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Development of new electrode materials for lithium ion batteries

Chao Zhong
University of Wollongong

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**DEVELOPMENT OF NEW ELECTRODE MATERIALS FOR
LITHIUM ION BATTERIES**

A thesis submitted in fulfilment of the requirements for the award of the
degree

MASTER OF ENGINEERING - RESEARCH

from

UNIVERSITY OF WOLLONGONG

by

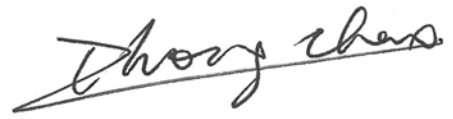
CHAO ZHONG, B. ENG.

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

2010

CERTIFICATION

I, Chao Zhong, declare that this thesis, submitted in fulfillment of the requirements for the award of Master of Engineering-Research, 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.

A handwritten signature in dark ink, appearing to read 'Chao Zhong', is written over a horizontal line.

Chao Zhong

16 February 2010

**For my father and mother,
who love and support me all the time**

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ABSTRACT

Rechargeable lithium-ion batteries that have been widely used in portable electronic devices are now extended to applications such as electric vehicles (EVs). Therefore, the performance of the rechargeable lithium-ion batteries must continue to be improved in terms of capacity, rate capability, cycle life, etc. In this Master's research study, to contribute to this goal, several materials were characterized and examined for possible applications as anode or cathode for rechargeable lithium-ion batteries. Among the anode candidates, nickel oxide (NiO), copper oxide (CuO) and copper oxide with carbon (CuO-C), and free-standing graphene-silicon (graphene-Si) were studied. Manganese dioxide (MnO_2) was also studied as a cathode material candidate for use in rechargeable lithium-ion batteries.

Hollow spherical NiO particles were prepared using the spray pyrolysis method with different concentrations of precursor for use in rechargeable lithium-ion battery anode. The electrochemical properties of the NiO electrodes, which contained a new type of binder, carboxymethyl cellulose (CMC), were examined for comparison with NiO electrodes with poly(vinylidene) fluoride (PVDF) binder. The electrochemical performance of NiO electrodes using CMC binder was significantly improved. For the cell made from 0.3 mol L^{-1} precursor, the irreversible capacity loss between the first discharge and charge was about 43% and 24% for the electrode with PVDF and CMC binder, respectively. The cell with NiO-CMC electrode has a much higher discharge capacity of 547 mAh g^{-1} compared to that of the cell with NiO-PVDF electrode, which is 157 mAh g^{-1} beyond 40 cycles.

Bare copper oxide and copper oxide–carbon composite were synthesized by a one-step spray pyrolysis method and tested as anode materials combined with CMC or PVDF binder for rechargeable lithium-ion batteries. The results demonstrate that the CuO-carbon composite in conjunction with CMC binder has excellent electrochemical performance, with a capacity of 633 mAh g^{-1} up to 250 cycles at a current density of 100 mA g^{-1} . Usage of the water soluble binder, CMC, not only further confirmed its potential for improving the electrochemical performance of transition metal oxides for use in lithium-ion batteries, but also makes the electrode fabrication process much easier and more environmentally friendly.

Flexible, free-standing, paper-like, graphene-silicon composite materials have been synthesised by a simple, one-step, in-situ filtration method. The Si nanoparticles are highly encapsulated in a graphene nanosheet matrix. The electrochemical results show that graphene-Si composite film has much higher discharge capacity beyond 100 cycles (708 mAh g^{-1}) than that of the cell with pure graphene (304 mAh g^{-1}). The graphene functions as a flexible mechanical support for strain release, offering an efficient electrically conducting channel, while the nanosized silicon provides the high capacity.

Finally, nanocrystalline MnO_2 powders were synthesized by a novel magnetic field assisted hydrothermal method and tested as cathode material in rechargeable lithium-ion batteries. It was found that the morphology of the MnO_2 prepared without magnetic field is characterized by an urchin-like structure, while the MnO_2 prepared in magnetic fields has a rambutan-like structure. A pronounced increase in the

Brunauer-Emmett-Teller (BET) specific surface area was obtained when the intensity of the pulsed magnetic field increased. The battery performance was improved for the samples prepared with magnetic fields. The MnO_2 prepared under a magnetic field of 4 T shows a capacity of 121.8 mAh g^{-1} after 30 cycles, while the MnO_2 prepared without magnetic field only shows 103.0 mAh g^{-1} after 30 cycles.

TABLE OF CONTENTS

CERTIFICATION	i
ACKNOWLEDGEMENTS	iii
ABSTRACT	v
TABLE OF CONTENTS	viii
LIST OF FIGURES	xi
LIST OF TABLES	xiv
CHAPTER 1 INTRODUCTION	15
CHAPTER 2 LITERATURE REVIEW	18
2. 1 Introduction to Rechargeable Lithium-ion Batteries	18
2.1.1 General Introduction	18
2.1.2 A Brief History	20
2.1.3 Basic Principles of Lithium-ion Batteries	21
2. 2 Anode Electrode Materials	24
2.2.1 Carbonaceous Materials	25
2.2.2 Lithium-metal Alloys	28
2.2.3 Transition Metal Oxides	29
2. 3 Cathode Electrode Materials	31
2.3.1 Nanostructured Lithium Transition Metal Oxides	33
2.3.2 Olivine	34
2.3.3 Other Oxide Materials	36
2. 4 Electrolytes for Lithium-ion Batteries	36
2. 5 Binders for Lithium-ion Batteries	37
CHAPTER 3 EXPERIMENTAL	39
3. 1 List of materials	39
3. 2 Experimental procedure	40
3.2.1 Overall Framework of the Experiments	40
3.2.2 Materials Preparation	41
3. 3 Electrode Preparation and Cell Fabrication	43
3. 4 Physical and Structural Characterization	44

3.4.1	X-ray Diffraction (XRD).....	44
3.4.2	Scanning Electron Microscopy (SEM)	45
3.4.3	Transmission Electron Microscopy (TEM)	45
3.4.4	Raman Spectroscopy	46
3.4.5	Thermogravimetric Analysis (TGA).....	46
3.4.6	Brunauer-Emmett-Teller (BET) Method	46
3.5	Electrochemical Characterization	47
3.5.1	Cyclic Voltammetry (CV).....	47
3.5.2	Galvanostatic Charge and Discharge Testing	47
3.5.3	Electrochemical Impedance Spectroscopy (EIS).....	48
CHAPTER 4 NANOCRYSTALLINE NICKEL OXIDE HOLLOW SPHERES IN CONJUNCTION WITH CMC BINDER AS ANODE MATERIALS FOR LITHIUM-ION BATTERIES		49
4.1	Introduction	49
4.2	Experimental	51
4.2.1	Synthesis of Hollow Spherical NiO	51
4.2.2	Structural and Electrochemical Characterization.....	51
4.3	Results and Discussion.....	52
4.4	Chapter Summary	60
CHAPTER 5 SPRAY PYROLYSIS SYNTHESIZED COPPER OXIDE- CARBON COMPOSITE COMBINED WITH CMC BINDER AS ANODE FOR LITHIUM-ION BATTERIES		61
5.1	Introduction	61
5.2	Experimental	63
5.2.1	Synthesis of the Materials	63
5.2.2	Structural and Electrochemical Characterization.....	63
5.3	Results and Discussion.....	64
5.3.1	Physical and Structural Characterization	64
5.3.2	Electrochemical Properties	69
5.4	Chapter Summary	73
CHAPTER 6 HIGH CAPACITY FLEXIBLE FREE-STANDING GRAPHENE- SILICON COMPOSITE FILM FOR LITHIUM-ION BATTERIES		75
6.1	Introduction	75
6.2	Experimental	77

6.2.1	Synthesis of graphite oxide	77
6.2.2	Preparation of graphene and graphene-Si composite films.....	77
6.2.3	Structural and Electrochemical Characterization.....	79
6. 3	Results and Discussion.....	80
6. 4	Chapter Summary	87
CHAPTER 7 HYDROTHERMAL SYNTHESIS OF NANOSTRUCTURED MANGANESE DIOXIDE UNDER MAGNETIC FIELD FOR RECHARGEABLE LITHIUM BATTERIES		88
7. 1	Introduction	88
7. 2	Experimental	89
7.2.1	Synthesis of Nanostructured MnO ₂	89
7.2.2	Physical and Electrochemical Characterization	90
7. 3	Results and discussion	91
7.3.1	Physical and Structural Characterization	91
7.3.2	Electrochemical Properties	94
7. 4	Chapter Summary	97
CHAPTER 8 CONCLUSIONS.....		99
REFERENCES.....		101
LIST OF PUBLICATIONS		110

LIST OF FIGURES

Figure 2.1 Energy densities of the different types of rechargeable batteries [3].	19
Figure 2.2 Schematic drawing showing the shape and components of various Li-ion battery configurations: a, Cylindrical; b, coin; c, prismatic; and d, thin and flat [3].	23
Figure 2.3 Voltage versus capacity for positive and negative electrode materials [3].	24
Figure 2.4 The structures of three different types of carbonaceous materials.	27
Figure 2.5 Schematic drawing of layered structure (e.g. LiTiS_2 , LiCoO_2 and LiNiO_2) which shows the lithium ions between the transition-metal oxide/sulfide sheets [36].	33
Figure 2.6 Structures of orthorhombic LiFePO_4 and trigonal quartz-like FePO_4 .	35
Figure 3.1 The overall framework of the experiments.	40
Figure 3.2 Schematic diagram of spray pyrolysis apparatus.	41
Figure 3.3 Filtration process using Whatman 47 mm filtration cell.	42
Figure 3.4 Cross-sectional schematic diagram of the coin-type cell.	44
Figure 4.1 X-ray diffraction patterns for NiO powders from spray pyrolysis solutions at different concentrations.	52
Figure 4.2 Images of NiO powder made from 0.3 M precursor: (a) SEM, (b) FE-SEM, (c) TEM, and (d) corresponding SAED pattern to (c).	54
Figure 4.3 Discharge capacities vs. cycle number for NiO electrodes made from spray solutions at different concentrations with PVDF and CMC binders.	55
Figure 4.4 Typical charge-discharge curves for NiO electrodes (0.3 mol L ⁻¹) with CMC and PVDF binders.	56
Figure 4.5 Nyquist impedance plots of NiO electrodes (0.3 mol L ⁻¹) with different binders (a) before and (b) after cycling.	58
Figure 4.6 SEM images of NiO electrodes (0.3 mol L ⁻¹) with CMC binder (left) and PVDF binder (right): (a-b) before cycling, (c-d) after cycling, (e-f) cross-sections of electrodes after cycling. Insets in (e) and (f) show enlargements of the indicated areas.	59

Figure 5.1 XRD patterns for the as-prepared (a) bare CuO and (b) CuO-carbon composite materials.....	65
Figure 5.2 SEM images of (a) pure CuO, (b) CuO:C=70:30 composite, and respective FESEM images (c-d).....	66
Figure 5.3 EDX mapping for the as-prepared CuO:C=70:30 composite material.....	67
Figure 5.4 TGA curves for the as-prepared materials.....	68
Figure 5.5 Cyclic voltammograms of the electrodes made from the as-prepared (a) bare CuO and (b) CuO-carbon materials at a scan rate of 0.1 mV s^{-1}	70
Figure 5.6 (a) Cycling behavior of the samples with CMC or PVDF binders at a scan rate of 100 mA g^{-1} ; (b) rate capability of the samples with CMC binder	72
Figure 5.7 Nyquist impedance plots (50th cycle) of the bare CuO and CuO:C=70:30 composite electrodes with different binders.	73
Figure 6.1 Schematic diagram of the composite film fabrication.....	78
Figure 6.2 X-ray diffraction patterns for free-standing graphene-Si film (a), Si nanopowder (b), and free-standing graphene film (c).....	80
Figure 6.3 Raman spectra for free-standing graphene-Si composite film, graphene film, and Si nanopowder.	82
Figure 6.4 FESEM images: top view of free-standing graphene film (a) with a cross-sectional view (inset), free-standing graphene-Si composite film (b), and cross-sectional views of the composite film at low (c) and high (d) magnification; TEM image of graphene-Si composite (e); FESEM image of graphene-Si (f), with corresponding EDS mapping of carbon and silicon.	83
Figure 6.5 TGA curves of graphene-Si composite film, graphene film, and Si nanopowder.....	84
Figure 6.6 Discharge capacity vs. cycle number for the electrodes made from graphene film and graphene-Si composite film.	86
Figure 7.1 XRD pattern of the MnO_2 obtained without and with a 4 T magnetic field.	91
Figure 7.2 SEM images (a), (b), and (c) for the MnO_2 obtained without magnetic field, and with 2 T and 4 T fields, respectively; EDX results for the MnO_2 obtained (d) without magnetic field and (e) with a 4 T field.	92
Figure 7.3 TEM images and SAED patterns (inset) of the MnO_2 obtained (a) without magnetic field and (b) with a 4 T field.....	93

Figure 7.4 Cyclic voltammograms for the MnO_2 materials synthesized with and without magnetic field. 95

Figure 7.5 (a) Discharge and charge curves for the MnO_2 materials prepared with different magnetic fields. (b) Discharge capacities vs. cycle number for the as-prepared MnO_2 97

LIST OF TABLES

Table 2.1 Advantages and disadvantages of lithium-ion batteries [2].	19
Table 2.2 History of battery development.	21
Table 2.3 List of alternative anode materials for lithium-ion batteries [9].	26
Table 3.1 Description of chemicals used during my Master's studies.....	39