

2007

## Nanostructured materials for electrodes in lithium-ion batteries

See How Ng  
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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

**UNIVERSITY OF WOLLONGONG**

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*

## **ACKNOWLEDGEMENTS**

It is my pleasure to acknowledge the considerable assistances that I have received from the people of the University of Wollongong (UoW), Australia and also from the Paul Scherrer Institute (PSI), Switzerland, during the course of my doctoral studies. I wish to express my utmost gratitude to my thesis supervisor, *Professor Hua Kun Liu*, and co-supervisor, *Dr. Jiazhao Wang*, for their invaluable advice, encouragement, understanding and trust during my stay at UoW. Many thanks also for their careful review of the manuscripts. Any remaining errors are my responsibility.

I would like to express my deepest appreciation to *Prof. Shi Xue Dou*, Director of the Institute for Superconducting & Electronic Materials (ISEM), and *Prof. Gordon Wallace*, Director of the ARC Center of Excellence for Electromaterials Science (ACES), for providing me with the appropriate facilities and expertise during the course of my studies. I would like to thank ISEM, ACES, and the University of Wollongong, for providing me with the financial support during my doctoral studies, by means of a Tuition Fee Waiver Scholarship and also a matching PhD Scholarship.

I would like to thank *P.D. Dr. Petr Novák*, Head of Batteries Group, *P.D. Dr. Thomas Lippert*, Head of Materials Group, and *Prof. Alexander Wokaun*, Head of the General Energy Department, all from the Paul Scherrer Institute, Switzerland, for their scientific assistance and support, during my appointment as a Visiting Scientist in PSI, from October 2006 till April 2007. I would also like to thank *Prof. Dr. Sotiris E. Pratsinis*,

Director of the Particle Technology Laboratory (PTL), Swiss Federal Institute of Technology Zurich, Switzerland, for providing me with the facilities for the production of nanoparticles via the flame spray pyrolysis process.

I wish to thank *Mrs. Franziska Simmen*, PhD student from PSI, for her assistance in preparing and analyzing the PLD-made  $\text{LiMn}_2\text{O}_4$  thin films for my thesis work. Many thanks also go to *Mr. Timothy Patey* (PhD student, PSI) and *Mr. Robert Büchel* (PhD student, PTL) for their assistance in the synthesis of vanadium-based oxides nanoparticles via the flame spray pyrolysis process, for use as cathode materials in my research work. During my Visiting Scientist appointment at the Paul Scherrer Institute, Switzerland, I had the pleasure working with a number of scientists and postgraduate students such as *Dr. Matthias Hahn*, *Dr. Nicolas Tran*, *Dr. Maire Pascal*, *Dr. Joachim Ufheil*, *Mr. Werner Scheifele*, *Mr. Hermann Kaiser*, *Mr. Patrick Ruch*, *Mr. Fabio La Mantia*, and *Mr. Fabio Roschiano*. Their help and discussion are greatly appreciated. Also the administrative help from *Ms. Isabella Kalt* is greatly acknowledged.

Technical assistance from the people of the University of Wollongong such as *Dr. David Wexler* (TEM), *Dr. Jun Chen* (FT-IR, Raman, and TGA), *Dr. Konstantin Konstantinov* (spray pyrolysis, BET, TGA/DTA, and SEM/EDX), *Dr. Zaiping Guo* (EIS), and *Assoc. Prof. Chee Too* (bucky paper) are gratefully acknowledged. It is also my pleasure to work with a number of overseas collaborators such as *Prof. Dayse dos Santos* (UNESP, Brazil), *Prof. Chuanqi Feng* (Wuhan University, China), *Mr. Yann Tournayre* (France), *Ms. Dong Yun Zhang* (Shanghai Jiao Tong University, China), and *Mr. Roshan Shanmukaraj* (India) during my studies in ISEM.

I also wish to thank *Mr. Kieran de Silva, Dr. Wai Kong Yeoh, Dr. Jung Ho Kim, Dr. Steve Bewlay, Dr. Scott Needham, Mr. Bernie Huang, Mr. Min-Sik Park, Mr. Jin-Soo Park, Mr. Joe Xu, Mr. Dapeng Chen, Ms. Olga Scherbakova, Mr. Andrey Scherbakov, Dr. Germanas Peleckis, Dr. Marie Roussel, Dr. Ling Yuan, Ms. Jane Yao, Mr. Brad Winton, Mr. Georgin Lao, and Mr. Jerry Zhao*, for all their friendly support and helpful discussions during my doctoral studies in ISEM. I wish to thank *Dr. Tania Silver* for the critical reading of all my publications, improving the standard of my written English, and also proofreading of my thesis. My heartfelt thanks also go to *Mr. Ron Kinnell*, for all the technical assistance with the maintenance of equipment and scientific facilities.

I would like to thank my mum, dad, and sisters, for their continue support and love, which translates into the strength and guidance path for me during my PhD studies. Finally, my greatest debt, however, is to my wife, *Ms. Sau Yen (Sophie) Chew*, who endured my long days in my study with particular grace and understanding. She has been, simply, indispensable.



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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 micro-sized powder as the electrode materials, which function 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



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the specific capacity, with a reversible capacity above 100 mAh g<sup>-1</sup> 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 °C showed the best cycling performance, retaining a specific capacity of 1120 mAh g<sup>-1</sup> 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<sub>2</sub>O<sub>5</sub> have been successfully synthesized via a precipitation process followed by heating in vacuum at 300 °C. The increase in crystallinity and higher yield of one-dimensional nanostructured oxides contributed significantly to the improved capacity and enhanced cycle life. V<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>O<sub>5</sub> nanoparticles show excellent cyclability when cycled between 2.5 V and 4.0 V vs. Li/Li<sup>+</sup>, retaining a discharge capacity of 120 mAh g<sup>-1</sup> beyond 100 cycles at a cycling rate of 100 mA g<sup>-1</sup>. LiV<sub>3</sub>O<sub>8</sub> nanoparticles (~24 nm in size) have been synthesized by FSP for the first time. The as-synthesized LiV<sub>3</sub>O<sub>8</sub> nanoparticles proved to be a promising cathode material for lithium rechargeable batteries, retaining a specific discharge capacity of 180 mAh g<sup>-1</sup> beyond 50 cycles. A series of LiMn<sub>2</sub>O<sub>4</sub> thin films on either Si (100) or stainless steel substrate were successfully prepared via pulsed laser deposition (PLD). The as-deposited LiMn<sub>2</sub>O<sub>4</sub> 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<sub>2</sub>O<sub>4</sub> thin film with the lowest deposition pulse rate (or thinnest film) exhibited the best electrochemical performance, retaining a charge capacity of 48 μAh cm<sup>-2</sup> μm<sup>-1</sup> beyond 100 cycles.

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## NOMENCLATURE

- List of Symbols

Symbol	Name	Unit
$a_i$	Activity of species $i$	$\text{mol dm}^{-3}$
$C$	Concentration	M
$C$ -rate	Rate of charge or current density	$\text{mA g}^{-1}$ or $\mu\text{A cm}^{-2}$
$C_C$	Charge capacity	$\text{Ah kg}^{-1}$ or $\text{mAh g}^{-1}$
$C_D$	Discharge capacity	$\text{Ah kg}^{-1}$ or $\text{mAh g}^{-1}$
$C_{dl}$	Double-layer capacitance	$\text{F m}^{-2}$
$D_P$	Average crystal size	nm
$d$	Distance between atomic layers in a crystal	$\text{\AA}$ 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
$\Delta G^0$	Standard Gibbs free energy	$\text{J mol}^{-1}$
$I$	Current	A or mA
$K$	Shape factor of the average crystallite	(dimensionless)

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- 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
$P_{O_2}$	Oxygen background pressure	mbar
$P_u$	Upstream pressure	bar
$P_v$	Power density	W dm <sup>-3</sup>
$p$	Specific power	W kg <sup>-1</sup>
$Q$	Solution flow rate	mL min <sup>-1</sup>
$Q$	Capacity	Ah or mAh
$Q_{irrev}$	Irreversible capacity loss	%
$q_{th}$	Theoretical specific charge capacity	Ah kg <sup>-1</sup> or mAh g <sup>-1</sup>
$R_n$	Reversible capacity at cycle $n$	Ah kg <sup>-1</sup> or mAh g <sup>-1</sup>
$R_{ct}$	Charge-transfer resistance	$\Omega$
$Q$	Capacity	Ah or mAh
$Q_{irrev}$	Irreversible capacity loss	%
$q_{th}$	Theoretical specific charge capacity	Ah kg <sup>-1</sup> or mAh g <sup>-1</sup>
$R_n$	Reversible capacity at cycle $n$	Ah kg <sup>-1</sup> or mAh g <sup>-1</sup>
$R_{ct}$	Charge-transfer resistance	$\Omega$
$S_{BET}$	Specific surface area	m <sup>2</sup> g <sup>-1</sup>
$T$	Temperature	K or °C
$T_s$	Substrate temperature	K or °C
$t$	Time	h
$v$	Scan rate	mV s <sup>-1</sup>
$v_i$	Stoichiometric coefficients of species $i$	(dimensionless)
$W_{V.th}$	Theoretical energy density	Wh dm <sup>-3</sup>
$w_{th}$	Theoretical specific energy	Wh kg <sup>-1</sup>
$\Delta x$	Amount of guest species	mol

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- List of Symbols (con't)

Symbol	Name	Unit
$\beta$	Full width at half maximum in radians	radians
$\omega_{RBM}$	RBM frequency	$\text{cm}^{-1}$
$\lambda$	Wavelength of the incident X-ray beam	nm
$\varphi$	Laser fluence	$\text{J cm}^{-2}$
$\theta$	Angle of incidence	° or degrees
$\sigma$	Electrical conductivity	$\text{S cm}^{-1}$
$\tau$	Pulse width	ns

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- List of Fundamental Constants

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

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- List of Conversion Factors

Value	Equivalence
1 eV	$1.602 \times 10^{-19} \text{ J}$ $86.5 \text{ kJ mol}^{-1}$ $8066 \text{ cm}^{-1}$
1 $\text{cm}^{-1}$	$1.986 \times 10^{-23} \text{ J}$
1 $\mu\text{m}$	$10^{-6} \text{ m}$
1 nm	$10^{-9} \text{ m}$
1 Å	$10^{-10} \text{ m}$

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- **List of Abbreviations**

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<b>Abbreviation</b>	<b>Meaning</b>
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

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- List of Abbreviations (con't)

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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

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