2011

Advanced materials for Lithium-Ion batteries

Mokhlesur Rahman MD
University of Wollongong

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ADVANCED MATERIALS FOR LITHIUM-ION BATTERIES

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

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

MD. MOKHLESUR RAHMAN

B.Sc. (Hons.), M.Sc.

INSTITUTE FOR SUPERCONDUCTING & ELECTRONIC MATERIALS,
FACULTY OF ENGINEERING

August 2011
CERTIFICATION

I, Md. Mokhlesur Rahman, 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, Australia, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Md. Mokhlesur Rahman

5 August 2011
DEDICATION

For my parents, parents in law, siblings, and beloved wife
ACKNOWLEDGEMENTS

It is my great pleasure to acknowledge the considerable assistances that I have received from the people of the University of Wollongong, Australia, during the course of my doctoral studies. I wish to express my deeply appreciation to my supervisor, Prof. Hua Kun Liu and co-supervisor, Dr. Jiazhao Wang for their encouragement, understanding, invaluable advice, and constant support during my study at University of Wollongong (UOW).

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 Centre of Excellence for Electromaterials Science (ACES), for providing me with appropriate facilities and expertise during the course of my studies.

I would like to thank ISEM, ACES, and the University of Wollongong, for financial support from the Australian Research Council (ARC) under an ARC Centre of Excellence Program (CE0561616) and an ARC Discovery project (DP0987805), by means of University Postgraduate Award (UPA) and Higher Degree Research (HDR) Tuition Fee Exemption Scholarship.

Technical assistance from people at UOW, such as Dr. David Wexler (TEM, FE-SEM), Mr. Darren Attard (FE-SEM), Dr. Konstantin Konstantinov (TGA, BET, and SEM), Dr. Shulei Chou (Electrochemical measurement), Dr. Zhixin Chen (TEM), Dr. Rong Zeng and Mr. Jyotish Chandra Debnath (Magnetic measurements), Mr.
Ron Kinnell and Mr. Robert Morgan (mechanical works), A/Prof. Peter Innis (Raman) and Dr. Germanas Peleckis (XRD) is also highly appreciated. My special thank to Dr. Tania Silver for critical reading of the manuscript and thesis as well.

I would like to thank Ms. Yu-Yuan Zhang and Prof. Xin-Jun Li, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, China and Mr. Xiao-Long Deng and Prof. Ying Li, School of Materials Science and Engineering, Shanghai University, China, for their collaborative research work.

I also wish to thank Prof. Chao Zhang, Prof. Xiaolin Wang, Dr. Md. Shahriar AL Hossain, Dr. Mohd Faiz Hassan, Dr. Zaiping Guo, Dr. Dongqi Shi, Mr. Chao Zhong, Mr. Peng Zhang, Mr. Guodong Du, Mr. Hao Liu, Ms. Lu Lin, Ms. Nurul Indris, Mr. Lukman Noerochim, and Dr. Fábio R. Bento, for helping me or sharing knowledge with me.

Finally, I would like to thank my parents, parents in law, brothers, brothers in law (Mr. Anwar Hossan, Mr. Shamim Ahmed, Mr. Anik) and sisters for their continue support and love, which translates into the strength and guidance path for me during my PhD studies. My heartiest thanks go to my wonderful wife, Mrs. Irin Sultana (Sumi), who is always with me and provides a lot of inspirations to achieve my PhD degree.
TABLE OF CONTENTS

CERTIFICATION...........................................................................................................i
DEDICATION..................................................................................................................ii
ACKNOWLEDGEMENTS...............................................................................................iii
TABLE OF CONTENTS......................................................................................................v
ABSTRACT......................................................................................................................x
NOMENCLATURE..........................................................................................................xv
LIST OF FIGURES.........................................................................................................xix
LIST OF SCHEMES.......................................................................................................xxv
LIST OF TABLES..........................................................................................................xxvi

CHAPTER 1 INTRODUCTION.........................................................................................1

1.1  General Background.............................................................................................1

1.2  Statement of Problem and Solution Approach..................................................2
   1.2.1  Cathode Materials..........................................................................................3
   1.2.2  Anode Materials............................................................................................4
   1.2.3  Approaches for Improving Electrode Performance......................................5

1.3  Significance of Study...........................................................................................9

1.4  Objectives of Research.........................................................................................11

1.5  Thesis Structure................................................................................................12

CHAPTER 2 LITERATURE REVIEW.............................................................................14

2.1  Introduction.........................................................................................................14

2.2  Lithium-ion Rechargeable Batteries...................................................................15

2.3  Fundamentals of Electrochemistry.....................................................................18
   2.3.1  Principle of Reaction Mechanism of Lithium-ion Battery.........................18
CHAPTER 4 NANOCRYSTALLINE POROUS $\alpha$-LiFeO$_2$-C COMPOSITE – AN ENVIRONMENTALLY FRIENDLY CATHODE FOR THE LITHIUM-ION BATTERY

4.1 Introduction.................................................................63
4.2 Materials Synthesis......................................................66
4.3 Physical and Structural Characterization.............................67
4.4 Electrochemical Characterization.......................................72
4.5 Conclusions......................................................................77

CHAPTER 5 ENHANCED LITHIUM STORAGE IN A VO$_2$-MULTIWALL CARBON NANOTUBE MICRO SHEET COMPOSITE PREPARED VIA AN IN-SITU HYDROTHERMAL PROCESS.................................................................78
5.1 Introduction...................................................................78
5.2 Materials Synthesis.......................................................80
5.3 Physical and Structural Characterization...........................81
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.4</td>
<td>Electrochemical Characterization</td>
<td>143</td>
</tr>
<tr>
<td>8.5</td>
<td>Conclusions</td>
<td>150</td>
</tr>
<tr>
<td>9</td>
<td>SPRAY PYROLYZED NiO-C NANOCOMPOSITE AS AN ANODE MATERIAL FOR THE LITHIUM-ION BATTERY WITH ENHANCED CAPACITY RETENTION</td>
<td>151</td>
</tr>
<tr>
<td>9.1</td>
<td>Introduction</td>
<td>151</td>
</tr>
<tr>
<td>9.2</td>
<td>Materials Synthesis</td>
<td>153</td>
</tr>
<tr>
<td>9.3</td>
<td>Structure and Morphology Analysis</td>
<td>154</td>
</tr>
<tr>
<td>9.4</td>
<td>Electrochemical Characterization</td>
<td>158</td>
</tr>
<tr>
<td>9.5</td>
<td>Conclusions</td>
<td>164</td>
</tr>
<tr>
<td>10</td>
<td>GENERAL DISCUSSION AND OUTLOOK</td>
<td>165</td>
</tr>
<tr>
<td>10.1</td>
<td>General Discussion</td>
<td>165</td>
</tr>
<tr>
<td>10.1.1</td>
<td>Cathode Materials</td>
<td>166</td>
</tr>
<tr>
<td>10.1.2</td>
<td>Anode Materials</td>
<td>168</td>
</tr>
<tr>
<td>10.2</td>
<td>Outlook</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>REFERENCES</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>APPENDIX A: LIST OF PUBLICATIONS</td>
<td>201</td>
</tr>
<tr>
<td></td>
<td>APPENDIX B: RECEIVED AWARDS</td>
<td>206</td>
</tr>
</tbody>
</table>
ABSTRACT

Lithium-ion batteries are in high demand for the large spectrum of applications encompassing portable, industrial, and traction/automotive categories. High-performance lithium-ion batteries must satisfy stringent requirements, including large reversible capacity, high rate capability, and long-term cycle life, with advanced materials providing the main solutions to these issues. Improved battery performance depends on the development of materials for the various battery components, with the key aspect improving the performance of the active materials used to fabricate the cathode and anode. The use of nanostructured and conductive composite materials is designed to enhance both ion transport and electron transport, and to promote liquid electrolyte diffusion into the bulk material by shortening the diffusion lengths of ions and increasing the conductivity within the whole electrode. In this doctoral work, several nanostructured and conductive composite materials were examined and characterized for possible application as electrode for lithium-ion batteries. In this respect, nanocrystalline porous \( \alpha \)-LiFeO\(_2\) carbon composite, VO\(_2\)(B)-multiwall carbon nanotube microsheet composite, carbon and iron phosphide incorporated LiFePO\(_4\) composite, amorphous carbon coated Li\(_4\)Ti\(_5\)O\(_{12}\)-TiO\(_2\) composite, nanostructured Co\(_3\)O\(_4\) materials, and carbon coated NiO nanocomposite were investigated.

Porous \( \alpha \)-LiFeO\(_2\)-C nanocomposites with high surface area were synthesized using the molten salt method, which was followed by a carbon coating process. For comparison, nanocrystalline \( \alpha \)-LiFeO\(_2\) was also investigated. Electrochemical measurements demonstrated that the \( \alpha \)-LiFeO\(_2\)-C nanocomposites delivered a significantly higher reversible capacity compared to pure \( \alpha \)-LiFeO\(_2\) and excellent
cycling stability (230 mAh g\(^{-1}\) at 0.5 C after 100 cycles) when using a selected binder, sodium carboxymethyl cellulose (CMC). Even at the high rate of 3 C, the electrode showed more than 50% of its capacity at low rate (0.1 C). The key features of the synthesis method are very simple and easily scaled up, involving only low temperature treatment. Since this method does not require the use of high temperature, the fabrication process is also energy saving. So, it is believed that the \(\alpha\)-LiFeO\(_2\)-C nanocomposite can be used as a novel cathode material in lithium-ion batteries, with significant advantages in terms of environmental friendliness, high capacity, good cycling stability, and high-rate capability, which can lead to a future generation of lithium-ion batteries capable of satisfying the new demands on energy storage devices.

VO\(_2\)(B)-multiwall carbon nanotube (MWCNT) microsheet composite was synthesized via an in situ hydrothermal process. Electrochemical tests showed that the VO\(_2\)(B)-MWCNT composite cathode features cycling stability and high discharge capacity (177 mAh g\(^{-1}\)) in the voltage range of 2.0-3.25 V at 1 C with a capacity retention of 92% after 100 cycles. The electrochemical impedance spectra (EIS) indicate that the VO\(_2\)(B)-MWCNT composite electrode has very low charge-transfer resistance compared with pure VO\(_2\)(B), indicating the enhanced ionic conductivity of the VO\(_2\)(B)-MWCNT composite. The stable cyclic retention is attributed to the fact that the MWCNTs enhance the electronic transport and reduce the resistance within the VO\(_2\)(B) nanosheets. Moreover, the VO\(_2\)(B)-MWCNT composite can prevent the aggregation of active materials and accommodate the large volume variation during charge/discharge processes because of the very good
mechanical properties provided by the MWCNTs. This work provides a simple and feasible platform for further advances in CNT-based composites.

Carbon and iron phosphide incorporated LiFePO$_4$ composite was achieved by using a simple ultra-fast solvent assisted manual grinding method, combined with solid state reaction, which can replace the time-consuming high-energy ball-milling method. The electrochemical performance was outstanding, especially at high C rates. The composite cathode was found to display specific capacity of 167 mAh g$^{-1}$ at 0.2 C and 146 mAh g$^{-1}$ at 5 C after 100 cycles, respectively. At the high current density of 1700 mA g$^{-1}$ (10 C rate), it exhibited long-term cycling stability, retaining around 96% (131 mAh g$^{-1}$) of its original discharge capacity beyond 1000 cycles, which can meet the requirements of a lithium-ion battery for large-scale power applications. The results have demonstrated that the fabrication of samples with strong and extensive antiferromagnetic (AFM) and ferromagnetic (FM) interface coupling of LiFePO$_4$/Fe$_2$P provides a versatile strategy toward improving the electrochemical properties of LiFePO$_4$ materials and also opens up a new window for material scientists to further study the new exchange bias phenomenon that is involved and its ability to enhance the electrochemical performance of lithium-ion battery electrode.

High grain boundary density, dual phase Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite was synthesized by a simple molten salt method, followed by a carbon coating process. For comparison, Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$-TiO$_2$ were also investigated. The Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite electrode yielded good electrochemical performance in terms of high capacity (166 mAh g$^{-1}$ at a current density of 0.5 C), good cycling stability, and excellent rate capability (110 mAh g$^{-1}$ at a current density
of 10 C up to 100 cycles). The excellent electrochemical performance of the carbon coated nanocomposite could be related to the combined effects of the nanostructure, the carbon layering on the nanoparticles, and the grain boundary interface areas embedded in a carbon matrix, which would contribute together to enhance structural stability and improve lithium storage kinetics by reducing the traverse time of electrons and lithium ions, and also stabilizing the solid electrolyte interphase (SEI) film, which would result in improved rate and cycling performance.

High pulsed magnetic field and an aging technique were used for the synthesis of nanocrystalline Co$_3$O$_4$ via the hydrothermal method. The pulsed magnetic field processing produces a more compact and smooth surface composed of Co$_3$O$_4$ microspheres that each consist of numerous nanograins. The aging technique introduced into the Co$_3$O$_4$ synthesis process results in large Co$_3$O$_4$ hollow spheres consisting of a large quantity of nanospheres. So, both processes were proved to be effective approaches in material processing. Electrochemical measurements showed that Co$_3$O$_4$ materials prepared by the aging technique (Co$_3$O$_4$-Aging) yielded the best electrochemical performance compared with the other samples. In view of this hollow sphere structural arrangement, it is proposed that redox reactions with Li could promote more efficient and easier lithium diffusion than in the other two samples. Thus, the morphology affects not only the discharge capacity, but also the cycling stability of Li-ion batteries.

NiO-C nanocomposite, with spherical shell-like clusters of nanosized NiO particles surrounded by amorphous carbon, was synthesised by a spray pyrolysis technique.
Electrochemical tests demonstrated that the NiO-C nanocomposites exhibited better capacity retention (382 mAh g\(^{-1}\) for 50 cycles) than that of the pure NiO (141 mAh g\(^{-1}\) for 50 cycles). The enhanced capacity retention can be mainly attributed to the NiO-C composite structure, composed of NiO nanoparticles surrounded by carbon, which can accommodate the volume changes during charge-discharge and improve the electrical conductivity between the NiO nanoparticles. To verify the effects of the amorphous carbon network on the electrical conductivity of the NiO-C nanocomposites, AC impedance measurements were conducted. The diameter of the semicircle in the medium frequency region for the NiO-C electrode is much smaller than that of the NiO electrode, revealing lower charge transfer resistance. This indicates that the electronic conductivity of NiO was improved after the incorporation of carbon.
### NOMENCLATURE

#### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full name</th>
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<tbody>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
</tr>
<tr>
<td>AB</td>
<td>Acetylene black</td>
</tr>
<tr>
<td>AFM</td>
<td>Antiferromagnetic</td>
</tr>
<tr>
<td>AIIM</td>
<td>Australian Institute for Innovative Materials</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmet-Teller</td>
</tr>
<tr>
<td>BS</td>
<td>Backscattered</td>
</tr>
<tr>
<td>BSE</td>
<td>Back-scattered electrons</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>CMC</td>
<td>Sodium carboxymethyl cellulose</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CPE</td>
<td>Constant phase-angle element</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>DEMS</td>
<td>Differential electrochemical mass spectroscopy</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EB</td>
<td>Exchange bias</td>
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xv
<table>
<thead>
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<th>Full name</th>
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<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>EDX/EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EV</td>
<td>Electric vehicle</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>FM</td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-width at half-maximum</td>
</tr>
<tr>
<td>GIC</td>
<td>Graphite intercalation compounds</td>
</tr>
<tr>
<td>HEV</td>
<td>Hybrid electric vehicle</td>
</tr>
<tr>
<td>HR-EELS</td>
<td>High resolution electron energy loss spectroscopy</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscopy</td>
</tr>
<tr>
<td>IPRI</td>
<td>Intelligent Polymer Research Institute</td>
</tr>
<tr>
<td>ISEM</td>
<td>Institute for Superconducting and Electronic materials</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint committee on powder diffraction standards</td>
</tr>
<tr>
<td>LIBs</td>
<td>Lithium-ion batteries</td>
</tr>
<tr>
<td>LiPF₆</td>
<td>Lithium hexafluorophosphate</td>
</tr>
<tr>
<td>MO</td>
<td>Metal oxide</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotube</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>NMP</td>
<td>1-methyl-2-pyrrolidinone</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>PHEVs</td>
<td>Plug-in hybrid electric vehicles</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full name</td>
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<tr>
<td>--------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>PPMS</td>
<td>Physical properties measurement system</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>RTIL</td>
<td>Room temperature ionic liquid</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>SBR</td>
<td>Styrene-butadiene rubber</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>vDW</td>
<td>van der Waals</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<thead>
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<th>Symbol</th>
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<th>Unit</th>
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<tr>
<td>$\theta$</td>
<td>Peak position of XRD</td>
<td>°</td>
</tr>
<tr>
<td>$C-rate$</td>
<td>Charged or discharged rate</td>
<td>mA</td>
</tr>
<tr>
<td>$E$</td>
<td>Electrode potential</td>
<td>V</td>
</tr>
<tr>
<td>$ED$</td>
<td>Energy density</td>
<td>Wh L$^{-1}$</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant = 96485</td>
<td>C</td>
</tr>
<tr>
<td>$I$</td>
<td>Current</td>
<td>mA</td>
</tr>
<tr>
<td>Symbol</td>
<td>Name</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>$K$</td>
<td>Shape factor of the average crystallite</td>
<td>-</td>
</tr>
<tr>
<td>$L$</td>
<td>Crystal size</td>
<td>nm</td>
</tr>
<tr>
<td>$m$</td>
<td>Active material weight</td>
<td>g</td>
</tr>
<tr>
<td>$PD$</td>
<td>Power density</td>
<td>W L$^{-1}$</td>
</tr>
<tr>
<td>$Q_c$</td>
<td>Specific charge capacity</td>
<td>mAh g$^{-1}$</td>
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<tr>
<td>$Q_d$</td>
<td>Specific discharge capacity</td>
<td>mAh g$^{-1}$</td>
</tr>
<tr>
<td>$Q_{TSC}$</td>
<td>Theoretical specific capacity</td>
<td>mAh g$^{-1}$</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>Charge transfer resistant</td>
<td>Ω</td>
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<tr>
<td>$R_Ω$</td>
<td>Ohmic resistance</td>
<td>Ω</td>
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<tr>
<td>$SE$</td>
<td>Specific energy</td>
<td>Wh kg$^{-1}$</td>
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<tr>
<td>$SP$</td>
<td>Specific power</td>
<td>W kg$^{-1}$</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>h or s</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K or °C</td>
</tr>
<tr>
<td>$W$</td>
<td>Warburg impedance</td>
<td>Ω</td>
</tr>
<tr>
<td>$Z_{imag}$</td>
<td>Imaginary part of the impedance</td>
<td>Ω</td>
</tr>
<tr>
<td>$Z_{real}$</td>
<td>Real part of the impedance</td>
<td>Ω</td>
</tr>
<tr>
<td>$ΔG$</td>
<td>Gibbs free energy</td>
<td>-</td>
</tr>
<tr>
<td>$η$</td>
<td>Coulombic efficiency</td>
<td>%</td>
</tr>
<tr>
<td>$λ$</td>
<td>X-ray wavelength</td>
<td>Å</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 2.1  Comparison of the different battery technologies in terms of specific power and specific energy density.  

Figure 2.2  The operating principle of the lithium-ion battery during charging and discharging.  

Figure 2.3  Potential vs. capacity for positive and negative electrode materials presently used or under serious consideration for the next generation of rechargeable Li-based cells.  

Figure 2.4  Two-dimensional crystal structure of LiMnO₂.  

Figure 2.5  Extended structure of LiMn₂O₄, shown with MnO₆ polyhedra with larger lattice parameters, where the Li ions can diffuse more freely through the structure.  

Figure 2.6  Ordered-olivine structure of LiFePO₄: (a) ball-stick model, (b) depiction of polyhedral connectivity.  

Figure 3.1  The overall scheme of experimental investigations.  

Figure 3.2  Schematic diagram of the spray pyrolysis process, with inset illustrating oxides-carbon nanocomposite formation.  

Figure 3.3  Reflection of X-rays from lattice planes according to Bragg’s law.  

Figure 3.4  A schematic diagram of the coin-type cell, CR2032, used at ISEM.  

Figure 3.5  Typical electrochemical impedance spectroscopy (EIS) curve of lithium-ion battery system.  

Figure 4.1  X-ray diffraction patterns of α-LiFeO₂ and α-LiFeO₂-C nanocomposite.  

Figure 4.2  Raman spectrum obtained from α-LiFeO₂-C nanocomposite (a) and TGA analysis of α-LiFeO₂ and α-LiFeO₂-C nanocomposite (b).  

Figure 4.3  FE-SEM images of α-LiFeO₂ and α-LiFeO₂-C nanocomposite: (a) low magnification image of large agglomerated clusters of α-LiFeO₂; (b) high magnification image.
image of clusters composed of numerous nanoparticles; (c) low magnification image of $\alpha$-LiFeO$_2$-C, consisting of numerous nanoclusters; (d) high-resolution image of individual nanocluster of $\alpha$-LiFeO$_2$-C, which is composed of very tiny nanoparticles joined by a porous architecture. The inset shows the same area at higher magnification.

Figure 4.4 (a) TEM image with its corresponding SAED pattern (inset), and (b) HRTEM image of the $\alpha$-LiFeO$_2$ sample; (c) TEM and (d) HRTEM images of the $\alpha$-LiFeO$_2$-C sample.

Figure 4.5 Electrochemical performance of $\alpha$-LiFeO$_2$ and $\alpha$-LiFeO$_2$-C nanocomposite electrodes: (a, b) galvanostatic charge-discharge profiles at 0.5 C for selected cycles; (c) cycling stability up to 100 cycles at 0.5 C; (d) consecutive cycling behaviour at different rates; (e) electrochemical impedance spectra after charge/discharge for 5 cycles.

Figure 5.1 X-ray diffraction patterns of VO$_2$(B) (a) and VO$_2$(B)-MWCNT microsheet composite (b).

Figure 5.2 TGA curves of MWCNT, VO$_2$(B), and VO$_2$(B)-MWCNT microsheet composite.

Figure 5.3 FE-SEM images of VO$_2$(B) and VO$_2$(B)-MWCNT microsheet composite: (a) low magnification image of large bundles of VO$_2$(B) nanosheets; (b) high magnification image of an individual bundle composed of numerous single nanosheets; (c) low magnification image of VO$_2$(B)–MWCNT composite, consisting of bundles of nanosheets of VO$_2$(B) with MWCNTs underneath; (d) high-resolution image of VO$_2$(B)–MWCNT composite, which is composed of numerous nanosheets along with MWCNTs attached to the surfaces of the nanosheets.

Figure 5.4 Typical TEM images of VO$_2$(B)-MWCNT microsheet composite: (a) image of the sample; (b) image of an individual VO$_2$(B) nanosheet and its SAED pattern (inset); (c) HRTEM image showing lattice fringes of an individual
VO$_2$(B) nanosheet from (b).

**Figure 5.5** Electrochemical performances of VO$_2$(B) and VO$_2$(B)-MWCNT electrodes at 1.0-3.25 V: (a) cyclic voltammograms for the initial cycle at a scan rate of 0.1 mV s$^{-1}$; (b, c) galvanostatic charge-discharge voltage profiles at 1 C for selected cycles; (d) cyclic performance up to 100 cycles at 1 C; (e) consecutive cyclic behaviour at different rates; (f) electrochemical impedance spectra after charge/discharge and the equivalent circuit (inset).

**Figure 5.6** Cycling behaviour of VO$_2$(B)-MWCNT electrode at discharge cut-off voltages of 1.5 V and 2.0 V. The current density applied was the 1 C rate.

**Figure 6.1** XRD patterns of the samples: (a) Bare-LiFePO$_4$ (0 wt.%C), (b) LiFePO$_4$-Fe$_2$P-C (1) (5.8 wt.%C), (c) LiFePO$_4$-Fe$_2$P-C (2) (10.4 wt.%C), and (d) LiFePO$_4$-Fe$_2$P-C (3) (19.9 wt.%C).

**Figure 6.2** TGA curves of bare-LiFePO$_4$ and LiFePO$_4$-Fe$_2$P-C composites powders estimated to contain (1) 5.8 wt.%C, (2) 10.4 wt.%C, and (3) 19.9 wt.%C.

**Figure 6.3** Secondary electron FESEM micrographs of (a) Bare-LiFePO$_4$, (b) LiFePO$_4$-Fe$_2$P-C (1), (c) LiFePO$_4$-Fe$_2$P-C (2), and (d) LiFePO$_4$-Fe$_2$P-C (3).

**Figure 6.4** High contrast backscattered (BS) FESEM micrographs of (a) Bare-LiFePO$_4$, (b) LiFePO$_4$-Fe$_2$P-C (1), (c) LiFePO$_4$-Fe$_2$P-C (2), and (d) LiFePO$_4$-Fe$_2$P-C (3).

**Figure 6.5** High contrast back-scattered FESEM image of LiFePO$_4$-Fe$_2$P-C (1) (5.8 wt.% C) composite powders (inset) with corresponding EDS spectra of the marked regions (a, b), and FESEM image showing the porous conductive architecture of the sample (c).

**Figure 6.6** The magnetic hysteresis loop measured at 5 K between ±10000 Oe after field cooling at 500 Oe.

**Figure 6.7** TEM and HRTEM images obtained from (a) bare-LiFePO$_4$
and (b)-(f) LiFePO₄-Fe₂P-C (1) (5.8 wt.%C) composite: 
(c)-(e) study of a region containing LiFePO₄ surrounded by 
a 3 nm carbon-rich layer, marked C, (f) HRTEM image of 
separate LiFePO₄ crystal surrounded by carbon-rich layer 
marked C. Inset is a fast Fourier transform of the image, 
and the orientation is close to (212).

**Figure 6.8** Short-term cycle life performance of all the sample 
electrodes (a), long-term cycle life performance beyond 
1000 cycles at 10 C for the LiFePO₄-Fe₂P-C (1) electrode 
(b), the 100th cycle galvanostatic charge-discharge profiles 
at different current densities from 0.2 to 10 C between 4.3 
and 2.5 V for LiFePO₄-Fe₂P-C (1) electrode (c), cyclic 
voltammograms of LiFePO₄-Fe₂P-C (1) electrode at a scan 
rate of 0.1 mV s⁻¹ for the first 5 cycles (d), EIS spectra of 
the bare-LiFePO₄ and LiFePO₄-Fe₂P-C electrodes, and the 
equivalent circuit (inset) (e).

**Figure 7.1** X-ray diffraction patterns of (a) Li₄Ti₅O₁₂, (b) Li₄Ti₅O₁₂-TiO₂, and (c) Li₄Ti₅O₁₂-TiO₂-C nanocomposite.

**Figure 7.2** Raman spectrum obtained from Li₄Ti₅O₁₂-TiO₂-C nanocomposite (a) and TGA curves of Li₄Ti₅O₁₂, 
Li₄Ti₅O₁₂-TiO₂, and Li₄Ti₅O₁₂-TiO₂-C nanocomposite (b).

**Figure 7.3** TEM results obtained from Li₄Ti₅O₁₂ calcined at 300 °C (a-c), Li₄Ti₅O₁₂-TiO₂ calcined at 400 °C (d-f), and 
Li₄Ti₅O₁₂-TiO₂-C calcined at 400 °C (g-i). Insets: selected 
area diffraction patterns in (a) and (d) contain reflections 
consistent with Li₄Ti₅O₁₂ (L) and anatase TiO₂ (A).

**Figure 7.4** (a) TEM image of Li₄Ti₅O₁₂-TiO₂-C sample and (b) semi-
quantiative EDS analysis of relatively large region of (a).

**Figure 7.5** Cyclic voltammograms of (a) Li₄Ti₅O₁₂, (b) Li₄Ti₅O₁₂-TiO₂, and (c) Li₄Ti₅O₁₂-TiO₂-C nanocomposite electrodes 
at a scan rate of 0.05 mVs⁻¹ between 1.0 and 2.5 V.

**Figure 7.6** The initial galvanostatic charge-discharge profiles of (a) 
Li₄Ti₅O₁₂, (b) Li₄Ti₅O₁₂-TiO₂, and (c) Li₄Ti₅O₁₂-TiO₂-C
electrodes at different current densities from 0.5 to 10 C between 2.5-1.0 V; (d) cyclic performance beyond 100 cycles at 10 C, (e) coulombic efficiency, and (f) rate capability (0.5-10 C) of the Li$_4$Ti$_5$O$_{12}$, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C electrodes, respectively.

**Figure 7.7** Nyquist plots for the Li$_4$Ti$_5$O$_{12}$, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C electrodes after charge-discharge and the equivalent circuit shown in the inset.

**Figure 8.1** XRD patterns of Co$_3$O$_4$ obtained at (a) 180 °C and 0 T magnetic field (Co$_3$O$_4$-0T), (b) 180°C and 4 T magnetic field (Co$_3$O$_4$-4T), and (c) with 12 hours aging time followed by 0 T processing at 180 °C (Co$_3$O$_4$-Aging).

**Figure 8.2** FE-SEM images of Co$_3$O$_4$ samples obtained at 180 °C and 0 T magnetic field (Co$_3$O$_4$-0T) (a, b); 180 °C and 4 T magnetic field (Co$_3$O$_4$-4T) (c, d).

**Figure 8.3** FE-SEM images of Co$_3$O$_4$ hollow sphere obtained with 12 hours aging time followed by 0 T processing at 180 °C for 10 hours (Co$_3$O$_4$-Aging): (a) low magnification image of the large hollow sphere; (b) high magnification image of the marked region of (a); (c) high magnification image of the spherical nanoparticles attached to the hollow sphere surface; (d) high-resolution image of the marked region of (b), which is composed of numerous spherical nanoparticles.

**Figure 8.4** Cyclic voltammograms of (a) Co$_3$O$_4$-0T, (b) Co$_3$O$_4$-4T, and (c) Co$_3$O$_4$-Aging electrodes at a scan rate of 0.1 mVs$^{-1}$ between 0.01 and 3.0 V.

**Figure 8.5** Typical charge-discharge curves at selected cycles of (a) Co$_3$O$_4$-0T, (b) Co$_3$O$_4$-4T, and (c) Co$_3$O$_4$-Aging electrodes at a current density of 30 mA g$^{-1}$ between 0.01 and 3.0 V.

**Figure 8.6** Cycling behaviour of Co$_3$O$_4$-0T, Co$_3$O$_4$-4T, and Co$_3$O$_4$-Aging electrodes at a current density of 100 mA g$^{-1}$.

**Figure 9.1** XRD patterns: (a) NiO powders and (b) NiO-C
Figure 9.2  TEM-EDS analysis of NiO-C nanocomposite: (a) low magnification image of spherical clusters of nanocrystals with indexed selected area electron diffraction pattern (inset) obtained from large cluster; (b) EDS output obtained from local region of large cluster in (a) located over a hole in the holey carbon support film; (c) and (d), high magnification images; (e) high resolution image of region of (d) in vicinity of holey carbon support film; (f) high resolution image and associated diffractogram (inset) showing NiO crystal with strong contrast, consistent with NiO (111) planes ($d_{111} \approx 0.24$ nm).

Figure 9.3  SEM images for (a) NiO powders, (b) NiO-C nanocomposite, and corresponding EDS mappings for image (b) as follows: (c) Ni mapping, (d) O mapping, and (e) C mapping.

Figure 9.4  TGA curves of NiO powders and NiO-C nanocomposite.

Figure 9.5  Galvanostatic discharge-charge voltage profiles of (a) NiO and (b) NiO-C electrodes at 100 mA g$^{-1}$ current density from 0.01-3.0 V for selected cycles.

Figure 9.6  Cyclic voltammograms of (a) NiO and (b) NiO-C electrodes measured between 0.01 and 3.0 V at a scan rate of 0.1 mV s$^{-1}$.

Figure 9.7  Capacity retention behaviour for NiO and NiO-C electrodes vs. cycle number from 0.01 to 3 V at different current densities: (a) 100 mA g$^{-1}$, (b) 400 mA g$^{-1}$, and (c) 700 mA g$^{-1}$.

Figure 9.8  Electrochemical impedance spectra, presented as Nyquist plots for the NiO and NiO-C electrodes.
LIST OF SCHEMES

Scheme 5.1  Schematic possible model of synthetic procedure: (a) mixed raw materials; (b) layered VO$_2$(B) with MWCNTs after hydrothermal reduction; (c) agglomerated nanocrystal seeds form sheets; (d) sheets tend further to split to form nanosheets; (e) bundles of nanosheets and MWCNTs attached to the surface and underneath the nanosheets.

Scheme 7.1  Schematic model of synthetic procedure: (a) mixed raw materials heated at 400 °C for 3 h, (b) solid molten salts and Li$_4$Ti$_5$O$_{12}$-TiO$_2$ nanoparticles with amorphous carbon, (c) Li$_4$Ti$_5$O$_{12}$-TiO$_2$ nanocrystals covered with thin layer of amorphous carbon and grain boundary interface areas embedded in carbon matrix.
LIST OF TABLES

Table 3.1 List of chemicals and materials used in this thesis. 43

Table 7.1 Specific surface areas and approximate crystal sizes of Li$_4$Ti$_5$O$_{12}$, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C samples. 120

Table 8.1 Cyclic performances of Co$_3$O$_4$-0T, Co$_3$O$_4$-4T, and Co$_3$O$_4$-Aging electrodes measured at a current density of 100 mA g$^{-1}$. 148

Table 8.2 Comparison of the electrochemical properties of Co$_3$O$_4$ materials investigated in this chapter with those of Co$_3$O$_4$ materials reported in the literature. 149
CHAPTER 1 INTRODUCTION

1.1 General Background

In the new century, clean and renewable energy storage devices have become the focus of both the power industry and research development. Fossil fuels have been and still are the major energy source, but society’s current individual mobility behaviour is creating a plethora of looming problems, such as fossil carbon intensity and the concomitant consequences regarding fossil resource supplies and emissions of pollutants such as nitrogen oxides (NO\textsubscript{x}), sulphur dioxide (SO\textsubscript{2}), and particulate matter [Liu and Cao, 2010; Notter et al., 2010]. Despite the prevalence of fossil fuels, lithium ion batteries have been one of the major power sources for small electronic devices since the last century. However, the current commercial lithium-ion batteries are still not good enough to completely satisfy the public need, and theoretically, there is much room for improvement. Apart from automotive applications, battery-operated devices are changing dramatically and are becoming more demanding and sophisticated with much room for future development. With the rapid advances in electronics and the increasing demand for clean sustainable energy, lithium-ion batteries with higher energy density, higher power density, and better cyclic stability are needed. Obviously, an improved electrochemical performance can be achieved in this system by developing electrode materials, as the electrode materials hold the key to fundamental advances in energy conversion and storage in the lithium-ion battery system, where electrochemical reactions take place [Arico et al., 2005]. In this doctoral work, research has been focused on developing electrode materials with
high discharge capacity, large charge/discharge rates, and long life cycles. To achieve these goals, considerable effort has been devoted to fabricating composites and nanostructured materials that best facilitate the intercalation behaviour of lithium ions and thus provide effective information for further research in the future.

1.2 Statement of Problem and Solution Approach

A lithium-ion battery, just like other types of batteries, consists of three major components: an anode, a cathode, and the electrolyte between them, and works by converting chemical potential to electric energy through Faradaic reactions, which include the heterogeneous charge transfer process occurring at the surface of an electrode [Winter and Brodd, 2004]. Advances in battery technology have been relying on the development and use of different types of materials for electrodes and electrolytes, and thus, with different electrochemical reactions [Adachi et al., 1996]. Since the electronic conductivity and viscosity of the electrode materials are very low in the lithium-ion battery, it is necessary to add an electrical conductor and a binder into the active material for producing electrodes. In spite of their commercial success in consumer electronics, such as laptop computers, digital cameras, and cellular phones, current lithium ion batteries are not good enough for use as power supplies for electric vehicle (EV) and hybrid electric vehicle (HEV), which require high energy and power density. To meet these demands, the development of rechargeable lithium-ion batteries has been the focus of considerable research, and active research is continuing on all aspects of lithium-ion batteries, i.e., anodes, cathodes, electrolytes, and cell construction. However, cathode and anode materials have been the central focus of this doctoral work.
1.2.1 Cathode Materials

Cathodes are very indispensable and a key part of lithium-ion batteries (LIBs), and great research efforts have been devoted to cathode materials in order to decrease costs and to address safety issues [Li et al., 2009]. Among all the cathode materials, the most widely studied systems include compounds with three-dimensional (LiMn$_2$O$_4$, LiFePO$_4$) or layered (LiMO$_2$ with M = Co, Ni) structures which exhibit good topotactic insertion/deinsertion properties [Amatucci and Tarascon, 2002]. Although LiCoO$_2$ is still being used as a successful cathode material in most commercial lithium-ion batteries, its raw materials are less available, more toxic, and more costly than other transition metals, such as manganese, nickel, and iron. In addition, LiCoO$_2$ is not as stable as other potential electrode materials and can undergo performance degradation or failure when overcharged [Belov and Yang, 2008a; Belov and Yang, 2008b; Doh et al., 2008]. In an attempt to develop alternative cathodes, layered LiNiO$_2$, spinel LiMn$_2$O$_4$, and olivine LiFePO$_4$ have become attractive, since Ni, Mn, and Fe are less expensive and less toxic than Co. However, LiNiO$_2$ suffers from structural changes, thermal runaway, and difficulties in synthesizing it as an ordered material with all Ni$^{3+}$ [Nakai and Nakagome, 1998; Hirano et al., 1995; Dutta et al., 1992]. Furthermore, LiMn$_2$O$_4$ suffers from severe capacity fade at elevated temperatures, with several factors, such as manganese dissolution, Jahn-Teller distortion, loss of crystallinity, and development of microstrain during cycling, reported to be responsible [Thackeray et al., 1998; Huang et al., 1999; Shin and Manthiram, 2002]. Also, LiMn$_2$O$_4$ has a limited capacity of $< 120$ mAh g$^{-1}$, which is less than that of LiCoO$_2$ (140 mAh g$^{-1}$). Olivine-like LiFePO$_4$ appears to be an interesting positive electrode material for lithium-ion batteries
because of its low toxicity, low cost, long cycle life, and cell safety. However, a major limitation of this material, which prevents it from being used in large-scale applications, is its poor high-rate performance, owing to its low electronic conductivity and low ionic diffusion coefficient [Huang et al., 2001; Chen and Dahn, 2002].

1.2.2 Anode Materials

As is well known, the ‘standard’ anode for a lithium ion battery is a carbonaceous compound, either graphite or coke [Megahed and Scrosati, 1994]. The main motivations to choose these materials are the low cost and the low operational voltage. The carbonaceous anode is coupled with a high voltage cathode, e.g. LiCoO$_2$, in order to obtain a battery operating in the 4 V range. In addition, the mechanism of lithium intercalation in the so-called ‘soft’ anodes, i.e. graphite or graphitizable carbons, is well known: It develops through well-identified, reversible stages, corresponding to progressive intercalation within discrete graphene layers, to reach the formation of LiC$_6$, with a maximum theoretical capacity of 372 mAh g$^{-1}$ [Scrosati, 2000]. However, the graphite anode has the disadvantages of low energy density, safety issues related to lithium deposition, and a significant irreversible loss in capacity after only one cycle [Shukla and Kumar, 2008; Winter et al., 1998]. Thus, new anode materials with high theoretical capacity (including Si (3579 mAh g$^{-1}$), Sn (992 mAh g$^{-1}$), and transition metal oxides (500-1000 mAh g$^{-1}$)), low cost, enhanced safety, and long cycle life, have been considered the most promising alternative anode materials. However, the main challenge for the implementation of such anodes is their large volume change during lithium insertion.
and extraction. The electrode suffers cracking and crumbling, and consequent loss of interparticle contact [Winter et al., 1998; Lee et al., 2001], resulting in the loss of capacity. In order to resolve the safety issues, spinel Li$\text{4}$$\text{Ti}_5\text{O}_{12}$ has been demonstrated as a potential candidate for the anode electrode material in high power lithium-ion batteries for HEV [Bai et al., 2008]. One of its most important properties is that its lattice parameters are almost unchanged when lithium ions are inserted/extracted, but it also suffered from poor rate capability due to low electronic conductivity.

### 1.2.3 Approaches for Improving Electrode Performance

In attempts to improve the energy storage capacity, rate capability, and cycling stability of electrodes, several strategies have been developed to reduce the detrimental effects of large volume variation and to alleviate the side reaction with electrolyte. These approaches are discussed below:

**Nanostructured electrodes**

Nanostructured materials lie at the heart of fundamental advances in efficient energy storage and/or conversion, in which surface processes and transport kinetics play determining roles. Nanoscale materials are endowed with unusual mechanical, electrical and optical properties by confining the dimensions of such materials, and the overall behaviours of nanostructured materials exhibit combinations of bulk and surface properties [Cao, 2004]. The lithium ion battery field is one of a number that have benefited from the introduction of nanostructures: the application of nanostructured electrodes has significantly improved the lithium ion intercalation
capability, e.g. storage capacity, intercalation rate, and cyclic stability [Takahashi et al., 2004; Bruce, 2008]. Considering the liquid/solid interface reaction characteristic of lithium ion intercalation, followed by diffusion into the electrode bulk, it is reasonable to expect that a large surface area and short lithium ion diffusion path can ensure complete Faradaic reaction at the interface and facilitate the diffusion into the bulk. Thus nanostructured electrodes which meet these requirements are highly favourable as intercalation hosts instead of bulk electrodes consisting of micrometre sized particles.

**Multiphase composites**

In the case of multiphase composites, the properties of each phase will affect the overall performance of the material. The primary purpose of dispersing active particles within a composite matrix (filler) is to use the host matrix to buffer the large volume changes of the active particles so that the electrode integrity and the electronic contact between the active particles and conductive phase can be maintained [Yang et al., 1996; Boukamp et al., 1981]. As a result, the host matrix must allow rapid transport of electrons and Li ions, as well as maintaining the microstructural stability of the whole electrode [Yang et al., 1999a]. The host matrix also acts as a spacer to reduce the aggregation of active particles during cycling [Yang et al., 1999a; Courtney et al., 1999]. It has been widely reported that higher amounts of host phases improve the cycling stability of the anode but reduce specific capacity [Yang et al., 1999a]. To avoid this problem, the host matrix must possess good ionic and electronic conductivities and appropriate mechanical strength. In terms of mechanical properties, it has been proposed that a matrix with a high yield
strength, low ductility, and a low elastic modulus will provide better volume compensation during cycling [Wang et al., 2001; Wolfenstine, 2003]. In other words, the matrix must be able to sustain a high stress with a large elastic deformation when the active particles expand so that the active particles are under high compressive residual stress during Li insertion. In this view, a matrix with high strength, low ductility, and a low elastic modulus may reduce the tendency towards active particle cracking.

**Carbon-based composites**

Carbon-based materials are a key component of electrodes, due to their high electronic conductivity and robustness, and the rich functional surface chemistry of carbon. Great research interest has been dedicated to the development of electrodes with advanced architectures using nanostructured carbon materials (carbon nanotubes or nanofibres, ordered mesoporous materials, etc.), in contrast to the “classical” carbon materials based on graphite, glassy carbon, and carbon black [Centi and Perathoner, 2010]. However, the beneficial effects of carbon addition or a carbon coating have been widely observed in many studies. The improved cycling performance of carbon-based composites could be attributed to the improved electric conductivity and the buffering effect of carbon [Park et al., 2006a; Yoon and Manthiram, 2009; Lee and Lee, 2004]. Carbon additives also have the advantages of good ionic conductivity, low volume expansion, tolerance to mechanical stress, and Li-storage capability [Park et al., 2006a; Lee and Lee, 2004]. It has also been suggested that a carbon coating exerts a compressive stress on the active particles, which acts as an opposing force against particle volume expansion during lithiation.
and thus limits the pulverization of the particles [Saint et al., 2007]. In addition to carbon coating, metal coating, such as with silver, has been successfully used to increase the conductivity as well [Croce et al., 2002].

**Porous structured materials**

One of the most promising approaches is to design porous structured materials with sufficient porosity to accommodate the large volume expansion during charge/discharge [Kim and Cho, 2008; Lou et al., 2006; Wang et al., 2006]. Porous materials have many advantages for use in electrodes for lithium-ion batteries such as [Zhao et al., 2008]: (a) the large pore surface area, which provides a large contact area between the active materials and the electrolyte; (b) the continuous network, which is expected to improve electrical conductivity; (c) numerous pores that can buffer the large volume changes caused by disintegration of the structure; and (e) suitable microporous structures that may block the re-aggregation of the superfine particles. As a result, these materials can show improved reversible capacity, enhanced cycling performance, and elevated rate capability.

**Binder**

The choice of binder is also very important to solve the problem of the large capacity fade observed with cycling for Si, Sn, and transition metal oxide anode materials. The conventional binder used for graphite and alloy anodes is polyvinylidene fluoride (PVDF), a thermoplastic material with poor elastomeric properties [Zhang, 2011]. However, a newer binder, sodium carboxymethyl cellulose (CMC), has been
proved to be even more effective in enhancing the capacity retention of Si anode than either PVDF or styrene-butadiene rubber (SBR) elastomer binder [Ding et al., 2009; Li et al., 2007]. CMC binder can also improve the cycling performance of iron-based materials [Li et al., 2008; Chou et al., 2010]. It was proposed that the CMC binder may act as a surface modifier promoting the formation of a stable solid electrolyte interphase (SEI) passive layer [Li et al., 2007], while the extended conformation of CMC in solution leads to more homogeneous dispersion and networking of the conductive carbon and active particles [Lestriez et al., 2007]. The reported results indicate that the choice of binder has a critical impact on the electrochemical performance of a battery electrode system.

1.3 Significance of Study

The past two decades have shown that the exploration of properties on the nanoscale can lead not only to substantially new insights regarding fundamental issues, but also to novel technological perspectives. Simultaneously, it became very fashionable to decorate activities with the prefix ‘nano’. So, it is now believed that the combination of composite science and nanotechnology could be the best way to achieve breakthroughs in the energy storage field, especially with respect to the lithium-ion battery. In this doctoral work, systematic experimental investigations were carried out to improve the performance of electrodes based on composite and nanostructured materials. Generally, the potential advantages for the use of composite and nanostructured materials as electrode can be summarized as follows:
(1) Nanostructured materials may not only introduce innovative reaction mechanisms, but also improve electrochemical properties over those of their bulk counterparts.

(2) Nanostructured materials provide a larger electrode/electrolyte contact area, which is beneficial to high current rate performance, because Li ion diffusion and electron transport are highly dependent on the transport length and accessible sites on the surface of active materials. On the other hand, conductive composites can enhance the transfer of electrons. Those compounds exhibiting low Li ion diffusion coefficients usually show low Li ion storage capacities in bulk form, especially at high current rates. From this point of view, micrometer-sized electrode materials are not beneficial for high-rate charge/discharge because of the long path length for Li ion transport and low contact area between the electrode and electrolyte.

(3) Besides their excellent high current rate charge/discharge performance, nanostructured electrode materials may also deliver good cycling stability. The capacity fading of lithium ion batteries upon cycling is usually caused by the large volume expansion/contraction associated with Li insertion/extraction or Li alloying/de-alloying. Nanostructured electrodes can absorb this large volume expansion/contraction, preserving the integrity of the electrode, which leads to stable cycling performance. Conductive composites are also beneficial for the electrolyte diffusion into the bulk of the electrode, provide fast transport channels for the Li ions, and accommodate the volume variation more effectively, thus increasing the structural stability of the electrode.

The overall goal is to contribute to a comprehensive insight into the factors controlling lithium-ion electrode performance, from the synthesis of nanostructured
and composite materials to the details of phase-related electrochemical behaviour. The ultimate goal is to investigate the mechanism involved during electrochemical cycling and to understand how nanostructured and composite materials influence the electrochemical performance of lithium-ion batteries. Therefore, in this thesis research, many different types of electrochemical, magnetic, and structural characterization techniques have been adopted, in the hope of accomplishing this goal.

1.4 Objectives of Research

Based on previous work at ISEM and published reports in relevant international journals, the author was initially motivated to explore synthesis techniques, structural characterization, and electrochemical performance evaluation of different types of composite/nanostructured materials as potential candidates for use as electrode materials for lithium-ion batteries. The following objectives have been addressed to achieve the main goals:

1. To synthesise novel conductive nanocomposite electrode materials for lithium-ion batteries.
2. To synthesise nanostructured electrode materials for lithium-ion batteries.
3. To characterize the synthesized materials by numerous techniques in order to understand the structural, morphological, physical, and also, most importantly, the electrochemical changes.
4. To increase the practical specific capacity of the electrode materials to near their theoretical capacity with excellent rate capability and cycling stability.
5. To contribute to the next technology breakthrough in order to open up a new window for the next generation lithium-ion batteries.

1.5 Thesis Structure

Some of the scope of the research which has been carried out in this doctoral work is briefly outlined below:

In this Chapter, a general background and major problems associated with lithium-ion battery electrode are presented. Possible approaches for improving electrode performance, and the significance and objectives of this study are also discussed.

In Chapter 2, a thorough literature review on the current state-of-the-art lithium-ion battery, especially with respect to the role of nanostructured/composite electrode materials and their possible synthesis techniques, is presented.

Chapter 3 presents the chemicals and methods used to synthesise nanostructured/composite materials and the instrumental analysis techniques used to characterize the electrode materials, including X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), energy dispersive X-ray (EDX) spectroscopy, the physical properties measurement system (PPMS), Brunauer-Emmet-Teller (BET) surface area measurements, Raman spectroscopy, cyclic
voltammetry, charge-discharge testing, and electrochemical impedance spectroscopy (EIS).

Synthesis techniques and electrochemical performances of the potential cathode materials, $\alpha$-LiFeO$_2$-C, VO$_2$(B)-MWCNT, and LiFePO$_4$-Fe$_2$P-C, are discussed in Chapters 4, 5, and 6, respectively.

Chapters 7, 8, and 9 describe the synthesis techniques and electrochemical performances of the potential anode materials, Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C, Co$_3$O$_4$, and NiO-C, respectively.

Chapter 10 summarizes the results of this doctoral work and provides some indications for further research work related to electrode materials.
CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

With economic, infrastructural, and technological advancement, the world’s hunger for energy is ever increasing. Finite fossil-fuel supplies, problems of nuclear waste, and global warming linked to CO₂ emissions necessitate the rapid development of alternative/“green” sources of energy [Mann et al., 2008; Armaroli and Balzani, 2007]. Electricity generated from renewable resources is intermittent, while available electricity may be required at any time in our daily lives. These crucial energy supply issues facing mankind, together with the enthusiasm and rapid advances in the electric automotive industry towards the development of electric vehicles (EVs) and hybrid electric vehicles (HEVs), have combined to make the development of radically improved rechargeable batteries a worldwide imperative [Armand and Tarascon, 2008]. Researchers then have the responsibility for providing the world with better and more efficient batteries. Advancement in battery technology has been relying on the development and use of different types of materials for electrodes and electrolytes, and thus with different electrochemical reactions [Adachi et al., 1996; Wang and Cao, 2006]. In order to compare the different battery types on the level of their performance, one can make use of the so-called Ragone chart (Figure 2.1), which plots specific power versus specific energy, where one can compare easily the different batteries suitable for use in either battery-electric vehicles (which primarily need energy) and hybrid vehicles (which primarily need power) [Bossche
et al., 2006]. Obviously, lithium-ion batteries offer a balanced combination of high power and energy density. However, the current technologies for producing rechargeable lithium-ion batteries do not completely satisfy all the requirements. In recent years, great efforts have been devoted to the development of various electrode materials and have moved closer towards reaching the requirements. Therefore, lithium-ion batteries will be investigated and discussed in detail in this doctoral work.

![Figure 2.1](image)

**Figure 2.1** Comparison of the different battery technologies in terms of specific power and specific energy density [Bossche et al., 2006].

### 2.2 Lithium-ion Rechargeable Batteries

The first lithium-based battery was demonstrated in the early 1970s and was a primary or non-rechargeable type, consisting of a SOCl₂ positive electrode and a lithium metal negative electrode [Robinson, 1974]. During the 1970s and 80s, many
researchers were involved in programs to develop rechargeable batteries and discovered that several inorganic compounds could react with lithium and sodium in a reversible way. This led to the development of alternative battery systems that utilized layered transition metal dichalcogenides, and in 1972, Whittingham [Whittingham, 1976] embarked on a large project using TiS$_2$ as the cathode electrode, Li metal as an anode electrode, and lithium perchlorate in dioxolane as the electrolyte. TiS$_2$ was the best intercalation compound available at the time, having a very favourable layered-type structure, and was the most promising one candidate for the energy storage electrode due to its light weight [Abraham et al., 1986; Holleck and Driscoll, 1977; Whittingham, 1973]. However, in spite of the impeccable operation of the positive electrode, the system was not viable. It soon encountered the shortcomings of a Li-metal/liquid electrolyte combination – uneven Li growth as the metal was replated during each subsequent discharge-recharge cycle, which led to explosion hazards. The safety issue, the low potential, and the high production cost of this material caused people to start to move to layered oxide materials [Patil et al., 2008]. Vanadium pentoxide (V$_2$O$_5$) and molybdenum trioxide (MoO$_3$) were two of the earliest studied oxides. Molybdenum oxide is of little interest due to its low rate capability [Dampier, 1974], whereas V$_2$O$_5$ has been investigated for 30 years [Walk and Gore, 1975; Walk and Margalit, 1997; Delmas et al., 1994; Dickens et al., 1979; Tarascon and Armand, 2001]. It has a layered structure with weak vanadium-oxygen bonds between the layers and is now known to react by an intercalation mechanism. However, the multiphase transition and rapid capacity loss on cycling makes this material unsuitable for commercial application in rechargeable batteries [Walk and Gore, 1975; Walk and Margalit, 1997; Delmas et al., 1994; Dickens et al., 1979]. In the 1980s, Goodenough and his co-workers discovered the open
framework Li$_x$MO$_2$ (M = Co, Ni or Mn) family of compounds as more suitable positive electrode materials. They recognized that LiCoO$_2$ had a similar structure to the layered structures of the dichalcogenides and showed that the lithium could be inserted and de-inserted electrochemically, thus making LiCoO$_2$ a very promising cathode material [Mizushima et al., 1980; Thackeray et al., 1983]. On the other hand, the introduction of carbon as an anode material in lithium-ion secondary batteries has an interesting history. Lithium insertion in graphite host lattices from conventional non-aqueous solvents was reported as early as 1976 [Besenhard, 1976]. Nevertheless, disintegration of the graphite host lattice during intercalation/de-intercalation has remained an unresolved issue. The search for new solvent-supporting electrolyte systems, including polymer electrolytes, would ensure reversible intercalation/de-intercalation which, in turn, would improve the cycle life of graphite material [Yazami and Touzain, 1983]. Sony Corporation, in a swift move, reported that lithium insertion could also be successfully carried out in disordered-carbon material [Kasei, 1987]. This opened up many possibilities in terms of carbon material sources and the choice of solvent-supporting electrolyte system. Following a parallel sequence of developments which resulted in the selection of LiCoO$_2$ as the cathode material, Sony Corporation introduced the first, successful, disordered-carbon based, Li-ion batteries [Nagura and Tozawa, 1990], which were commercialized in 1991 [Nishi, 2001]. These lithium-ion batteries had a strong impact on the battery community all over the world because of their high operating voltage, and they rapidly became the power source of choice for portable electronic devices, especially wireless telephones and laptop computers, over the past 16 years. Today, the modern world cannot be described without considering lithium-ion batteries.
2.3 Fundamentals of Electrochemistry

Electrochemistry includes the study of chemical properties and reactions involving ions either in solution or in solids. In order to study these properties, generally electrochemical cells are constructed. A typical cell consists of two solid electrodes, the cathode and anode, in contact with an ionic conducting electrolyte. A galvanic cell is an electrochemical cell that is capable of converting chemical energy into electrical energy. It generates electricity as a result of a spontaneous electrode reaction inside it.

2.3.1 Principle of Reaction Mechanism of Lithium-ion Battery

In the current type of lithium-ion battery, normally the cathode (positive electrode) is comprised of materials with a layered structure, such as lithium transition metal oxides, and the anode (negative electrode) is based on graphitic layered carbon materials, such as natural graphite and other carbonaceous materials. A non-aqueous electrolyte (e.g. LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC)) with a separator, or a polymer gel or solid polymer electrolyte is placed between the two electrodes for ion transfer. A schematic diagram of the charge/discharge process in a rechargeable lithium-ion battery is shown in the Figure 2.2.
The mechanism of the lithium-ion battery can be considered as based on the flow of lithium ions inside the battery between anode and cathode, and at the same time, transport of electrons outside the battery (external circuit) between anode and cathode. As the lithium-ions are included in the cathode material (such as lithium transition metal oxide, LiCoO$_2$), the cells need to be charged first to allow lithium ions to be de-intercalated from the cathode and spread throughout the electrolyte to be placed in the negative electrode material (such as graphite, C). During the discharge process, lithium ions are extracted from the negative electrode and are inserted into the positive electrode through the electrolyte. The generation of lithium ions and electrons occurs simultaneously from the reaction, Li → Li$^+$ + e$^-$, where the cathode electrode is oxidised and the anode electrode is reduced during charge.
respectively. The reactions involved in the charge and discharge process are described below [Nishi, 2001; Wakihara, 2001]:

At positive electrode:

\[
Li\text{MO}_2 \leftrightarrow Li_{1-x}\text{MO}_2 + x Li^+ + x e^- \tag{2.1}
\]

At negative electrode:

\[
6C + x Li^+ + x e^- \leftrightarrow Li_xC_6 \tag{2.2}
\]

Overall reaction:

\[
6C + Li\text{MO}_2 \leftrightarrow Li_{1-x}\text{MO}_2 + Li_xC_6 \tag{2.3}
\]

However, the electrode must allow for the flow of both lithium ions and electrons, and thus, the electrode must have both good ionic conductivity and good electronic conductivity. Simply, the lithium ions (Li\(^+\)) move back and forth between the cathode and anode upon charging and discharging, which gives rise to a potential difference of about 4 V between the two electrodes, while the battery capacity is dependent on the amount of lithium ions that can be extracted from the cathode material. The name “lithium ion” for the batteries originates from this simple mechanism, that is, the transfer of lithium ions between the anode and cathode.

2.3.2 Fundamental Properties

To evaluate the properties of electrodes in a secondary cell some general concepts are introduced below:

Active mass: Active mass is the material that generates electrical current by means of chemical reaction within the battery.
Open circuit voltage (OCV): Open circuit voltage is the voltage across the terminals of a cell or battery when no external current flows. It is usually close to the thermodynamic voltage for the system.

Potential: The cell potential is determined by the difference between the chemical potential of the lithium in the anode and cathode,

\[ \Delta G = -EF \] (2.4)

where \( \Delta G \) = Gibbs free energy

\( F \) = Faraday constant (96485 C)

\( E \) = Electrode potential

For the rechargeable lithium-ion cell, the terms cathode and anode are defined as the higher potential and lower potential electrode, respectively. Typically, the electrochemistry of the total lithium cell reactions can be investigated using a half cell with lithium metal as counter and reference electrode, denoted as vs. Li\(^+\)/Li for the convenience of research. Therefore, the active materials we will discuss later are all working as cathode materials in the half cell, but what they really are is determined by the potential. Normally, the cathode materials show a potential vs. Li\(^+\)/Li higher than 2 V, while the anode materials show a potential vs. Li\(^i\)/Li lower than 2 V. Figure 2.3 summarizes the electrochemical potential and the typical lithium ion storage capacities of both anodic and cathodic materials.

Discharging: Discharging is the operation in which a battery delivers electrical energy to an external load.

Charging: Charging is the operation in which the battery is restored to its original charged condition by reversal of the current flow.
Figure 2.3 Potential vs. capacity for positive and negative electrode materials presently used or under serious consideration for the next generation of rechargeable Li-based cells [Tarascon and Armand, 2001].

**Overcharging:** Attempting to charge a battery beyond its electrical capacity can also lead to a battery explosion, leakage, or irreversible damage to the battery. It may also cause damage to the charger or device in which the overcharged battery is later used.

**Short circuiting:** A short circuit can lead to a battery fire or explosion. It often occurs when a battery is connected to itself, creating two points on a circuit with different potentials connected with zero or near-zero resistance.

**Memory effect:** The memory effect is a vague description of a temporary loss of capacity for the Ni-Cd battery. "Memory effect" refers to the phenomenon where a nickel/cadmium battery loses the ability to deliver full capacity if it is utilised only partially for a prolonged period of time. In practice, every kind of temporary capacity loss is often called a "memory effect".
**Theoretical specific capacity:** Other than the potential, the specific capacity is also an important parameter to evaluate the active materials. The theoretical specific capacity ($Q_{TSC}$) can be calculated from the equation:

$$Q_{TSC} = \frac{n \times F}{M} \tag{2.5}$$

where $n$ is the number of mol of electron transfer in the electrochemical reaction, $F$ is the Faraday constant (96485 C), and $M$ is the molecular weight of the active materials.

**Specific charge capacity/Specific discharge capacity:** The specific charge capacity ($Q_c$) or specific discharge capacity ($Q_d$) is calculated based on the total amount of charge transferred:

$$Q_c \text{ or } Q_d = \frac{I \times t}{m} \tag{2.6}$$

where $I$ is the current (mA), $t$ is the time (h), and $m$ is the mass of active materials. So the $Q_c$ or $Q_d$ is in the units of mAh g$^{-1}$.

**Energy:** It is usually desirable that the amount of energy stored in a given mass or volume is as high as possible. The concepts of specific energy ($SE$, Wh kg$^{-1}$) or energy density ($ED$, Wh L$^{-1}$) allow comparison of the energy content or energy density.

$$SE = \frac{E \times Q}{1000} \tag{2.7}$$

$$ED = \frac{E \times Q \times m}{1000 \times V} \tag{2.8}$$

where $E$ is the voltage (V) of the cell, $Q$ is the specific capacity (mAh kg$^{-1}$), $m$ is the weight of the cell (kg), and $V$ is the volume of the cell (L).

**Power:** Specific power ($SP$, W kg$^{-1}$) and power density ($PD$, W L$^{-1}$) are the ability of the cell to deliver power per unit mass and unit volume, respectively.
where \( t \) is the discharge time (h).

**Rate capability:** Rate capability is another parameter to evaluate electrode performance. The term charge/discharge rate or C-rate is often used to describe how fast the cell can be charged or discharged. C denotes either the theoretical charge capacity of a cell or battery (mAh) or the nominal capacity of a cell or battery, as indicated by the manufacturer. For example, a battery rated at 1000 mAh provides 1000 mA for one hour if discharged at 1 C rate. 1 C is often referred to as a one-hour discharge; a 0.5 C would be a two-hour, and a 0.1 C a 10 hour discharge. A C-rate between 2 and 10 C is called a medium high rate. A C-rate higher than 10 C is considered as a high rate.

**Irreversible capacity loss:** It is also important to define how much capacity is lost after each cycle. The irreversible capacity can reflect the stability of cells upon cycling. Irreversible capacity loss is therefore explained by the following equation:

For anode materials:

\[
\text{Irreversible capacity loss} = \frac{n_{\text{th}} Q_{\text{d}} - n_{\text{th}} Q_{\text{c}}}{n_{\text{th}} Q_{\text{d}}} \times 100\% \tag{2.11}
\]

For cathode materials:

\[
\text{Irreversible capacity loss} = \frac{n_{\text{th}} Q_{\text{c}} - n_{\text{th}} Q_{\text{d}}}{n_{\text{th}} Q_{\text{c}}} \times 100\% \tag{2.12}
\]

**Capacity retention:** Capacity retention is the ratio of the last cycle to the 1st cycle discharge capacity and is calculated as a percentage as follows:

\[
(C_{100} / C_1) \times 100\% \tag{2.13}
\]
where $C_{100}$ is the discharge capacity at the 100th cycle and $C_1$ is the initial discharge capacity.

**Coulombic efficiency:** Coulombic efficiency ($\eta$) is another important parameter to represent the ratio of the discharge capacity to the charge capacity.

$$\eta = \frac{n_{th}Q_d}{n_{th}Q_c} \times 100\%$$

(2.14)

### 2.4 Materials for Cathode

The choice of the cathode materials depends on whether we are dealing with rechargeable Li-metal or Li-ion batteries. For rechargeable Li batteries, owing to the use of metallic Li as an anode, the cathode does not need to be lithiated before cell assembly. In contrast, for Li-ion batteries, because the carbon anode is empty (no Li); the cathode must act as the source of Li, thus requiring use of air-stable Li-based intercalation compounds to facilitate the cell assembly [Patil et al., 2008]. There is a wide range of materials that can be used as positive electrodes for Li-ion batteries. The best ones are those with little or no structural modification during cycling. Typical insertion or intercalation compounds are therefore preferred candidates. However, the key criteria to screen potential cathode materials are as follows [Whittingham, 2004]:

- high free energy of reaction with lithium
- wide range of $x$ (amount of Li-ion insertion)
- little structural change upon reaction
- highly reversible reaction
- rapid diffusion of lithium within the host lattice
• good electronic conductivity
• no solubility in electrolyte
• readily available or easily synthesized from low cost reactants

Here, an overview is provided on selected developments in the area of cathode electrode materials in both Li-ion and Li batteries in the past decade, and particularly in the past few years. Three major structures of cathode materials reviewed here are the lithium transition metal oxides, the spinel oxides, and the olivines.

2.4.1 Lithium Transition-Metal Oxides

The two-dimensional lithium transition metal oxides with the general formula LiMO$_2$, with M = V, Fe, Co, Mn, and Ni, adopt the $\alpha$-NaFeO$_2$-type structure, which can be regarded as a distorted rock salt superstructure [Kobayashi et al., 1969; Liao et al., 2006; Han et al., 2003; Yamaki et al., 2006; Liu et al., 2006]. In a cubic close-packed oxygen array, the lithium and transition-metal atoms are distributed in the octahedral interstitial sites, in such a way that MO$_2$ layers are formed, consisting of edge-sharing [MO$_6$] octahedra. In between these layers, lithium resides in octahedral [LiO$_6$] coordination, leading to alternating (111) planes of the cubic rock salt structure. This (111) ordering induces a slight distortion of the lattice to hexagonal symmetry. The layered framework provides a two dimensional path, which allows for relatively facile extraction and insertion of lithium ions. Figure 2.4 shows the typical two-dimensional crystal structure of LiMnO$_2$. However, LiCoO$_2$ is the most popular cathode materials, owing to the convenience and simplicity of preparation [Wang and Cao, 2008]. The Li$_x$CoO$_2$ system has been studied extensively and exhibits excellent cyclability at room temperature for $1 > x > 0.5$. The specific
capacity of the material is limited to the range of 137 to 140 mAh g\(^{-1}\), although the theoretical capacity of LiCoO\(_2\) is 273 mAh g\(^{-1}\) [Ohzuku and Ueda, 1994]. Despite the commercial success of LiCoO\(_2\), substitutes for LiCoO\(_2\) are necessary, as it has several drawbacks than other transition metals [Belov and Yang, 2008a; Belov and Yang, 2008b; Doh et al., 2008].

![Two-dimensional crystal structure of LiMnO\(_2\) [Patil et al., 2008].](image)

**Figure 2.4** Two-dimensional crystal structure of LiMnO\(_2\) [Patil et al., 2008].

Isostructural LiNiO\(_2\) was first proposed by Dahn et al. [Dahn et al., 1990] as an alternative to LiCoO\(_2\) because of its lower cost, higher reversible capacity (~200 mAh g\(^{-1}\)), and lower toxicity, but LiNiO\(_2\) suffers from structural changes, thermal runaway, and difficulties in synthesizing it as an ordered material with all Ni\(^{3+}\) ions as it was mentioned in Chapter 1. [Nakai and Nakagome, 1998; Hirano et al., 1995; Dutta et al., 1992]. From an economic and environmental point of view, layered LiMnO\(_2\) is a very attractive material for cathode. However, layered LiMnO\(_2\) is a metastable phase. Therefore, it is not possible to synthesize it via the conventional
solid-state method used to make its layered Co or Ni analogues. Some research groups [Armstrong and Bruce, 1996; Capitaine et al., 1996] have reported the preparation of layered LiMnO$_2$ via ion exchange of thermodynamically stable layered NaMnO$_2$ with Li, but layered Li$_{0.5}$MnO$_2$ is converted into the LiMn$_2$O$_4$ spinel structure during cycling, resulting in poor electrochemical properties and a spinel-like drop in the voltage profile [Vitins and West, 1997]. Various strategies have been proposed and tested to avoid some of these drawbacks, and scientists are still struggling to minimize these problems. On the other hand, iron-based compounds have been widely concerned as electrode materials for lithium-ion battery. Among them, nanosized different polymorphs of lithium ferrite, LiFeO$_2$, were also studied as potential alternatives to Li-Co-O positive electrodes. The use of these ferric materials as electrodes is subject to major constraints arising from their low cycling efficiency and also low operating voltage [Kanno et al., 1997; Lee et al., 2002; Sakurai et al., 1997]. However, Li-Fe-O systems provide similar capacities to those of LiCoO$_2$ and LiFePO$_4$. Among various candidate cathode materials, another class of transition metal oxide, vanadium oxides, VO$_x$ (e.g., V$_2$O$_5$, V$_2$O$_4$, V$_2$O$_3$, VO$_2$, V$_6$O$_{13}$) [Cao et al., 2005; Wang and Cao, 2006; Livage, 1991; Tipton et al., 1996; Wei et al., 2005; Odani et al., 2006; Onnerud et al., 1995; West et al., 1985] has been attracted continuous attention, due to their splendid electrochemical properties; it is thus expected that these vanadium oxides have great potential to be used as cathode materials in the next generation rechargeable batteries, not only because of their low cost, relatively low toxicity, and the abundance of their raw materials in nature with respect to commercially available layered LiCoO$_2$, but also their high energy density and moderate work-potential, which is particularly important for application in electric vehicles (EVs) or hybrid EVs (HEVs). Of these vanadium oxides, VO$_2$(B), a
metastable phase of vanadium dioxide, is of great interest, owing to its layered structure and promising properties in the nanometer domain [Onnerud et al., 1995; Balberb and Trokman, 1975].

### 2.4.2 Spinel Oxides

Manganese oxides are among the most popular cathode materials in lithium batteries, due to their abundant raw materials, low cost, favourable charge density, rather high electronic conductivity, better stability on overcharge, and suitable electrode potential [Patil et al., 2008]. LiMn$_2$O$_4$ exhibits an operating voltage of 4.1 V vs. Li$^+$/Li. Spinels have been the subject of exhaustive studies in the 1990s, as well as in the present [Tarascon and Guyomard, 1993; Tarascon et al., 1993; Thackeray, 1995]. The discharge proceeds in predominantly two steps, one around 4 V and the other around 3 V. Usually only the 4 V plateau is used, so that the cell is constructed in the discharged state and must be charged before use, just as for LiCoO$_2$.

\[
\text{LiMn}_2\text{O}_4 \rightarrow \text{Mn}_2\text{O}_4 + \text{Li}^+ + e^- \quad \text{(Charge)} \quad (2.15)
\]

The advantages of the three-dimensional framework structure of LiMn$_2$O$_4$ over two-dimensional layered structures such as the structures of LiCoO$_2$ and LiMnO$_2$ is: (i) the possibility of avoiding, for steric reasons, the co-insertion of bulky species such as solvent molecules; (ii) the smaller degree of expansion/contraction of the framework structure upon lithium insertion/de-insertion; (iii) the spinel structure of LiMn$_2$O$_4$, in contrast to LiCoO$_2$ and LiNiO$_2$, which explain why it is more common in large batteries. Figure 2.5 shows a polyhedral structural representation of LiMn$_2$O$_4$, where MnO$_6$ octahedra are colored maroon and the green lithium ions fill the interstitial sites. The size of the channels must be sufficiently large to
accommodate the ions. The structure consists of Mn atoms octahedrally coordinated to six oxygens and lithium atoms tetrahedrally coordinated to four oxygens.

Figure 2.5 Extended structure of LiMn$_2$O$_4$, shown with MnO$_6$ polyhedra with larger lattice parameters, where the Li ions can diffuse more freely through the structure [Li et al., 2001].

However, LiMn$_2$O$_4$ suffers from severe capacity fade at elevated temperatures, and several factors, such as manganese dissolution, Jahn-Teller distortion, loss of crystallinity, and development of microstrain during cycling, have been reported to be responsible for the capacity fade [Thackeray et al., 1998; Huang et al., 1999; Shin and Manthiram, 2002]. Unfortunately the LiMn$_2$O$_4$ batteries have not proven to be as reproducible as the LiCoO$_2$ batteries in terms of cell resistivity and cycling stability. Numerous elements have been introduced into LiMn$_2$O$_4$ to investigate doping effects. LiFe$_x$Mn$_{2-x}$O$_4$ spinel can be used as a 5 V cathode material, whereas cobalt exists in the spinel structure of LiCo$_y$Mn$_{2-y}$O$_4$, increasing the conductivity of
LiCo$_y$Mn$_{2-y}$O$_4$, which is much higher than that of LiMn$_2$O$_4$ [Shigemura et al., 2001; Armstrong et al., 1999]. Furthermore, after doping with cobalt, the particle size becomes larger, and the specific surface area decreases, and consequently, the contact area between active materials and electrolytes also becomes smaller, and the decomposition rate of electrolytes and self-discharge rate decrease. The presence of cobalt inhibits the passivation process occurring on the cathode surface, increases the exchange current density, and facilitates the charge-transfer reaction of the active material [Avora et al., 1998]. Recently, there have also been some reports on the use of nanostructured spinels to enhance electrochemical properties. For example, ordered mesoporous [Jiao et al., 2008], and nanorod morphologies [Kim et al., 2008] of LiMn$_2$O$_4$ have shown particularly high rate capability. Many studies have also been done on high voltage Li[Ni$_{0.5}$Mn$_{1.5}$]O$_4$ spinel cathode [Wakihara, 2005; Kunduraci and Amatucci, 2008; Talyosef et al., 2005; Park et al., 2007 (a)], and Imazaki et al. [Imazaki et al., 2009] reported a promising new generation of 12 V batteries by using Li[Ni$_{0.5}$Mn$_{1.5}$]O$_4$ and LiMn$_2$O$_4$ spinel cathode in combination with an elevated anode electrode, such as Li$_4$Ti$_5$O$_{12}$. It is expected that the current ongoing research will produce materials with improved energy.

2.4.3 Olivines

Iron-based compounds that contain compact tetrahedral ‘polyanion’ structural units (XO$_4$)$^{n-}$ (X = S, P, As, W, or Mo) have been investigated intensively as potential cathode materials for lithium ion batteries. Amongst the various polyanion compounds, the olivine structure has the most extensive interconnection of octahedra, with the cations that occupy the M2 sites (Fe site in LiFePO$_4$) forming a corner-sharing network of octahedra in the (010) plane, and the cations on M1 (Li)
sites forming edge-sharing chains of octahedra in the [100] direction (Figure 2.6) [Chung et al., 2002].

![Ordered-olivine structure of LiFePO₄: (a) ball-stick model, (b) depiction of polyhedral connectivity [Chung et al., 2002].](image)

**Figure 2.6** Ordered-olivine structure of LiFePO₄: (a) ball-stick model, (b) depiction of polyhedral connectivity [Chung et al., 2002].

However, LiFePO₄ has become of great interest as an active material for storage cathodes in rechargeable lithium batteries, because of their high energy density, low cost of their raw materials, environmental friendliness, high thermal stability in the fully charged state, and greater safety than conventional materials [Patil et al., 2008]. LiFePO₄ has a high lithium intercalation voltage (~3.5 V relative to lithium metal) and no obvious capacity fading, even after several hundred cycles. Its capacity approaches 170 mAh g⁻¹, which is higher than the 140 mAh g⁻¹ for LiCoO₂. In practice one could not obtain the full capacity of the material due to its low electrical conductivity (10⁻⁹ to 10⁻¹⁰ S cm⁻¹). LiFePO₄ electrodes are actually composed of two separate phases, LiFePO₄ and FePO₄, which are both poor electronic conductors because they each contain Fe cations with just one oxidation state (2⁺ or 3⁺, respectively); as a result, this material has been largely ignored. Therefore, in order
to obtain acceptable energy and power from the lithium cells, it is necessary to use small LiFePO$_4$ particles, coated or in intimate contact with electronically conductive carbon [Huang et al., 2001]. This simultaneously reduces the distance for Li$^+$ transport, and increases the electronic contact between the particles. Procedures of this kind have led to a greatly improved electrochemical response, and the full capacity of the material is now accessible. However, the long term cycling stability at high current rate is still a great challenge for this material, as it is a compulsory requirement for lithium ion batteries to have long cycle life for EV/HEV application. Other than carbon, conducting polymer (polyprrole) was also proposed as a good conductive matrix for LiFePO$_4$ particles, and it also showed excellent mechanical properties [Park et al., 2007 (b)]. Olivine LiMnPO$_4$, on the other hand, which is isostructural with LiFePO$_4$, has a similar theoretical electrochemical capacity (170 mAh g$^{-1}$) and shows a higher voltage of 4.1 V vs. Li$^+$/Li) [Padhi et al., 1997]. Up to now, a few promising reports on the electrochemistry of this compound have been published. Unfortunately, LiMnPO$_4$ has low intrinsic electronic and ionic conductivity and hence a poor discharge rate capability. The electrochemical performance is especially poor at high current density, which is attributed to the slow lithium diffusion kinetics within the grains and the low intrinsic electronic conductivity [Delacourt et al., 2005; Yonemura et al., 2004]. Thus far, several researchers have made efforts to enhance its electrochemical properties by particle-size reduction [Delacourt et al., 2004; Drezen et al., 2007], cation doping [Dominko et al., 2006; Shiratsuchi et al., 2009], carbon coated LiMnPO$_4$ [Yang and Xu, 2006; Murugan et al., 2009], or LiMnPO$_4$/carbon composite [Dominko et al., 2006; Shiratsuchi et al., 2009; Bramnik and Ehrenberg, 2008].
2.5 Materials for Anode

Since the technological breakthrough on anode materials at the end of the 1980s and in the early 1990s, resulting in the birth and commercialization of the lithium ion battery, research on anode materials has been a focus of attention. However, to the best of our knowledge, carbonaceous-based materials are the most attractive and widely investigated materials for use as anode in lithium-ion batteries so far.

2.5.1 Carbon-based Materials

Mostly carbons are used as the anode in commercial lithium-ion batteries, because they function as the host structure for lithium intercalation, and their structures are flexible enough to offer reversibility by allowing effortless insertion and de-insertion of lithium. They also exhibit both higher specific charges and more negative potentials than most metal oxides, chalcogenides, and polymers. Graphite can be obtained in a variety of forms, ranging from a crystalline state to a nearly amorphous state. Carbonaceous materials can be classified into three groups: graphite, graphitizable carbon, and non-graphitized carbons.

**Graphite:**

Graphite is a classic carbonaceous material that consists of hexagonal sheets of \( sp^2 \) carbon atoms (called graphene sheets), weakly bonded together by van der Waals (vdW) forces. Lithium ions and other kinds of ions and molecules can be intercalated between the graphite sheets, and the resulting complexes are called “graphite
intercalation compounds” (GIC) [Zabel and Solin, 1992]. The GICs have an essential characteristic property which is called the staging phenomenon, which governs the intercalated layers that are occasionally organised in the matrix of graphite sheets. Lithium intercalation takes place through well-identified, reversible stages, corresponding to progressive intercalation within discrete graphene layers, to reach the formation of LiC₆ with a maximum theoretical capacity of 372 mAh g⁻¹. This process extends to the range of few mV versus lithium, i.e. well below the decomposition limit of the most common electrolytes. Electrolyte decomposition results in the formation of a surface protective film (SEI, or surface electrolyte interface), which allows the continuous operation of the carbonaceous anodes [Fong et al., 1990; Aurbach et al., 1995].

**Graphitizable Carbons:**

Graphitizable carbons are also called soft carbons. They have a structure composed of misoriented crystallites formed after heat-treatment at high temperature (2000-3000 °C) [Azuma et al., 1999; Dahn et al., 1993]. Their reversible capacities are normally lower than that of graphite because their maximum stoichiometric factor x in LiₓC₆ is typically ~ 0.5 to ~ 0.8 (for graphite, x = 1). The quality of sites capable of lithium accommodation strongly depends on the crystallinity, the microstructure, and the micromorphology of the carbonaceous material [Park et al., 2006; Dahn et al., 1994; Beguin et al., 2005]. Thus, this kind of carbon determines the current/potential characteristics of the electrochemical intercalation reaction. Their relatively low capacity is mainly due to the lower number of sites available to accommodate lithium in “wrinkled” and “buckled” defect structural segments.
Non-graphitized Carbons:

Non-graphitized carbons are derived from low temperature treatment of organic compounds. Typically, these carbons have a highly disordered structure, a large amount of micro-or nano-porosity, and heteroatoms remaining from the precursors [Sato et al., 1994; Xiang et al., 1997]. They deliver much higher capacities than graphite (e.g. 1000 mAh g$^{-1}$ for a coke-type material) [Mabuchi et al., 1995], but have very high irreversible capacities in the first cycle with a large hysteresis in the potential profile.

2.5.2 Lithium Metal Alloys

The replacement of metallic lithium by lithium alloys has been under investigation since Dey [Dey, 1971] demonstrated the feasibility of electrochemical formation of lithium alloys in liquid organic electrolytes in 1971. The reaction usually proceeds reversibly according to the general scheme shown in Equation 2.16.

\[ \text{Li}_x\text{M} \leftrightarrow x \text{Li}^+ + x e^- + \text{M} \]  

(2.16)

With only a few exceptions (such as hard metals, M = Ti, Ni, Mo, Nb), Li alloys are formed at ambient temperature by polarizing the metal M sufficiently negatively in a Li$^+$ containing electrolyte. In most cases even the binary systems Li-M are very complex. Sequences of stoichiometric intermetallic compounds and phases Li$_x$M with considerable phase ranges are usually formed during lithiation of the metal M, which is characterized by several steps and/or slopes in the charge diagram. The formation of Li-M phases is in many cases reversible, so that subsequent steps and slopes can also be observed during discharge. However, lithium metal alloys are of great interest due to their high theoretical capacities and also their similar potential
range to graphite materials, but unfortunately, the main problem encountered with these alloys is the huge volume change when lithium is either incorporated or removed [Besenhard et al., 1997]. As a result, mechanical stress and cracks occur during cycling, which leads to electrochemically inactive particles and thus quite poor cycling stabilities. Today, the use of lithium alloys as anodic materials in lithium-ion batteries is an interesting field of research, on account of the promising results provided by silicon-based and tin-based compounds. Among all the anode materials, silicon is the most promising candidate, owing to its high natural abundance, low discharge potential, and high theoretical capacity (3579 mAh g\(^{-1}\)) [Weydanz et al., 1998; Obrovac and Christensen, 2004]. However, the large volume changes (up to 270 % for the Li\(_{3.75}\)Si phase) and loss of electrical contact during lithium insertion and extraction result in capacity fading [Wolfenstine, 1999]. In recent years, several methods have been examined to attempt to achieve higher reversible capacity of Si anodes with respect to graphite and better capacity retention for practical commercial applications. Reducing the Si particle size to the nanoscale [Chan et al., 2008; Li et al., 1999; Ma et al., 2007] or dispersing the electroactive particles in a carbon matrix are the most promising approaches [Cahen et al., 2008; Ng et al., 2006]. It is believed that carbon based materials buffer the volume changes and improve the electronic and ionic conductivities. However, the initial coulombic efficiency (< 80%) and the capacity retention are still quite low, which hinders commercial application in lithium-ion batteries. On the other hand, Sn-based materials with high theoretical specific capacity (992 mAh g\(^{-1}\)) have been proposed as another type of promising candidate, due to their high theoretical capacity, high packing density, and safe thermodynamic potentials compared to carbonaceous materials for lithium secondary batteries [Yang et al., 1996; Wachter and Besenhard,
However, they usually undergo severe structural and volume change during the process of Li uptake and removal, which results in mechanical disintegration of the electrode and consequent capacity fade, greatly limiting the potential for commercialization [Wachter and Besenhard, 2001; Li et al., 2002; Zhao et al., 2005]. Numerous research works have been focused on alleviating the volumetric change in alloy composite anodes, including the use of intermetallic alloys containing an active or inactive host matrix, such as SnNi [Liao et al., 2003; Dong et al., 2004] and SnCo [Xia et al., 2001; Kim and Kang, 2002; Larcher and Beaulieu, 2000]. The active metal element can provide the high capacity, while the inactive element is able to buffer the volume change, release the mechanical stress, and thus increase the cycling stability of the electrode. On the other hand, surface-coated/composite SnO$_2$ has shown better electrochemical performance than the bare material due to the improved solid electrolyte interphase (SEI) layer and/or buffered volume change. Among the buffer materials, carbon has to be considered as the best choice because of its cheap, light, and conductive nature. To date, carbon coated onto or added into the SnO$_2$ has been prepared by spray pyrolysis, polymer coating, and afterwards, carbonization and hydrothermal/solvothermal methods. Although the electrochemical performance of these Sn-based alloy composites has been significantly improved, the cycling stability and the high fabrication cost are still make them inadequate for practical use [Larcher and Beaulieu, 2000; Wada and Sakal, 2002; Holmes, 2001; Yang et al., 1999].
2.5.3 Transition Metal Oxides

Recently, Poizot et al. [Poizot et al. 2000] reported that nano-sized 3d transition metal oxides (MxOy, where M is Fe, Co, Ni, Cu or Mn) which are inactive towards Li could be a new class of anode materials for lithium ion batteries. These transition-metal oxides demonstrated electrochemical capacities over 700 mAh g\(^{-1}\) and excellent cycling performances. These oxides with rock-salt structure have no sites for insertion/deinsertion of Li ions. There is a new mechanism which can be written as:

\[
\text{M}_x\text{O}_y + 2y\text{Li} \leftrightarrow y\text{Li}_2\text{O} + x\text{M}
\]  

(2.17)

During the discharge, the M\(_x\)O\(_y\) particle is completely disintegrated into highly dispersed metallic nanoparticles (< 10 nm) and Li\(_2\)O matrix, but the global shape of the starting particle is preserved. During the subsequent charge, the Li\(_2\)O matrix decomposes, and M nanoparticles are converted back to M\(_x\)O\(_y\) nanograins. The existence of this thermodynamically infeasible reaction is attributed to the highly active metallic nanoparticles [Tarascon and Armand, 2001]. An SEI will also be formed during the discharge process, but it can be partially decomposed during the subsequent charge process, which is attributed to the catalytic activity of metallic nanoparticles [Grugeon et al., 2001]. The partially reversible formation/decomposition of the SEI will lead to extra capacity. Among these oxides, there has been a growing interest in cubic Co\(_3\)O\(_4\), owing to its broad practical applications in several important technological fields, such as heterogeneous catalysis [Kim et al., 1998], solid state sensors [Li et al., 2005], electrochromic sensors [Maruyama and Arai, 1996], energy storage [Noguchi and Mizuhashi, 1981], pigments [Sugimoto and Matijevic, 1979], etc. As it is an important magnetic
material [Makhlouf, 2002], the synthesis of nanocrystalline Co$_3$O$_4$ has been the target of material chemists [Yin and Wang, 1999; Lakshmi et al., 1997]. Owing to the influence of particle size and morphology on the properties of materials, the controlled preparation of Co$_3$O$_4$ particles of different sizes and morphologies is always the researcher’s purpose. Currently, Co$_3$O$_4$ has an important application as an anode material for lithium-ion batteries, and its electrochemical properties have been extensively studied [Yuan et al., 2003; Binotto et al., 2007; Li et al., 2005; Liu et al., 2008]. NiO, another important anode material, has a theoretical capacity of 718 mAh g$^{-1}$. However, its reversible capacity is lower and its cycling performance is worse than those of other transition metal oxides such as CoO and Co$_3$O$_4$ [Poizot et al. 2000; Poizot et al., 2002]. To improve the electrochemical properties of NiO, one effective way is preparing nanostructured materials [Wang et al., 2003; Wang and Qin, 2002], since the nanoparticles facilitate the transportation of Li$^+$ and electrolyte ions by offering a shorter solid-state diffusion length. However, the most critical problem for nanomaterials is the aggregation of nanoparticles, which results in poor cycling performance. There are also other factors that affect the cycling performances, such as pulverization of the active particles during charge and discharge, and poor conductivity of the active materials, especially for transition metal oxides. To avoid the problems mentioned above, one promising method is forming composites with carbon [Huang et al., 2007]. The carbon can act as a barrier to suppress the aggregation of active particles, thus increasing their structure stability during cycling [Lee et al., 2003b; Fan et al., 2004; Fu et al., 2006], and also acts as a buffering matrix to relax the expansion that occurs within the electrode from the lithiation/delithiation process [Wang et al., 2004; Wen et al., 2003]. Furthermore, the carbon has a high electronic conductivity, and it can improve the conductance of the
active materials [Wang et al., 2006]. Other metal oxides such as Fe₂O₃ [Sarradin et al., 1998; Larcher et al., 2003; Chen et al., 2005] and CuO [Gao et al., 2004; Grugeon et al., 2001] have also been extensively investigated by researchers. As one of the most promising anode materials, hematite (α-Fe₂O₃) has been investigated intensively, due to its great advantages such as high theoretical capacity (1007 mAh g⁻¹), low cost, good stability, environmental friendliness, and high resistance to corrosion [Chen et al., 2005; Wu et al., 2006].

2.5.4 Titanium Compounds

Being inherently safe and chemically compatible with the electrolyte, titanium oxide-based materials, including both Li-titanates and various TiO₂ polymorphs, are considered alternatives to carbonaceous anodes in Li-ion batteries [Yang et al., 2009]. Due to findings of promising Li-insertion properties in the titanate spinels, lately, there has been increasing interest in various TiO₂ polymorphs, in particular, in their nanostructures. Titanium oxide (anatase) has been found to be one of the best candidates as a host for lithium ions, because it is a fast Li insertion/extraction host with a high theoretical capacity of 336 mAhg⁻¹, and it has the added advantages of low cost, non-toxicity, low volume expansion (3-4%) during lithium insertion [Qiao et al., 2008], and environmental friendliness [He et al., 2007]. The anatase form of titanium dioxide (TiO₂) and titanium spinel (Li₄Ti₅O₁₂) allow the insertion of lithium at potentials around 1.78 and 1.56 V vs. Li/Li⁺, respectively [Sudant et al., 2005; Strobel et al., 1996]. This potential would lead to a low overall cell voltage and poor energy densities. Nevertheless, these materials are of interest because of their rapid discharge and charge properties, due to a high diffusion rate of lithium within them.
One drawback, however, is the poor conductivity of Li$^+$ and the accompanying electrons in its bulk form, limiting the electrochemical performance of TiO$_2$ electrode materials. To improve the charge/ion transport properties, TiO$_2$ polymorphs have been fabricated into varied nanostructures that promote improved Li insertion properties. On the other hand, the relatively high potential vs. Li makes the titanate electrodes intrinsically safer compared to graphite, which has an operating voltage close to the Li electroplating potential, which raises concerns over its safety. Li$_4$Ti$_5$O$_{12}$ accommodates Li with a theoretical capacity of 175 mAh g$^{-1}$, based on the mass of the starting host material, according to the following equation [Yang et al., 2009].

$$\text{[Li]}^{8}[\text{Li}_{1/3}, \text{Ti}_{5/3}]^{16d}[\text{O}_4]^{32e} + e^- + \text{Li}^+ \leftrightarrow \text{[Li}_2]^{16c}[\text{Li}_{1/3}, \text{Ti}_{5/3}]^{16d}[\text{O}_4]^{32e}$$ (2.18)

In spite of several advantages, Li$_4$Ti$_5$O$_{12}$ still suffers from low electronic conductivity, which negatively affects its potential for applications where high power density and good rate performance for the batteries are required. However, rate capability of dual or multi phase systems induced by pseudocapacitive effect, which not only provides a faster surface charge-transfer, but also offers extra interfacial electrochemical lithium storage [Lai et al., 2010; Lin et al., 2011; Jamnik and Maier, 2003; Guo et al., 2011; Yu et al., 2009]. In recent reports, the interface in some dual-phase materials is demonstrated to be more sensitive for storing the extra lithium [Jamnik and Maier, 2003; Guo et al., 2011; Yu et al., 2009]. In some nanostructured TiO$_2$ and Li$_4$Ti$_5$O$_{12}$, the pseudocapacitive effect is induced due to the presence of abundant phase interfaces in the dual-phase Li$_4$Ti$_5$O$_{12}$-TiO$_2$ nanocomposite, which is beneficial to the enhanced high rate capability and good cycle stability for lithium ion batteries [Li et al., 2011, Zhang et al., 2007].
3.1 Materials

The materials and chemicals used during my PhD studies for the synthesis, characterization, and electrochemical testing are summarized in Table 3.1. The details of the suppliers are also provided for reference.

**Table 3.1** List of chemicals and materials used in this thesis.

<table>
<thead>
<tr>
<th>Materials/Chemicals</th>
<th>Formula</th>
<th>Purity (%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-methyl-2-pyrrolidinone (NMP)</td>
<td>C₅H₉NO</td>
<td>99.5</td>
<td>Sigma Aldrich, Australia</td>
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<tr>
<td>Sodium carboxymethyl cellulose</td>
<td>C₈₂H₃₀Na₸O₂₇ N/A</td>
<td>N/A</td>
<td>Sigma Aldrich, Australia</td>
</tr>
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<td>Polyvinylidene fluoride (PVDF)</td>
<td>(CH₂CF₂)ₙ N/A</td>
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<td>-</td>
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<td>Milli-Q Water</td>
<td>H₂O</td>
<td>5 ppb (TOC)</td>
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</tr>
<tr>
<td>Polypropylene separator</td>
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<td>Celgard</td>
<td>Hoechst Celanese Corporation, USA</td>
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<tr>
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<td>H₂O₂</td>
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<td>Riedel-de-Haën, Germany</td>
</tr>
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<td>Materials/Chemicals</td>
<td>Formula</td>
<td>Purity (%)</td>
<td>Supplier</td>
</tr>
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<td>---------------</td>
<td>------------</td>
<td>---------------------------</td>
</tr>
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<td>China</td>
</tr>
<tr>
<td>Copper foil</td>
<td>Cu</td>
<td>N/A</td>
<td>China</td>
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<td>Lithium metal</td>
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<td>CR2032 type coin cells</td>
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<td>N/A</td>
<td>China</td>
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<td>Iron (II) oxalate dihydrate</td>
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<tr>
<td>Citric acid</td>
<td>C$_6$H$_8$O$_7$</td>
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<tr>
<td>Iron (II) chloride tetrahydrate</td>
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<tr>
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<td>LiOH·H$_2$O</td>
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<td>Materials/Chemicals</td>
<td>Formula</td>
<td>Purity (%)</td>
<td>Supplier</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>----------------------------</td>
<td>------------</td>
<td>------------------------</td>
</tr>
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<td>Titanium (IV) butoxide</td>
<td>Ti[O(CH₂)₃CH₃]₄</td>
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<td>Multi-walled carbon nanotube</td>
<td>C</td>
<td>90+</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>H₂SO₄</td>
<td>98</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>69</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>LP30 electrolyte</td>
<td>LiPF₆ in EC/DMC (1:1)</td>
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<td>Merck KgaA, Germany</td>
</tr>
<tr>
<td>Vanadium (V) oxide</td>
<td>V₂O₅</td>
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</tr>
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<td>99</td>
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</tr>
<tr>
<td>Diethyl carbonate (DEC)</td>
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<td>99+</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
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<td>CH₃-CO-CH₃</td>
<td>99.9</td>
<td>Sigma Aldrich, Australia</td>
</tr>
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<td>Reagent</td>
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<td>Cyclohexane</td>
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<td>99+</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Nickel nitrate hexahydrate</td>
<td>(Ni(NO₃)₂·6 H₂O</td>
<td>97+</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Polyethylene glycol (PEG)</td>
<td>H(OCH₂CH₂)nOH</td>
<td>N/A</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Materials/Chemicals</td>
<td>Formula</td>
<td>Purity (%)</td>
<td>Supplier</td>
</tr>
<tr>
<td>------------------------------</td>
<td>---------------</td>
<td>------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>99.99</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Lithium hexafluorophosphate</td>
<td>LiPF₆</td>
<td>99.99</td>
<td>Sigma Aldrich, Australia</td>
</tr>
<tr>
<td>Ammonium phosphate monobasic</td>
<td>NH₄H₂PO₄</td>
<td>98.5+</td>
<td>Sigma Aldrich, Australia</td>
</tr>
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<td>Cobalt nitrate hexahydrate</td>
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<td>99</td>
<td>Sigma Aldrich, Australia</td>
</tr>
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<td>Ammonium chloride</td>
<td>NH₄Cl</td>
<td>99.99</td>
<td>Sigma Aldrich, Australia</td>
</tr>
</tbody>
</table>

### 3.2 Experimental Procedures

This PhD research work consists of main two parts: the first part is the synthesis of nanostructured/composite materials and their characterization using different instrumental analysis techniques; while the second part involves the application of these electrochemically active nanostructured/composite materials as electrode for use in lithium-ion batteries. The overall experimental procedures of this PhD research work are shown in Figure 3.1.

### 3.3 Synthesis of Nanostructured/Composite Materials

The electrochemically active nanostructured/composite materials used in this study were synthesised via different methods. In this section, the methods and the
procedures used in preparing the electrochemically active materials are discussed in detail.

**Figure 3.1** The overall scheme of experimental investigations.
3.3.1 Hydrothermal Method

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures, also termed the "hydrothermal method". Hydrothermal synthesis can be defined as a method of synthesis of minerals in hot water under high pressure. The hydrothermal autoclaves used in this doctoral work are 4748 Acid Digestion Bombs with 125 ml capacity from the Parr Instrument Company. The outside parts are made of stainless steel and the inside contains a polytetrafluoroethylene (PTFE) cup. The temperature can reach up to 250 °C. This hydrothermal technique has been extensively used in crystal growth and nanomaterials synthesis. The factors affecting the products in terms of composition, morphology, and crystal structure mainly include the volume of the solvent, which is related to the pressure, the concentration of the precursors, the temperature, and the use of a surfactant. To achieve desired materials with desired morphology and crystal structure, all the parameters need to be further investigated.

3.3.2 Molten Salt Method

In this doctoral work, a simple, easily scaled-up molten salt method to synthesize nanostructured/porous nanocomposite electrode materials at very low temperature (300°C) has been developed. The compounds were mixed thoroughly and ground in a mortar with a pestle. The powder mixture was vacuum dried at 120 °C for 24 h. The drying process was used to minimize the water content in the starting material mixture, and then the mixture was immediately transferred to a muffle furnace and calcined at 300°C. At this temperature, the LiNO₃-LiOH.H₂O-Li₂O₂ mixture, for
example, was melted to become a molten salt near the eutectic composition. This is significantly different from an aqueous solution, and the water content in the molten salt mixture was reduced as much as possible. The mixture thus became very basic, which led to the production of desired stable phases. The molten salt method shows an accelerated reaction rate and controllable particle morphology, because the salt melt acts as a strong solvent and exhibits a high ionic diffusion rate. Furthermore, this method is easy to achieve and scale up, the treatment temperature is low, and the raw molten salt materials are recyclable, so it is economical and promising for industrial application.

### 3.3.3 Spray Pyrolysis

A schematic diagram of the spray pyrolysis experimental set-up is presented in Figure 3.2. The spray pyrolysis system is composed of a peristaltic pump, a nozzle, the air compressor, a 3-zone vertical tube furnace, the sample collector, and a suction system. The precursor solution is sprayed with the aid of compressed air (carrier gas) into the quartz tube, which has an inner diameter of 20 cm and a length of 2 m. The furnace consists of 3 heating zones, which can be controlled accurately for a wide temperature range (150-1400°C). The precursor solution is first prepared in an aqueous solution. The solution is then atomized into small droplets in the pyrolysis chamber in order to produce a fine powder, which is subsequently sucked into the particle collector via the extractor pump. At the end of the spray pyrolysis process, the power of the extractor pump is slowly reduced, and the fine powder is carefully collected while using safety gloves and a respiratory mask. The morphology and crystal structure of the product can be easily controlled via changing the precursor
concentration, temperature, and nozzle size. The advantages of this system are that it is one-step, fast, and industrially oriented.

Figure 3.2 Schematic diagram of the spray pyrolysis process, with inset illustrating oxides-carbon nanocomposite formation [Needham, 2007].

3.3.4 Modified Solid State Reaction

A solid state reaction, also called a dry media reaction or a solventless reaction, is a chemical reaction in which solvents are not used. In a normal reaction, the reacting agents, also called the reactants, are placed in a solvent before the reaction can take place. These reactants react to form a new substance. After the reaction is completed, the new product can be removed from the solvent. A solid-state reaction, however, allows the reactants to chemically react without the presence of a solvent. The advantages of solid state reaction ripple through many industries. In this doctoral
work, a simple ultra-fast solvent assisted manual grinding method, combined with solid state reaction, has been developed to synthesize composite materials with a porous conductive architecture. The reactants for preparing the precursor were ground thoroughly, and a slurry was made by a mortar and a pestle in acetone solvent to ensure intimate and homogeneous mixing at the atomic level. The resulting slurry was dried in an oven at 60°C to remove acetone from the slurry before transfer to a tube furnace for the solid state reaction.

3.4 Physical and Structural Characterization of Nanostructured/Composite Materials

Physical and structural investigations of the synthesised nanostructured/porous nanocomposite electrode materials were conducted using the techniques described below. The equipment belonged to both our Institute and the Intelligent Polymer Research Institute (IPRI) under the Australian Institute for Innovative Materials (AIIM).

3.4.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive technique used to characterise the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples. The samples can be reused for other tests after XRD measurements. The X-rays are scattered by each set of lattice planes at a characteristic angle, and the scattered intensity is a function of the arrangement of atoms in the crystal. The scattering from all the different sets of planes results in a
pattern, which is unique to the crystal structure of a given compound. The X-rays are generated in X-ray tubes when the anode material (usually copper) is irradiated with a beam of high-energy electrons that is accelerated by a high voltage electric field to a very high speed. In addition, photons with energies characteristic of the target material are emitted. A monochromator is used that preferentially suppresses photons with other energies than the desired characteristic one. The X-rays produced are directed to the sample being studied, and X-rays with a wavelength in the range of 10 to 0.01 nanometers, which is on the order of the lattice spacing, are elastically diffracted from the atomic planes in the crystalline material. Re-emitted X-rays interfere, giving constructive or destructive interference. Bragg’s law (Eq. 3.1) describes the diffraction condition from planes with spacing, \(d\):

\[ n\lambda = 2d \sin \theta \]  

(3.1)

where \(d\) is the distance between atomic layers in a crystal, \(\lambda\) is the wavelength of the incident X-ray beam, \(n\) is an integer, and \(\theta\) is the angle of incidence experienced by the X-ray beam reflection from the faces of the crystal [Bragg and Bragg, 1913]. Figure 3.3 illustrates the interference between waves scattered from two adjacent planes of atoms in a crystal. In this PhD study, only X-ray powder diffraction was used. The powder sample is loaded into a small disc-shaped sample holder with a flattened surface. The sample holder is put on one axis of the diffractometer and tilted by an angle \(\theta\), while a detector rotates around it on an arm at a \(2\theta\) angle. This configuration is known under the name Bragg-Brentano. Each crystalline solid produces a distinctive diffraction pattern. Both the positions (corresponding to lattice spacings) and the relative intensities of the lines act to characterize the "fingerprint" for materials. In addition to identifying crystalline phases, X-ray diffraction can also
be used to determine the crystal size. This can be obtained from the broadening of the peaks according to the Scherrer formula (Eq. 3.2): 

$$\beta(2\theta) = \frac{K\lambda}{L \cos \theta} \quad (3.2)$$

where $L$ is the crystal size (nm), $\lambda$ is the X-ray wavelength (Å), $K$ is the shape factor of the average crystallite (with a typical shape factor around 0.9), $\beta$ is the full width at half maximum (FWHM) in radians, and $\theta$ is the peak position (°). XRD patterns were collected in a $2\theta$ configuration using either a Philips PW 1730 or a GBC MMA 017 diffractometer (Cu Kα radiation, $\lambda = 1.5418$ Å).

**Figure 3.3** Reflection of X-rays from lattice planes according to Bragg’s law [Giacovazzo, 2002].
3.4.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a type of investigation performed on samples that determines changes in weight in relation to changes in temperature. In this doctoral work, TGA was used to determine the amount of amorphous carbon and multiwall carbon nanotubes (MWCNTs) in the composite materials. A Mettler-Toledo thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) 1 Star® System was employed. Samples could be heated up to 1000 °C in air or high purity argon, with a typical heating rate of 5-10 °C per min. The container for the sample is made of platinum, and the loading mass of a sample is generally 2-20 mg, depending on the density of the sample.

3.4.3 Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray (EDX) Spectroscopy

Scanning electron microscopy (SEM) is used primarily to observe the electrode’s surface topography or the morphology of powder samples. During the SEM measurements, the sample is bombarded with a scanning beam of electrons. The electrons interact with the atoms that make up the sample, producing signals that contain information about topography, composition, and other properties of the sample surface, such as electrical conductivity. The types of signals produced by an SEM include those from secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light specimen currents, and transmitted electrons. Secondary electron detectors are common in all SEM. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. Secondary electron
imaging (SEI) allows one to observe the surface of a sample. SEM (JEOL JSM 6460A, 30 kV) and field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7500FA, 15 kV) were used to observe the morphology of the materials or electrodes. X-rays, which are produced by the interaction of electrons with the sample, can also be detected in an SEM equipped with an energy-dispersive X-ray (EDX) spectrometer to obtain the elemental composition of a sample. In this doctoral work, morphologies, elemental analysis, and elemental mapping of the samples were generally used. The powder sample was either dispersed in ethanol or directly loaded onto an aluminium holder using carbon conductive tape for SEM observation. A sample for EDX was loaded onto a piece of indium metal to eliminate contamination from the sample holder and the carbon tape. All SEM and FE-SEM measurements were carried out at ISEM.

3.4.4 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a charge-coupled device (CCD) camera. TEM is capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. TEM can be used to observe morphology, crystal structure, and electronic structure. Selected area electron diffraction (SAED) is a crystallographic experimental technique that can be performed inside a transmission electron microscope (TEM). A thin crystalline
specimen is subjected to a parallel beam of high-energy electrons. As the electrons pass through the sample, electrons are treated as wave-like, rather than particle-like. Because the wavelength of high-energy electrons is a fraction of a nanometer, and the spacings between atoms in a solid are only slightly larger, the atoms act as a diffraction grating for the electrons. That is, some fraction of the electrons will be scattered to particular angles, as determined by the crystal structure of the sample, while others continue to pass through the sample without deflection. As a result, the image on the screen of the TEM will be a series of spots, with each spot corresponding to a satisfied diffraction condition of the sample's crystal structure. If the sample is tilted, the same crystal will stay under illumination, but different diffraction conditions will be activated, and different diffraction spots will appear or disappear. Transmission electron microscopy (TEM) investigations were performed using a 200 keV JEOL 2011 instrument, with a JEOL-Energy Dispersive X-ray Spectroscopy (EDS) detector and a JEOL EDS software analysis system. TEM samples were prepared by deposition of ground particles onto holey/lacey carbon support films. Most of the TEM measurements in this research work were performed with the kind collaboration of Dr. David Wexler from the Faculty of Engineering, University of Wollongong.

3.4.5 Brunauer Emmett Teller (BET) Specific Surface Area Measurement

Specific surface areas of the nanostructured/composite particles were measured with a Quantachrome Nova 1000 nitrogen gas analyzer using the Brunauer-Emmett-Teller (BET) method. The BET specific surface area was determined through a 15-points nitrogen adsorption isotherm at 77 K after degassing the powder samples with
nitrogen at 150°C. Typically, a sample mass of approximately 200-500 mg is required, depending on the sample density.

### 3.4.6 Magnetic Measurement

The physical properties measurement system (PPMS) is an automated low-temperature and magnet system for the measurement of material properties such as specific heat, magnetic AC- and DC-susceptibility, and both electrical and thermal transport properties. The base unit of the PPMS consists of a cryostat with a superconducting magnet coil. The different measurement possibilities (options) result from the use of different measurement inserts or sample holders and the corresponding software mode. PPMS MultiVu is Windows™-based control software that contains all the functions essential for each measurement application. Its advanced expandable design combines many features in one instrument to make the PPMS the most versatile system. In this doctoral work, magnetic measurements were performed with the kind collaboration of Dr. Rong Zeng, ISEM, University of Wollongong. Magnetic measurements were carried out using a physical properties measurement system (PPMS) 14T magnetometer in the temperature range from 5-305 K and magnetic fields up to 1 T.

### 3.4.7 Raman Spectroscopy

Raman spectroscopy, which provides a fingerprint of molecules due to the vibration of chemical bonds and symmetry of molecules, is commonly used in chemistry to identify materials. Raman spectra were recorded using a JOBIN Yvon Horiba Raman
Spectrometer model HR800, employing a 10 mW helium/neon laser at 632.8 nm, which was filtered by a neutral density filter to reduce the laser intensity, and a charge-coupled detector (CCD). This Raman system was provided by the Intelligent Polymer Research Institute (IPRI), and spectroscopy was performed with the kind collaboration of Dr. Shulei Chou from ISEM.

3.5 Electrode Preparation and Test Cell Assembly

3.5.1 Electrode Preparation

The working electrodes for lithium-ion battery tests were prepared by mixing nanostructured/composite active materials with 10-20 wt.% acetylene black (AB) and 5-10 wt.% polyvinylidene fluoride (PVDF) or sodium carboxymethyl cellulose (CMC) in a solvent, consisting of either N-methyl-2-pyrrolidone (99.5%, Aldrich) or water, respectively. The slurry was uniformly pasted onto pieces of Cu (anode) or Al (cathode) foil with an area of 1 cm². The typical active mass loading of the electrodes was 2-5 mg cm⁻², depending on the density of the electrochemically active samples. Subsequently, the coated electrodes (average thickness of ~ 50 μm) were dried in a vacuum oven at 90-120°C for 24 h. The electrode was then either pressed under a pressure of approximately 3000 kg cm⁻² for 10 s to enhance the contact between the electrochemically active materials and the conductive carbon black, or used without pressing, depending on the materials. All measurements were performed using metallic lithium as the counter electrode because the potential of metallic lithium is nearly constant at moderate or low current densities. The counter
electrode also acts as the reference electrode. These working electrodes were used for electrochemical cell assemblies for further electrochemical testing.

3.5.2 Test Cell Assembly

The electrochemical cells (CR2032 coin type cell) contained active materials on Cu or Al foil as the working electrode, Li foil as the counter electrode and reference electrode, a porous polypropylene film as separator, and 1 M LiPF$_6$ in a 50:50 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte. The cells were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany) with O$_2$ and H$_2$O levels less than 1 ppm. The specific capacity has been calculated based on the mass of active materials in the electrode. A schematic diagram of the coin-type cell used in ISEM (Chou, 2010) is shown in Figure 3.4.

![Figure 3.4](image)

**Figure 3.4** A schematic diagram of the coin-type cell, CR2032, used at ISEM (Chou, 2010).
3.6  Electrochemical Characterization

When an electrochemical system is subjected to the passage of current between the two electrodes, it is then out of equilibrium. Usually we are interested in investigating the electrode process at one electrode, which is the working electrode. The other electrode, the counter electrode, is used to complete the external circuit. Occasionally a third electrode is employed, the reference electrode. When this is the case, the electrode potential is monitored with respect to the reference electrode. Electrochemical measurements, including cyclic voltammetry, charge-discharge testing, and electrochemical impedance spectroscopy, were used to characterize the performance of the electrodes in a lithium-ion battery system.

3.6.1  Cyclic Voltammetry (CV)

Cyclic Voltammetry (CV) is perhaps the most effective and versatile electroanalytical technique available for lithium-ion batteries, especially for the determination of the thermodynamics and kinetics of electron transfer at the electrode-electrolyte interface. It enables the electrode potential to be rapidly scanned in search of redox couples. It is used most often as a diagnostic tool for elucidating electrode mechanisms. The important parameters are the maximum and minimum potential ranges, which define the potential window. The choice of this potential window must take into account the stability range of the chosen electrolyte, to thereby avoid its decomposition. The cell is cycled in the potential window, where the potential applied on the working electrode is scanned at a constant rate. The change in potential as a function of time is called the scan rate. By measuring the
current change over a whole cycle (cathodic and anodic scan), one can tell that a particular electrochemical reaction happens and is associated with the observation of a current peak. A positive sweep rate causes the oxidation of the working electrode, and the resulting current has a positive sign. With a negative sweep rate, the reduction of the working electrode causes a negative current. Cyclic voltammetry (CV) measurements were conducted via a CHI 660 electrochemical workstation (CH Instruments, Cordova, TN) at ISEM.

### 3.6.2 Charge and Discharge

The charge-discharge tests were conducted at a constant current density. The capacity (Q) can be calculated based on the charge or discharge time using the formula $Q = I \times t$, where $I$ is current density and $t$ is the time. The instrument used here to obtain the data was a Neware battery tester (China) at ISEM.

### 3.6.3 Electrochemical Impedance Spectroscopy (EIS)

AC impedance spectroscopy is a powerful technique to determine the kinetic parameters of the electrode process, including those in the electrolyte, passivation layers, charge transfer, and Li$^+$ diffusion. Charge-transfer resistance ($R_{ct}$) is one of the important parameters for quantitatively characterizing the speed of an electrode reaction. Normally, a large charge-transfer resistance indicates a slow electrochemical reaction. The $R_{ct}$ can be calculated from electrochemical impedance spectroscopy (EIS), with the value equal to the diameter of the compressed semicircle in the medium-frequency region, as shown in Figure 3.5. Typically, the
impedance curves of a lithium-ion battery show one compressed semicircle in the medium-frequency region, which could be assigned to the charge-transfer resistance ($R_{ct}$), and an inclined line at approximately 45° in the low frequency range, which could be considered as Warburg impedance. The ac impedance spectroscopy measurements were carried out at ISEM using a CHI660B/CHI 660C electrochemical workstation system (CH Instruments, Cordova, TN) by applying a sine wave of 5 mV amplitude over a frequency range of 100.00 kHz to 0.01 Hz.

Figure 3.5 Typical electrochemical impedance spectroscopy (EIS) curve of lithium-ion battery system.
CHAPTER 4

NANOCRYSTALLINE POROUS α-LiFeO$_2$-C COMPOSITE – AN ENVIRONMENTALLY FRIENDLY CATHODE FOR THE LITHIUM-ION BATTERY

4.1 Introduction

The rapid progress in electronics and increasing public awareness of environmental issues have recently been putting more pressure on clean sustainable energy sources, including lithium ion batteries [Liu and Cao, 2010]. Thus, achieving the goals of low cost combined with higher energy density, better cycling stability, and non- or less toxic and more environmentally friendly materials as electrodes for lithium ion batteries has become mandatory if clean renewable technologies are to be developed for the future [Liu and Cao, 2010; Scrosati and Garche, 2010]. Among various cathode materials, layered LiCoO$_2$ is the most widely used in commercial Li-ion batteries due to its high energy density, high operating voltage and good electrochemical performance with charge cut-off voltage lower than 4.2V. However, when the charge cut-off voltage increases to 4.4 from 4.2V, the $x$ in Li$_x$CoO$_2$ decreased from 0.45 to 0.3, resulting in a rapid capacity loss and a large anisotropic volume change of over 3 % because of the phase transition among hexagonal, monoclinic, and H1-3 phases [Li et al., 2008a]. LiNiO$_2$, which also forms a distorted rock-salt structure, is lower in cost and has a higher energy density [Yamada et al., 2001], but is less stable [Amriou et al., 2005; Liu et al., 2007a], and less ordered
[Rougier et al., 1996], as compared to LiCoO₂. In the case of LiMn₂O₄, the paths for lithiation and delithiation are a 3-dimensional network of channels rather than planes, as in the distorted rock-salt structure. LiMn₂O₄ is less expensive and safer than LiCoO₂ [Whittingham, 2004; Pasquier et al., 2009; Belharouak et al., 2007], but it has a lower capacity. Another of the challenges in the use of LiMn₂O₄ as a cathode material is that phase changes can occur during cycling [Liu et al., 2007b; Molenda et al., 2007; Thackeray, 1999]. Various strategies have been proposed and tested to avoid some of these drawbacks, and scientists are still struggling to minimize these problems. Recently, iron-based compounds have attracted much attention as active materials for rechargeable Li batteries. Lithium ferrite (LiFeO₂), with a theoretical capacity of 282 mAhg⁻¹, has important advantages compared to LiCoO₂ and LiNiO₂ for practical use, because it is non-toxic, environmentally friendly, and contains iron, the most abundant and low cost metal available in the world [Uzunova et al., 2006; Lee et al., 2002]. Five different polymorphs of lithium ferrite, LiFeO₂, have been studied as potential alternatives to Li-Co-O positive electrodes [Lee et al., 2002; Kanno et al., 1997; Sakurai et al., 1997; Sakurai et al., 1998; Matsumura et al., 2002; Wang et al., 2004c; Morales and Santos-Pena, 2007]. In the α-LiFeO₂ structure, which crystallizes in the cubic system, Li⁺ and Fe³⁺ randomly occupy the octahedral sites, while γ-LiFeO₂ has a tetragonal structure in which the Li⁺ and Fe³⁺ ions are ordered along the tetragonal c axis. β-LiFeO₂ appears to be an intermediate phase formed during the ordering process [Uzunova et al., 2006; Morales and Santos-Pena, 2007]. However, many problems still remain, such as low operating voltage (2 V), poor electrochemical activity, especially for the cubic α- and γ-forms, and low capacity retention during cycling tests [Uzunova et al., 2006; Lee et al., 2003a]. It has been reported that the electrochemical properties in lithium batteries of a
A nanosized form of $\alpha$-LiFeO$_2$ included long cycle life with capacities up to 150 mAh g$^{-1}$ at C/4 (0.25 C) in the range of 4.5-1.5 V over at least 50 cycles, and these values were several times higher than those reported for several other polymorphs or even the $\alpha$-form itself [Sakurai et al., 1998; Wang et al., 2004c; Morales and Santos-Pena, 2007]. Very recently, it was reported that an $\alpha$-LiFeO$_2$-Ag composite film had delivered a reversible capacity of 160 mAh g$^{-1}$ at C/5 after 40 cycles in the 4.75-1.5 V range [Martin et al., 2010]. It should be noted that almost all the previous reports were focused on very low rate charge/discharge current densities. It is still a great challenge to improve both the cycling stability and the rate capability of iron-based materials. Furthermore, it has been shown that the capacity retention of iron oxide can be improved via fabricating active materials into hollow/nano-structures which could accommodate volume changes and shorten the lithium diffusion length [Chen et al., 2005; Wu et al., 2006; Wu et al., 2008; Zeng et al., 2007; Zeng et al., 2008]. In addition, a selected binder, sodium carboxymethyl cellulose (CMC), can also improve the cycling performance of iron-based materials [Li et al., 2008; Chou et al., 2010]. The rate capability in a lithium-ion battery system is particularly limited by the transportation of both lithium ions and electrons [Bruce et al., 2008; Taberna et al., 2006; Guo et al., 2008]. By producing nanostructured materials in/on a conducting matrix (metal or carbon), the high rate capability can be significantly improved [Taberna et al., 2006; Guo et al., 2007]. A relatively low mass, good electronic conductivity, reasonable Li-insertion capability, and small volume expansion coupled with softness and compliance make carbon the best active matrix [Kurita and Endo, 2002; Ng et al., 2006a]. The beneficial effect of the carbon coating, not only buffer the great volume changes during the cycling process, but also avoid possible agglomeration and alleviate mechanical stress of the distributed
particles [Ng et al., 2007; Guo et al., 2009]. In this Chapter, the synthesis of porous \( \alpha \)-LiFeO\(_2\)-C nanocomposite by a simple molten salt method using very low temperature, followed by a carbon coating process, is reported. This method is unlike the previous method used by other researchers, as it does not require the use of high temperature; the fabrication process is also energy saving. Furthermore, electrochemical measurements have demonstrated that the \( \alpha \)-LiFeO\(_2\)-C nanocomposite can be used as a novel cathode material in lithium-ion batteries, with significant advantages in terms of environmental safety issues, high capacity, good cycling stability, and high-rate capability compared with those previously reported results.

4.2 Materials Synthesis

The \( \alpha \)-LiFeO\(_2\) powder was synthesized by mixing together FeCl\(_2\)·4H\(_2\)O (Aldrich, 95%), LiOH·H\(_2\)O (Sigma-Aldrich, 98 %), LiNO\(_3\) (Sigma-Aldrich, 99.9 %), and Li\(_2\)O\(_2\) (Sigma-Aldrich, 90 %) with a molar ratio of 0.01:0.1:0.1:0.01, respectively, followed by grinding the mixture in a mortar with a pestle until it became homogenous. The powder mixture was vacuum dried at 120 °C for 24 h. The drying process was used to minimize the water content in the starting material mixture for the molten salt (LiNO\(_3\)-LiOH·H\(_2\)O). The mixture was immediately placed in an alumina crucible, and heated to and kept at 300 °C for 3 h in a muffle furnace in air. At this temperature, the LiNO\(_3\)-LiOH·H\(_2\)O:Li\(_2\)O\(_2\) mixture was melted to become a molten salt near the eutectic composition. This is significantly different from an aqueous solution, and the water content in the molten salt solution was reduced as much as possible. The resulting products were washed with large amounts of ethanol.
and distilled water, followed by drying at 100 °C for 12 h under a vacuum pressure of 0.1 MPa. The synthesized α-LiFeO₂ nanoparticles were then coated with amorphous carbon. Toluene (C₇H₈, 99.5%) and malic acid (C₄H₆O₅, 99%) were used as the solvent and the carbon source during the coating process, respectively. Both α-LiFeO₂ and malic acid were dispersed together in toluene with continuous stirring at room temperature for 2 h. The slurry was dried at 100 °C for 6 h at a vacuum pressure of 0.1 MPa and then further heat-treated at 300 °C for 3 h in air. The resultant particles were collected, washed, and vacuum treated again at 120 °C for 24 h to eliminate residual water on the particle surfaces.

### 4.3 Physical and Structural Characterization

The XRD patterns of the resulting products with and without carbon coating are shown in Figure 4.1. These patterns exhibit several peaks that could be ascribed to α-LiFeO₂ and were indexed in the cubic system with lattice parameter \(a = 4.158 \, \text{Å}\), which is quite consistent with the reported value (JCPDS 17-938). The main peaks for the pattern of the carbon-coated composite show a decrease in intensity, with a shift of the (111) peak compared to the uncoated material. Since the heat treatment temperature is low, it is proposed that the coated carbon is amorphous and that the amorphous carbon coating on the surface is responsible for weakening of the intensities of the XRD peaks [Cao et al., 2007]. An additional small and broad peak at \(\sim 30^\circ\) may be due to the presence of amorphous phase, as the synthesis method is conducted at relatively low temperature. The approximate crystallite sizes of the α-LiFeO₂ and α-LiFeO₂-C powder samples were calculated using the Debye-Scherrer equation applied to the marked peaks, assumed to be originating from (220), where
the Si standard 220 peak was used as the full-width half-maximum (FWHM) reference (0.204°) for the un-broadened peak. The crystal sizes were found to be 6.45 nm for the uncoated material and 5.42 nm for the carbon coated composite. The specific surface areas were also measured to be 97.98 m²g⁻¹ for the α-LiFeO₂ and 115.52 m²g⁻¹ for the α-LiFeO₂-C by the 15 points BET N₂ adsorption method.

![X-ray diffraction patterns of α-LiFeO₂ and α-LiFeO₂-C nanocomposite.](image)

**Figure 4.1** X-ray diffraction patterns of α-LiFeO₂ and α-LiFeO₂-C nanocomposite.

However, to detect and estimate the amount of amorphous carbon in the α-LiFeO₂-C composite materials, Raman spectroscopy (Figure 4.2(a)) and TGA (Figure 4.2(b)) were carried out, respectively. In the range of 1000-1800 cm⁻¹ (Figure 4.2(a)), it can be observed that the Raman spectra exhibit a typical characteristic of amorphous carbon, a broad peak located approximately in the range of 1200-1700 cm⁻¹, which is usually fitted to two peaks at approximately 1605 cm⁻¹ (G band) and 1357 cm⁻¹ (D band) [Garcia-Zarco et al., 2009]. On the other hand, TGA was carried out in air (Figure 4.2(b)). As the α-LiFeO₂ powders remained stable over the selected temperature range, any weight change is believed to correspond to the oxidation of
amorphous carbon [Ng et al., 2007]. It was estimated that the amount of total weight loss in the composite was approximately 25 wt.%, where ~ 6 wt.% weight loss could be considered as from loss of moisture and volatile organic compounds in the α-LiFeO2-C, starting from 50 °C. The remaining amount, ~ 19 wt.%, was attributed to the amorphous carbon produced by the decomposition of malic acid (C4H6O5) in the precursor.

Figure 4.2 Raman spectrum obtained from α-LiFeO2-C nanocomposite (a) and TGA analysis of α-LiFeO2 and α-LiFeO2-C nanocomposite (b).

Typical field emission scanning electron microscope (FE-SEM) observations of the two samples are shown in Figure 4.3. A low magnification FE-SEM image of α-LiFeO2 (Figure 4.3(a)) shows that the sample consists of large agglomerated clusters.
Under high magnification, it can be seen that each cluster is composed of numerous spherical nanoparticles, each having a smooth surface and a typical diameter of ~ 10-20 nm (Figure 4.3(b)). In the case of the $\alpha$-LiFeO$_2$-C sample, a low magnification image (Figure 4.3(c)) reveals that the sample consists of numerous agglomerated nanoclusters. These nanoclusters are composed of very tiny nanoparticles joined by a porous architecture, as can be clearly seen under high magnification (Figure 4.3(d) and inset), which can account for the high surface area of the $\alpha$-LiFeO$_2$-C sample.

Figure 4.3 FE-SEM images of $\alpha$-LiFeO$_2$ and $\alpha$-LiFeO$_2$-C nanocomposite: (a) low magnification image of large agglomerated clusters of $\alpha$-LiFeO$_2$; (b) high magnification image of clusters composed of numerous nanoparticles; (c) low magnification image of $\alpha$-LiFeO$_2$-C, consisting of numerous nanoclusters; (d) high-resolution image of individual nanocluster of $\alpha$-LiFeO$_2$-C, which is composed of very tiny nanoparticles joined by a porous architecture. The inset shows the same area at higher magnification.
TEM investigations further revealed that the samples consist of tiny particles with a spheroidal shape (Figure 4.4). Figure 4.4(a) shows an intermediate magnification image and the corresponding selected area electron diffraction (SAED) pattern (inset) of the $\alpha$-LiFeO$_2$ sample, where all of the ring spots are evaluated to represent $d$-spacings of 0.24, 0.20, and 0.14 nm, which can be referred to the crystallographic directions of (111), (200), and (220), respectively. These results are also consistent with the standard information provided by the XRD patterns. Figure 4.4 (b) presents a high resolution TEM (HRTEM) image of the same sample. Amorphous carbon incorporated into the pores can be clearly observed among the nanoparticles of the $\alpha$-LiFeO$_2$-C sample (Figure 4.4(c)).

**Figure 4.4** (a) TEM image with its corresponding SAED pattern (inset), and (b) HRTEM image of the $\alpha$-LiFeO$_2$ sample; (c) TEM and (d) HRTEM images of the $\alpha$-LiFeO$_2$-C sample.
High resolution imaging of the C-containing sample (Figure 4.4(d)) also resulted in contrast consistent with the presence of carbon incorporated into pores among the nanocrystals, and some nanocrystals are covered by a thin layer of carbon, as well.

### 4.4 Electrochemical Characterization

To test the electrochemical performance, sample powders were mixed with acetylene black (AB) and a binder, carboxymethyl cellulose (CMC), in a weight ratio of 80:15:5 in a solvent (distilled water). The slurry was spread onto aluminium foil substrates. The coated electrodes were dried in a vacuum oven at 110 °C for 24 h to remove water molecules. The electrode was then pressed using a disc with a diameter of 14 mm to enhance the contact between the aluminium foil, active materials, and conductive carbon. Subsequently, the electrodes were cut to a 1 × 1 cm² size. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume, provided by MERCK KgaA, Germany). The cells were galvanostatically charged and discharged in the range of 4.5-1.5 V at different current densities using a computer-controlled charger system manufactured by Neware Battery Testers. The calculated capacity was based on the weight of active materials (α-LiFeO₂). Electrochemical impedance spectroscopy (EIS) was performed on the electrodes using a CHI 660C electrochemistry workstation. The AC amplitude was 5 mV, and the frequency range applied was 100 kHz - 0.01 Hz. Figure 4.5 shows typical charge-discharge curves for different cycles of α-LiFeO₂ (a) and α-LiFeO₂-C (b) electrodes in coin test cells using lithium as the counter and reference electrode between 1.5 and 4.5 V (vs. Li⁺/Li). The profiles are somewhat different from those obtained for the Swagelok cell configuration [Morales et al.,
2008]. The coin cells used herein (CR2032 model) have some advantages over Swagelok cells. The coin cell has a bigger diameter that allows the use of a greater amount of electrolyte, increasing the electrolyte-electrode interface, and the cell components are more tightly packed than those of the Swagelok cells, thus decreasing the cell impedance. As a result, the cell activity in the first charge was better for the coin cells [Morales and Santos-Pena, 2007]. On charging the cell with the $\alpha$-LiFeO$_2$ electrode, the voltage exhibited a rapid increase from 2.3 to 3.0 V, followed by a steep increase to 4.0 V and then a gradual increase to 4.5 V, as a plateau is observed in the initial charge curve between 4.0 and 4.5 V. During the first discharge, the cell voltage decreased quickly to 4.0 V, followed by a steep decrease to 3.25 V and then a slow decrease to the cut-off voltage of 1.5 V, with a voltage plateau in the 1.9-2.2 V region. Subsequent charge/discharge curves were S-shaped, similarly to those of iron oxides with various structures, including $\alpha$-LiFeO$_2$ [Sakurai et al., 1998; Wang et al., 2004c; Morales and Santos-Pena, 2007], corrugated layered LiFeO$_2$ [Lee et al., 2002; Lee et al., 2003c; Lee et al., 2003], goethite-type LiFeO$_2$ [Sakurai et al., 1997], and spinel-type LiFe$_5$O$_8$ [Kim and Manthiram, 1999]. However, a significant difference is observed in the initial charge-discharge curve for the $\alpha$-LiFeO$_2$-C electrode compared with $\alpha$-LiFeO$_2$. On charging the cell with the $\alpha$-LiFeO$_2$-C electrode, the voltage increased gradually to 3.0 V, followed by a steep increase to 4.0 V and then a gradual increase to 4.5 V. For the initial discharge, the cell voltage decreased rapidly to 3.5 V and then decreased slowly to the cut-off voltage of 1.5 V, with subsequent charge/discharge curves following the same trend as for the $\alpha$-LiFeO$_2$ electrode. The reversible electrochemical reaction occurring in the $\alpha$-LiFeO$_2$ cathode might be due to the participation of the redox couple Fe$^{2+}$/Fe$^{3+}$ in the reaction:
Li_{1+x}FeO_2 \rightarrow LiFeO_2 + xLi^+ + xe^-, \quad (4.1)
as proposed for other LiFeO_2 isomers [Lee et al., 2003; Kanno et al., 1996]. A
different mechanism has also been proposed based on the reaction:

LiFe^{III}O_2 \rightarrow xLi^+ + xe^- + Li_{1-x}Fe^{III}_{1-x}Fe^{IV}_xO_2, \quad (4.2)
on charging the cell [Morales et al., 2008]. However, there is no experimental
evidence reported for the formation of Fe^{4+} in the charged electrode at 4.5 V
[Matsumura et al., 2002; Armstrong et al., 2008]. The cycling stabilities of \( \alpha \)-LiFeO_2
and \( \alpha \)-LiFeO_2-C nanocomposite electrodes at 0.5 C are shown in Figure 4.5(c). The
\( \alpha \)-LiFeO_2 electrode shows an initial discharge capacity of 284 mAh g\(^{-1}\), and the
capacity drops rapidly after 30 cycles. After 100 cycles, the discharge capacity was
measured to be 120 mAh g\(^{-1}\), which is only around 42% of the initial discharge
capacity, confirming the poor cycling stability of the \( \alpha \)-LiFeO_2 electrode. It can be
seen that the \( \alpha \)-LiFeO_2-C nanocomposite electrode shows greatly enhanced capacity
retention. The \( \alpha \)-LiFeO_2-C electrode shows an initial discharge capacity of 287 mAh
\( g^{-1} \), and after 100 cycles, it was measured to be 230 mAh \( g^{-1} \), which is around 80% of
the initial discharge capacity, confirming that there is only 20% capacity fading in
this electrode. Furthermore, the cycling performance of the \( \alpha \)-LiFeO_2 and \( \alpha \)-LiFeO_2-C
nanocomposite electrodes at different charge/discharge rates, measured after 5
cycles at each rate from 0.1 to 3 C in an ascending order, followed by a return to 0.1
C, is shown in Figure 4.5(d). The \( \alpha \)-LiFeO_2-C nanocomposite electrode presents
excellent cycling stability at each rate, and reversible capacities were measured to be
255, 219, 195, 170, and 153 mAh \( g^{-1} \) at the rates of 0.1, 0.5, 1, 2, and 3 C,
respectively. After 35 cycles, the reversible capacity of the \( \alpha \)-LiFeO_2-C
nanocomposite at 0.1 C was still 245 mAh \( g^{-1} \) (96 % of the initial reversible capacity
of 255 mAh \( g^{-1} \)), illustrating its excellent cycling performance, even after cycling at
high rates, which is clearly much better than the performance of the $\alpha$-LiFeO$_2$ electrode (173 mAh g$^{-1}$).

**Figure 4.5** Electrochemical performance of $\alpha$-LiFeO$_2$ and $\alpha$-LiFeO$_2$-C nanocomposite electrodes: (a, b) galvanostatic charge-discharge profiles at 0.5 C for selected cycles; (c) cycling stability up to 100 cycles at 0.5 C; (d) consecutive cycling behaviour at different rates; (e) electrochemical impedance spectra after charge/discharge for 5 cycles.
EIS spectra for the $\alpha$-LiFeO$_2$ and $\alpha$-LiFeO$_2$-C composite electrodes were collected after charge-discharge for five cycles. The Nyquist plots (Figure 4.5(e)) show one compressed semicircle in the high to medium frequency range, which expresses the charge transfer resistance ($R_{ct}$) for both electrodes, and an approximately 45° inclined line in the low-frequency range, which could be considered as Warburg impedance. By comparing the diameters of the semicircles, the impedance of the $\alpha$-LiFeO$_2$ electrode is significantly larger than that of the $\alpha$-LiFeO$_2$-C electrode. The values of $R_{ct}$ for the $\alpha$-LiFeO$_2$ and $\alpha$-LiFeO$_2$-C electrodes were calculated to be 349 and 147 $\Omega$, respectively. Obviously, the $R_{ct}$ of the $\alpha$-LiFeO$_2$-C electrode is much smaller than that of the $\alpha$-LiFeO$_2$ electrode, indicating the enhanced ionic conductivity of the $\alpha$-LiFeO$_2$-C composite.

In brief, several reasons could be given for the excellent electrochemical performance of the $\alpha$-LiFeO$_2$-C nanocomposite electrode. The porous nanostructured $\alpha$-LiFeO$_2$-C composite could provide better contact between the electrode and electrolyte, reducing the traverse time for both electrons and lithium ions. This also offers flexibility and toughness to absorb the contraction and expansion processes during lithium-ion insertion/extraction, which would help to enhance the electrochemical performance [Mai et al., 2007; Maier, 2005; Hu et al., 2006; Mai et al., 2003; Guo et al., 2009]. On the other hand, carbon incorporated into the pores among the nanoparticles and the carbon layer around the nanocrystals, which could further extend the surface area and provides the carbon shell on the surface of the $\alpha$-LiFeO$_2$ nanoparticles, are also beneficial for the electrolyte diffusion into the bulk of the cathode, provide fast transport channels for the Li ions, and accommodate the volume variation more effectively, thus increasing the structural stability of the
electrode and protecting the film from further high volume expansion during cycling [Hassan et al., 2010; Fu et al., 2009]. Similar effects have also been shown to improve the performance of LiCoO₂, LiFePO₄, and LiMn₂O₄ materials, especially at high charge/discharge rates, where the carbon provides a path for electrons without blocking the access for Li⁺ ions [Cao et al., 2007; Chang et al., 2009; Joachin et al., 2009; Patey et al., 2009]. So, it is believed that the carbon incorporated into the porous conductive architecture among the nanoparticles not only has benefits in terms of decreasing the absolute volume changes and improving the mobility of the lithium ions, but also offers a conductive pathway along the whole interconnected wall in the structure, which is favourable for the transport of electrons, promotes liquid electrolyte diffusion into the bulk material, and acts as a protective layer during the redox reaction between Fe²⁺ and Fe³⁺.

4.5 Conclusions

In this study, porous α-LiFeO₂-C nanocomposite with high surface area has been successfully produced using the molten salt method, which was followed by a carbon coating process. For comparison, nanocrystalline α-LiFeO₂ was also investigated. TEM observations demonstrated that a thin layer of amorphous carbon exists around the nanocrystals, and amorphous carbon is also incorporated into the pores among the nanocrystals. The α-LiFeO₂-C nanocomposite electrode delivered a higher reversible capacity and very stable cycle life compared to α-LiFeO₂ electrode, which makes this novel nanostructured porous composite a very promising cathode material for the lithium ion battery.
CHAPTER 5

ENHANCED LITHIUM STORAGE IN A VO2-MULTIWALL CARBON NANOTUBE MICROSHET COMPOSITE PREPARED VIA AN IN-SITU HYDROTHERMAL PROCESS

5.1 Introduction

Vanadium oxides have attracted great attention because of their outstanding properties and potential applications in catalysis [Magg et al., 2004], chemical sensors [Liu et al., 2002a], high energy density lithium batteries [Sudant et al., 2004], and electrochemical and optical devices [Azens et al., 2003]. For Li-ion intercalation applications, vanadium oxides are a promising alternative, as vanadium is known to exist in a wide range of oxidation states from +2, as in VO, to +5, as in V2O5, and the vanadium oxides have the potential to offer much higher capacities along with the essential advantages of low cost, abundant source material, and easy synthesis. Among the various known vanadium oxides, metastable oxides such as VO2(B), H2V3O8, V2O5-δ, V2O5, and LiV3O8 have been found to show interesting cathode properties in lithium cells [Kannan and Manthiram, 2003; Qiao et al., 2006; Zhang et al., 2001; Reddy et al., 2007]. VO2 exhibits four different polymorphic structures, including the most stable, VO2(R) with rutile structure, the monoclinic VO2(B) with a slightly distorted rutile structure, the tetragonal structure of VO2(A), and the metastable VO2(B) with monoclinic structure [Chirayil et al., 1998]. VO2(B), in particular, with its metastable monoclinic structure, is a promising cathode material.
for both organic and aqueous lithium-ion batteries [Li et al., 1994; James, 1994; Li and Dahn, 1995]. The crystal structure of VO$_2$(B) consists of sheets of edge sharing VO$_6$ octahedra linked by corner sharing to adjacent sheets along the c-direction of the unit cell [Baudrin et al., 2006]. This sharing structure is related to the structural stability and the consequent resistance to lattice shearing during cycling in the lithium-ion battery [Tsang and Manthiram, 1997]. Recently, considerable efforts have been made toward the preparation of VO$_2$(B) nanocrystals. Several nanostructured VO$_2$(B) materials, including nanowires, nanobelts, nanorods, nanoneedles, nanoribbons, and urchin-like morphologies have been obtained [Chen et al., 2004a; Armstrong et al., 2008b; Liu et al., 2004; Zhang et al., 2006; Sediri and Gharbi, 2009; Liu et al., 2008a; Chen et al., 2004b; Li et al., 2007b; Sediri et al., 2006; Liu et al., 2007; Mao and Liu, 2008; Li et al., 2009a]. However, its poor cycling lifetime (usually less than 20 cycles) greatly limits practical applications. The capacity fading of nanoscale VO$_2$(B) is probably due to vanadium dissolution as in other polymorphs below a discharge voltage of 2 V [Sudant et al., 2004; Chernova et al., 2009] and also the nanosized forms of VO$_2$(B), which have large specific surface areas and high surface energies, making it easier to form the agglomerated state during the electrochemical cycling, thus increasing the charge transfer resistance [Rahul et al., 2009; Liu et al., 2009].

Recently, material scientists have shown that three-dimensional (3D), hierarchical, micro-/nano-structures, such as VO$_2$(B) microflowers [Zhang et al., 2009] and VO$_2$(B) hollow microspheres [Liu et al., 2009a], exhibit improved electrochemical properties because they not only inherit the properties of the nano-units, but also have collective properties from the self-assembly of nano-units into microscale
structures. From this point of view, microscale structures (composed of nano-units) could be the best choice of material, rather than single nano-units. In addition, coating the surface of the electrode material with carbon has also been proven to be an effective way to increase the cycling stability [Kim et al., 2008; Luo et al., 2008; Luo and Xia, 2007]. The detailed mechanism responsible for this improvement remains unclear; one possible explanation is the enhanced electronic conductivity resulting from the carbon layer [Mi et al., 2008].

Inspired by this concept, a novel VO$_2$(B)-multiwall carbon nanotube (MWCNT) microsheet composite has been synthesized. The controlled synthesis of VO$_2$(B) is relatively difficult because vanadium is known to exist in a wide range of oxidation states from +2 to +5, and VO$_2$(B) tends to be transformed (> 300 °C) to thermodynamically more stable rutile VO$_2$ [Tsang and Manthiram, 1997], which is not usable as a cathode material for the lithium-ion battery. Electrode using carboxymethyl cellulose (CMC) binder is also being reported for the first time for this material. The composite microstructure exhibits high lithium storage properties and provides good electronic contact owing to the good mechanical properties and high conductivity provided by MWCNTs. Furthermore, the electrochemical measurements demonstrate that the VO$_2$(B)-MWCNT microsheet composite can be used as an alternative cathode material in lithium-ion batteries with high capacity, good cycling stability, and high-rate capability.

5.2 Materials Synthesis

First, MWCNTs were treated by a mixture of H$_2$O$_2$ (35%, Riedel-de Haën) and sulphuric-nitric acid (3:1 ratio) using a reflux process. The system was heated at 120
℃ for 2 h. The product was washed with deionized water and dried in a vacuum oven at 60 ℃ overnight. VO₂(B)-MWCNT microsheet composite precursor was prepared by an in-situ hydrothermal process. In a typical synthesis, a suitable amount of treated MWCNTs, 0.365 g V₂O₅ powder (purissima, Riedel-de Haën), 10 mL n-butanol (> 99.0%, Sigma-Aldrich), and 30 mL de-ionized H₂O were mixed together for 4 h using an ultrasonic probe, which was followed by vigorous magnetic stirring at room temperature for 4 h. An orange suspension was obtained. The resultant mixture was then transferred to a 40 mL autoclave and kept in an oven at 180 ℃ for 48 h under a vacuum pressure of 0.1 MPa. The product was washed with anhydrous ethanol and cyclohexane several times. The produced VO₂(B)-MWCNT composite precursor was dried at 80 ℃ in vacuum oven for 12 h. The crystalline VO₂(B)-MWCNT microsheet composite was obtained by annealing the precursor at 250 ℃ for 10 h under argon atmosphere. For a comparison study, VO₂(B) microsheet was also prepared using the same procedure.

5.3 Physical and Structural Characterization

Figure 5.1 presents typical XRD patterns of the VO₂(B) (a) and VO₂(B)-MWCNT microsheet composite (b). All the diffraction peaks can be indexed to the monoclinic structure of VO₂(B) with lattice constants \( a = 12.03 \, \text{Å} \), \( b = 3.693 \, \text{Å} \), \( c = 6.42 \, \text{Å} \), and \( \beta = 106.6^\circ \) (JCPDS # 31-1438). Compared with the standard data, the relative intensities of the (001), (002), and (003) peaks for the VO₂(B) sample were stronger than those of the other peaks to an extraordinary degree, indicating that the as-obtained VO₂(B) may have a special morphology and that the (0 0 l) planes are most probably the preferred growth direction of the VO₂(B) nanosheets [Li et al., 2006;
Liu et al., 2009b]. No peaks of any other phases or impurities were observed, demonstrating that VO$_2$(B) microsheet with high purity could be obtained using the present synthetic process, where $n$-butanol served as the reducing agent. The products were black after the hydrothermal process, which indicated that V$^{5+}$ cations had been reduced to V$^{4+}$ cations [Chen et al., 2004].

Figure 5.1 X-ray diffraction patterns of VO$_2$(B) (a) and VO$_2$(B)-MWCNT microsheet composite (b).

To estimate the amount of multiwalled carbon nanotubes (MWCNTs) in the VO$_2$(B)-MWCNT microsheet composite, thermogravimetric analysis (TGA) was carried out in air (Figure 5.2). The samples were heated from 50 to 900 °C at a rate of 5°C min$^{-1}$. Figure 5.2 shows a typical TGA analysis of the VO$_2$(B)-MWCNT composite sample along with samples of VO$_2$(B) and MWCNT powders. As can be seen from Figure 5.2, both VO$_2$(B) and VO$_2$(B)-MWCNT powders started to oxidize slowly in air at temperatures above 365 °C, with rapid oxidation above 470 °C. The retained
mass of the VO$_2$(B) powder was increased by 4 wt.%, which could be attributed to the transformation of VO$_2$ to V$_2$O$_5$. Meanwhile, the VO$_2$(B)-MWCNT composite powder shows rapid mass loss between 470-600 °C. As the conversion of VO$_2$ to V$_2$O$_5$ for the VO$_2$(B) sample remains stable in the temperature range of 470-900 °C, any weight change for the VO$_2$(B)-MWCNT sample around this temperature range corresponds to the oxidation of MWCNTs. Therefore, the difference in weight between VO$_2$(B) and VO$_2$(B)-MWCNT after the oxidation could be directly translated into the amount of MWCNTs in the VO$_2$(B)-MWCNT composite. With the use of this method, it was estimated that the amount of MWCNTs in the composite microstructure was approximately 4.5 wt.%.

**Figure 5.2** TGA curves of MWCNT, VO$_2$(B), and VO$_2$(B)-MWCNT microsheet composite.

Morphological characterization of the two samples was carried out by means of FE-SEM analysis. Figure 5.3 shows FE-SEM images of the as-prepared VO$_2$(B) and the VO$_2$(B)-MWCNT microsheet composite. As shown in Figure 5.3, both samples
exhibited a sheet-like morphology, with the nanosheets frequently grown together in the form of bundles (Figure 5.3(a, c)). These bundles are composed of numerous nanosheets, each having a smooth surface and a typical length of 300-500 nm, width of 50-150 nm, and thickness of 10-50 nm.

Figure 5.3  FE-SEM images of VO$_2$(B) and VO$_2$(B)-MWCNT microsheet composite: (a) low magnification image of large bundles of VO$_2$(B) nanosheets; (b) high magnification image of an individual bundle composed of numerous single nanosheets; (c) low magnification image of VO$_2$(B)–MWCNT composite, consisting of bundles of nanosheets of VO$_2$(B) with MWCNTs underneath; (d) high-resolution image of VO$_2$(B)–MWCNT composite, which is composed of numerous nanosheets along with MWCNTs attached to the surfaces of the nanosheets.
Furthermore, the MWCNTs were randomly distributed during the *in-situ* hydrothermal process. MWCNTs can be observed underneath the nanosheets/bundles and attached to the surfaces of the nanosheets (Figure 5.3 (c, d)).

In this study, the exact processes occurring during the growth of the nanosheet microstructure in the hydrothermal system is still unclear. The following chemical reaction takes place in the hydrothermal system, resulting in the formation of the VO$_2$(B) phase.

\[
\text{C}_4\text{H}_9\text{-OH} + \text{V}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{VO}_2(\text{B}) + \text{C}_4\text{H}_8\text{O} + 2\text{H}_2\text{O} \quad (5.1)
\]

We believe that *n*-butanol (C$_4$H$_9$-OH) plays an important role in the system for the formation of VO$_2$(B) phase and acts as a reducing agent for the reduction of V$_2$O$_5$ to form VO$_2$(B) during the reaction process [Chen et al., 2010]. It is assumed that in the initial stage of the reaction, V$_2$O$_5$ is partly dissolved in the C$_4$H$_9$-OH-H$_2$O solution system. On increasing the temperature and pressure of the hydrothermal conditions, the V(+5) in V$_2$O$_5$ is reduced slowly to V(+4) by butanol to form small VO$_2$ nanocrystals, which can serve as seeds for further growth of VO$_2$ nanostructures [Chen et al., 2010; Li et al., 2010]. It is well known that VO$_2$(B) has a layered structure and tends to exfoliate, and this results in the formation of sheets. As the system moves to a lower total energy, sheets tend to further split to form nanosheets. These poorly-crystallized nanosheets then undergo further calcination at 250 °C for 10 h under argon atmosphere. During this calcination period, nanosheets are partially aggregated and form a microstructure with a bundle-like morphology and improved crystallinity. The overall possible synthetic model is schematically described in Scheme 5.1.
Scheme 5.1 Schematic possible model of synthetic procedure: (a) mixed raw materials; (b) layered VO$_2$(B) with MWCNTs after hydrothermal reduction; (c) agglomerated nanocrystal seeds form sheets; (d) sheets tend further to split to form nanosheets; (e) bundles of nanosheets and MWCNTs attached to the surface and underneath the nanosheets.

To obtain additional information concerning structural and morphological evolution of the samples, TEM measurements were carried out (Figure 5.4). The TEM image in Figure 5.4(a) gives further support to the observation that the MWCNTs are located underneath the nanosheets and attached to the surfaces of the sheets as well. The selected-area electron diffraction (SAED) pattern (inset) was taken from the individual nanosheet region of Figure 5.4(b), demonstrating that the synthesised nanosheets are single-crystal with preferential growth along the [0 1 0]$^*$ direction.
Furthermore, the high-resolution TEM (HRTEM) image of an individual nanosheet shown in Figure 5.4(c) clearly exhibits lattice fringes, where the lattice planes with a \(d\) spacing of 0.352 nm correspond to the (1 1 0) planes, which is a good match to monoclinic VO\(_2\)(B) (JCPDS No: 31-1438), as was confirmed by XRD.

**Figure 5.4** Typical TEM images of VO\(_2\)(B)-MWCNT microsheet composite: (a) image of the sample; (b) image of an individual VO\(_2\)(B) nanosheet and its SAED pattern (inset); (c) HRTEM image showing lattice fringes of an individual VO\(_2\)(B) nanosheet from (b).
5.4 Electrochemical Characterization

To test the electrochemical performance, sample powders were mixed with acetylene black (AB) and a binder, carboxymethyl cellulose (CMC), in a weight ratio of 80:15:5 in a solvent (distilled water). The slurry was spread onto aluminium foil substrates. The coated electrodes were dried in a vacuum oven at 110 °C for 24 h to remove water molecules. The electrode was then pressed using a disc with a diameter of 14 mm to enhance the contact between the aluminium foil, active materials, and conductive carbon. Subsequently, the electrodes were cut to a 1×1 cm² size. CR 2032 coin-type cells were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany), using lithium metal foil as the counter electrode. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume, provided by MERCK KgaA, Germany). The cells were cycled galvanostatically between 3.25 V and various discharge cut-off voltages from 1.0 to 2.0 V. Cyclic voltammetry (CV), with a scan rate of 0.1 mVs⁻¹ between 1.0-3.25 V versus Li/Li⁺, and electrochemical impedance spectroscopy (EIS) were performed on the electrodes using a CHI 660C electrochemistry workstation. The AC amplitude was 5 mV, and the frequency range applied was 100 kHz -0.01 Hz.

Electrochemical properties of the prepared samples were investigated systematically and are shown in Figure 5.5 within the voltage range of 1.0-3.25 V. Figure 5.5(a) shows cyclic voltammograms of VO₂(B) and VO₂(B)-MWCNT electrodes with a scan rate of 0.1 mVs⁻¹. The cathodic peak located at around 2.4 V for both electrodes corresponds to the voltage platform of the discharge process, in which Li⁺ is intercalated into the VO₂(B) and VO₂(B)-MWCNT electrodes, whereas the anodic
peak located at around 2.7 V for both electrodes corresponds to the voltage platform of the charge process, in which Li\(^+\) is deintercalated from the VO\(_2\)(B) and VO\(_2\)(B)-MWCNT electrodes, respectively. The cathodic/anodic peaks in the cyclic voltammograms are in good agreement with the plateaus observed in the voltage-capacity profiles (Figure 5.5(b, c)). Compared with VO\(_2\)(B), the redox peaks of VO\(_2\)(B)-MWCNT electrode are slightly shifted, which may be due to the effect of MWCNTs [Wang et al., 2010]. Figure 5.5(d) compares the cycling performance of the VO\(_2\)(B)-MWCNT electrode at 1 C (323 mAh g\(^{-1}\)) with that of the VO\(_2\)(B) in the voltage range of 1.0-3.25 V, and their corresponding discharge-charge voltage profiles are shown in Figure 5.5(b, c). Figure 5.5(b) and (c) shows the 1\(^{st}\), 2\(^{nd}\), 25\(^{th}\), 45\(^{th}\), 75\(^{th}\), and 100\(^{th}\) cycle discharge-charge curves for the VO\(_2\)(B) and VO\(_2\)(B)-MWCNT electrodes, respectively. The VO\(_2\)(B) electrode shows an initial discharge capacity of 184 mAh g\(^{-1}\), with an initial coulombic efficiency of 95 %. The capacity drops rapidly to 94 mAh g\(^{-1}\) at the 100\(^{th}\) cycle, confirming the poor cycling stability of VO\(_2\)(B) electrode. On the contrary, the initial discharge capacity for the VO\(_2\)(B)-MWCNT electrode was measured to be 228 mAh g\(^{-1}\), with an initial coulombic efficiency of 98 %. After 100 cycles, the VO\(_2\)(B)-MWCNT composite electrode retains a discharge capacity of 170 mAh g\(^{-1}\), which is around 75 % of the initial discharge capacity. It can be seen that the capacity retention and initial coulombic efficiency of the VO\(_2\)(B)-MWCNT composite electrode represent a significant improvement over that of the VO\(_2\)(B) electrode. The consecutive cycling behaviours at various current densities of 0.1, 0.3, 1, 3, and 5 C were also examined, as shown in Figure 5.5(e). The initial discharge capacities at the low current density of 0.1 C were measured to be 363 mAh g\(^{-1}\) and 377 mAh g\(^{-1}\), and at the 5\(^{th}\) cycle, capacity retention was 87 % and 78 % of the initial discharge capacity for the VO\(_2\)(B) and
VO$_2$(B)-MWCNT electrodes, respectively. This trend was continued up to 35 cycles for both electrodes, and capacity retention measured at every 5$^{th}$ cycle was only 66% at 0.3 C, 44% at 1 C, 24% at 3 C, and 17% at 5 C of the initial discharge capacity for the VO$_2$(B) electrode. In the case of the VO$_2$(B)-MWCNT composite electrode, capacity retention was 67% at 0.3 C, 56% at 1 C, 42% at 3 C, and 34% at 5 C of initial discharge capacity. On returning to 0.1 C, the VO$_2$(B) and VO$_2$(B)-MWCNT composite electrodes delivered a discharge capacity of 259 mAh g$^{-1}$ (71% of initial discharge capacity) and 273 mAh g$^{-1}$ (73% of initial discharge capacity), respectively. Figure 5.5(f) presents the Nyquist plots of the VO$_2$(B) and VO$_2$(B)-MWCNT electrodes at a discharge potential of 1.0 V vs. Li/Li$^+$ after charge-discharge for five cycles. The impedance curves show one compressed semicircle in the medium-frequency region, which could be assigned to the charge-transfer resistance ($R_{ct}$), and an approximately 45° inclined line in the low-frequency range, which could be considered as Warburg impedance. The equivalent circuit for the Nyquist plots of the VO$_2$(B) and VO$_2$(B)-MWCNT electrodes is shown as the inset in Figure 5.5(f). In this equivalent circuit, $R_{eq}$ and $R_{ct}$ are the ohmic resistance (total resistance of the electrolyte, separator, and electrical contacts) and the charge-transfer resistance, respectively. CPE is the constant phase-angle element, involving double layer capacitance, and W represents the Warburg impedance, reflecting the solid-state diffusion of Li ions into the bulk of the active materials, which is associated with the inclined line at low frequencies. The $R_{ct}$ is calculated to be 469 and 230 $\Omega$ cm$^{-2}$ for the VO$_2$(B) and VO$_2$(B)-MWCNT composite electrode, respectively. The VO$_2$(B)-MWCNT composite electrode shows less than 50% of the charge-transfer resistance of the VO$_2$(B) electrode, indicating the enhanced ionic conductivity of the VO$_2$(B)-MWCNT composite.
Figure 5.5  Electrochemical performances of VO\textsubscript{2}(B) and VO\textsubscript{2}(B)-MWCNT electrodes at 1.0-3.25 V: (a) cyclic voltammograms for the initial cycle at a scan rate of 0.1 mV s\textsuperscript{-1}; (b, c) galvanostatic charge-discharge voltage profiles at 1 C for selected cycles; (d) cyclic performance up to 100 cycles at 1 C; (e) consecutive cyclic behaviour at different rates; (f) electrochemical impedance spectra after charge/discharge and the equivalent circuit (inset).
Furthermore, in order to fully estimate the cycling stability of the VO$_2$(B)-MWCNT composite electrode, cells were cycled galvanostatically between 1.5-3.25 V and 2.0-3.25 V at 1 C (Figure 5.6). After 100 cycles, the VO$_2$(B)-MWCNT composite electrode shows a discharge capacity of 166 mAh g$^{-1}$ over 1.5-3.25 V and 177 mAh g$^{-1}$ over 2.0-3.25 V, with a capacity retention of 85 % and 92 % of the initial discharge capacity, respectively.

![Figure 5.6](image)

**Figure 5.6** Cycling behaviour of VO$_2$(B)-MWCNT electrode at discharge cut-off voltages of 1.5 V and 2.0 V. The current density applied was the 1 C rate.

The VO$_2$(B)-MWCNT composite electrode shows improved cycle life when the cut-off voltage for discharging is increased from 1.0 to 2.0 V, as increasing the cut-off voltage to 2.0 V gave less capacity fading (See Figures 5.5 and 5.6). The significant capacity loss might be related to the dissolution of vanadium and the structural changes upon cycling in the larger potential span [Ng et al., 2007b]. However, the VO$_2$(B)-MWCNT microsheet composite shows good cycling stability and high
capacity, which are comparable with or better than results in previous reports [Kannan and Manthiram, 2003; Armstrong et al., 2008b; Wang et al., 2010; Ding et al., 2009a; Li et al., 2006]. The electrochemical behaviour leads to the conclusion that the microsheet composite structure of VO$_2$(B)-MWCNT is important to the improved cycling performance, where MWCNTs contribute to maintaining the electronic conduction, as well as preventing the aggregation of active materials during a long cycling process and accommodating the volume variation more effectively [He et al., 2010; Park et al., 2007]. Thus, the combination of MWCNTs with the microsheet structure morphology of VO$_2$(B) (composed of numerous nanosheets) strongly influences the electrochemical characteristics of the composite material. The possible reason is that MWCNTs are attached to the surface and randomly distributed underneath the nanosheets, so that the electronic transport is enhanced and reduces the resistance within the VO$_2$(B) nanosheets.

5.5 Conclusions

In summary, VO$_2$(B)-MWCNT microsheet composite has been successfully synthesized via an *in-situ* hydrothermal process. FE-SEM and TEM images confirmed that the composite exhibited sheet-like morphology and illustrated that the nanosheets are frequently grown together in the form of bundles, whereas MWCNTs are attached to the nanosheet surfaces and randomly distributed underneath the nanosheets. The electrochemical measurements demonstrated that VO$_2$(B)-MWCNT composite possesses better capacity retention during the charge/discharge process compared with pure VO$_2$(B). The stable cyclic retention is attributed to the fact that the MWCNTs enhance the electronic transport and reduce the resistance within the
VO$_2$(B) nanosheets. Moreover, the VO$_2$(B)-MWCNT composite can prevent the aggregation of active materials and accommodate the large volume variation because of the very good mechanical properties provided by the MWCNTs. This work provides a simple and feasible platform for further advances in CNT-based composites.
CHAPTER 6

LiFePO$_4$-Fe$_2$P-C COMPOSITE CATHODE: AN ENVIRONMENTALLY FRIENDLY HIGH PERFORMANCE LITHIUM-ION BATTERY MATERIAL FOR EV/HEV APPLICATION

6.1 Introduction

In the new century, clean and renewable energy storage devices have become the focus of research interest for the energy, electronics, and transportation industries [Liu and Cao, 2010]. Lithium ion batteries are considered close to becoming state-of-the-art technology for a range of advanced electrochemical energy storage and conversion systems. These include hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and stationary energy storage for solar and wind electricity generation, as well as smart grids [Liu and Cao, 2010; Wang et al., 2010a]. However, for a range of EV/HEV applications, commercialized lithium-ion batteries do not yet meet the required combinations of high energy density, high power, and high rate capability. Apart from the search for new or improved electrode materials with higher energy densities [Zhang et al., 2006a; Zhang et al., 2006b; Noh et al., 2005], the enhancement of electrode capacity retention at high charge/discharge rates is one main challenges in lithium-ion battery research. Following the pioneering work by Padhi et al., 1997, olivine-like LiFePO$_4$ has appeared as an attractive electrode material for lithium-ion batteries, in particular, for high power applications. This is because of its high theoretical capacity (170 mAh g$^{-1}$), acceptable operating
voltage (3.4 V vs. Li+/Li), low cost, environmental friendliness, long cycle life, cell safety, and high thermal stability [Wang et al., 2010a; Padhi et al., 1997; Yamada et al., 2001]. Nevertheless, a major limitation of this material, which prevents it from being used in large-scale applications, is its poor high-rate performance, owing to its low electronic conductivity and low ionic diffusion coefficient [Huang et al., 2001; Chen and Dahn, 2002]. Furthermore, long term cycling stability at high current rate is still a great challenge for this material, as it is a compulsory requirement for lithium ion batteries to have long cycle life for EV/HEV applications. Recently, ultra-fast charging and discharging at very high rates has been reported for LiFePO4 material via creation of an ion conducting lithium phosphate coating on the surface of LiFePO4 nanoparticles. However, the reported cycle number is not good enough [Kang and Ceder, 2009]. Satisfactory long term cycling stability has been achieved through the formation of mesoporous LiFePO4/C nanocomposite (118 mAh g⁻¹ at 10 C after 1000 cycles) [Wang et al., 2010a] and by synthesising LiFePO4/carbon composite (∼ 85 mAh g⁻¹ at 10 C after 2400 cycles) via high-energy ball milling combined with a spray-drying method [Kwon et al., 2004]. Both of these reported results satisfy the long term cycling requirements, but their specific discharge capacities are not as high as we expect, and there is definitely more room for further improvement.

In this investigation, the synthesis strategy has involved the creation of a porous conductive architecture of LiFePO4-C composite, which includes distinct regions or clusters containing antiferromagnetic (AFM) LiFePO4 in close proximity to ferromagnetic (FM) Fe2P. The microstructure is achieved by using a solvent assisted modified solid state reaction method, which is quite different from others reported in
the literature. The evidence that is presented is consistent with the occurrence of an AFM/FM “exchange bias (EB)” effect, based on a particular type of shifting of magnetic hysteresis loops, which is attributed to the occurrence of LiFePO$_4$/Fe$_2$P interface coupling. Using these results and those of others, the electrochemical performance of LiFePO$_4$-Fe$_2$P-C composite cathodes is enhanced, at least in part, by increased volume fraction of fine distributions of LiFePO$_4$/Fe$_2$P. Electrochemical measurements demonstrated that the synthesised LiFePO$_4$-Fe$_2$P-C composite delivered a high capacity of 167 mAh g$^{-1}$ at 0.2 C at the 100$^{th}$ cycle and displayed long term cycling stability with a capacity retention of around 96 % (131 mAh g$^{-1}$), even after 1000 cycles at 10 C.

6.2 Materials Synthesis

A simple ultra-fast solvent assisted manual grinding method combined with solid state reaction has been developed to synthesize LiFePO$_4$-Fe$_2$P-C composite with a porous conductive architecture. The present grinding method replaces the time consuming high-energy ball milling method. LiCO$_3$, FeC$_2$O$_4$.2H$_2$O, and NH$_4$H$_2$PO$_4$ in a stoichiometric molar ratio of 1:1:1 were used as the starting materials, and citric acid (C$_6$H$_8$O$_7$) was used as both the reducing agent and the carbon source. The reactants for preparing the precursor were ground thoroughly, and a slurry was made by a mortar and a pestle in acetone solvent to ensure intimate and homogeneous mixing at the atomic level. The slurry was then dried in an oven at 60 °C to remove acetone from the slurry. To decompose the carbonate, oxalate, and phosphate, the dried mixture was placed in a tube furnace and heat-treated at 350 °C for 10 h in flowing argon. The resultant powders were cooled to room temperature and
thoroughly reground. The powders were again calcined at 600 °C for 10 h under argon flow. The bare-LiFePO₄ and the LiFePO₄-Fe₂P-C composite containing 5.8 wt.% C [LiFePO₄-Fe₂P-C, sample (1)], 10.4 wt.% C [LiFePO₄-Fe₂P-C, sample (2)], and 19.9 wt.% C [LiFePO₄-Fe₂P-C, sample (3)] were obtained using different amounts of citric acid.

6.3 Physical and Structural Characterization

XRD results obtained from the samples are shown in Figure 6.1. The profiles of the diffraction peaks could be indexed according to the olivine LiFePO₄ phase (JCDPS Card Number 40-1499), with additional peak positions consistent with Li₄P₂O₇, Li₃PO₄, and Fe₂P. Any broad peaks or lines corresponding to amorphous or crystalline carbon were of insufficient intensity to be detected against the background in the XRD patterns of LiFePO₄-Fe₂P-C composite. XRD patterns obtained from the carbon coated samples indicate that iron phosphide phase (barringerite Fe₂P, peak at 2θ = 40.28°) begins to form during the annealing process. According to the literature, it usually exists in the form of nanosized clusters [Salah et al., 2006]. XRD patterns were also collected from bare-LiFePO₄, but there was no evidence of Fe₂P peaks. It is therefore possible that carbon originating from the citrate framework has acted as a reductant under the Ar atmosphere during the annealing process in this synthesis system. To estimate the amount of amorphous carbon in the LiFePO₄-Fe₂P-C composites, TGA was carried out in air (Figure 6.2). The samples were heated from 50 to 1000 °C at a rate of 5° C min⁻¹. As can be seen from Figure 6.2, bare-LiFePO₄ and LiFePO₄-Fe₂P-C powders started to oxidize slowly in air at temperatures above 365 °C, with rapid oxidation above 450 °C.
Figure 6.1 XRD patterns of the samples: (a) Bare-LiFePO$_4$ (0 wt.%C), (b) LiFePO$_4$-Fe$_2$P-C (1) (5.8 wt.%C), (c) LiFePO$_4$-Fe$_2$P-C (2) (10.4 wt.%C), and (d) LiFePO$_4$-Fe$_2$P-C (3) (19.9 wt.%C).

Figure 6.2 TGA curves of bare-LiFePO$_4$ and LiFePO$_4$-Fe$_2$P-C composites powders estimated to contain (1) 5.8 wt.%C, (2) 10.4 wt.%C, and (3) 19.9 wt.%C.
The retained mass of the bare-LiFePO₄ powder was increased by 4.8 wt.%, which could be attributed to the oxidation of Fe(II) to Fe(III). Meanwhile, the LiFePO₄-Fe₂P-C composite powders show rapid mass loss between 400-700°C, which is corresponds to the burn-off of carbon. Therefore, the change in weight before and after the oxidation of carbon directly translates into the amount of amorphous carbon in the composite. Using this method, it was estimated that the amount of amorphous carbon in the composites was approximately 5.8 wt.% C [LiFePO₄-Fe₂P-C (1)], 10.4 wt.% C [LiFePO₄-Fe₂P-C (2)], and 19.9 wt.% C [LiFePO₄-Fe₂P-C (3)], respectively, obtained from different amount of citric acid used. The specific surface areas of the synthesised products were also measured by the 15 points BET N₂ adsorption method. The LiFePO₄-Fe₂P-C (1) composite containing 5.8 wt% C shows the highest specific surface area (33.14 m²g⁻¹), while bare-LiFePO₄, LiFePO₄-Fe₂P-C (2) (10.4 wt.%C), and LiFePO₄-Fe₂P-C (3) (19.9 wt.%C) have specific surface areas of 1.17, 16.74, and 14.25 m²g⁻¹, respectively.

Secondary electron field emission scanning electron microscope (FESEM) images of the bare-LiFePO₄ and LiFePO₄-Fe₂P-C composites with different carbon content are shown in Figure 6.3. It was observed that the growth of the LiFePO₄ grains is inhibited by the carbon and Fe₂P formed during the heat treatment process. According to previous investigations, the particle size and electrochemical polarization can be reduced effectively when the LiFePO₄ particle surface is coated by conductive carbon [Huang et al., 2001; Wang et al., 2008]. In Figure 6.3(b-d), the FESEM images indicate an abrupt particle growth with increasing carbon content in the sample, which may be caused by the agglomeration of the excess carbon in the samples, where Fe₂P nanoclusters are being trapped. A porous network structure
along with small particles and rough surfaces can be clearly observed in Figure 6.3(b). As shown in Figure 6.3(c, d), it is obvious that with increasing carbon content, the porous network structure with rough surfaces gradually disappears and agglomerated larger particles with smooth surfaces appear.

**Figure 6.3** Secondary electron FESEM micrographs of (a) Bare-LiFePO₄, (b) LiFePO₄-Fe₂P-C (1), (c) LiFePO₄-Fe₂P-C (2), and (d) LiFePO₄-Fe₂P-C (3).

FESEM high-contrast backscattered imaging (Figure 6.4) of sectioned powders was performed with qualitative calibration of the three most distinct phases (Fe₂P, LiFePO₄, and C). This was achieved using EDS spot analysis performed on regions of constant grey level (Figure 6.5(a, b)). Examination of Figure 6.4(b-d) reveals the presence of inhomogeneous distributions of nano-Fe₂P particles (white), in a highly porous architecture of LiFePO₄ (light grey) and carbon (dark grey). Despite the inhomogeneous nature of the microstructures, it was observed that the LiFePO₄-
Fe$_2$P-C composite containing 5.8 wt.% C (Figure 6.4(b)) exhibited the largest fraction of local areas comprising fine distributions of Fe$_2$P particles in close contact with LiFePO$_4$ and carbon, as can be seen by comparing Figure 6.4(b) with Figure 6.4(c) and (d)). It was also observed that this sample (5.8 wt.% C) had a particularly porous and highly porous conductive architecture (Figure 6.5 (c)). These observations are consistent with the formation of a higher fraction of LiFePO$_4$/Fe$_2$P interface coupling, with implications for magnetic properties, and thus, magnetic hysteresis loops were collected. With increasing carbon content, the Fe$_2$P particles become connected with the primary particles of LiFePO$_4$, and the samples also become denser, which is caused by the agglomeration of the excess carbon, with the agglomerates acting as traps for the Fe$_2$P particles (Figure 6.4(d)).

**Figure 6.4** High contrast backscattered (BS) FESEM micrographs of (a) Bare-LiFePO$_4$, (b) LiFePO$_4$-Fe$_2$P-C (1), (c) LiFePO$_4$-Fe$_2$P-C (2), and (d) LiFePO$_4$-Fe$_2$P-C (3).
Figure 6.5 High contrast back-scattered FESEM image of LiFePO$_4$-Fe$_2$P-C (1) (5.8 wt.% C) composite powders (inset) with corresponding EDS spectra of the marked regions (a, b), and FESEM image showing the porous conductive architecture of the sample (c).
Preliminary magnetic measurement investigations revealed additional information which can be associated with structural evolution in the samples. The exchange interaction at the interface between a ferromagnetic (FM) and antiferromagnetic (AFM) component often results in an interesting phenomenon called “exchange bias” (EB), which is manifested by a shift in the hysteresis loop along the field axis when the system is cooled down in an external magnetic field [Meiklejohn and Bean, 1956; Nogués et al., 2005]. However, so far, there has been no experimental determination of an exchange bias (EB) effect in LiFePO₄/Fe₂P interface coupling in LiFePO₄ materials, even though the magnetic structure and properties of LiFePO₄ have been re-examined theoretically and experimentally [Streltsov et al., 1993; Rousse et al., 2003]. Compared to the other samples investigated, a large shift was observed in the magnetic hysteresis loop for the sample containing 5.8 wt% C. Assuming that this shift is associated with an exchange bias effect, the magnitude of this shift in the field axis can be defined as the EB (exchange bias) field, $-H_E = (H_1 + H_2)/2$, where $H_1$ and $H_2$ are the left and right coercive fields, respectively [Meiklejohn and Bean, 1956]. Results for different samples are shown in Figure 6.6. The maximum value of $H_E$ is 634 Oe at 500 Oe cooling field for the 5.8 wt% C containing sample, which is larger than the value for the other samples at 5 K. Comparison of the EB effect among the samples indicates that the effect is stronger for the 5.8 wt% C containing sample, with the effect in descending order of LiFePO₄-Fe₂P-C (1) > LiFePO₄-Fe₂P-C (2) > LiFePO₄-Fe₂P-C (3). This trend is coincident with the observation that the fraction of local areas comprising a fine distribution of Fe₂P particles in close contact with LiFePO₄ also decreases in the same way, where the largest fraction is observed in the sample containing 5.8 wt% C. The same trend was also observed for surface area measurements, with BET surface
areas of 33.14, 16.74, 14.25, and 1.17 m\(^2\)g\(^{-1}\) for 5.8, 10.4, and 19.9 wt.% C containing samples and bare-LiFePO\(_4\), respectively, and by electrochemical impedance spectroscopy (EIS) analysis (described later).

**Figure 6.6** The magnetic hysteresis loop measured at 5 K between ±10000 Oe after field cooling at 500 Oe.

Transmission electron microscopy (TEM) was used to investigate the morphology and structure of the bare sample and the LiFePO\(_4\)-Fe\(_2\)P-C (1) (5.8 wt.%C) composite. It was clearly observed that the crystallite size of this composite is much smaller than that of the bare LiFePO\(_4\). The set of images in Figure 6.7(c)-(e) shows a LiFePO\(_4\) particle at increasing magnification. The particle (bottom right of Figure 6.7(c)) is located over a hole in the holey carbon support film and is surrounded by a layer of carbon ~2-3 nm thick, marked C in Figure 6.7(d) and (e).
Figure 6.7 TEM and HRTEM images obtained from (a) bare-LiFePO$_4$ and (b)-(f) LiFePO$_4$-Fe$_2$P-C (1) (5.8 wt.%C) composite: (c)-(e) study of a region containing LiFePO$_4$ surrounded by a 3 nm carbon-rich layer, marked C, (f) HRTEM image of separate LiFePO$_4$ crystal surrounded by carbon-rich layer marked C. Inset is a fast Fourier transform of the image, and the orientation is close to (212).
High resolution TEM (HRTEM) imaging (Figure 6.7(e)) revealed lattice plane contrast consistent with (020) LiFePO$_4$ ($d_{020} = 0.51$ nm) and contrast around the edge of the particle consistent with amorphous carbon. HRTEM imaging of other regions containing single LiFePO$_4$ particles revealed similar contrast associated with the presence of a layer of amorphous carbon around the edges of the particles (marked C in Figure 6.7(f)), a result consistent with a real carbon-rich reaction product, rather than, for example, a contamination build up during electron microscope examination. In the case of Figure 6.7(f), the lattice image and associated fast Fourier transform (inset, Figure 6.7(f)) are consistent with a single LiFePO$_4$ crystal with orientation close to (212).

### 6.4 Electrochemical Characterization

To test the electrochemical performance, powder samples were mixed with acetylene black (AB) (Cabot Australasia Pty Ltd.) and a binder, polyvinylidene fluoride (PVDF, Sigma-Aldrich), in a weight ratio of 80:15:5 in a solvent, $N$-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, anhydrous, 99.5 %). The slurry was uniformly spread onto aluminium foil substrates with an area of 1 cm$^2$. The coated electrodes were dried in a vacuum oven at 100 °C for 24 h and then pressed. CR 2032 coin-type cells were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany). The electrochemical coin cells contained the above-mentioned materials coated on aluminium foil as the working electrode, lithium foil as counter electrode and reference electrode, porous polypropylene as the separator, and 1 M LiPF$_6$ in a 50:50 (v/v) mixture of ethylene carbonate and dimethyl carbonate (MERCK KgaA, Germany) as the electrolyte. The cells were galvanostatically charged and discharged
in the range of 4.3-2.5 V at different rates of 0.2-10 C using a computer-controlled charger system manufactured by Neware Battery Testers. The calculated capacity was based on the weight of active materials (LiFePO$_4$). Cyclic voltammetry (with a scan rate of 0.1 mVs$^{-1}$ between 4.3 and 2.5 V (versus Li/Li$^+$)) and electrochemical impedance spectroscopy (EIS) were performed on the electrodes using a CHI 660C electrochemistry workstation. The AC amplitude was 5 mV, and the frequency range applied was 100 kHz - 0.01 Hz. The electrochemical performances of the prepared electrodes were evaluated systematically and are shown in Figure 6.8. The cycle life performances up to 120 cycles for the bare-LiFePO$_4$ and LiFePO$_4$-Fe$_2$P-C composite electrodes at 10 C charge/discharge rates are shown in Figure 6.8(a). The initial discharge capacities were measured to be 43, 59, 89, and 137 mAh g$^{-1}$, with a capacity retention of 40, 56, 84, and 136 mAh g$^{-1}$ at the 120$^{th}$ cycle at the 10 C rate for the bare-LiFePO$_4$, LiFePO$_4$-Fe$_2$P-C (3), LiFePO$_4$-Fe$_2$P-C (2), and LiFePO$_4$-Fe$_2$P-C (1) electrodes, respectively. The electrochemical performances of the carbon coated samples is in descending order of LiFePO$_4$-Fe$_2$P-C (1) > LiFePO$_4$-Fe$_2$P-C (2) > LiFePO$_4$-Fe$_2$P-C (3). The electrode composed of LiFePO$_4$-Fe$_2$P-C (1) (5.8 wt.%C) shows the best electrochemical performances, even at the high current density of 10 C. In order to fully estimate the electrochemical performance of the LiFePO$_4$-Fe$_2$P-C (1) (5.8 wt.%C) composite electrode, the cycling behaviour at the different current densities of 0.2, 2, 5 and 10 C was measured up to the 100$^{th}$ cycle, and the corresponding charge-discharge voltage profiles are shown in Figure 6.8(c). The LiFePO$_4$-Fe$_2$P-C (1) (5.8wt.%C) composite electrode shows long and flat voltage plateaus in the 3.4-3.5 V range, and the small voltage difference between the charge-discharge plateaus indicates its good kinetics. This observation is also supported by the cyclic voltammograms (CV curves) shown in Figure 6.8(d). The well defined
sharp redox peaks in the range of 3.26 -3.70 V can be attributed to the Fe$^{2+}$/Fe$^{3+}$ redox couple reaction, corresponding to lithium extraction and insertion in the LiFePO$_4$ crystal structure [Wang et al., 2010a]. The 100$^{th}$ cycle discharge capacities were measured to be 167 mAh g$^{-1}$ at 0.2 C, 159 mAh g$^{-1}$ at 2 C, 146 mAh g$^{-1}$ at 5 C, and 136 mAh g$^{-1}$ at 10 C for the LiFePO$_4$-Fe$_2$P-C (1) (5.8 wt.%C) electrode, respectively. At the low current density of 0.2 C (5 hours charge and 5 hours discharge), the discharge capacity (167 mAh g$^{-1}$) is very close to the theoretical capacity of LiFePO$_4$ (170 mAh g$^{-1}$). Even at the high current rate of 10 C (6 minutes for charging and 6 minutes for discharging), a capacity of 136 mAh g$^{-1}$ is still obtained, demonstrating that the LiFePO$_4$-Fe$_2$P-C (1) (5.8 wt.% C) composite can tolerate high rate charge and discharge. The capacity fading is only ~18 % with increasing charge-discharge rate from 0.2 to 10 C. The composite electrode was life tested at a high current density of 1700 mA g$^{-1}$ (10 C rate) for long term cycling, as batteries are required to operate at high current density and to have a cycle life of more than 2000 cycles for EV/HEV applications [Liu et al., 2009]. Therefore, we cycled LiFePO$_4$-Fe$_2$P-C (1) (5.8 wt.% C) electrode at the 10 C rate (6 minutes for charging and 6 minutes for discharging) for 1000 cycles (Figure 6.8(b)). Surprisingly, the LiFePO$_4$-Fe$_2$P-C (1) (5.8 wt.% C) electrode exhibited superior electrochemical performance, with a capacity retention of around 96% (131 mAh g$^{-1}$) of its original discharge capacity after 1000 cycles at the high current rate of 10 C. Such outstanding electrochemical performance certainly can meet the demands of many high power applications. However, to understand the effects of LiFePO$_4$/Fe$_2$P interface coupling along with carbon coating on the charge transfer resistance of electrodes, ac impedance measurements were carried out at room temperature (Figure 6.8(e)). The impedance curves show one compressed semicircle in the
medium-frequency region, which could be assigned to the charge-transfer resistance ($R_{ct}$). The spike at the low frequency end indicates the Warburg impedance ($W$) of long-range lithium-ion diffusion [Gao and Tang, 2008; Shin et al., 2006; Chang et al., 2008]. The charge transfer resistance ($R_{ct}$) was calculated to be 148 $\Omega$ cm$^{-2}$ for the bare-LiFePO$_4$, 28 $\Omega$ cm$^{-2}$ for the LiFePO$_4$-Fe$_2$P-C (1), 37 $\Omega$ cm$^{-2}$ for the LiFePO$_4$-Fe$_2$P-C (2), and 60 $\Omega$ cm$^{-2}$ for the LiFePO$_4$-Fe$_2$P-C (3) electrodes, respectively. According to a previous report [Zhi et al., 2010], higher carbon content samples show lower charge transfer resistance ($R_{ct}$), and generally, this trend is also logical. Under this consideration, the $R_{ct}$ should be in order of LiFePO$_4$-Fe$_2$P-C (3) (19.9 wt.% C) < LiFePO$_4$-Fe$_2$P-C (2) (10.4 wt.% C) < LiFePO$_4$-Fe$_2$P-C (1) (5.8 wt.% C), but the reality is the inverse: LiFePO$_4$-Fe$_2$P-C (1) < LiFePO$_4$-Fe$_2$P-C (2) < LiFePO$_4$-Fe$_2$P-C (3). At this point, the argument is that this $R_{ct}$ is not only influenced by the carbon content, but also strongly influenced by the interface coupling of LiFePO$_4$/Fe$_2$P clusters. The LiFePO$_4$-Fe$_2$P-C (1) sample exhibits more and stronger interface coupling of antiferromagnetic (AFM) and ferromagnetic (FM) clusters than the other samples, which increases the effective interface areas, facilitates more rapid charge transfer, and reduces the charge transfer resistance, leading to the huge shift in the magnetic hysteresis loop [De et al., 2008; Liu et al., 2009c]. So, the excellent electrochemical performance of the LiFePO$_4$-Fe$_2$P-C (1) (5.8 wt.% C) composite could be attributed to the porous conductive architecture with huge and strong interface coupling of LiFePO$_4$/Fe$_2$P that increases the contact area among the carbon, the Fe$_2$P clusters, and the LiFePO$_4$ particles, providing multidimensional channels for charge transfer and reducing the resistance for lithium ion migration. Moreover, the composite with porous architecture can suck up electrolyte to shorten enormously the distance for lithium ion diffusion.
Figure 6.8 Short-term cycle life performance of all the sample electrodes (a), long-term cycle life performance beyond 1000 cycles at 10 C for the LiFePO$_4$-Fe$_2$P-C (1) electrode (b), the 100$^{th}$ cycle galvanostatic charge-discharge profiles at different current densities from 0.2 to 10 C between 4.3 and 2.5 V for LiFePO$_4$-Fe$_2$P-C (1) electrode (c), cyclic voltammograms of LiFePO$_4$-Fe$_2$P-C (1) electrode at a scan rate of 0.1 mV s$^{-1}$ for the first 5 cycles (d), EIS spectra of the bare-LiFePO$_4$ and LiFePO$_4$-Fe$_2$P-C electrodes, and the equivalent circuit (inset) (e).
In the case of LiFePO$_4$-Fe$_2$P-C (3) (19.9 wt.% C), the excessive carbon cannot help to restrict the particle growth, where the Fe$_2$P particles become connected with the primary particles of LiFePO$_4$, and the samples become denser, which will result in less permeability for Li$^+$ ions and could impedes charge-transfer through the cathode, thus leading to the decrease of discharge capacity at high rates [Zhi et al., 2010; Dominko et al., 2007].

### 6.5 Conclusions

In conclusion, the results demonstrated that the facilitation of antiferromagnetic (AFM) and ferromagnetic (FM) interface coupling of LiFePO$_4$/Fe$_2$P provides versatile strategies toward improving the electrochemical properties of LiFePO$_4$ materials and also opens a new window for material scientists to further study this new phenomenon (exchange bias in LiFePO$_4$ composite) and its ability to enhance the electrochemical performance of lithium-ion battery electrode.
7.1 Introduction

Besides searching for novel electrode materials with high energy density [Zhang et al., 2006a; Zhang et al., 2006b; Noh et al., 2005], enhancing their capacity retention at high rate, or rate performance, is one of the main research topics in the battery field, and it has great challenges. Traditional Li-storage materials suffer serious capacity loss when charged and discharged at high rates, which is mainly due to large polarization and slow diffusion of lithium ions and electrons in the active materials [Yan et al., 2003]. Adopting electrode materials with fine particle size and tunable morphology/architecture has been attempted to solve these problems. Being inherently safe and chemically compatible with the electrolyte [Yang et al., 2009], titanium oxide-based materials, including both Li-titanates and various TiO$_2$ polymorphs, are considered alternatives to carbonaceous anodes in Li-ion batteries. Given the commercial success of the spinel lithium titanates, TiO$_2$ polymorphs, in nanostructured forms in particular, have been fabricated and investigated for applications [Yang et al., 2009]. Spinel lithium titanate (Li$_4$Ti$_5$O$_{12}$) has been demonstrated as a potential candidate for the anode electrode material in high power Li-ion batteries, as well as in hybrid supercapacitors [Colbow et al., 1989; Zaghib et
al., 1998; Ohzuku et al., 1993; Zaghib et al., 1999; Guerfi et al., 2003; Scharner et al., 1999; Thackeray et al., 1984; Ohzuku et al., 1995; Peramunage and Abraham, 1998], because it has some unique characteristics as compared with carbon based anode materials. It has good structural stability, with an almost negligible volume change during the Li$^+$ insertion and extraction processes, which suggests virtually unlimited cycle life. It features a flat operating voltage of about 1.5 V versus lithium, which is higher than the reduction potential of most electrolyte solvents. This material accommodates Li$^+$ with a theoretical capacity of 175 mAh g$^{-1}$, and the actual discharge capacity is $> 160$ mAh g$^{-1}$ [Sorensen et al., 2006]. On the other hand, anatase TiO$_2$ is generally considered to be one of the best candidates as a lithium ion host among these TiO$_2$ polymorphs, because anatase is a fast Li$^+$ insertion/extraction host and characterized by low cost, non-toxicity, an appropriate insertion potential (~2.0V), low volume expansion (3-4%) during lithium insertion [Qiao et al., 2008], and environmental friendliness [He et al., 2007]. However, it is well-known that electronic transport properties can be tuned by interfacial design and by varying the spacing of interfaces down to the nano-regime, in which the grain boundaries apparently act as channels to allow Li$^+$ to enter the particles. The lithium ions then reversibly react with atoms at and within the grain boundaries [Jamnika and Maier, 2003; Beaulieu et al., 2000]. So, it is very much expected that if materials have high grain boundary density with large interfacial areas, they will show very high lithium storage properties. To increase grain boundary density with large interfacial areas, it could be wise to choose binary or multinary compounds rather than single compounds. Morphological stability can also be further improved if several materials are combined in an appropriately structured composite [Idota et al., 1997; Li et al., 2002a]. From this point of view, binary Li$_4$Ti$_5$O$_{12}$-TiO$_2$ compounds are the
best choice of material, rather than pure Li$_4$Ti$_5$O$_{12}$ compound. Furthermore, the raw Li$_4$Ti$_5$O$_{12}$ and TiO$_2$ powders have low electrical conductivity, resulting in poor electrochemical rate performance [Che et al., 2001; Yan et al., 2008], and this trait of Li$_4$Ti$_5$O$_{12}$ and TiO$_2$ bars them from wide practical applications. Various research groups have focused on developing strategies to overcome this problem, such as reducing particle size [Cheng et al., 2006; Jiang et al., 2007], doping with other metals or metal oxides [Cheng et al., 2007; Huang et al., 2007a], and coating with conductive carbons [Wang et al., 2007; Huang et al., 2008; Hao et al., 2007; Xu et al., 2008]. In contrast to the metal additives, carbon has a low mass density, and carbon is a cheap way to enhance the conductivity, improve the morphology, and the electrochemical performance of materials. In addition, carbon can improve the diffusion coefficient of lithium ions in Li$_4$Ti$_5$O$_{12}$ [Wang et al., 2007]. In order to prepare Li$_4$Ti$_5$O$_{12}$, multifarious methods, such as high temperature solid state reaction [Colbow et al., 1989; Pyun et al., 1999; Amatucci et al., 2001; Pasquier et al., 2002], high energy ball-milling-assisted solid state reaction [Guerfi et al., 2003; Wang et al., 2008a], sol-gel synthesis [Bach et al., 1999; Shen et al., 2002; Rho et al., 2002; Jung et al., 2003], hydrothermal synthesis [Fattakhova and Krtíl, 2002], template synthesis [Sorensen et al., 2006; Woo et al., 2007], the rheological phase method [Liu et al., 2008b], and the microwave method [Li et al., 2007a; Yang et al., 2008], have all been under investigation. Nevertheless, most of the above-mentioned methods need some special instruments, harsh conditions, or a relatively high processing temperature, so that the production of nanocrystalline, high grain boundary density, dual phase Li$_4$Ti$_5$O$_{12}$-TiO$_2$ is difficult and inconvenient.
In this chapter, a simple, inexpensive synthetic fabrication route for an amorphous carbon coated, high grain boundary density, dual phase nanocomposite, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, through the *in situ* conversion of citric acid (C$_6$H$_8$O$_7$) to amorphous carbon by a low temperature molten salt precipitation method has been reported. This synthesis route is suitable for large-scale production and the synthesised nanocomposite (Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C) is new and is being reported for the first time, so far. The material was tested as an anode for the lithium ion battery, presenting high charge-discharge capacity, good cycling performance, and excellent rate capability.

### 7.2 Materials Synthesis

The precursors of Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$-TiO$_2$ powder samples were synthesized using LiNO$_3$ (Sigma-Aldrich, 99.9%), LiOH·H$_2$O (Sigma-Aldrich, 98%), Li$_2$O$_2$ (Sigma-Aldrich, 90%), and Ti[O(CH$_2$)$_3$CH$_3$]$_4$ (Sigma-Aldrich, 97%) as starting materials. The molar ratio of the eutectic mixture of LiNO$_3$:LiOH·H$_2$O:Li$_2$O$_2$ was fixed at 0.05:0.1:0.1. The compounds were mixed thoroughly and ground in a mortar with a pestle. Ti[O(CH$_2$)$_3$CH$_3$]$_4$ (0.5 mol) solution was added to the mixture dropwise with further grinding to form a homogeneous slurry. The powder mixture was vacuum dried at 120 °C for 24 h. The drying process was used to minimize the water content in the starting material mixture for the molten salt (LiNO$_3$-LiOH·H$_2$O). The mixture was immediately transferred to a muffle furnace and calcined at 300°C for 3 h to yield Li$_4$Ti$_5$O$_{12}$ and at 400 °C for 3 h to yield Li$_4$Ti$_5$O$_{12}$-TiO$_2$, respectively.

To obtain the Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite, a suitable amount of citric acid was simply added to the mixture as a carbon source, and calcination was performed at 400 °C for 3 h. The heating rate was 10°C min$^{-1}$ for all temperature settings. The
LiNO$_3$-LiOH-H$_2$O-Li$_2$O$_2$ mixture became a molten salt near the eutectic composition. This is significantly different from an aqueous solution, and the water content of the molten salt solution was reduced as much as possible. The solution thus became very basic, which led to the production of stable Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$-TiO$_2$ phases. A black powder was immediately precipitated in the molten salt solution. After cooling and solidification, this solid mixture was immersed in de-ionized water, and all of the salt elements were dissolved. The precipitated black powders, which are the metal oxide particles, are insoluble in water, so that all of the precipitates could be separated. The resultant particles were collected and vacuum treated again at 120 °C for 24 h to eliminate residual water on the particle surfaces. The dried powders were then subjected to structural characterization and electrochemical measurements.

### 7.3 Structure and Morphology Analysis

Molten salt compositions with their low melting points are helpful in preventing the excessive growth of Li$_4$Ti$_5$O$_{12}$ and TiO$_2$ particles in a eutectic environment. The method is characterized by an accelerated reaction rate and controllable particle morphology, because the salt melt acts as a strong solvent and exhibits a high ionic diffusion rate [Tang et al., 2002]. The synthesised Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanostructured composites are composed of nanocrystallites or grains with different crystallographic orientations. The grain-boundary atoms are not in regular crystallographic sites and may therefore be reactive to Li$^+$ [Beaulieu et al., 2000]. Furthermore, the amorphous carbon produced by the decomposition of citric acid (C$_6$H$_8$O$_7$) suppressed aggregation of nanoparticles and was dispersed at grain boundaries. An overall schematic model of the synthetic procedure is presented in Scheme 7.1.
Scheme 7.1 Schematic model of synthetic procedure: (a) mixed raw materials heated at 400 °C for 3 h, (b) solid molten salts and Li₄Ti₅O₁₂-TiO₂ nanoparticles with amorphous carbon, (c) Li₄Ti₅O₁₂-TiO₂ nanocrystals covered with thin layer of amorphous carbon and grain boundary interface areas embedded in carbon matrix.

The structures and phases present in the synthesised products were investigated by X-ray diffraction (XRD). XRD patterns for the samples of Li₄Ti₅O₁₂, Li₄Ti₅O₁₂-TiO₂, and Li₄Ti₅O₁₂-TiO₂-C are shown in Figure 7.1. In all samples, diffraction peaks consistent with the cubic spinel phase, Li₄Ti₅O₁₂ [Space group Fd-3m (227), JCPDS No. 49-0207], were observed, and the individual sets of planes are indexed in Figure 7.1. Additional narrow peaks were observed for the Li₄Ti₅O₁₂-TiO₂ and Li₄Ti₅O₁₂-TiO₂-C samples, consistent with the TiO₂ anatase phase (JCPDS No. 89-4921), and are also indexed in Figure 7.1. Any broad peaks or lines corresponding to amorphous or crystalline carbon were of insufficient intensity to be detected against the background in the XRD pattern of Li₄Ti₅O₁₂-TiO₂-C nanocomposite. The
approximate crystallite sizes of the Li$_4$Ti$_5$O$_{12}$, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C powder samples were estimated using the Debye-Scherrer equation applied to the marked peaks, assumed to be originating from (400) Li$_4$Ti$_5$O$_{12}$ and (200) TiO$_2$, where the Si standard 220 peak was used as the full-width half-maximum (FWHM) reference (0.204°) for the un-broadened peak.

![X-ray diffraction patterns](image)

**Figure 7.1** X-ray diffraction patterns of (a) Li$_4$Ti$_5$O$_{12}$, (b) Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and (c) Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite.

The specific surface areas of the synthesised products were also measured by the 15 points BET N$_2$ adsorption method. Approximate crystallite sizes and specific surface areas of the samples are shown in Table 7.1. The Li$_4$Ti$_5$O$_{12}$ sample shows the highest specific surface area (110.92 m$^2$g$^{-1}$), while the Li$_4$Ti$_5$O$_{12}$-TiO$_2$ and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C samples have specific surface areas of 76.43 m$^2$g$^{-1}$ and 49.92 m$^2$g$^{-1}$, respectively.
Table 7.1. Specific surface areas and approximate crystal sizes of Li$_4$Ti$_5$O$_{12}$, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Li$_4$Ti$<em>5$O$</em>{12}$</th>
<th>Li$_4$Ti$<em>5$O$</em>{12}$-TiO$_2$</th>
<th>Li$_4$Ti$<em>5$O$</em>{12}$-TiO$_2$-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment time (h)</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Crystallite sizes of Li$_4$Ti$<em>5$O$</em>{12}$ (nm)</td>
<td>1.9</td>
<td>2.43</td>
<td>8.82</td>
</tr>
<tr>
<td>Crystallite sizes of TiO$_2$ (nm)</td>
<td>-</td>
<td>23.26</td>
<td>10.06</td>
</tr>
<tr>
<td>BET surface areas (m$^2$ g$^{-1}$)</td>
<td>110.92</td>
<td>76.43</td>
<td>49.92</td>
</tr>
</tbody>
</table>

However, to detect and quantify the amount of amorphous carbon in the Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C composite materials, Raman spectroscopy (Figure 7.2 (a)) and TGA (Figure 7.2 (b)) were carried out, respectively. In the range of 1000-1800 cm$^{-1}$ (Figure 7.2(a)), it can be observed that the Raman spectra exhibit a typical characteristic of amorphous carbon, a broad peak located approximately in the range of 1200-1700 cm$^{-1}$, which is usually fitted to two peaks at approximately 1605 cm$^{-1}$ (G band) and 1357 cm$^{-1}$ (D band) [Garcia-Zarco et al., 2009]. On the other hand, TGA was carried out in air (Figure 7.2(b)). The samples were heated from 60 to 800 °C at a rate of 5 °C min$^{-1}$. As can be seen from Figure 7.2(b), Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite powders start to lose weight slowly in air with increasing temperature, and maximum weight loss was found to take place around 300-500 °C, while the Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$-TiO$_2$ powders remain stable over the entire temperature range.
Figure 7.2 Raman spectrum obtained from Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite (a) and TGA curves of Li$_4$Ti$_5$O$_{12}$, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite (b).
As the Li$_4$Ti$_5$O$_{12}$-TiO$_2$ powders remain stable over this temperature range, any weight change is believed to correspond to the oxidation of amorphous carbon [Ng et al., 2007]. According to Figure 7.2(b), weight loss for the sample of Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C starts at 60 °C, which could be attributed to the loss of moisture and volatile organic compounds (~ 3 wt.%) contained in the sample. Therefore, the change in weight before and after the oxidation of carbon directly translates into the amount of amorphous carbon in the Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C composite. With the use of this method, it was estimated that the amount of total weight loss in the composite was approximately 14.30 wt. %, where ~ 3 wt.% weight loss could be considered to be due to moisture and volatile organic compounds. The remaining amount, ~ 11.3 wt.%, was attributed to the decomposition of citric acid (C$_6$H$_8$O$_7$) in the precursor.

Transmission electron microscope images are shown in Figure 7.3, which compares the nanostructures found in the carbon containing sample with the results obtained from the Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$-TiO$_2$ samples, which did not contain carbon. In the TEM investigation it was demonstrated that the products formed after calcination at 300°C, the Li$_4$Ti$_5$O$_{12}$ sample, (Figure 7.3(a-c)) contained only nanostructured Li$_4$Ti$_5$O$_{12}$, while the Li$_4$Ti$_5$O$_{12}$-TiO$_2$ sample calcined at 400 °C (Figure 7.3(d-i)) consisted of a high grain boundary density, duplex nanostructure consisting of both coarse (anatase TiO$_2$) and fine (Li$_4$Ti$_5$O$_{12}$) particles (Figure 7.3(e)). For the carbon containing composite, carbon incorporation into the nanostructure was confirmed by semi-quantitative EDS analysis of relatively large regions located over holes in the holey carbon support film (Figure 7.4). This preliminary investigation revealed only slight variations in the carbon to Ti to oxygen ratios for the different regions.
examined. Bright-field TEM contrast indicated that the carbon is located on Li$_4$Ti$_5$O$_{12}$ and anatase TiO$_2$ grain surfaces and at the grain boundaries. At low magnification, sharpness of the nanocrystalline structure is more evident in the samples which do not contain carbon (comparing Figure 7.3(a) and (d) without C to Figure 7.3(g) with C), while at intermediate and high magnifications, the contrast indicated that carbon was also distributed between the grain boundaries.

**Figure 7.3** TEM results obtained from Li$_4$Ti$_5$O$_{12}$ calcined at 300 °C (a-c), Li$_4$Ti$_5$O$_{12}$-TiO$_2$ calcined at 400 °C (d-f), and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C calcined at 400 °C (g-i). Insets: selected area diffraction patterns in (a) and (d) contain reflections consistent with Li$_4$Ti$_5$O$_{12}$ (L) and anatase TiO$_2$ (A).
For example, the cellular contrast of Figure 7.3(h) is consistent with the presence of grain boundary carbon, while the comparatively clearer grain boundary contrast in Figure 7.3(e) is also consistent with a microstructure composed of just TiO$_2$ and Li$_4$Ti$_5$O$_{12}$. High resolution imaging of the C-containing sample (Figure 7.3(i)) also resulted in contrast consistent with the presence of TiO$_2$ and Li$_4$Ti$_5$O$_{12}$ nanocrystals covered by a thin layer of amorphous carbon and grain boundary interface areas embedded in carbon matrix.

![TEM image and EDS analysis](image)

**Figure 7.4 (a)** TEM image of Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C sample and (b) semi-quantitative EDS analysis of relatively large region of (a).

### 7.4 Electrochemical Characterization

To test the electrochemical performance, Li$_4$Ti$_5$O$_{12}$, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C powders were mixed with acetylene black (AB) (Cabot Australasia Pty Ltd.) and a binder, polyvinylidene fluoride (PVdF, Sigma-Aldrich), in a weight ratio of 80:10:10 in a solvent, N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, anhydrous, 99.5%). The slurry was uniformly spread onto copper foil substrates with an area of 1 cm$^2$. The coated electrodes (average thickness ~50 µm) were dried in a vacuum.
oven at 100 °C for 24 h and then pressed in a hydraulic press for 10 s. Subsequently, the electrodes were cut to a 1 × 1 cm² size, and CR 2032 coin-type cells were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany). The electrochemical coin cells contained the coated material on Cu foil as the working electrode, lithium foil as the counter electrode and reference electrode, porous polypropylene as the separator, and 1 M LiPF₆ in a 50:50 (v/v) mixture of ethylene carbonate and dimethyl carbonate (MERCK KgaA, Germany) as the electrolyte. Electrochemical measurements, including charge-discharge, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were performed using a Neware battery tester and a CHI 660b electrochemistry workstation, respectively. The cells were galvanostatically discharged and charged in the range of 1.0-2.5 V at different current densities. Cyclic voltammograms of the electrodes were collected with a scan rate of 0.05 mVs⁻¹ between 1.0 and 2.5 V vs. Li/Li⁺.

Cyclic voltammograms (CV) of the Li₄Ti₅O₁₂, Li₄Ti₅O₁₂-TiO₂, and Li₄Ti₅O₁₂-TiO₂-C composite electrodes are shown in Figure 7.5. The cathodic peak located around 1.5 V for all samples corresponds to the voltage platform of the discharge process, in which Li-ions are inserted into the spinel Li₄Ti₅O₁₂. The anodic peak located at 1.66 V for the Li₄Ti₅O₁₂ electrode, 1.63 V for the Li₄Ti₅O₁₂-TiO₂ electrode, and 1.59 V for the Li₄Ti₅O₁₂-TiO₂-C electrode corresponds to the voltage platform of the charge process, in which Li-ions are extracted from the spinel Li₄Ti₅O₁₂. It should be noted that both the Li₄Ti₅O₁₂-TiO₂ and Li₄Ti₅O₁₂-TiO₂-C electrodes have two voltage plateaus. The plateaus at around 1.7 V and 2.0 V correspond to the discharge and charge plateaus of anatase TiO₂ [Li et al., 2007a]. Only one oxidation/reduction peak is observed for the Li₄Ti₅O₁₂ electrode, and no peak with characteristics of 125
lithium ion insertion or extraction for anatase TiO$_2$ is observed. Since there are no other redox peaks in the cyclic voltammogram, the spinel Li$_4$Ti$_5$O$_{12}$ is evidently synthesized in pure form at very low temperature (300 °C), whereas with increasing temperature (400 °C), the Li$_4$Ti$_5$O$_{12}$ phase is partially transformed to anatase TiO$_2$, in accordance with the XRD results. Moreover, the anodic and cathodic peaks are sharp, indicating the good electrode kinetics of the Li$_4$Ti$_5$O$_{12}$-TiO$_2$ and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C electrodes. The voltage difference between the anodic and the cathodic peaks can reflect the degree of polarization of the electrode. The Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C composite has the lowest value compared with the other two electrodes, showing the weak polarization of the electrode. This is consistent with the excellent rate capability of the Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite. The following Equations (7.1) and (7.2) explain the lithium ion insertion and extraction into and from the spinel Li$_4$Ti$_5$O$_{12}$ and anatase TiO$_2$, respectively, during cycling processes. The insertion and extraction processes are associated with the redox reactions of Ti$^{4+}$/Ti$^{3+}$ [He et al., 2007; Venkateswarlu et al., 2005].

\[
\text{Li}_4\text{Ti}_5\text{O}_{12} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_{4+x}\text{Ti}_5\text{O}_{12} \quad (7.1)
\]
\[
\text{TiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2 \quad (7.2)
\]

The amount of lithium insertion may depend on the crystalline nature and the microstructure of the material [Yuan et al., 2009a].
Figure 7.5 Cyclic voltammograms of (a) Li$_4$Ti$_5$O$_{12}$, (b) Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and (c) Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite electrodes at a scan rate of 0.05 mVs$^{-1}$ between 1.0 and 2.5 V.

The initial charge-discharge profiles for the Li$_4$Ti$_5$O$_{12}$, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite electrodes at the 0.5 to 10 C charge/discharge rates are shown in Figure 7.6(a-c). Initial discharge capacities were measured to be 147, 167, and 166 mAh g$^{-1}$ at 0.5 C for the Li$_4$Ti$_5$O$_{12}$, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C electrodes; and 57, 107, and 135 mAh g$^{-1}$ at 10 C for the Li$_4$Ti$_5$O$_{12}$, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C electrodes, respectively. The discharge capacity decreases for all samples with increasing current density, and some
irreversible capacity loss was observed in the first cycle, which might be due to irreversible electrochemical decomposition of the electrolyte or impurity phase over the Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}/TiO\textsubscript{2} surface [Yuan et al., 2009b]. The Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} sample prepared at low temperature (300 °C) delivers sloping charge/discharge curves instead of a flat plateau (Figure 7.6(a)), which is consistent with material prepared by the thermohydro method at low temperature [Li et al., 2005a]. Differences in the charge/discharge profiles are mostly correlated with crystal structure. As can be seen in Figure 7.6(b) (Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}-TiO\textsubscript{2}) and Figure 7.6(c) (Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}-TiO\textsubscript{2}-C), both the discharge and the charge curves have two voltage plateaus due to the formation of the two phases of spinel Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} and anatase TiO\textsubscript{2}. This also agrees with the results on cathodic and anodic peak potential in the cyclic voltammograms. Figure 7.6(d) compares the cycling performance of the Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}-TiO\textsubscript{2}-C nanocomposite at 10 C with that of the Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} and Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}-TiO\textsubscript{2} in the voltage range of 1.0-2.5 V. The Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}-TiO\textsubscript{2}-C nanocomposite electrode shows a higher capacity and better cycling performance. After 100 cycles, the discharge capacity for the Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}-TiO\textsubscript{2}-C electrode was measured to be 110 mAh g\textsuperscript{-1} at 10 C (82 % of initial discharge capacity) with an initial coulombic efficiency of 99 % (Figure 7.6(e)). On the contrary, the discharge capacities for the Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} and Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}-TiO\textsubscript{2} electrodes were only 40 mAh g\textsuperscript{-1} (70 % of initial discharge capacity) and 83 mAh g\textsuperscript{-1} (77 % of initial discharge capacity) at 10 C, with an initial coulombic efficiency of 93 and 97%, respectively. The high capacity and good cycling performance delivered by the Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}-TiO\textsubscript{2}-C electrode could be attributed to its high electronic conductivity due to the thin layer of amorphous carbon around each nanocrystal and the grain boundary areas embedded in a carbon matrix, which has significant implications for
both the improvement of electronic conductivity and the enhancement of Li$^+$ transfer as well.

Figure 7.6 The initial galvanostatic charge-discharge profiles of (a) Li$_4$Ti$_5$O$_{12}$, (b) Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and (c) Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C electrodes at different current densities from 0.5 to 10 C between 2.5-1.0 V; (d) cyclic performance beyond 100 cycles at 10 C, (e) coulombic efficiency, and (f) rate capability (0.5-10 C) of the Li$_4$Ti$_5$O$_{12}$, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C electrodes, respectively.
Figure 7.6 (f) shows the variation in the cell capacity as a function of the applied rate, expressed in terms of C. The lowest slope indicates the best rate capability. The rate capabilities are in the order of Li$_4$Ti$_5$O$_{12}$ < Li$_4$Ti$_5$O$_{12}$-TiO$_2$ < Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C. That is to say, the Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite electrode shows the best rate capability. Here, the carbon content in the nanocomposite could increase the electron transfer and reduce the resistance within the particles, and such a sample would then show the best rate capability. At the low current density of 0.5 C, the differences between the specific capacities of the electrodes are not so large. This is reasonable because Li$^+$ insertion/extraction is sufficient at this relatively low current rate. The difference increases with increasing rate. This result confirms that the carbon coated nanoparticles can affect the rate-capability of the Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C electrodes.

Electrochemical impedance spectroscopy (EIS) measurements were carried out in order to compare the conductivity of the prepared Li$_4$Ti$_5$O$_{12}$, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite electrodes. The Nyquist plots of the three electrodes and the equivalent circuit are depicted in Figure 7.7. In this equivalent circuit (inset), $R_\Omega$ and $R_{ct}$ are the ohmic resistance (total resistance of the electrolyte, separator, and electrical contacts) and charge-transfer resistance, respectively. CPE is the constant phase-angle element, involving double layer capacitance, and $W$ represents the Warburg impedance reflecting the solid-state diffusion of Li ions into the bulk of the active materials, which is associated with the inclined line at low frequencies [Fey et al., 2003]. The resistance of the combination of the electrolyte, separator, and electrical contacts ($R_\Omega$) is similar for the Li$_4$Ti$_5$O$_{12}$ ($R_\Omega = 2.32$), Li$_4$Ti$_5$O$_{12}$-TiO$_2$ ($R_\Omega = 1.91$), and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C ($R_\Omega = 1.26$) electrodes. This is because the electrodes were prepared by adding a conductive carbon black agent,
which induces good conductivity in the electrode. It can be seen clearly that the $R_{ct}$ is much smaller for the Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C ($R_{ct} = 108.60 \ \Omega$) electrode than for the Li$_4$Ti$_5$O$_{12}$ ($R_{ct} = 273.59 \ \Omega$) and Li$_4$Ti$_5$O$_{12}$-TiO$_2$ ($R_{ct} = 179.25 \ \Omega$) electrodes, which indicates that the carbon coating could enable much easier charge transfer at the electrode/electrolyte interface and consequently, decrease the overall battery internal resistance. The in situ carbon coating applied in the synthesis significantly enhances the conductivity of the Li$_4$Ti$_5$O$_{12}$-TiO$_2$ material, since the conductive carbon facilitates electronic conductive paths in the Li$_4$Ti$_5$O$_{12}$-TiO$_2$ particle surroundings, which is considered a key factor in improving the discharge capacity, rate capability, and cycle life of the Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite material.

**Figure 7.7** Nyquist plots for the Li$_4$Ti$_5$O$_{12}$, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C electrodes after charge-discharge and the equivalent circuit shown in the inset.
This enhanced kinetics, better cycling performance, and excellent high rate capability of the Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite could be explained as follows:

Nanostructured materials offer the possibility to make use of small transport lengths and small separation distances in almost the same way as in fluids. The materials synthesized in this study are obviously nanoparticles. The first difference between Li$_4$Ti$_5$O$_{12}$, Li$_4$Ti$_5$O$_{12}$-TiO$_2$, and Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C is the surface area, which is in the order of Li$_4$Ti$_5$O$_{12}$ > Li$_4$Ti$_5$O$_{12}$-TiO$_2$ > Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C. Since the number of insertion sites is directly proportional to the surface area, a larger number of lithium insertion sites would be expected in the samples with higher surface area [Allen et al., 2006]. Under these considerations, the electrochemical performance should be in the order of Li$_4$Ti$_5$O$_{12}$ > Li$_4$Ti$_5$O$_{12}$-TiO$_2$ > Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C, but the reality is the inverse (Li$_4$Ti$_5$O$_{12}$ < Li$_4$Ti$_5$O$_{12}$-TiO$_2$ < Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C). This may be due to the presence of very dense agglomerations or the weak crystallinity of ultra-fine particles (Figure 7.3(c)) in the Li$_4$Ti$_5$O$_{12}$ sample, which may hinder the insertion reaction, as intercalation can only occur with the outer atoms and is therefore limited. On the other hand, the Li$_4$Ti$_5$O$_{12}$-TiO$_2$ sample has high grain boundary density (Figure 7.3(e)) with higher theoretical capacity compared to Li$_4$Ti$_5$O$_{12}$. In the case of Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C, the kinetics of the lithium insertion/removal reaction and consequently the lithium storage capacity are not only dependent on the crystallite size and grain boundary density of Li$_4$Ti$_5$O$_{12}$-TiO$_2$, but also show strong dependence on the amorphous carbon coating. The carbon coating suppresses particle agglomeration and growth, and provides better electronic conductivity. Additionally, the carbon coating influences the lithium insertion kinetics in Li$_4$Ti$_5$O$_{12}$-TiO$_2$, causing facile lithium insertion/removal, and provides structural stability minimizing lithium trapping sites [Das et al., 2010]. Besides this absorptive mechanism.
(insertion reaction), there is another adsorptive mechanism (reversible interfacial reaction), the capacity of which depends on the grain size in the first instance and, indeed, relies on the presence of nanoparticles. Different possibilities for interfacial reactions have been discussed in the literature: one is under-potential deposition [Conway, 1993], and a second possible mechanism is lithium storage by reaction with the grain boundary phase in polycrystalline materials [Beaulieu et al., 2000] or by reaction with the liquid electrolyte at the solid/liquid interface [Grugeon et al., 2001; Li et al., 2002b]. Here, the second possible mechanism is being considered: lithium storage by reaction with the grain boundary phase. Lithium storage in these samples relates to the presence of grain boundary interfaces between spinel Li$_4$Ti$_5$O$_{12}$ and anatase TiO$_2$. Heat treatment affects both the surface to volume ratio of the nanostructures and the total area of the interface between the anatase and the lithium titanate nanostructures, as indicated by the TEM observations (Figure 7.3). The sample of Li$_4$Ti$_5$O$_{12}$ is too dense or weakly crystalline, and the reversible interfacial reaction paths along the grain boundaries are too long. The sample of Li$_4$Ti$_5$O$_{12}$-TiO$_2$ has a large area of interface between the anatase and the lithium titanate, while in the carbon coated sample, there is a thin layer of amorphous carbon around each nanocrystal, as well as grain boundary interface areas embedded in a carbon matrix, which can store electrolyte and allow more channels for the reactions of Li$^+$ ion insertion/extraction. At the same time, electrolyte can penetrate easily to minimize the ionic resistance [Wang et al., 2010b], thereby leading to superior electrochemical performance.
7.5 Conclusions

High grain boundary density, dual phase Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite was synthesized by a simple molten salt process, and its electrochemical characteristics were investigated in this study. For comparison, Li$_4$Ti$_5$O$_{12}$ and Li$_4$Ti$_5$O$_{12}$-TiO$_2$ were also investigated. The TEM results indicate that a thin layer of amorphous carbon exists around each nanocrystal of Li$_4$Ti$_5$O$_{12}$ and TiO$_2$ for the Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C sample, and their grain boundary interface areas are embedded in a carbon matrix. The electrochemical results clearly demonstrated that the electrode properties of the Li$_4$Ti$_5$O$_{12}$-TiO$_2$-C nanocomposite were much better than those of the Li$_4$Ti$_5$O$_{12}$ or Li$_4$Ti$_5$O$_{12}$-TiO$_2$ nanoparticles. The excellent electrochemical performance of the carbon coated nanocomposite could be related to the combined effects of the nanostructure, the carbon layering on the nanoparticles, and the grain boundary interface areas embedded in a carbon matrix, which would contribute together to enhance structural stability and improve lithium storage kinetics by reducing the traverse time of electrons and lithium ions, and also stabilizing the solid electrolyte interphase (SEI) film, which would result in improved rate and cycling performance. The synthesis process employed is very simple, convenient, and requires only a low treatment temperature. The method presented here could also be adopted to synthesize other metal oxide composites.
CHAPTER 8

HYDROTHERMAL SYNTHESIS OF NANOSTRUCTURED \( \text{Co}_3\text{O}_4 \) MATERIALS UNDER PULSED MAGNETIC FIELD AND WITH AN AGING TECHNIQUE, AND THEIR ELECTROCHEMICAL PERFORMANCE AS ANODE FOR THE LITHIUM-ION BATTERY

8.1 Introduction

In recent years, great efforts have been put into the reinvestigation of materials that were thought of as being electrochemically inactive in bulk form, but that could present improved electrochemical performance at the nanoscale. One good example is the demonstration that nanoparticles of some simple transition metal oxides, sulfides, fluorides, and nitrides can provide innovative anode materials for lithium ion batteries [Zhou et al., 2006]. Transition-metal oxides in the nanometer size regime display many interesting size-dependent optical, electronic, magnetic, and chemical properties [Spear and Tamhuser, 1993; Hagel, 1965; Tarasevich et al., 1980]. Such nanoscale materials have potential applications in chemical sensors, spintronics, magnetic data storage systems, and shape memory alloys [Mo et al., 2005; Maye et al., 2005; Hu et al., 2004]. Among these oxides, \( \text{Co}_3\text{O}_4 \) is universally known as a widely applied material used in electrodes [Wang et al., 2002], catalysts [Wang et al., 2005], and gas sensors [Li et al., 2005]. With continuing progress on electrode materials, \( \text{Co}_3\text{O}_4 \) has attracted considerable attention due to its high theoretical reversible capacity of 1100 mAh g\(^{-1}\) when discharged to 0 V vs. Li\(^+\)/Li.
As is well known, Co$_3$O$_4$ particles have magnetic properties [Hou et al., 2005; Makhlouf, 2002], so there may be advantages to their fabrication under external field. As an example of using such properties, single-crystalline Fe$_3$O$_4$ (an allomer of Co$_3$O$_4$) nanowires [Wang et al., 2004b; Zhang et al., 2007b] have been successfully
synthesized under low magnetic field. However, most of the above methods may be not compatible with magnetic field, or the magnetic field involved can only be very small. Recently, high magnetic field has been recognized not only for study of the physical properties of a material, but also as a tool to control the microstructure and functions of the material [Yanwei et al., 2006]. Yet until now, there have been scarcely any reports on the synthesis of Co$_3$O$_4$ nanoparticles under high magnetic field. So, it is very interesting to explore the synthesis of Co$_3$O$_4$ nanoparticles by the hydrothermal method under pulsed magnetic field and with an aging technique, and to examine their electrochemical performance as anode for the lithium-ion battery.

8.2 Materials Synthesis

Based on a collaboration with Shanghai University, the samples were made in Shanghai University, China. The starting chemicals were cobalt nitrate, ammonia, ammonium chloride, hydrogen peroxide, polyethylene glycol (PEG), n-butanol, and absolute ethanol. Cobalt nitrate (0.0378 mole) and PEG (0.125 g) as surfactant were dissolved in an appropriate amount of deionized water, and then an excess amount of NH$_3$-NH$_4$Cl buffer solution (pH value of 10) was added under electromagnetic stirring to form the Co(OH)$_2$ precursor. 30 % (mass fraction) H$_2$O$_2$ was slowly dropped into the suspension. The above mixture was stirred vigorously for 30 min and then transferred into a 25 mL Teflon-lined stainless steel autoclave. In addition, one mixture was aged for 12 hours at room temperature before being transferred into the autoclave. Then, the autoclave was filled with n-butanol up to 70 % of the total capacity. Finally, the autoclave was sealed, heated to and maintained at 180 °C temperature for 10 hours, and then cooled to room temperature naturally. For one
sample, pulsed magnetic field (Shanghai University facility, Model: DCD-1100/5-384T; Power source: AC 220 V, 50-60 Hz, 40 A; Maximum output current: 60000 A; Charging time: 9 seconds; Output voltage: 50-1100 V (continuously variable); Capacitance: 38400 μF; Maximum output energy: 23.232 J) was used over the whole thermal reaction process with a frequency of two pulses per minute. The product was filtered and washed several times each with deionized water and absolute ethanol, and then dried in an oven at 80°C for 10 hours. The essential chemical reaction equation is as follows:

\[
3 \text{Co(NO}_3\text{)}_2 + 6 \text{NH}_3\cdot\text{H}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{Co}_3\text{O}_4 + 6 \text{NH}_4\text{NO}_3 + 4\text{H}_2\text{O} \quad (8.1)
\]

8.3 Structure and Morphology Analysis

Figure 8.1 shows the XRD patterns for the samples produced at 180 °C and 0 T magnetic field (Co$_3$O$_4$-0T), at 180 °C and 4 T magnetic field (Co$_3$O$_4$-4T), and with 12 hours aging time followed by 0 T processing at 180 °C (Co$_3$O$_4$-Aging). All the diffraction peaks are readily indexed to cubic structure [space group: Fd3m (227)] Co$_3$O$_4$, which is consistent with the literature results (Joint Committee on Powder Diffraction Standards (JCPDS) File No. 43-1003). Comparing these data with standard Co$_3$O$_4$ (JCPDS File No. 43-1003), there are slight differences in the lattice constant (8.1016 Å for Co$_3$O$_4$-0T, 8.0850 Å for Co$_3$O$_4$-4T, and 8.0876 Å for Co$_3$O$_4$-Aging) and in the displacement of peak positions, which confirms the existence of minor strain in the as-prepared samples, owing to their nanocrystalline nature [Tripathy et al., 2008]. It can also be seen that the lattice constant of the as-prepared sample obtained under the 4 T magnetic field is closer to the literature value (8.084 Å for standard Co$_3$O$_4$, JCPDS File No. 43-1003). The explanation could be that the
high pulsed magnetic field generates magnetic force, and this magnetic force produces pressure on the object, which causes strong vibrations in the autoclave solution and promotes more nucleation. It also makes the microsphere surface smooth and compact. So, the pulsed magnetic field has positive effects in terms of reducing strain in the nanocrystals. Moreover, there are also positive effects resulting from the 12 hour aging process, which is described in detail in the surface morphology section. The XRD pattern for this material indicates that the prepared sample is pure Co$_3$O$_4$ (Figure 8.1).

![XRD patterns of Co$_3$O$_4$](image)

**Figure 8.1** XRD patterns of Co$_3$O$_4$ obtained at (a) 180 °C and 0 T magnetic field (Co$_3$O$_4$-0T), (b) 180°C and 4 T magnetic field (Co$_3$O$_4$-4T), and (c) with 12 hours aging time followed by 0 T processing at 180 °C (Co$_3$O$_4$-Aging).

The surface morphology, one of the prime factors that govern the physical and electrochemical properties of materials, was investigated by means of FE-SEM analysis. Figure 8.2 shows FE-SEM images of the Co$_3$O$_4$ samples obtained using different synthesis conditions. Figure 8.2(a, b) and (c, d) contains images of the
samples obtained at a temperature of 180 °C over 10 hours in 0 T and 4 T magnetic field, respectively. From Figure 8.2(b) it can be seen that the morphology of nanocrystalline Co$_3$O$_4$ is spherical, with the typical particle size around 30 nm for the sample obtained under 0 T magnetic field. The sample obtained under 4 T magnetic field consists of large agglomerated spheres (Figure 8.2(c)). These spheres are composed of numerous quasi-spherical nanoparticles with a typical diameter of ~ 25 nm (Figure 8.2(d)). Co$_3$O$_4$ nanospheres with compact and smooth surfaces are observed for the magnetic field processing compared to processing with no magnetic field. It is found that pulsed magnetic field processing makes the prepared nanoparticle surface more compact and smooth (Figure 8.2 (d)), with less strain.

![Figure 8.2](image)

**Figure 8.2** FE-SEM images of Co$_3$O$_4$ samples obtained at 180 °C and 0 T magnetic field (Co$_3$O$_4$-0T) (a, b); 180 °C and 4 T magnetic field (Co$_3$O$_4$-4T) (c, d).
In other words, the pulsed magnetic field has a significant influence on the morphology of the Co$_3$O$_4$ crystals, and on the structure and size of the Co$_3$O$_4$ grains. The possible reason is as follows: the formation of a crystal includes the two processes of nucleation and growth; it is probable that the pulsed magnetic field provides energy to the processes, or it changes the conditions of nanocrystalline nucleation and growth, so that it influences the dynamics and thermodynamics of nanocrystal formation, resulting in some differences in the nanostructure of the prepared samples. The vigorous vibration produced by the pulsed magnetic field is likely to promote nucleation and break up some crystal grains that have already formed. These broken grains may become new nucleating centres to form crystal grains again. All these behaviours affect the crystal nucleation and growth.

Figure 8.3 shows FE-SEM images of the Co$_3$O$_4$ sample obtained with 12 hours aging time followed by 0 T processing at 180 °C for 10 hours. It can be seen that the sample consists of large Co$_3$O$_4$ hollow spheres with a typical diameter of ~ 2.5 μm (Figure 8.3(a)). The hollow sphere in this image is composed of numerous spherical nanoparticles with a typical diameter of ~ 20 nm (Figure 8.3(d)). Furthermore, agglomerated nanoparticles are observed on the surface of the hollow sphere, and the microstructure of these spherical nanoparticles attached to the hollow sphere surface was scanned under high magnification (Figure 8.3(c)). Compared with Figure 8.2, it was found that the Co$_3$O$_4$ hollow sphere grains produced by aging technique are smaller than for the sample without aging. The aging process thus also has an impact on the morphology and grain refinement of Co$_3$O$_4$. The processes occurring during aging are not yet fully understood. One possibility is that nucleation was occurring due to chemical rearrangement during the aging of the starting solution at room
temperature before hydrothermal treatment. The small particles formed during this stage are actually ‘germ’ nuclei that undergo further growth on heating [White et al., 1998; Twomey et al., 1994]. However, if the aging time is long enough, small crystals with a similar particle morphology that formed during the initial stage of hydrothermal synthesis can be obtained [White et al., 1998].

**Figure 8.3** FE-SEM images of Co$_3$O$_4$ hollow sphere obtained with 12 hours aging time followed by 0 T processing at 180 °C for 10 hours (Co$_3$O$_4$-Aging): (a) low magnification image of the large hollow sphere; (b) high magnification image of the marked region of (a); (c) high magnification image of the spherical nanoparticles attached to the hollow sphere surface; (d) high-resolution image of the marked region of (b), which is composed of numerous spherical nanoparticles.
8.4 Electrochemical Characterization

To test the electrochemical performances, Co$_3$O$_4$ nanomaterials were mixed with acetylene black (AB) and a binder, carboxymethyl cellulose (CMC), in a weight ratio of 80:15:5 in a solvent (distilled water). The slurry was spread onto copper foil substrates. The thickness of the electrode was approximately 50-60 µm with a loading of 1-2 mg. The coated electrodes were dried in a vacuum oven at 110 °C for 24 hours to remove water molecules. Subsequently, the electrodes were cut to a 1 × 1 cm$^2$ size. CR 2032 coin-type cells were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany) using lithium metal foil as the counter electrode. The electrolyte was 1 M LiPF$_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume, provided by MERCK KgaA, Germany). The cells were galvanostatically discharged and charged in the range of 0.01-3.0 V at current densities of 30 and 100 mA g$^{-1}$. Cyclic voltammetry was conducted on fresh cells using a CHI 660C electrochemical workstation system. Cyclic voltammetry measurements were performed to examine the electrochemical properties of the Co$_3$O$_4$ electrodes during the galvanostatic charge-discharge processes. Figure 8.4 presents the initial five cycles collected at sweep rates of 0.1 mVs$^{-1}$ between 0.01 and 3.0 V. An irreversible reduction peak appears at 0.7 V in the first discharge cycle, corresponding to the initial reduction of Co$_3$O$_4$ to metallic cobalt, the electrochemical formation of amorphous Li$_2$O, and the formation of a partially irreversible solid electrolyte interphase (SEI) layer [Poizot et al., 2001]. In the oxidation scan, two main anodic peaks at around 1.3 and 2.06 V reveal the multi-step extraction process where Co is re-oxidised to Co$_3$O$_4$ and Li$_2$O decomposes [Grugeon et al., 2001]. In the second cycle, the reduction peaks consist of main peaks at around 0.90 V, and the
intensities of the cathodic peaks gradually decrease in the subsequent scanning cycles. After the electrode activation via the 1\textsuperscript{st} cycle, the strongly overlapping trend of the 2\textsuperscript{nd}, 3\textsuperscript{rd}, 4\textsuperscript{th}, and 5\textsuperscript{th} cycles indicates that electrochemical reversibility has set in after the initial cycle. The overall electrochemical processes can be expressed as follows:

\[ \text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \underset{\text{Charge}}{\rightleftharpoons} 3\text{Co} + 4\text{Li}_2\text{O} \] (8.2)

**Figure 8.4** Cyclic voltammograms of (a) Co$_3$O$_4$-0T, (b) Co$_3$O$_4$-4T, and (c) Co$_3$O$_4$-Aging electrodes at a scan rate of 0.1 mVs$^{-1}$ between 0.01 and 3.0 V.

The Li storage capacities and cycling performance of the Co$_3$O$_4$ electrodes were investigated by galvanostatic charge-discharge measurements. Figure 8.5 shows the 1\textsuperscript{st}, 2\textsuperscript{nd}, 15\textsuperscript{th}, and 25\textsuperscript{th} cycle (numbers in graph represent the cycle number)
galvanostatic charge-discharge curves of Li/Co$_3$O$_4$ cells cycled between 0.01 and 3.0 V at a constant current density of 30 mA g$^{-1}$. The first discharge curve of each electrode has a longer sloping part, and the voltage trend strongly indicates typical characteristics of Co$_3$O$_4$ electrode, that is, a long voltage plateau at about 1.08 V followed by a sloping curve down to the cut-off voltage of 0.01 V during the first discharge step. Similar results were obtained for cobalt oxides by the research group of Thackeray and co-workers [Thackeray et al., 1985; Larcher et al., 2002]. The initial discharge capacities were found to be 1168, 1230, and 1246 mAh g$^{-1}$ for the Co$_3$O$_4$-0T, Co$_3$O$_4$-4T, and Co$_3$O$_4$-Aging electrodes, respectively. The discharge capacity is higher than the theoretical capacity. The extra capacity could be attributed to the formation of a polymer-like SEI, with the formation of the SEI dominant over the Co$_3$O$_4$ → Co conversion [Pralong et al., 2004], corresponding to an irreversible reduction process from 1.08 V with a maximum peak at 0.7 V, as shown in Figure 8.4. The first charge process in Figure 8.5 exhibits a higher and more sloping voltage profile, with two inconspicuous plateaus and lower capacities of 802, 762, and 1066 mAh g$^{-1}$ for the Co$_3$O$_4$-0T, Co$_3$O$_4$-4T, and Co$_3$O$_4$-Aging electrodes, respectively. In the second discharge process, the voltage plateau appears at a higher voltage of about 1.25 V, while the amplitude of the plateau is reduced and reversible capacity of 831 mAh g$^{-1}$ for the Co$_3$O$_4$-0T electrode, 806 mAh g$^{-1}$ for the Co$_3$O$_4$-4T electrode, and 1108 mAh g$^{-1}$ for the Co$_3$O$_4$-Aging electrode can be achieved. There are no obvious differences in subsequent cycles.
Figure 8.5 Typical charge-discharge curves at selected cycles of (a) Co$_3$O$_4$-0T, (b) Co$_3$O$_4$-4T, and (c) Co$_3$O$_4$-Aging electrodes at a current density of 30 mA g$^{-1}$ between 0.01 and 3.0 V.
The cycling behaviours of the Co$_3$O$_4$-0T, Co$_3$O$_4$-4T, and Co$_3$O$_4$-Aging electrodes at a current density of 100 mA g$^{-1}$ are presented in Figure 8.6. It can be seen that higher capacity and better cyclic retention are obtained for the Co$_3$O$_4$-Aging electrode. The discharge capacities and capacity retention for the electrodes composed of Co$_3$O$_4$-0T, Co$_3$O$_4$-4T, and Co$_3$O$_4$-Aging are summarised in Table 8.1. The Co$_3$O$_4$-Aging electrode shows the highest initial capacity (1334 mAh g$^{-1}$), with a capacity retention of 407 mAh g$^{-1}$ after 100 cycles, which is about 30% of the initial discharge capacity. The capacity loss is in the order of Co$_3$O$_4$-Aging < Co$_3$O$_4$-4T < Co$_3$O$_4$-0T. Thus, the morphologies affect not only the discharge capacity, but also the cycling stability of Li-ion batteries. Furthermore, the capacities of all electrodes decrease sharply with initial cycling and stabilise after several cycles. The capacities in the first cycle are higher than the theoretical capacity. This may be related to the gradual activation of Co$_3$O$_4$ and the formation of the electroactive polymer/gel-like film on the surface of the electrodes that has been discussed earlier. However, similar results are also reported in the literature [Liu et al., 2008; Lou et al., 2008; Du et al., 2007]. For comparison purposes, the electrochemical properties of the Co$_3$O$_4$-0T, Co$_3$O$_4$-4T, and Co$_3$O$_4$-Aging materials that have been investigated in this chapter and those of Co$_3$O$_4$ materials reported in the literature are summarized in Table 8.2. Although the electrodes prepared in this study have nearly identical initial discharge capacity compared with some Co$_3$O$_4$ samples, the initial coulombic efficiency for the Co$_3$O$_4$-Aging electrode is higher than those of the individual oxides. The capacity retention after 100 cycles is also notable.
Table 8.1 Cyclic performances of Co₃O₄-0T, Co₃O₄-4T, and Co₃O₄-Aging electrodes measured at a current density of 100 mA g⁻¹.

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Initial discharge capacity (mAh g⁻¹)</th>
<th>Capacity after 100 cycles (mAh g⁻¹)</th>
<th>Capacity retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₃O₄-0T</td>
<td>1057</td>
<td>274</td>
<td>26</td>
</tr>
<tr>
<td>Co₃O₄-4T</td>
<td>1280</td>
<td>348</td>
<td>27</td>
</tr>
<tr>
<td>Co₃O₄-Aging</td>
<td>1334</td>
<td>407</td>
<td>30</td>
</tr>
</tbody>
</table>

Figure 8.6 Cycling behaviour of Co₃O₄-0T, Co₃O₄-4T, and Co₃O₄-Aging electrodes at a current density of 100 mA g⁻¹.
Table 8.2 Comparison of the electrochemical properties of Co$_3$O$_4$ materials investigated in this chapter with those of Co$_3$O$_4$ materials reported in the literature.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Current density (mA g$^{-1}$)</th>
<th>Initial capacity (mAh g$^{-1}$)</th>
<th>Initial coulombic efficiency (%)</th>
<th>Capacity retention (mAh g$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_3$O$_4$-0T</td>
<td>100</td>
<td>1057</td>
<td>63</td>
<td>274</td>
<td>This work (100 cycles)</td>
</tr>
<tr>
<td>Co$_3$O$_4$-4T</td>
<td>100</td>
<td>1280</td>
<td>65</td>
<td>348</td>
<td>This work (100 cycles)</td>
</tr>
<tr>
<td>Co$_3$O$_4$-Aging</td>
<td>100</td>
<td>1334</td>
<td>73</td>
<td>407</td>
<td>This work (100 cycles)</td>
</tr>
<tr>
<td>Aging</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanosized</td>
<td>220</td>
<td>1411</td>
<td>34</td>
<td>913</td>
<td>[Yuan et al., 2003]</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(20 cycles) 2003</td>
</tr>
<tr>
<td>Nanosized</td>
<td>110</td>
<td>1380</td>
<td>67</td>
<td>550</td>
<td>[Yang et al., 2007]</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(10 cycles) 2007</td>
</tr>
<tr>
<td>Microsphere</td>
<td>100</td>
<td>4259</td>
<td>59</td>
<td>267</td>
<td>[Liu et al., 2008]</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(45 cycles) 2008</td>
</tr>
<tr>
<td>Co$_3$O$_4$ hollow</td>
<td>60</td>
<td>1241</td>
<td>-</td>
<td>633</td>
<td>[Liu and Zhang, 2009]</td>
</tr>
<tr>
<td>hollow microspheres</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanosized</td>
<td>20</td>
<td>780</td>
<td>-</td>
<td>460</td>
<td>Wang et al., 2002</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(30 cycles) 2002</td>
</tr>
</tbody>
</table>

149
8.5 Conclusions

This chapter explores the synthesis of Co$_3$O$_4$ nanoparticles by the hydrothermal method under pulsed magnetic field and with an aging technique. Processing with pulsed magnetic field produces a more compact and smooth surface than without it, and the product is composed of Co$_3$O$_4$ microspheres that consist of numerous nanograins. The aging technique introduced into the Co$_3$O$_4$ synthesis process makes large Co$_3$O$_4$ hollow spheres consisting of a large quantity of nanospheres. So, both processes have been proved to be effective approaches in material processing. The electrochemical measurements demonstrated that the Co$_3$O$_4$ hollow spheres formed by the aging technique showed the best electrochemical performance, including the highest discharge capacity and capacity retention as well. In view of this hollow-sphere structural arrangement, it is proposed that redox reactions with Li could promote more efficient and easier lithium diffusion than in the other two samples. This method could also be used to improve the electrochemical properties of other metal oxides for lithium-ion batteries.
CHAPTER 9

SPRAY PYROLYZED NiO-C NANOCOMPOSITE AS AN ANODE MATERIAL FOR THE LITHIUM-ION BATTERY WITH ENHANCED CAPACITY RETENTION

9.1 Introduction

Nanosized materials are known to exhibit profound differences in properties in comparison to those of bulk single crystals, microcrystalline powders, or thin films with the same chemical composition. Now-a-days, there is an increasing interest in nanomaterials (nanoparticles, nanostructured materials, etc.) for fundamental scientific reasons and potential applications as well [Parada and Morán, 2006]. This point is clearly illustrated in the transition metal oxide (MO) system (M = Fe, Co, Cu, and Ni) by considering the applicability of these materials to Li-ion batteries. These oxides offer a promising alternative to carbon as negative electrode materials in lithium-ion batteries [Huang et al., 2007b]. Nevertheless, the anodes based on pure transition metal oxides suffer from poor cycling performance owing to their tendency to agglomerate during lithium insertion/extraction processes and the mechanical instabilities caused by the huge volume changes, resulting in increased diffusion lengths and electrical disconnection from the current collector [Fan et al., 2004; Cheng et al., 2008]. Among them, NiO is an interesting material due to its applications in diverse fields, including magnetic thin films [Fujii et al., 1996], the active layer for gas sensors [Hotovy et al., 1999], electrochromic materials.
[Porqueras and Bertran, 2001], smart windows [Ferreira et al., 1996; Scarminio et al., 1992; Fantini et al., 1996], lithium-ion batteries [Chiu et al., 2005; Wang and Qin, 2002; Poizot et al., 2000], and so forth. NiO has a theoretical capacity of 718 mAh g\(^{-1}\) when it is used as anode material for lithium-ion batteries, but stoichiometric NiO shows very low electrical conductivity, less than \(10^{-13} \Omega^{-1} \text{ cm}^{-1}\) at room temperature, and is classified as a Mott-Hubbard insulator [Morin, 1954; Lukenheimer et al., 1991]. However, its reversible capacity is lower and its cycling performance is worse than those of other transition metal oxides such as CoO and Co\(_3\)O\(_4\) [Poizot et al., 2000; Poizot et al., 2002]. To improve the electrochemical properties of NiO, one effective way is preparing nanostructured materials [Wang et al., 2003; Wang and Qin, 2002], since the nanoparticles facilitate the transportation of Li\(^+\) and electrolyte ions by offering a shorter solid-state diffusion length. However, the most critical problem for nanomaterials is the aggregation of nanoparticles, which results in poor cycling performances. It has been reported that the cycling performance of other active materials, including Sn [Lee et al., 2003b; Noh et al., 2005], SnO\(_2\) [Wang et al., 2006], Si [Wang et al., 2004; Ng et al., 2006], and TiO\(_2\) [Huang et al., 2007], was significantly enhanced by forming composites with carbon. To prevent the pulverization during the charge-discharge cycle and improve the conductivity, an effective way is forming a composite with carbon, as carbon can act as a barrier to suppress the aggregation and pulverization of active particles, and thus increase their structural stability during cycling [Lee et al., 2003b; Fan et al., 2004; Fu et al., 2006]. Furthermore, carbon has high electronic conductivity, and it can improve the conductance of the active materials [Wang et al., 2006]. In efforts to improve the performance of NiO, net-structured NiO-C [Fu et al., 2006] and spherical NiO-C composite [Huang et al., 2007b] via the hydrothermal method have demonstrated
better capacity retention than pure NiO. However, these previous reports involved a series of complex steps, including calcination, dispersion, hydrothermal processes, and centrifugation, which makes these methods unsuitable for industrial application. In addition, the role of binders is becoming increasingly important in terms of the energy density of the whole battery. CMC (carboxymethyl cellulose) is an environmentally friendly and inexpensive material compared to the conventional binder, polyvinylidene difluoride (PVdF). The water solubility of CMC also decreases the processing costs during the production of negative electrodes [Li et al., 2007]. In this chapter, the preparation of NiO-C nanocomposite by a spray pyrolysis method is discussed, which is a simple and low-cost alternative for producing large scale submicron-/nano-particles with controlled composition and morphology. The synthesised NiO-C nanocomposite, with spherical shell clusters of nanosized NiO particles surrounded by amorphous carbon, shows enhanced electrochemical performance.

### 9.2 Materials Synthesis

Nanocrystalline NiO powders were synthesised by the spray pyrolysis method [Ng et al., 2006a]. Nickel oxide powders were prepared using a 0.5 M aqueous solution of nickel nitrate hexahydrate (Ni(NO₃)₂·6 H₂O, ≥ 97.0%, Sigma-Aldrich) as the precursor, while the carbon composite materials were prepared by mixing the initial solution with citric acid (C₆H₈O₇, ≥ 99.5%, Sigma-Aldrich) to a concentration of 0.06 M, with a theoretical weight ratio of NiO : carbon = 90 : 10. The solution was peristaltically pumped into a three-zone spray pyrolysis furnace at an operating temperature of 600 °C, using compressed air as the carrier gas. The resultant powder
was separated from the hot gas stream via a collecting jar and collected into airtight sample bottles.

### 9.3 Structure and Morphology Analysis

XRD patterns of the NiO powders (a) and NiO-C nanocomposite (b) are shown in Figure 9.1. All the peaks can be assigned to cubic NiO, and no impurities can be observed, indicating a complete decomposition of the precursor. The diffraction peaks of NiO powders can be indexed as the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) crystal planes of the crystalline cubic structure [space group: Fm-3 m, JCPDS No. 03-065-5745]. In the pattern of the NiO-C composite, only peaks of cubic NiO can be observed, indicating that the carbon in the composite is amorphous.

![XRD patterns: (a) NiO powders and (b) NiO-C nanocomposite.](image)

**Figure 9.1** XRD patterns: (a) NiO powders and (b) NiO-C nanocomposite.
TEM-EDS analysis of the NiO-C nanocomposite is shown in Figure 9.2. TEM and TEM-EDS examination of the NiO-C nanocomposite revealed spherical shell clusters of nanosized NiO particles surrounded by amorphous carbon. The spherical shells range in size from ~10-50 nm to greater than 500 nm (Figure 9.2(a)), with the NiO nanostructure confirmed by selected area electron diffraction (inset, Figure 9.2(a)). EDS examination of regions of the spherical shells protruding over holes in the holey carbon films (Figure 9.2(b)) confirmed the presence of Ni and O, with standardless analysis indicating carbon contents of around 2-4 wt.%. High magnification images of the nano-NiO particles (Figure 9.2(c) and (d)) revealed crystallite sizes of ~5-10 nm with a plate-like morphology. Figure 9.2(e) shows a high resolution image of a region of (d) in the vicinity of the holey carbon support film. In the case of Figure 9.2(f), lattice imaging also confirmed individual NiO planes, with a $d$ spacing consistent with (111) type, which is also consistent with the associated diffractogram (inset, Figure 9.2(f)).

Further SEM investigations were used to confirm the presence of carbon in the composites. Scanning electron micrographs of NiO powders and NiO-C nanocomposites are shown in Figure 9.3(a) and (b), respectively. To verify the formation of the NiO-C nanocomposite, EDS mapping analysis was used (see Figure 9.3(b)-(e)). The bright spots correspond to the presence of the elements Ni, O, and C, respectively. The results show that carbon particles are distributed uniformly throughout the whole area of NiO nanoparticles.
Figure 9.2 TEM-EDS analysis of NiO-C nanocomposite: (a) low magnification image of spherical clusters of nanocrystals with indexed selected area electron diffraction pattern (inset) obtained from large cluster; (b) EDS output obtained from local region of large cluster in (a) located over a hole in the holey carbon support film; (c) and (d), high magnification images; (e) high resolution image of region of (d) in vicinity of holey carbon support film; (f) high resolution image and associated diffractogram (inset) showing NiO crystal with strong contrast, consistent with NiO (111) planes ($d_{111} \approx 0.24$ nm).
Figure 9.3 SEM images for (a) NiO powders, (b) NiO-C nanocomposite, and corresponding EDS mappings for image (b) as follows: (c) Ni mapping, (d) O mapping, and (e) C mapping.

For quantifying the amount of amorphous carbon in the NiO-C nanocomposite materials, TGA analysis was carried out in air. Figure 9.4 shows the TGA analysis of the NiO powders and NiO-C nanocomposite. The samples were heated from 100 to
800 °C at the rate of 5 °C min\(^{-1}\). As can be seen from Figure 9.4, NiO-C nanocomposite powders start to lose weight slowly in air at a temperature of approximately 150 °C, while the bare NiO powders remain stable over the temperature range used for this experiment. As the bare NiO powders remain stable from 150 to 480 °C, any weight change can be assigned to amorphous carbon [Ng et al., 2007]. Therefore, the amount of amorphous carbon in the NiO-C composite can be estimated to be approximately 4 wt. % for the precursor solutions.

![Figure 9.4 TGA curves of NiO powders and NiO-C nanocomposite.](image)

9.4 Electrochemical Characterization

The anode slurry was made by mixing 80 wt.% active materials with 10 wt. % carbon black and 10 wt.% carboxymethyl cellulose (CMC) binder in water solvent to form a homogeneous slurry. The slurry was spread onto copper foil substrates. The coated electrodes were dried in a vacuum oven at 110 °C for 24 h and then pressed.
Subsequently, the electrodes were cut to a 1 × 1 cm² size. CR 2032 coin-type cells were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany) using lithium metal foil as the counter electrode. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume). The cells were galvanostatically discharged and charged in the range of 0.01-3.0 V at various current densities. Cyclic voltammetric measurements of the electrodes were performed on a CHI 660B electrochemical workstation with a scan rate of 0.1 mV s⁻¹ between 0.01 and 3.0 V (versus Li/Li⁺). AC impedance was measured for the fresh cells at open potential using the three electrode configuration. This was also carried out using the CHI 660C electrochemical workstation system. The AC amplitude was 5 mV, and the frequency range applied was 100 kHz – 0.01 Hz.

Figure 9.5 shows the 1st, 2nd, 20th, and 50th cycle discharge-charge curves for the NiO and NiO-C electrodes, measured between 0.01 and 3.0 V at a current density of 100 mA g⁻¹. In the first discharge process, the potential of both electrodes rapidly falls, followed by a long plateau between 0.42 and 0.6 V. The first discharge capacities of the NiO and NiO-C electrodes were 1133 and 1155 mAh g⁻¹, respectively, which are higher than the theoretical capacity (718 mAh g⁻¹) for NiO→Ni reduction. The extra capacity is due to the formation of the solid electrolyte interphase (SEI) [Débart et al., 2001]. The first charge process exhibits a higher voltage than subsequently, with two sloping potential ranges at about 1.5 and 2.25 V, respectively. The first charge capacities of the NiO and NiO-C electrodes were measured to be 712 and 715 mAh g⁻¹, which is very close to the theoretical capacity, indicating the totally reversible nature of the reaction from Ni to NiO.
Figure 9.5 Galvanostatic discharge-charge voltage profiles of (a) NiO and (b) NiO-C electrodes at 100 mA g$^{-1}$ current density from 0.01-3.0 V for selected cycles.

Figure 9.6 shows cyclic voltammograms of NiO and NiO-C electrodes between 0.01 and 3.0 V. Both samples exhibit similar curves, as reported previously [Varghese et al., 2008; Huang et al., 2006]. For the first cathodic scan, there is a strong peak at 0.25-0.5 V, corresponding to the decomposition of NiO into Ni, and the formation of amorphous Li$_2$O and the SEI. This peak becomes broader and weaker, and shifts to about 0.98 V for the NiO electrode and 0.97 V for the NiO-C electrode at subsequent scans. In the subsequent cycles, the two oxidation peaks of NiO and NiO-C, located at about 1.5 and around 2.25 V, could be attributed to the decomposition of the SEI and the formation of NiO, respectively [Dèbart et al., 2001; Grugeon et al., 2001]. The peaks in the cyclic voltammograms are consistent with the plateaus or sloping potential ranges in the voltage-capacity profiles. From the analysis of the CV curves with respect to the peak potential separation in the anodic and cathodic regions, the peak separation of the NiO-C electrode decreases in comparison with that of the NiO, indicating weaker polarization and better reversibility. This is because the high electronic conductivity of the carbon in the NiO spheres is beneficial for the
diffusion of lithium ions. Similar results were obtained for core/shell TiO$_2$-C composite prepared by emulsion polymerization [Fu et al., 2006].

![Figure 9.6](image)

**Figure 9.6** Cyclic voltammograms of (a) NiO and (b) NiO-C electrodes measured between 0.01 and 3.0 V at a scan rate of 0.1 mV s$^{-1}$.

The discharge capacity versus cycle number plots for the NiO and NiO-C electrodes at the different current densities of 100, 400, and 700 mA g$^{-1}$ are shown in Figure 9.7. As can be seen, when applying a current density of 100 mA g$^{-1}$, the discharge capacities were measured to be 367 and 428 mAh g$^{-1}$ at the end of the 50th cycle for the NiO and NiO-C electrodes, respectively. After 50 cycles, the discharge capacity was maintained at 32 and 37% of initial discharge capacity for the NiO and NiO-C electrodes, respectively. However, capacity retention was maintained at 18% for the NiO electrode and 35% for the NiO-C electrode at the end of the 50th cycle when the current density was 400 mA g$^{-1}$. In the case of 700 mA g$^{-1}$ current density, the discharge capacities were measured to be 1002 and 1102 mAh g$^{-1}$ in the initial cycle, and 141 and 382 mAh g$^{-1}$ in the 50th cycle, with 14 and 35% capacity retention after 50 cycles for the NiO and NiO-C electrodes, respectively. The capacity retention behaviour was almost the same for the two electrodes at the current density of 100
mA g⁻¹. It can be observed that the capacity and cycling stability of the NiO-C have been significantly improved compared with the bare NiO electrode, when discharging is conducted at a high rate.

![Figure 9.7 Capacity retention behaviour for NiO and NiO-C electrodes vs. cycle number from 0.01 to 3 V at different current densities: (a) 100 mA g⁻¹, (b) 400 mA g⁻¹, and (c) 700 mA g⁻¹.](image)

Figure 9.7 Capacity retention behaviour for NiO and NiO-C electrodes vs. cycle number from 0.01 to 3 V at different current densities: (a) 100 mA g⁻¹, (b) 400 mA g⁻¹, and (c) 700 mA g⁻¹.

However, amorphous carbon in the NiO-C composite is able to keep the NiO network electrically connected and thus facilitates the charge transportation [Huang et al., 2007]. In this investigation, carbon further provides a good conductive matrix, which not only maintains the integrity of the electrodes, but also decreases the polarization, thus enhancing the capacity retention. Moreover, the good interface
affinity between the oxide and the carbon particles ensures structural stability during cycling and results in better electrochemical performance of the composite. In order to verify the effects of the amorphous carbon network on the electrical conductivity of the NiO-C nanocomposites, AC impedance measurements (three electrode configuration) were conducted. Figure 9.8 shows the electrochemical impedance spectra (EIS) of the NiO and NiO-C electrodes, respectively. The semicircle in the medium frequency region is assigned to the charge transfer resistance ($R_{ct}$), and the inclined line at an approximate 45° angle to the real axis corresponds to the lithium diffusion process within the electrodes [Yang et al., 2006]. It can be seen that the diameter of the semicircle in the medium frequency region for the NiO-C electrode is much smaller than that of the NiO electrode, revealing lower charge transfer resistance. This indicates that the electronic conductivity of NiO was improved after the incorporation of carbon.

Figure 9.8 Electrochemical impedance spectra, presented as Nyquist plots for the NiO and NiO-C electrodes.
9.5 Conclusions

In this study, NiO-C nanocomposite, with spherical shell clusters of nanosized NiO particles surrounded by amorphous carbon, was synthesised by a spray pyrolysis technique using nickel nitrate hexahydrate as the precursor and citric acid as the carbon source. The microstructure and morphology of the NiO-C composite were characterized by means of X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS) mapping, and thermogravimetric analysis (TGA). Electrochemical tests demonstrated that the NiO-C nanocomposites exhibited better capacity retention (382 mAh g$^{-1}$ for 50 cycles at a current density of 700 mA g$^{-1}$) than that of pure NiO (141 mAh g$^{-1}$ for 50 cycles at a current density of 700 mA g$^{-1}$), which was also prepared by spray pyrolysis using only Ni(NO$_3$)$_2$ as precursor. The enhanced capacity retention can be mainly attributed to the NiO-C composite structure, composed of NiO nanoparticles surrounded by carbon, which can accommodate the volume changes during charge-discharge and improve the electrical conductivity between the NiO nanoparticles.
CHAPTER 10

GENERAL DISCUSSION AND OUTLOOK

10.1 General Discussion

The aim of this doctoral work was to broaden our knowledge in the field of advanced energy storage materials, especially nanostructured and composite materials, their synthesis, characterization, and their application as electrode in advanced lithium-ion batteries. The synthesised nano/composite materials show several advantages as electrode materials for lithium-ion batteries. Nanostructured electrodes may not only introduce innovative reaction mechanisms, but also improve electrochemical properties, such as specific energy storage capacity, accessibility of electrolyte, and short path lengths for both electronic and Li ion transport (permitting operation even with low electronic or low Li ion conductivity), enhancing the reactivity and cycling stability over the performance of their bulk counterparts. On the other hand, conductive composite materials not only have benefits in terms of decreasing the absolute volume changes and improving the mobility of the lithium ions, but also offer a conductive pathway along the whole interconnected wall in the structure, which is favourable for the transport of electrons to improve the high rate capability, promote liquid electrolyte diffusion into the bulk material, and act as a protective layer during the redox reaction. In the following sections, a summary of the outcomes is given.
10.1.1 Cathode Materials

A novel nanocrystalline porous α-LiFeO$_2$-C composite with a high surface area of around 115 m$^2$ g$^{-1}$ was synthesized by a simple molten salt method, followed by a carbon coating process. The structure and morphology were confirmed by X-ray diffraction, field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). FESEM observations demonstrated that the morphology consists of α-LiFeO$_2$-C nanoclusters composed of very tiny nanoparticles joined together by a porous architecture. TEM investigations revealed that amorphous carbon was incorporated into the pores among the nanoparticles and that some nanoparticles were covered by a thin layer of carbon as well. Electrochemical measurements showed that the α-LiFeO$_2$-C nanocomposite delivered a significantly higher reversible capacity compared to α-LiFeO$_2$ and excellent cycle stability (230 mAh g$^{-1}$ at 0.5 C after 100 cycles) using a selected binder, sodium carboxymethyl cellulose (CMC). Even at the high rate of 3 C, the electrode showed more than 50% of the capacity at low rate (0.1 C). In this respect, nanocrystalline porous α-LiFeO$_2$-C composite could be suitable as a very promising cathode material in lithium-ion batteries, with significant advantages in terms of environmental friendliness, high capacity, good cycling stability, and high-rate capability, which can lead to a future generation of lithium-ion batteries that are capable of satisfying new demands in the field of energy storage devices. Furthermore, owing to the water solubility of CMC, the usage of CMC as binder makes the whole electrode fabrication process cheaper and more environmentally friendly.
A novel VO$_2$(B)-multiwall carbon nanotube (MWCNT) composite with a sheet-like morphology was synthesized by a simple in situ hydrothermal process. The morphology and structural properties of the samples were investigated by X-ray diffraction (XRD), thermogravimetric analysis (TGA), FE-SEM, and TEM. FE-SEM observations demonstrated that the nanosheets are frequently grown together in the form of bundles composed of numerous nanosheets, each with a smooth surface and a typical length of 300-500 nm, width of 50-150 nm, and thickness of 10-50 nm. Electrochemical measurements were carried out using different discharge cut-off voltages. Electrochemical tests showed that the VO$_2$(B)-MWCNT composite cathode features long-term cycling stability and high discharge capacity (177 mAh g$^{-1}$) in the voltage range of 2.0-3.25 V at 1 C with a capacity retention of 92% after 100 cycles. The electrochemical impedance spectra (EIS) indicate that the VO$_2$(B)-MWCNT composite electrode has very low charge-transfer resistance compared with pure VO$_2$(B), indicating the enhanced ionic conductivity of the VO$_2$(B)-MWCNT composite. The enhanced cycling stability is attributed to the fact that the VO$_2$(B)-MWCNT composite can prevent the aggregation of active materials, accommodate the large volume variation with cycling, and maintain good electronic contact. It is concluded that the VO$_2$(B)-MWCNT composite could be considered as a potential cathode material for lithium-ion batteries.

LiFePO$_4$-Fe$_2$P-C composite was achieved by using a simple ultra-fast solvent assisted manual grinding method, combined with solid state reaction, which can replace the time-consuming high-energy ball-milling method. In this investigation, the synthesis strategy involved the creation of LiFePO$_4$-Fe$_2$P-C composites with a porous conductive architecture, which includes distinct regions or clusters containing
antiferromagnetic LiFePO\textsubscript{4} in close proximity to ferromagnetic Fe\textsubscript{2}P. The crystalline structure, morphology, and electrochemical characterization of the synthesised product were investigated systematically. The electrochemical performance was outstanding, especially at high C rates. The composite cathode was found to display specific capacity of 167 mAh g\textsuperscript{-1} at 0.2 C and 146 mAh g\textsuperscript{-1} at 5 C after 100 cycles, respectively. At the high current density of 1700 mA g\textsuperscript{-1} (10 C rate), it exhibited long-term cycling stability, retaining around 96% (131 mAh g\textsuperscript{-1}) of its original discharge capacity beyond 1000 cycles, which can meet the requirements of a lithium-ion battery for large-scale power applications.

\textbf{10.1.2 Anode Materials}

High grain boundary density, dual phase Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}-TiO\textsubscript{2}-C nanocomposite was synthesized by a simple molten salt method, followed by a carbon coating process. The microstructure and morphology of the Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}-TiO\textsubscript{2}-C product were characterized systematically. The Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}-TiO\textsubscript{2}-C nanocomposite electrode yielded good electrochemical performance in terms of high capacity (166 mAh g\textsuperscript{-1} at a current density of 0.5 C), good cycling stability, and excellent rate capability (110 mAh g\textsuperscript{-1} at a current density of 10 C up to 100 cycles). The likely contributing factors to the excellent electrochemical performance of the Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}-TiO\textsubscript{2}-C nanocomposite could be related to the improved morphology, including the presence of high grain boundary density among the nanoparticles, carbon layering on each nanocrystal, and grain boundary interface areas embedded in a carbon matrix, where electronic transport properties were tuned by interfacial design and by varying the spacing of interfaces down to the nano-regime, in which the grain boundary
interfaces embedded in the carbon matrix can store electrolyte and allow more channels for the reactions of Li$^{+}$ ion insertion/extraction. These results suggest that the carbon-coated dual phase Li$_4$Ti$_5$O$_{12}$-TiO$_2$ nanocomposite could be suitable for use as high rate performance anode for lithium-ion batteries.

Co$_3$O$_4$ nanoparticle samples were prepared as anode materials for lithium-ion batteries by the hydrothermal synthesis method without magnetic field (Co$_3$O$_4$-0T), under pulsed magnetic field (Co$_3$O$_4$-4T), and by using an aging technique (Co$_3$O$_4$-Aging), respectively. The morphology and structural properties of the Co$_3$O$_4$ nanoparticles were investigated by FE-SEM and XRD. FE-SEM measurements demonstrated that the Co$_3$O$_4$ sample formed under a 4 T magnetic field consisted of large agglomerated spheres composed of numerous quasi-spherical nanoparticles with a typical diameter of $\sim$25 nm and that it had more compact and smoother surfaces compared to a reference sample prepared without magnetic field. After the aging process, large Co$_3$O$_4$ hollow spheres composed of numerous spherical nanoparticles with a typical diameter of $\sim$ 20 nm were formed. Electrochemical measurements showed that Co$_3$O$_4$ materials prepared by the aging technique (Co$_3$O$_4$-Aging) yielded the best electrochemical performance compared with the other samples. Capacities were maintained at 274, 348, and 407 mAh g$^{-1}$ up to 100 cycles for the Co$_3$O$_4$-0T, Co$_3$O$_4$-4T, and Co$_3$O$_4$-Aging materials, which are about 26, 27, and 30 % of initial discharge capacities, respectively. The capacity loss is in the order of Co$_3$O$_4$-Aging < Co$_3$O$_4$-4T < Co$_3$O$_4$-0T. Thus, the morphology affects not only the discharge capacity, but also the cycling stability of Li-ion batteries.
NiO-C nanocomposite, with spherical shell clusters of nanosized NiO particles surrounded by amorphous carbon, was synthesised by a spray pyrolysis technique using nickel nitrate hexahydrate as the precursor and citric acid as the carbon source. The microstructure and morphology of the NiO-C composite were characterized by means of XRD, TEM, energy dispersive spectroscopy (EDS) mapping, and TGA. Electrochemical tests demonstrated that the NiO-C nanocomposites exhibited better capacity retention (382 mAh g\(^{-1}\) for 50 cycles) than the pure NiO (141 mAh g\(^{-1}\) for 50 cycles), which was also prepared by spray pyrolysis using only Ni(\(\text{NO}_3\))\(_2\) as precursor. The enhanced capacity retention can be mainly attributed to the NiO-C composite structure, composed of NiO nanoparticles surrounded by carbon, which can accommodate the volume changes during charge-discharge and improve the electrical conductivity between the NiO nanoparticles.

### 10.2 Outlook

All topics discussed in this thesis can be further extended, as every new finding opened the door for additional scientific questions and technical improvements. Collected here are some recommendations to be considered as starting ideas for future development. In this thesis, the experimental work was mainly focused on the synthesis of nanostructured and composite materials, and their application as electrode materials for use in lithium-ion batteries. The synthesis methods presented here, including molten salt followed by a carbon coating process, the hydrothermal method, the hydrothermal method under magnetic field, modified solid state reaction, and spray pyrolysis, are also applicable to the preparation of other metal oxide nanomaterials or composite materials.
Amorphous carbon incorporated porous conductive nanocomposite needs to be further investigated for other cathode materials, such as LiCoO₂, LiNiO₂, LiFePO₄, LiV₃O₈, LiMnPO₄, LiMn₂O₄, LiNi₁/₂Mn₃/₂O₄, and LiNi₁/₃Mn₁/₃Co₁/₃O for improving the cycling stability and high rate capability. The binder and electrolyte effects on the performance of lithium-ion batteries are still worth further investigation. CMC could be used as a binder for improving the cycling performance of other anode or cathode materials. Room temperature ionic liquid (RTIL) can also be used for the lithium-ion battery system to replace flammable solvents and improve the safety.

The cycling stability of VO₂(B)-multiwall carbon nanotube (MWCNT) composite can be further improved via doping with other transition metal elements or amorphous carbon incorporation in the system.

The fabrication of samples with strong and extensive antiferromagnetic and ferromagnetic interface coupling of LiFePO₄/Fe₂P provides a versatile strategy toward improving the electrochemical properties of LiFePO₄ materials and also opens up a new window for material scientists to further study the new exchange bias phenomenon and its ability to enhance the electrochemical performance of lithium-ion battery electrode.

In the case of carbon incorporated high grain boundary density dual phase Li₄Ti₅O₁₂-TiO₂ nanocomposite anode, interfacial reactions were considered as a possible lithium storage mechanism. Lithium storage in these samples relates to the presence of grain boundary interfaces between spinel Li₄Ti₅O₁₂ and anatase TiO₂. However, to
understand the exact lithium storage mechanism, this high grain boundary density dual phase system needs to be further investigated.

High pulsed magnetic field and an aging technique have successfully been used in the synthesis of nanocrystalline Co$_3$O$_4$ via the hydrothermal method. The pulsed magnetic field processing produces a more compact and smooth surfaces, whereas the aging technique introduces hollow spheres consisting of a large quantity of nanospheres. The electrochemical performances of these materials are also notable. This method with some changes in parameters can also be used for further study and to improve the electrochemical properties of other metal oxides for lithium-ion batteries.

As for the carbon coated NiO nanocomposite, attention needs to be focused on fully understanding the reasons behind the greatly improved electrochemical performance of the composite compared to pure nanocrystalline NiO particles. This could be done by investigating the role of the amorphous carbon, with assistance from *in-situ* measurement techniques, such as X-ray photoelectron spectroscopy (XPS), high resolution electron energy loss spectroscopy (HR-EELS), and differential electrochemical mass spectroscopy (DEMS). Furthermore, the influence of other spray parameters, such as the type of solvent used, the NiO particle size, and also the different types of low-temperature carbon sources used, should be investigated and reviewed in detail in order to fully understand the role of carbon in the composite.
In addition, the disadvantages of nanomaterials, which are due to their high surface area, also need to be taken into account. The nanomaterials typically show low density and high reactivity in terms of side reactions, resulting in more irreversible capacity and causing safety issues. Further research will also focus on the safety issues associated with the size effect. In order to ameliorate the disadvantages of nanomaterials, surface modification and selection of the correct size of the particles need to be further investigated. However, *in-situ* characterization tools are other possible ways to move forward in order to drive further breakthroughs in lithium-ion battery performance. Nevertheless, the author believes that the scientific challenges are being slowly overcome and that research is moving in the right direction with a well defined goal, as proven in this thesis, so that the future for the next generation of Li-ion batteries is likely to be brighter ahead.
REFERENCES


177


*J. Power Sources*, **174**, 949.


179


183


APPENDIX A: LIST OF PUBLICATIONS


21. Irin Sultana†, M. M. Rahman, Sha Li, Jiazhao Wang, G.G. Wallace, Hua-Kun Liu, “Highly flexible and bendable free-standing polypyrrole (PPy)/Indigo carmine (IC) film as anode for lithium-polymer battery” (manuscript under preparation).
22. Irin Sultana†, **M. M. Rahman**, Sha Li, Jiazhao Wang, G.G. Wallace, Hua-Kun Liu, “Electrodeposited polypyrrole (PPy)/poly (vinyl sulfonic acid) (PVS) free standing film for lithium-polymer battery application” (manuscript under preparation).


Papers listed are all during PhD study. † is corresponding author. Impact factor (IF) is from 2010.
APPENDIX B: RECEIVED AWARDS

1. University Postgraduate Award (UPA) and Higher Degree Research (HDR) Tuition Fee Exemption Scholarship (2008-2011) for pursuing a PhD through the Australian Research Council (ARC) Centre of Excellence for Electromaterials Science (CE0561616), University of Wollongong, Australia

2. Excellent Research Top-Up Award-2009, ISEM, University of Wollongong, Australia

3. ISEM Merit Award-2009, University of Wollongong, Australia

4. Student Travel grant to attend international conference-2010

5. Research Student Grant Award (2007-2010) for pursuing a PhD under E-science project (Project Vote: 79077) provided by the Universiti Teknologi Malaysia

6. Research Student Grant Fellowship Award (2004-2006) for pursuing a M.Sc. (by research) from the Ministry of Science, Technology and Innovation, Malaysia (Project Vote: 74187, Universiti Teknologi Malaysia)

7. Bangladesh Government Talent-Pool Scholarship at Secondary and Higher Secondary level

8. Shafder Ali Memorial Award-1990 for obtaining starring mark in Secondary level examination