode
SSM	Stainless steel mesh
SWCNT	Single-walled carbon nanotube
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis

Abbreviation	Full name
XRD	X-ray diffraction

List of Symbols

Symbol	Name	Unit
2θ	Peak position of XRD	$^{\circ}$
C_{dl}	Electrical double layer capacitance	F
ΔQ	Charged or discharged capacity	C
C_{dm}	Specific capacitance of the electrochemical double layer	$F g^{-1}$
C_p	Pseudo-capacitance	F
$C\text{-rate}$	Charged or discharged rate	mA
C_S	Specific capacitance	$F g^{-1}$
E	Energy stored in a supercapacitor	$Wh kg^{-1}$
E_a	Apparent activation energies	$kJ mol^{-1}$
ED	Energy density	$Wh L^{-1}$
$EDLC$	Electrical double layer capacitance	F
E_O	Oxidation peak potential	V
E_R	Reduction peak potential	V
f	Frequency in the EIS test	Hz
F	Faradic constant = 96485	C
I	Current density,	$A cm^{-2}$
i_0	Exchange currents	A
I_O	Current density of oxidation peak	$mA g^{-1}$
I_R	Current density of reduction peak	$mA g^{-1}$
L	Crystal size	nm
m	Active material weight	g
N	Avogadro's number = 6.022×10^{23}	mol^{-1}
P	Equilibrium pressure	P
P_0	Saturation pressure	P
PD	Power density	$W L^{-1}$
Q	Specific capacity	$mAh kg^{-1}$

Symbol	Name	Unit
Q_c	Specific charge capacity	mAh g^{-1}
Q_d	Specific discharge capacity	mAh g^{-1}
Q_{TSC}	Theoretical specific capacity	mAh g^{-1}
R	Gas constant = 8.319	$\text{J K}^{-1} \text{mol}^{-1}$
R_{ct}	Charge transfer resistant	Ω
S_{BET}	Specific BET surface area	$\text{m}^2 \text{g}^{-1}$
SE	Specific energy	Wh kg^{-1}
S_E	Electrochemically active surface area	$\text{m}^2 \text{g}^{-1}$
SP	Specific power	W kg^{-1}
t	Time	h or s
T	Temperature	K or $^{\circ}\text{C}$
W_{PVdF+C}	Percentage of PVDF and carbon	%
W_{TL}	Total-weight loss	%
W_{VL}	Weight loss of V_2O_5	%
Z_{img}	Imaginary part of the impedance	Ω
Z_{real}	Real part of the impedance	Ω
η	Coulombic efficiency	%
λ	X-ray wavelength	\AA

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