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Nanostructured materials for electrodes in lithium-ion batteries

See How Ng
University of Wollongong

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NANOSTRUCTURED MATERIALS FOR

ELECTRODES IN LITHIUM-ION BATTERIES

A thesis submitted in fulfillment of the

requirements for the award of the degree

DOCTOR OF PHILOSOPHY

from

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by

SEE HOW NG, B. ENG. (HONS.), M. ENG.

INSTITUTE FOR SUPERCONDUCTING

& ELECTRONIC MATERIALS,

FACULTY OF ENGINEERING

2007

CERTIFICATION

I, See How Ng, 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.

See How Ng

25 September 2007

For my parents, siblings, and Sau Yen

who wonder what I do all day

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ABSTRACT

The commercially available lithium-ion cells, which are the most advanced among the rechargeable battery systems available so far, employ polycrystalline microsized powder as the electrode materials, which functions as the Li-ion insertion hosts. With the advancement of nanotechnology, there is an interest in the replacement of conventional materials by nanostructured materials. The use of nanoparticles in composite electrodes for Li-ion batteries may have considerable kinetic advantages due to the reduction of the diffusion length for lithium-ion insertion into the active mass, and also because of the reduction of the overall charge transfer resistance of the electrodes. In this doctoral work, several nanostructured materials were examined and characterized for possible application as electrode materials in Li-ion rechargeable batteries. Among the anode candidates studied were free-standing single-walled carbon nanotube (SWCNT) paper, lead oxide (PbO) and lead oxide-carbon (PbO-C) nanocomposite, and carbon-coated silicon (Si-C) nanocomposite materials. Meanwhile, several cathode candidates were also studied: nanostructured vanadium oxide (V_2O_5), lithium trivanadate (LiV_3O_8) nanoparticles, and lithium manganese oxide ($LiMn_2O_4$) thin film electrode.

Free-standing SWCNT paper electrodes have been synthesized by a simple filtration method via positive pressure. The free-standing electrode was produced without any binder or metal substrate, which reduced the weight significantly. The free-standing SWCNT paper electrodes were also flexible and had good electrical conductivity. With the addition of both carbon black and nanosized Si particles, the electrical conductivity and specific capacity of the free-standing SWCNT paper electrode were greatly enhanced, so that they retained a capacity of 400 mAh g^{-1} beyond 100 cycles. A new approach has been used to prepare nanostructured PbO and PbO-C composites via the spray pyrolysis technique. The prepared powders consist of fine nanocrystalline PbO homogeneously distributed within an amorphous carbon matrix with highly developed surface area. The combination of spray technology and carbon addition increased the specific surface area (above 6 m^2 g^{-1}) and the conductivity of PbO, and also improved

the specific capacity, with a reversible capacity above 100 mAh g^{-1} retained beyond 50 cycles. An effective, inexpensive, and industrially oriented approach was applied to produce carbon-coated Si nanocomposites. Carbon-coated Si nanocomposites spray-pyrolyzed in air at 400 ^{o}C showed the best cycling performance, retaining a specific capacity of 1120 mAh g^{-1} beyond 100 cycles, with a capacity fading of less than 0.4 % per cycle. The beneficial effect of the carbon-coating in enhancing the dimensional stability of the Si nanoparticles appears to be the main reason for this markedly improved electrochemical performance.

One-dimensional (1D) nanostructures of V_2O_5 have been successfully synthesized via a precipitation process followed by heating in vacuum at 300 ^{o}C. The increase in crystallinity and higher yield of one-dimensional nanostructured oxides contributed significantly to the improved capacity and enhanced cycle life. V_2O_5 nanoparticles were also synthesized via the flame spray pyrolysis (FSP) process in air. They showed an improved cycle life when the cut-off potential for discharging was increased from 1.5 V to 2.5 V. The significant capacity loss when discharging to 1.5 V is possibly related to the dissolution of vanadium active mass and the structural changes upon cycling in the larger potential span. The flame spray pyrolyzed V_2O_5 nanoparticles show excellent cyclability when cycled between 2.5 V and 4.0 V vs. Li/Li^{+}, retaining a discharge capacity of 120 mAh g^{-1} beyond 100 cycles at a cycling rate of 100 mA g^{-1}. LiV_3O_8 nanoparticles (~24 nm in size) have been synthesized by FSP for the first time. The as-synthesized LiV_3O_8 nanoparticles proved to be a promising cathode material for lithium rechargeable batteries, retaining a specific discharge capacity of 180 mAh g^{-1} beyond 50 cycles. A series of $LiMn_2O_4$ thin films on either Si (100) or stainless steel substrate were successfully prepared via pulsed laser deposition (PLD). The as-deposited $LiMn_2O_4$ thin films on stainless steel substrate are highly lithium- and oxygen-deficient, as confirmed by ERDA/RBS and Raman analysis. Lithium and oxygen content increased when the pulse rate was increased, leading to thicker films. However, the $LiMn_2O_4$ thin film with the lowest deposition pulse rate (or thinnest film) exhibited the best electrochemical performance, retaining a charge capacity of 48 μAh cm^{-2} μm^{-1} beyond 100 cycles.

NOMENCLATURE

- **List of Symbols**

Symbol	Name	Unit
a_i	Activity of species i	mol dm^{-3}
C	Concentration	M
C-rate	Rate of charge or current density	mA g^{-1} or µA cm^{-2}
C_C	Charge capacity	Ah kg^{-1} or mAh g^{-1}
C_D	Discharge capacity	Ah kg^{-1} or mAh g^{-1}
C_{dl}	Double-layer capacitance	F m^{-2}
D_P	Average crystal size	nm
d	Distance between atomic layers in a crystal	Å or nm
d_t	Tube diameter	nm
d_{t-s}	Target-substrate distance	cm
E	Potential of half-reactions	V or mV
E_{dc}	DC potential	V or mV
E_f	Final potential	V or mV
E_i	Initial potential	V or mV
E_s	Switching potential	V or mV
E^0	Standard electrode potential	V or mV
$E^{0,(-)}$	Negative electrode potential	V or mV
$E^{0,(+)}$	Positive electrode potential	V or mV
$\Delta E^0, U^0$	Cell potential	V or mV
f	Frequency	Hz
ΔG^0	Standard Gibbs free energy	J mol^{-1}
I	Current	A or mA
K	Shape factor of the average crystallite	(dimensionless)

- **List of Symbols (con't)**

Symbol	Name	Unit
L	Crystal size	nm
M_p	Mass of the target atom	kg or g
M_r	Mass of the incident ion	kg or g
m, m_i	Mass of species i	kg or g
N^0	Number of pulses	(dimensionless)
n	Number of electrons exchanged or integer	(dimensionless)
P_d	Downstream pressure	bar
P_{O2}	Oxygen background pressure	mbar
P_u	Upstream pressure	bar
P_v	Power density	$W\ dm^{-3}$
p	Specific power	$W\ kg^{-1}$
Q	Solution flow rate	$mL\ min^{-1}$
Q	Capacity	Ah or mAh
Q_{irrev}	Irreversible capacity loss	%
q_{th}	Theoretical specific charge capacity	$Ah\ kg^{-1}$ or $mAh\ g^{-1}$
R_n	Reversible capacity at cycle n	$Ah\ kg^{-1}$ or $mAh\ g^{-1}$
R_{ct}	Charge-transfer resistance	Ω
Q	Capacity	Ah or mAh
Q_{irrev}	Irreversible capacity loss	%
q_{th}	Theoretical specific charge capacity	$Ah\ kg^{-1}$ or $mAh\ g^{-1}$
R_n	Reversible capacity at cycle n	$Ah\ kg^{-1}$ or $mAh\ g^{-1}$
R_{ct}	Charge-transfer resistance	Ω
S_{BET}	Specific surface area	$m^2\ g^{-1}$
T	Temperature	K or ^{o}C
T_s	Substrate temperature	K or ^{o}C
t	Time	h
v	Scan rate	$mV\ s^{-1}$
v_i	Stoichiometric coefficients of species i	(dimensionless)
$W_{V.th}$	Theoretical energy density	$Wh\ dm^{-3}$
w_{th}	Theoretical specific energy	$Wh\ kg^{-1}$
Δx	Amount of guest species	mol

- **List of Symbols (con't)**

Symbol	Name	Unit
β	Full width at half maximum in radians	radians
ω_{RBM}	RBM frequency	cm^{-1}
λ	Wavelength of the incident X-ray beam	nm
φ	Laser fluence	J cm^{-2}
θ	Angle of incidence	° or degrees
σ	Electrical conductivity	S cm^{-1}
τ	Pulse width	ns

- **List of Fundamental Constants**

Quantity	Symbol	Value	Power of Ten	Unit
Avogadro constant	N_A	6.022	10^{23}	mol^{-1}
Boltzmann constant	k	1.381	10^{-23}	J K^{-1}
Elementary charge	e	1.602	10^{-19}	C
Faraday constant	$F = N_A \times e$	9.6487	10^{4}	C mol^{-1}
Gas constant	$R = N_A \times k$	8.319	10^{0}	J K^{-1} mol^{-1}

- **List of Conversion Factors**

Value	Equivalence
1 eV	1.602×10^{-19} J
	86.5 kJ mol^{-1}
	8066 cm^{-1}
1 cm^{-1}	1.986×10^{-23} J
1 μm	10^{-6} m
1 nm	10^{-9} m
1 Å	10^{-10} m

- **List of Abbreviations**

Abbreviation	Meaning
AFM	Atomic force microscopy
a.u.	Arbitrary unit
BET	Brunauer Emmett Teller
CB	Carbon black
CCCC	Computer controlled cell capture
CNT	Carbon nanotube
CV	Cyclic voltammetry
CVD	Chemical vapor deposition
DC	Disordered carbon
dc	Dynamic current
DEG	Diethylene glycol
DMC	Dimethyl carbonate
DWCNT	Double-walled carbon nanotube
EC	Ethylene carbonate
EDS	Energy dispersive spectroscopy
EIS	Electrochemical impedance spectroscopy
ERDA	Elastic recoil detection analysis
ETH	Swiss Federal Institute of Technology
EV	Electric vehicle
FE-SEM	Field-emission scanning electron microscopy
FSP	Flame spray pyrolysis
FWHM	Full width at half maximum
hcp	Hexagonal-close-packed
HEV	Hybrid electric vehicle
HR-TEM	High-resolution transmission electron microscopy
IPRI	Intelligent Polymer Research Institute
ISEM	Institute for Superconducting and Electronic Materials
JCPDS	Joint committee on powder diffraction standards
LTB	Lithium tert-butoxide
MWCNT	Multi-walled carbon nanotube
Ni-Cd	Nickel-cadmium

- **List of Abbreviations (con't)**

Abbreviation	Meaning
Ni-MH	Nickel-metal hydride
NMP	1-methyl-2-pyrrolidinone
NMR	Nuclear magnetic resonance
NNI	National nanotechnology initiative
NRA	Nuclear reaction analysis
OCP	Open circuit potential
OEM	Original equipment manufacturer
PC	Propylene carbonate
PLD	Pulsed laser deposition
PSI	Paul Scherrer Institute
PSPD	Position sensitive photo-detector
PVDF	Polyvinylidene fluoride
PZT	Piezo-electric
RBM	Radial breathing mode
RBS	Rutherford backscattering spectrometry
R & D	Research and development
rms	Root mean square
SAEDP	Selected area electron diffraction pattern
SEI	Solid-electrolyte interphase
SEM	Scanning electron microscopy
SEM	Scanning electron microscopy
SHE	Standard hydrogen electrode
SS	Stainless steel
SWCNT	Single-walled carbon nanotube
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TMO	Transition metal oxide
UV	Ultra-violet
XRD	X-ray diffraction

LIST OF FIGURES