

# Electrode Materials for Lithium-ion Batteries and Supercapacitors

This thesis is submitted in fulfilment of the requirements for the degree of

**Doctor of Philosophy** 

from

University of Technology, Sydney

by

# Anjon Kumar Mondal

B. Sc. (Hons) & M. Sc.

Centre for Clean Energy Technology Faculty of Science 2015

### **CERTIFICATE OF ORIGINAL AUTHORSHIP**

I, Anjon Kumar Mondal certify that the work presented in this thesis has not previously been submitted for a degree nor has been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Anjon Kumar Mondal Sydney, Australia May, 2015

# DEDICATION

This thesis is dedicated to my family. Thank you for all of your love and support.

#### ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my supervisor, Professor Guoxiu Wang for his invaluable advice and supervision throughout this research work. His inventive research ideas and motivation enlightened and encouraged me during my PhD study.

I am grateful to my co-supervisor Assoc. Professor Alison Ung for her constant suggestion, contribution to reviewing my thesis and the fruitful discussion. I also acknowledge Assoc. Professor Andrew McDonagh for his kind help and suggestion.

Special thanks are given to my colleagues, Dr. Hao Liu, Dr. Zhimin Ao, Dr. Xiaodan Huang, Dr. Ali Reza Ranjbartoreh, Dr. Bei Wang, Dr. Bing Sun, Dr. Ying Wang, Dr. Dawei Su, Mr. Shuangqiang Chen, Mr. Kefei Li, Mr. Yiying Wei, Mr. Xiuqiang Xie, Mr. Jinqiang Zhang, Miss Yufei Zhao, Miss Katja Kretschmer, Miss Jing Xu, and Mr. Linfeng Zheng for their innovative ideas, kind co-operation and assistance during the period of this research. It is my pleasure to have worked with all of you and I really appreciate everyone's efforts in creating an intimate atmosphere for the research work.

I would like to acknowledge Dr. Jane Yao for her kind help and support in many ways throughout this study period.

I appreciate the administrative and technical support I received from Dr. Ronald Shimmon, Dr. Linda Xiao, Mrs. Rochelle Seneviratne, Mrs. Era Koirala, Ms. Sarah King, and Ms. Emaly Black.

Finally, I would like to express my sincere gratitude to my wife, my son, my daughter my parents, my family members and relatives. Without their support and encouragement, it would have been impossible for me to complete the research. Their

iii

love is the mental strength that supported me to study abroad and it will hold a special place in my heart forever.

## **RESEARCH PUBLICATIONS**

- 1 A. K. Mondal, D. Su, S. Chen, A. Ung, H. S. Kim, G. X. Wang, Mesoporous MnCo<sub>2</sub>O<sub>4</sub> with a flake-like structure as advanced electrode materials for lithium ion batteries and supercapacitors, *Chemistry–A European Journal*, 2015, 21, 1526-1532. IF: 5.696
- A. K. Mondal, D. Su, S. Chen, K. Kretschmer, X. Xie, H. J. Ahn, G. X. Wang, A microwave synthesis of mesoporous NiCo<sub>2</sub>O<sub>4</sub> nanosheets as electrode materials for lithium ion batteries and supercapacitors, *ChemPhysChem*, 2015, 16, 169-175. IF: 3.36
- 3 A. K. Mondal, D. Su, S. Chen, X. Xie, G. X. Wang, Highly porous NiCo<sub>2</sub>O<sub>4</sub> nanoflakes and nanobelts as anode materials for lithium ion batteries with excellent rate capability, *ACS Applied Materials & Interfaces*, 2014, 6, 14827-14835. IF: 5.9
- A. K. Mondal, D. Su, S. Chen, J. Zhang, A. Ung, G. X. Wang, Microwave-assisted synthesis of spherical β-Ni(OH)<sub>2</sub> superstructures for electrochemical capacitors with excellent cycling stability, *Chemical Physics Letters*, 2014, 610-611, 115–120. IF: 1.991
- 5 A. K. Mondal, D. Su, S. Chen, B. Sun, K. Li, G. X. Wang, A simple approach to prepare nickel hydroxide nanosheets for enhanced pseudocapacitive performance, *RSC Advances*, 2014, 4, 19476-19481. IF: 3.708
- 6 A. K. Mondal, B. Wang, D. Su, Y. Wang, S. Chen, X. Zhang, G. X. Wang, Graphene/MnO<sub>2</sub> hybrid nanosheets as high performance electrode materials for supercapacitors, *Materials Chemistry and Physics*, 2014, 143, 740-746. IF: 2.129
- 7 A. K. Mondal, D. Su, Y. Wang, S. Chen, Q. Liu, G. X. Wang, Microwave hydrothermal synthesis of urchin-like NiO nanospheres as electrode materials for lithium-ion batteries and supercapacitors with enhanced electrochemical performances, *Journal of Alloys and Compounds*, 2014, 582, 522-527. IF: 2.726
- 8 A. K. Mondal, S. Chen, D. Su, H. Liu, G. X. Wang, Fabrication and enhanced electrochemical performances of MoO<sub>3</sub>/graphene composite as anode material for lithium-ion batteries, *International Journal of Smart Grid and Clean Energy*, 2014, 3, 142-148.
- 9 A. K. Mondal, D. Su, Y. Wang, S. Chen, G. X. Wang, Hydrothermal synthesis of nickel oxide nanosheets for lithium-ion batteries and supercapacitors with excellent performance, *Chemistry - An Asian Journal*, 2013, 8, 2828-2832. IF: 3.935
- 10 A. K. Mondal, B. Wang, D. Su, Y. Wang, X. Zhang, G. X. Wang, Preparation and enhanced electrochemical performance of MnO<sub>2</sub> nanosheets for supercapacitors, *Journal of the Chinese Chemical Society*, 2012, 59, 1275-1279. IF: 0.856

TABLE OF	CONTENTS
----------	----------

CERTIFICATE OF AUTHORSHIP	i
DEDICATION	ii
ACKNOWLEDGEMENTS	iii
RESEARCH PUBLICATIONS	V
TABLE OF CONTENTS	vi
LIST OF TABLES	xii
LIST OF FIGURES	xiii
ABSTRACT	xxiv
INTRODUCTION	xxviii
CHAPTER 1 Literature Review	1
1.1 Lithium-ion Batteries	1
1.1.1 History and Development	1
1.1.2 Basic Concepts and Energy Storage Mechanism	2
1.1.3 Advantages and Disadvantages of Lithium-ion Batteries	4
1.1.4 Nanostructured Electrode Materials	9
1.1.4.1 Anode Materials	11
1.1.4.2 Cathode Materials	
1.2 Supercapacitors	41
1.2.1 History and Development	41
1.2.2 Energy Storage Mechanism	
1.2.3 Electrode Materials	44
1.2.4 Electrolytes	
CHAPTER 2 Experimental	63
2.1 Overview	63
2.2 Materials and Chemicals	63

2.3 Materials Preparation
2.3.1 Hydrothermal Method65
2.3.2 Microwave Method
2.3.3 Precipitation Method
2.4 Materials Characterization
2.4.1 X-ray Diffraction (XRD)68
2.4.2 Field-emission Scanning Electron Microscopy (FESEM)69
2.4.3 Transmission Electron Microscopy (TEM)70
2.4.4 Brunauer-Emmett-Teller (BET) Nitrogen Adsorption-Desorption
Isotherms
2.4.5 Thermogravimetric Analysis
2.4.6 Raman Spectroscopy
2.4.7 Atomic Force Microscopy
2.4.8 Fourier Transform Infrared Spectroscopy
2.5 Electrode Fabrication and Cell Assembly
2.5.1 Electrode fabrication
2.5.2 Cell Assembly
2.5.2.1 Lithium ion batteries
2.5.2.2 Supercapacitors74
2.6 Electrochemical Measurements74
2.6.1 Cyclic voltammetry
2.6.2 Galvanostatic charge-discharge
2.6.3 Electrochemical Impedance Spectroscopy76
CHAPTER 3 Hydrothermal synthesis of nickel oxide nanosheets for lithium
-ion batteries and supercapacitors with excellent performance78
3.1 Introduction
3.2 Experimental

3.2.1 Preparation of NiO nanosheets	79
3.2.2 Materials characterization.	79
3.2.3 Electrochemical testing	80
3.3 Results and Discussion	81
3.3.1 Structural and morphological analysis	
3.3.2 Electrochemical performance of NiO nanosheets for lithium ion b	patteries and
supercapacitors	
3.4 Conclusions	90
CHAPTER 4 Microwave-assisted synthesis of spherical β-Ni(OH) <sub>2</sub> su	perstructures
for electrochemical capacitors with excellent cycling stability	92
4.1 Introduction	92
4.2 Experimental	94
4.2.1 Preparation of spherical β-Ni(OH) <sub>2</sub>	94
4.2.2 Materials characterization	95
4.2.3 Electrochemical measurements	95
4.3 Results and Discussion	96
4.3.1 Physical and structural characterization	96
4.3.2 Electrochemical properties for supercapacitors	101
4.4 Conclusions	105
CHAPTER 5 Microwave synthesis of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> nanoparticles and their	r lithium
storage properties: A comparative study	106
5.1 Introduction.	106
5.2 Experimental	107
5.2.1 Preparation of Fe <sub>2</sub> O <sub>3</sub> nanoparticles	107
5.2.2 Materials Characterization	108
5.2.3 Electrochemical testing	108

5.3 Results and Discussion	109
5.3.1 Structural and morphological analysis	
5.3.2 Electrochemical performances	114
5.4 Conclusions	123
CHAPTER 6 Highly porous NiCo <sub>2</sub> O <sub>4</sub> nanoflakes and nanobelts as a	node
Materials for lithium ion batteries with excellent rate capability	124
6.1 Introduction	124
6.2 Experimental	126
6.2.1 Synthesis of NiCo <sub>2</sub> O <sub>4</sub> nanoflakes and nanobelts	126
6.2.2 Materials characterization	127
6.2.3 Electrochemical measurements	127
6.3 Results and Discussion	128
6.3.1 Physical and structural characterization	128
6.3.2 Electrochemical performances for lithium ion batteries	137
6.4 Conclusions	145
CHAPTER 7 Graphene/MnO <sub>2</sub> hybrid nanosheets as high performan	ice
electrode materials for supercapacitors	147
7.1 Introduction	147
7.2 Experimental	150
7.2.1 Synthesis of graphene nanosheets	150
7.2.2 Synthesis of MnO <sub>2</sub> nanosheets	150
7.2.3 Preparation of graphene-MnO <sub>2</sub> hybrid nanosheets	151
7.2.4 Materials Characterization	151
7.2.5 Electrochemical testing	151
7.3 Results and Discussion	152
7.3.1 Structural and morphological characterization	152

7.3.2 Electrochemical performances for supercapacitors	.157
7.4 Conclusions	161
CHAPTER 8 A microwave synthesis of mesoporous NiCo <sub>2</sub> O <sub>4</sub> nanosheets as	
electrode materials for lithium ion batteries and supercapacitors	163
8.1 Introduction	163
8.2 Experimental	165
8.2.1 Synthesis of NiCo <sub>2</sub> O <sub>4</sub> nanosheets	165
8.2.2 Materials characterization	166
8.2.3 Electrochemical testing	166
8.3 Results and Discussion	167
8.3.1 Structural analysis and surface characterization	167
8.3.2 Electrochemical performances for lithium ion batteries and	
supercapacitors	172
8.4 Conclusions	179
CHAPTER 9 Mesoporous MnCo <sub>2</sub> O <sub>4</sub> with a flake-like structure as advanced	
electrode materials for lithium ion batteries and supercapacitors	180
9.1 Introduction	180
9.2 Experimental	182
9.2.1 Preparation of flake-like MnCo <sub>2</sub> O <sub>4</sub>	182
9.2.2 Physical Characterization	182
9.2.3 Electrochemical measurements	182
9.3 Results and discussion	183
9.3.1 Structural and morphological analysis	183
9.3.2 Electrochemical properties of like MnCo <sub>2</sub> O <sub>4</sub> for lithium ion batteries and	
supercapacitors	191
9.4 Conclusions	199

CHAPTER 10 Conclusions and future perspective	
10.1 Conclusions	
10.2 Future perspective	201
APPENDIX: NOMENCLATURE	203
REFERENCES	206

# LIST OF TABLES

Table 1.1 Nonaqueous electrolytes for lithium ion batteries	7
Table 1.2 Density, resistivity and operating voltage window for different	
electrolytes	60
Table 2.1 Materials and chemicals	63

#### **LIST OF FIGURES**

Figure 1.1 Schematic illustration of the charge/discharge process involved in a lithium-	ion
Cell	3
Figure 1.2 Voltage versus capacity for electrode materials for the next generation	of
rechargeable Li-based cells	.5

**Figure 1.8** SEM images of the nickel oxide nanocone arrays (Ni NCAs) before and after oxidation. (a, b) SEM images of Ni NCAs deposited on Ni foam; the inset in (a) xiii

**Figure 1.9** (a) Overview SEM image of  $Fe(OH)_x$  nanotubes; (b) SEM image of cracked nanotubes showing exposed interior; (c and d) TEM images of Fe(OH)x nanotubes; (e) wall structure of the nanotubes. (f) Discharge/charge voltage profiles of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanotubes cycled between 0.01–3.0 V at 0.5 C; (b) cycling performance of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanotubes and nanoparticles at 0.5 C. All potentials are with reference to Li/Li<sup>+</sup>.....29

**Figure 1.14** (a) XRD pattern, (b) SEM image, (c and d) TEM images and (e) Cycling performance and coulombic efficiency of the urchin-like NiCo<sub>2</sub>O<sub>4</sub> nanostructures....54

Figure 2.3 Microwave Synthesizer (Model: NOVA-II)......67

**Figure 2.6** (a) A UniLab glove box, manufactured by MBraun, Germany (b) An electrochemistry workstation (CHI660D model) and (c) Neware battery testers.....75

Figure 3.1 XRD patterns of as-synthesized (a)  $\alpha$ -Ni(OH)<sub>2</sub> and (b) NiO nanosheets...81

**Figure 4.1** XRD pattern of spherical β-Ni(OH)<sub>2</sub>.....96

Figure 4.4 TGA curve of as-synthesized spherical β-Ni(OH)<sub>2</sub>.....99

**Figure 4.5** FTIR spectrum of the prepared spherical β-Ni(OH)<sub>2</sub>.....100

**Figure 4.7** (a) Galvanostatic charge/discharge curves at different current densities (1 to  $10 \text{ A g}^{-1}$ ) and (b) CV curves at various scan rates ranging from 2 to 50 mV s<sup>-1</sup> for the spherical  $\beta$ -Ni(OH)<sub>2</sub> electrode in 2 M KOH electrolyte......102

**Figure 4.8** (a) Specific capacitance at various discharge current densities and (b) cycling performance of spherical  $\beta$ -Ni(OH)<sub>2</sub> at a scan rate of 50 mV s<sup>-1</sup>. The charge and discharge curves of  $\beta$ -Ni(OH)<sub>2</sub> for the first ten cycles (the inset in Fig. 8(b))......103

**Figure 5.1** XRD patterns of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (a) small particles (precursor concentration 0.5 mmol) and (b) big particles (precursor concentration 5 mmol).....109

**Figure 5.2** FESEM images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> small particles (precursor concentration 0.5 mmol) (a), (b) low magnification and (c), (d) high magnification......110

particles	(b)	big	particle	s at a	a scan	rate	of 0.1	mV s	s <sup>-1</sup> ir	n the	voltage	range	of	0.01	-3.0
V														1	116

**Figure 5.6** Nitrogen adsorption-desorption isotherms of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (a) small particles (b)

Figure 5.7 Cyclic voltammograms of the electrodes made from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (a) small

Figure 5.8 Discharge/charge profiles of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (a) small particles and (b) big particles at a current density of 100 mA g<sup>-1</sup>, in the potential range of 0.01-3.0 V......117

Figure 5.9 Cycling performances of the electrodes made of small and big particles of  $\alpha$ - $Fe_2O_3$  at the current density of (a) 100 mA g<sup>-1</sup> and (b) 500 mA g<sup>-1</sup>.....118

Figure 5.10 FESEM images of $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> nanoparticles after charge-discharge	cycling
(a), (b) small particles and (c), (d) big particles	119

Figure 5.11 Rate performances of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrodes at different cur	rrent densities
(a) small particles and (b) big particles	121

Figure 5.12 Electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> electrochemical impedance spectra of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	etrode (small and big
particles) (a) fresh cell (b) after 80 cycles	

Figure 6.1 XRD par	tterns of NiCo <sub>2</sub> O <sub>4</sub>	calcinated at	500 °C for	r 3 h (a) n	anoflakes (b)
nanobelts					128

Figure 6.2 FESEM images of the Ni-Co based intermediate (a and b) nanoflakes (low and high magnification), (c and d) nanobelts (low and high magnification)......130

Figure 6.3 FESEM images of porous NiCo <sub>2</sub> O <sub>4</sub> nanc	oflakes (a and b) low magnification,
(c and d) high magnification	

 Figure 6.5
 SEM-EDX pattern of (a) NiCo<sub>2</sub>O<sub>4</sub> nanoflakes and (b) NiCo<sub>2</sub>O<sub>4</sub>

 nanobelts
 133

Figure 6.9 TGA curves for the NiCo<sub>2</sub>O<sub>4</sub> nanoflakes (a) and NiCo<sub>2</sub>O<sub>4</sub> nanobelts (b)..136

Figure	6.13	Rate	perform	nances	for	the	NiCo <sub>2</sub> O	elect	rode a	at v	various	current	densities
(a) nano	oflake	s and	(b) nan	obelts						••••			141

**Figure 7.2** FESEM images of (a) graphene nanosheets, (b)  $MnO_2$  nanosheets, (c) graphene/MnO<sub>2</sub> (1:4 in weight ratio) hybrid nanosheets (low magnification), and (d) graphene/MnO<sub>2</sub> (1:4 in weight ratio) hybrid nanosheets (high magnification)......153

 Figure 7.5 SEM-EDX elemental analysis of graphene/MnO2 (1:4 in weight ratio)

 hybrid nanosheets
 156

 Figure 7.6 Raman spectrum of graphene/MnO2 (1:4 in weight ratio) hybrid

 nanosheets
 156

Figure 7.7	CV curves of graphene/MnO <sub>2</sub> (1:4 in weight ratio) hybrid nat	nosheets at
different sca	an rates of 5 mV s <sup>-1</sup> , 10 mV s <sup>-1</sup> , 20 mV s <sup>-1</sup> , 50 mV s <sup>-1</sup> and 100 mV	/ s <sup>-1</sup> in 1 M
$Na_2SO_4$ solu	ution	157

**Figure 7.8** Charge/discharge profiles of graphene/ $MnO_2$  (1:4 in weight ratio) hybrid nanosheets at the current density of 500 mA g<sup>-1</sup> in 1 M Na<sub>2</sub>SO<sub>4</sub> solution......158

Figure 7.9 Comparison of cycling performance of graphene/MnO<sub>2</sub> hybrid nanosheets with different ratios in 1 M Na<sub>2</sub>SO<sub>4</sub> at the current density of 500 mA  $g^{-1}$ ......159

Figure 7.10 Cycling performance	of MnO <sub>2</sub> nanosheets at the	current density of 500 mA

$g^{-1}$ in 1 M Na <sub>2</sub> S	\$04	
-----------------------------------	------	--

Figure 8.1 XRD	pattern of NiCo <sub>2</sub> O <sub>4</sub>	nanosheets	167
----------------	---	------------	-----

Figure 8.2 FI	ESEM images	of the Ni-C	o based	intermediate	(a) low	magnification	and
(b) high magn	ification					1	68

**Figure 8.9** (a) Rate performance of NiCo<sub>2</sub>O<sub>4</sub> nanosheets......175

**Figure 8.11** (a) Galvanostatic discharge and charge curves at different current densities (2 to 20 A  $g^{-1}$ ) and (b) CV curves at various scan rates ranging from 2 to 20 mV s<sup>-1</sup> for the porous NiCo<sub>2</sub>O<sub>4</sub> nanosheet electrode in 2 M KOH electrolyte......177

Figure 9.1 XRD pattern of flake-like MnCo<sub>2</sub>O<sub>4</sub>......184

**Figure 9.3** FESEM images of mesoporous flake-like  $MnCo_2O_4$  ((a) and (b)) low magnification, ((c) and (d)) high magnification......185

 Figure 9.5 FESEM images (without Na2SO4) (a) low magnification and (b) high magnification.

 187

 Figure 9.6 FESEM images (temperature less than 180 °C) (a) low magnification and (b)

 high magnification

 188

**Figure 9.10** The first three consecutive CV curves of the electrode made from flake-like  $MnCo_2O_4$  in the potential range of 0.01–3.0 V at a scan rate of 0.1 mV s<sup>-1</sup>.....192

 Figure 9.12 Rate capability test for the flake-like MnCo<sub>2</sub>O<sub>4</sub> electrode at different

 current densities
 195

**Figure 9.15** Cycling performance of flake-like  $MnCo_2O_4$  at a scan rate of 50 mV s<sup>-1</sup>. The charge and discharge curves for the first ten cycles (the inset in Fig. 10)......198

#### ABSTRACT

With the increasing demand for energy and growing concern about environmental pollution caused by the enormous consumption of fossil fuels, it is an urgent need of renewable energy and clean energy sources. Development of suitable mobile electronics or energy storage technologies that can be used in electric vehicles would help to address problem. As energy storage devices, lithium-ion batteries have attracted attention due to their high energy density and storage capacity. Supercapacitors have attracted enormous attention due to high power density and long cycle life. The exploration of new electrode materials for lithium-ion batteries and supercapacitors is the focus of research to satisfy the ever-rising demands for better performance including longer cycle life and improved safety. Nanostructured materials exhibit excellent electrochemical performances, and they are regarded as promising materials for highperformance lithium-ion batteries and supercapacitors. In this doctoral study, various nanostructured materials such as, nanosheets, nanospheres, nanobelts, nanoflakes, hybrid nanostructures and mesoporous structures have been successfully synthesized and characterised, using different methods. Their electrochemical properties have also been evaluated by cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectra.

Nickel oxide (NiO) nanosheets have been synthesized, using a simple ethylene glycol mediated hydrothermal method. When evaluated as anode materials for lithium ion batteries, NiO nanosheets exhibited high reversible capacities of 1193 mA h g<sup>-1</sup> at the current density of 500 mA g<sup>-1</sup> with enhanced rate capability and good cycling stability. While as electrode materials for supercapacitors, NiO nanosheets also demonstrated a

xxiv

superior specific capacitance of 999 F  $g^{-1}$  at the current density of 20 A  $g^{-1}$  with excellent cycling performance.

The spherical  $\beta$ -Ni(OH)<sub>2</sub> superstructures was successfully synthesised in a single-step microwave-assisted process, without using any templates. Due to its unique morphology, the prepared  $\beta$ -Ni(OH)<sub>2</sub> electrode displayed a high and specific capacitance of 2147 F g<sup>-1</sup> at a discharge current of 1 A g<sup>-1</sup> with excellent cycling stability (99.5 % capacitance retained after 2000 cycles).

A straight forward microwave reaction was employed to successfully prepare  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles with two different sizes. When used as anode materials for lithium ion batteries of both the materials showed good electrochemical performances. Remarkably, the electrode made of larger particles (200-300 nm) exhibited higher reversible capacity of 1012 mA h g<sup>-1</sup> with better rate capability and excellent cycling stability (88 % retention after 80 cycles) than those of the smaller particles (20-30 nm) (49 % retention after 80 cycles). The better lithium storage properties of the large particles can be attributed to their structural integrity during cycling, which offers adequate spaces to accommodate volume expansion during Li<sup>+</sup> insertion/extraction and shortens the diffusion paths of lithium ions.

Highly porous NiCo<sub>2</sub>O<sub>4</sub> nanoflakes and nanobelts were prepared in two steps; the NiCo<sub>2</sub>O<sub>4</sub> intermediates were first formed by a hydrothermal method and the intermediates were simply thermal treated to the final product. Owing to their unique porous structural features, the NiCo<sub>2</sub>O<sub>4</sub> nanoflakes and nanobelts exhibited high specific capacities of 1033 mA h g<sup>-1</sup> and 1056 mA h g<sup>-1</sup>, respectively, good cycling stability and rate capability. These exceptional electrochemical performances could be attributed to the unique structure of high surface area and void spaces within the surface of

nanoflakes and nanobelts, which provides large contact areas between electrolyte and active materials for electrolyte diffusion and cushions the volume change during charge-discharge cycling.

Graphene/MnO<sub>2</sub> hybrid nanosheets were prepared by the incorporating graphene and  $MnO_2$  nanosheets in ethylene glycol. As electrode materials for supercapacitors, graphene/MnO<sub>2</sub> hybrid nanosheets of different ratios were investigated. The graphene/MnO<sub>2</sub> hybrid nanosheets with a weight ratio of 1:4 (graphene: MnO<sub>2</sub>) delivered the highest specific capacitance of 320 F g<sup>-1</sup>, and exhibited good capacitance retention on 2000 cycles.

Mesoporous NiCo<sub>2</sub>O<sub>4</sub> nanosheets were synthesized by microwave method and applied as electrode materials for lithium ion batteries and supercapacitors. Due to its porous nanosheet structure, the NiCo<sub>2</sub>O<sub>4</sub> electrodes exhibited a high reversible capacity of 891 mA h g<sup>-1</sup> at the current density of 100 mA g<sup>-1</sup> with good rate capability and stable cycling performance. When used as electrode materials for supercapacitors, NiCo<sub>2</sub>O<sub>4</sub> nanosheets demonstrated a specific capacitance of 400 F g<sup>-1</sup> at the current density of 20 A g<sup>-1</sup> and superior cycling stability over 5000 cycles. The excellent electrochemical performance could be ascribed to the thin porous nanosheet structure, which provided high specific surface area to increase electrode-electrolyte contact area and facilitate rapid ion transport.

Mesoporous flake-like Manganese-cobalt composite oxide ( $MnCo_2O_4$ ) was successfully synthesized, using the hydrothermal method. The flake-like  $MnCo_2O_4$  was evaluated as anode materials for lithium ion batteries. It exhibited superior rate capability and good cycling stability with a high reversible capacity of 1066 mA h g<sup>-1</sup>. As electrode materials for supercapacitors,  $MnCo_2O_4$  also demonstrated a high super capacitance of 1487 F  $g^{-1}$  at the current density of 1 A  $g^{-1}$  and superior cycling stability over 2000 charge-discharge cycles.