2011

Nanostructured anode materials for lithium-ion batteries

Guodong Du

University of Wollongong

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NANOSTRUCTURED ANODE MATERIALS FOR LITHIUM-ION BATTERIES

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

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

GUODONG DU, B. ENG., M. ENG.

INSTITUTE FOR SUPERCONDUCTING & ELECTRONIC MATERIALS,
FACULTY OF ENGINEERING

September 2011
I, Guodong Du, declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting and Electronic Materials, Faculty of Engineering, University of Wollongong, is wholly original work unless otherwise referenced or acknowledged. This thesis has not been submitted for qualifications at any other academic institution.

Guodong Du

26/Sep/2011
ACKNOWLEDGEMENTS

The experimental work in my thesis was undertaken during the past three and half years in the Institute for Superconducting and Electronic Materials (ISEM) at the University of Wollongong in Australia. I wish to express my sincere gratitude to my supervisors, Prof. Zai Ping Guo and Prof. Hua Kun Liu, for their expertise, academic supervision and guidance, encouragement, understanding and invaluable advice. I would also like to thank Prof. Shi Xue Dou, the director of ISEM, for his great support during my study.

Financial support from Australian Research Council (ARC) through Discovery Projects (DP0878611 and DP1094261) and a Linkage Project (LP0991012), a University Postgraduate Award (UPA) and an International Postgraduate Tuition Award (IPTA) is gratefully acknowledged.

Technical support from Dr. Zhi Xin Chen (TEM), Dr. David Wexler (TEM), Dr. Konstantin Konstantinov (TGA), Dr. Germanas Peleckis (XRD), Mr. Darren Attard (SEM, EDS, and Raman), Charlie Kong from UNSW (FIB), Mr. Ron Kinnell, and Mr. Robert Morgan is highly appreciated. Special thanks go to Dr. Tania Silver, who spent lots of time on critical reading of manuscripts and this thesis.

I wish to thank my collaborators Dr. Neeraj Sharma, Dr. Vanessa K Peterson, Dr. Andrew Studer from the Bragg Institute, Australian Nuclear Science and Technology
Organisation (ANSTO), Dr. Justin Kimpton, Dr. Qinfen Gu, and Dr. Kia Wallwork from the Australian Synchrotron powder diffraction beamline. It has also been a pleasure to work with a number of overseas collaborators, Assoc. Prof. Xian Jun Zhu (Central China Normal Univ.), Prof. Jie Qiang Wang (Jinan Univ.), Assoc. Prof. Zun Xian Yang (Fuzhou Univ.), Prof. Xue Bin Yu (Fudan Univ.), Prof. Chuan Qi Feng (Hubei Univ.), Prof. Ying Li (Shanghai Univ.), Prof. Dian Zeng Jia (Xinjiang Univ.), Dr. Bin Wan (Shanghai University of Science and Engineering), Dr. Dong Mei Han (Sun Yat Sen Univ.), Prof. Yun Long Xu (East China University of Science and Technology), and Dr. Jun Liu (Central South Univ.).

I would also like to thank Dr. Wen Xian Li, Dr. Wei Min Zhang, Dr. Zheng Wei Zhao, Dr. Zhen Guo Huang, Dr. Hao Liu, Dr. Shu Lei Chou, Dr. Brad Winton, Dr. Md. Faiz Hassan, Dr. Peng Zhang, Dr. Yi Du, Dr. Da Peng Chen, Dr. Jia Zhao Wang, Prof. Xiao Lin Wang, Prof. Chao Zhang, Assoc. Prof. Joseph Horvat, Dr. Rong Zeng, Dr. Yun Zhang, Dr. Lin Wang, Dr. Md. Mokhlesur Rahman, Dr. Jian Feng Mao, Mr. Chao Zhong, Mr. Qi Li, Ms. Lin Lu, Mr. Kuok Hau Seng, Mr. Chao Feng Zhang, Ms. Li Li, Ms. Dan Li, and other staff and students in ISEM, for their readiness to freely share their knowledge and valuable suggestions.

I would like to express my gratitude to my parents and sister for their continued support, love, and understanding. Their encouragement always kept me going forward during my study aboard.
# TABLE OF CONTENTS

CERTIFICATION ........................................................................................................ i  
ACKNOWLEDGEMENTS .......................................................................................... ii  
TABLE OF CONTENTS ............................................................................................ iv  
ABSTRACT ................................................................................................................ ix  
NOMENCLATURE ................................................................................................... xii  
LIST OF FIGURES ................................................................................................... xv  
LIST OF TABLES .................................................................................................. xxxi  
CHAPTER 1 INTRODUCTION ............................................................................... 1  
CHAPTER 2 LITERATURE REVIEW .................................................................... 6  
    2.1 Lithium ion batteries ..................................................................................... 6  
    2.1.1 Brief History ............................................................................................ 8  
    2.1.2 Working mechanism ............................................................................. 10  
    2.1.3 Electrochemical Principles .................................................................... 14  
    2.1.4 Opportunities and challenges ............................................................... 16  
    2.2 Anode materials ......................................................................................... 21  
    2.2.1 Carbonaceous anode ............................................................................. 21  
    2.2.2 Lithium-Alloy anode ............................................................................. 23  
    2.2.3 Metal oxide ............................................................................................ 25  
    2.2.4 Sulfides ................................................................................................. 33  
    2.2.5 Nitrides/Phosphides/Fluorides ............................................................... 34  
    References ......................................................................................................... 36  
CHAPTER 3 EXPERIMENT ................................................................................. 43  
    3.1 General procedure ....................................................................................... 43  
    3.2 Chemicals .................................................................................................... 44  
    3.3 Fabrication procedure ................................................................................ 45
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.1 Molten Salt Reaction</td>
<td>45</td>
</tr>
<tr>
<td>3.3.2 Hydrothermal synthesis</td>
<td>46</td>
</tr>
<tr>
<td>3.3.3 Electrospinning</td>
<td>47</td>
</tr>
<tr>
<td>3.3.4 Chemical Solution Reaction</td>
<td>48</td>
</tr>
<tr>
<td>3.3.5 Anodization</td>
<td>49</td>
</tr>
<tr>
<td>3.3.6 Solid State Reaction</td>
<td>50</td>
</tr>
<tr>
<td>3.3.7 Spray Pyrolysis</td>
<td>50</td>
</tr>
<tr>
<td>3.4 Techniques for characterization</td>
<td>51</td>
</tr>
<tr>
<td>3.4.1 X-ray powder diffraction</td>
<td>52</td>
</tr>
<tr>
<td>3.4.2 Neutron powder diffraction</td>
<td>53</td>
</tr>
<tr>
<td>3.4.3 Raman spectroscopy</td>
<td>54</td>
</tr>
<tr>
<td>3.4.4 Scanning electron microscopy and Energy-dispersive X-ray spectroscopy</td>
<td>54</td>
</tr>
<tr>
<td>3.4.5 Transmission electron microscopy</td>
<td>55</td>
</tr>
<tr>
<td>3.4.6 X-ray photoelectron spectroscopy</td>
<td>56</td>
</tr>
<tr>
<td>3.4.7 Surface area measurement</td>
<td>57</td>
</tr>
<tr>
<td>3.4.8 Thermogravimetric analysis</td>
<td>58</td>
</tr>
<tr>
<td>3.4.9 Magnetic measurements</td>
<td>58</td>
</tr>
<tr>
<td>3.5 Electrode preparation and coin-cell assembly</td>
<td>58</td>
</tr>
<tr>
<td>3.6 Electrochemical measurements</td>
<td>60</td>
</tr>
<tr>
<td>3.6.1 Galvanostatic charge-discharge</td>
<td>60</td>
</tr>
<tr>
<td>3.6.2 Cyclic voltammetry</td>
<td>60</td>
</tr>
<tr>
<td>3.6.3 Electrochemical impedance spectroscopy</td>
<td>61</td>
</tr>
<tr>
<td>CHAPTER 4 Ultra-fine Porous SnO₂ and SnO₂/Carbon Composite</td>
<td>62</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>62</td>
</tr>
<tr>
<td>4.2 Experimental</td>
<td>63</td>
</tr>
<tr>
<td>4.2.1 Sample Preparation</td>
<td>63</td>
</tr>
</tbody>
</table>
4.2.2 Electrochemical Characterization....................................................... 64
4.3 Physical Characterization ........................................................................ 64
4.4 Electrochemical performance .................................................................. 69
4.5 Summary....................................................................................................... 71
References ........................................................................................................... 72

CHAPTER 5 One Dimensional SnO$_2$/CNT Composites and SnO$_2$ Nanofibre...... 74
5.1 Introduction................................................................................................... 74
5.2 SnO$_2$/CNT composite ............................................................................ 75
5.2.1 Experimental....................................................................................... 75
5.2.2 Physical Characterization ................................................................... 76
5.2.3 Electrochemical Performance............................................................. 80
5.3 SnO$_2$ and SnO$_2$/C nanofibres ............................................................... 85
5.3.1 Synthesis............................................................................................. 85
5.3.2 Physical Characterization ................................................................... 86
5.3.3 Electrochemical Performance............................................................. 95
5.4 Summary....................................................................................................... 98
References......................................................................................................... 99

CHAPTER 6 Superior Restacked MoS$_2$ Anode and MoS$_2$/SnO$_2$ Composites ...... 103
6.1 Introduction................................................................................................. 103
6.2 In-situ neutron diffraction .......................................................................... 105
6.2.1 Experimental setup ........................................................................... 105
6.2.2 Electrochemical performance............................................................. 109
6.3 Restacked MoS$_2$ ....................................................................................... 116
6.3.1 Experimental..................................................................................... 116
6.3.2 Characterization................................................................................ 117
6.3.3 Electrochemical performance............................................................. 121
6.4 MoS$_2$/SnO$_2$ composites........................................................................... 129
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4.1</td>
<td>Synthesis</td>
<td>129</td>
</tr>
<tr>
<td>6.4.2</td>
<td>Characterization</td>
<td>130</td>
</tr>
<tr>
<td>6.4.3</td>
<td>Electrochemical performance</td>
<td>138</td>
</tr>
<tr>
<td>6.5</td>
<td>Summary</td>
<td>142</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>143</td>
</tr>
<tr>
<td>7.1</td>
<td>Introduction</td>
<td>146</td>
</tr>
<tr>
<td>7.2</td>
<td>TiO$_2$(B)</td>
<td>150</td>
</tr>
<tr>
<td>7.2.1</td>
<td>Synthesis</td>
<td>150</td>
</tr>
<tr>
<td>7.2.2</td>
<td>Characterization</td>
<td>150</td>
</tr>
<tr>
<td>7.2.3</td>
<td>Electrochemical performance</td>
<td>153</td>
</tr>
<tr>
<td>7.3</td>
<td>TiO$_2$ nanotube array</td>
<td>156</td>
</tr>
<tr>
<td>7.3.1</td>
<td>Synthesis</td>
<td>156</td>
</tr>
<tr>
<td>7.3.2</td>
<td>Characterization</td>
<td>157</td>
</tr>
<tr>
<td>7.3.3</td>
<td>Electrochemical performance</td>
<td>159</td>
</tr>
<tr>
<td>7.4</td>
<td>SnO$_2$ nanocrystal/TiO$_2$ nanotube composites</td>
<td>163</td>
</tr>
<tr>
<td>7.4.1</td>
<td>Synthesis</td>
<td>163</td>
</tr>
<tr>
<td>7.4.2</td>
<td>Characterization</td>
<td>164</td>
</tr>
<tr>
<td>7.4.3</td>
<td>Electrochemical performance</td>
<td>171</td>
</tr>
<tr>
<td>7.5</td>
<td>Summary</td>
<td>177</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>178</td>
</tr>
<tr>
<td>8.1</td>
<td>Introduction</td>
<td>183</td>
</tr>
<tr>
<td>8.2</td>
<td>Spray Pyrolysis Preparation of Li$_4$Ti$<em>5$O$</em>{12}$</td>
<td>185</td>
</tr>
<tr>
<td>8.2.1</td>
<td>Synthesis</td>
<td>185</td>
</tr>
<tr>
<td>8.2.2</td>
<td>Characterization</td>
<td>186</td>
</tr>
</tbody>
</table>
Table of contents

8.2.3 Electrochemical performance ......................................................... 195

8.3 Br doping of Li$_4$Ti$_5$O$_{12}$ ............................................................................ 199
  8.3.1 Experimental .................................................................................. 199
  8.3.2 Characterization ........................................................................... 201
    8.3.2.1 Li$_4$Ti$_5$O$_{12-x}$Br$_x$ ................................................................. 201
    8.3.2.2 Composite Li$_4$Ti$_5$O$_{12}$/TiO$_2$ Anode ...................................... 209

8.4 Summary .............................................................................................. 216

References .................................................................................................. 218

CHAPTER 9 CONCLUSIONS AND OUTLOOK ...................................................... 222
  9.1 General Conclusions ........................................................................ 222
  9.2 Outlook .............................................................................................. 224

APPENDIX: LIST OF PUBLICATIONS ........................................................... 227
Abstract

ABSTRACT

Lithium ion batteries have served as power sources for portable electronic devices for the past two decades. To date, they have employed polycrystalline microsized powder electrode materials. However, many next-generation electronic devices or wireless communication devices demand thin and flexible electrodes with higher energy density than ever before. Moreover, the large-scale potential lithium ion battery applications, such as in electric vehicles, (plug-in) hybrid electric vehicles, or energy storage systems in smart grids, require batteries exhibiting high rate capability, high power, and long cycle life. Due to the advantages of nanostructured electrode materials, i.e., high surface area, more lithium active sites, and shorter lithium diffusion length, the electrochemical performance of nanomaterial electrodes are more likely to meet the specific requirements in the potential new applications. In this doctoral work, various nanostructured materials were synthesized, characterized by different physical techniques and tested as potential anode electrode materials for lithium ion batteries. The nanomaterials include porous SnO$_2$, SnO$_2$/C composite, one-dimensional SnO$_2$/carbon nanotube (CNT) composite, SnO$_2$ nanofibre, SnO$_2$/C composite nanofibre, restacked MoS$_2$, MoS$_2$/SnO$_2$ composite, one-dimensional TiO$_2$(B) nanowire, three-dimensional TiO$_2$ nanotube arrays, SnO$_2$ nanocrystal/TiO$_2$ nanotube array composite, and nanosized polycrystalline Li$_4$Ti$_5$O$_{12}$.

Various nanostructured SnO$_2$ and SnO$_2$/C composites were prepared by the molten salt, solvothermal, and electrospinning techniques. The porous SnO$_2$ and SnO$_2$/C nanocomposite prepared by the molten salt method exhibit high surface area, giving more contact area between the active material and the electrolyte, as well as a
Abstract
decreased lithium diffusion length. At the same time, the pores could accommodate the volume expansion. Porous SnO₂ electrode delivers a reversible capacity of 410 mAh g⁻¹ after 100 cycles in the voltage range of 0.05-1.5 V, while the composite shows better capacity retention (85.3 wt%) than bare nano-SnO₂ (64.8 wt%) after 100 cycles. SnO₂/CNT composite synthesized by the solvothermal method consists of a conductive CNT core and SnO₂ nanocrystals about 5 nm in size that are deposited and pinned onto the CNTs. Very large area uniform SnO₂ and SnO₂/C composite nanofibre with fibre diameters around 80 nm, consisting of orderly bonded SnO₂ nanoparticles ~10 nm in size have been obtained by the electrospinning technique and a thermal pyrolysis process under optimized synthesis conditions. The uniformly distributed carbon greatly improved the electrochemical performance even at high rate.

Restacked MoS₂ with an enlarged c-axis parameter was prepared by exfoliation and then restacking in a hydrothermal process. The enlarged c parameter and the increased surface area are favourable to the intercalation reaction. The restacked MoS₂ anode exhibited large reversible capacity of about 800 mAh g⁻¹ and stable cycling performance, as well as good rate capability. A similar strategy was applied to prepare MoS₂/SnO₂ composite by exfoliation and restacking of commercial MoS₂ with SnO₂ nanocrystals ~ 5 nm in size deposited between the MoS₂ layers.

One-dimensional TiO₂(B)/anatase nanowires were synthesized by the hydrothermal method, which delivered a high reversible capacity of 196 mAh g⁻¹ up to 100 cycles at 30 mA g⁻¹ (0.1 C). It also exhibited a reversible discharge capacity as high as 125 mAh g⁻¹, even when cycled at 4500 mA g⁻¹ (15 C). Three-dimensional TiO₂ nanotube
arrays were prepared by anodization, and then SnO₂ nanocrystals were deposited into/onto the TiO₂ nanotube array to make a composite anode in which the TiO₂ could serve both as an electroactive material, as mechanical support, and as a buffer to accommodate SnO₂ volume expansion during the charge/discharge process. The much increased capacity is due to the SnO₂. The total capacity depends on the TiO₂ tube length and the amount of SnO₂ loading.

Carbon-incorporated Li₄Ti₅O₁₂ nanocrystals were synthesized by spray pyrolysis and examined as a promising anode material. The molecular level mixing of the organic lithium and the titanium precursor allows a shorter annealing time afterwards at high temperature, which is energy saving in large-scale production. Furthermore, annealing in N₂ atmosphere preserved the carbon from the organic precursor and distributed it uniformly, which could improve the conductivity. The Li₄Ti₅O₁₂ electrode exhibits excellent cyclability and rate capability, as well as stable cycling in full battery tests. Br-doped Li₄Ti₅O₁₂ was investigated by synchrotron X-ray diffraction to understanding the structural and impurity effects on the electrochemical behaviour. Because TiO₂ impurity always appears in the Li₄Ti₅O₁₂ preparation process, Li₄Ti₅O₁₂/TiO₂ composite anode was investigated by in-situ neutron diffraction to understand the electrochemical behaviour.
## Nomenclature

### List of Symbols

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<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Unit</th>
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<tr>
<td>2θ</td>
<td>Angle of incident beam and diffraction beam</td>
<td>°</td>
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<tr>
<td>D</td>
<td>Diffusion coefficient</td>
<td>m s⁻¹</td>
</tr>
<tr>
<td>E°</td>
<td>Standard electrode potential</td>
<td>V</td>
</tr>
<tr>
<td>E(binding)</td>
<td>binding energy</td>
<td>eV</td>
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<tr>
<td>E(kinetic)</td>
<td>kinetic energy</td>
<td>eV</td>
</tr>
<tr>
<td>E(work function)</td>
<td>work function</td>
<td>eV</td>
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<tr>
<td>F</td>
<td>Faraday’s constant</td>
<td>C mol⁻¹</td>
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<tr>
<td>ΔG</td>
<td>Gibbs free energy</td>
<td>kJ mol⁻¹</td>
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<tr>
<td>ΔH</td>
<td>Enthalpy</td>
<td>kJ mol⁻¹</td>
</tr>
<tr>
<td>I</td>
<td>Current</td>
<td>A</td>
</tr>
<tr>
<td>iₚ</td>
<td>peak current</td>
<td>A</td>
</tr>
<tr>
<td>J</td>
<td>Flux of diffusing specie</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>Diffusion length</td>
<td>M</td>
</tr>
<tr>
<td>N</td>
<td>Avogadro’s number</td>
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<tr>
<td>P</td>
<td>Pressure</td>
<td>Pa</td>
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<tr>
<td>Q</td>
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<td>t</td>
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<tr>
<td>V</td>
<td>Molar volume</td>
<td>L mol⁻¹</td>
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<tr>
<td>$V_{oc}$</td>
<td>Open-circuit voltage</td>
<td>V</td>
</tr>
<tr>
<td>w</td>
<td>Weight of adsorbate</td>
<td>g</td>
</tr>
<tr>
<td>$\eta_c$</td>
<td>Coulombic efficiency</td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Activity factor</td>
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<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
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</tr>
</tbody>
</table>

**List of Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
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</tr>
</thead>
<tbody>
<tr>
<td>0D</td>
<td>Zero dimensional</td>
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<td>One dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three dimensional</td>
</tr>
<tr>
<td>AIIM</td>
<td>Australian Institute of Innovative Materials</td>
</tr>
<tr>
<td>ANSTO</td>
<td>Australian Nuclear Science and Technology Organisation</td>
</tr>
<tr>
<td>AS</td>
<td>Australian Synchrotron</td>
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<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BEV</td>
<td>Battery electric vehicle</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
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<td>Energy-dispersive X-ray spectroscopy</td>
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<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
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<tr>
<td>EV</td>
<td>Electric vehicle</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
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<tr>
<td>HEV</td>
<td>Hybrid electric vehicle</td>
</tr>
<tr>
<td>IPRI</td>
<td>Intelligent Polymer Research Institute</td>
</tr>
<tr>
<td>IT</td>
<td>Information technology</td>
</tr>
<tr>
<td>MEMS</td>
<td>Microelectromechanical systems</td>
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<tr>
<td>ND</td>
<td>Neutron diffraction</td>
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<tr>
<td>NPD</td>
<td>Neutron powder diffraction</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-2-pyrrolidinone</td>
</tr>
<tr>
<td>PHEV</td>
<td>Plug-in hybrid electric vehicles</td>
</tr>
<tr>
<td>PPMS</td>
<td>Physical properties measurement system</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene difluoride</td>
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<td>SAED</td>
<td>Selected area electron diffraction</td>
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<td>SCiB</td>
<td>Super Charge ion Batteries</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>TCO</td>
<td>Amorphous tin composite oxide</td>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

| Figure 2.1 | Comparison of various electrochemical energy conversion systems with the internal combustion engine and turbine in terms of specific power and energy. |
| Figure 2.2 | Comparison of the different battery technologies in terms of volumetric and gravimetric energy density. |
| Figure 2.3 | Schematic of reaction mechanism in a rechargeable lithium ion battery. |
| Figure 2.4 | Requirements of lithium ion batteries for the three most important types of applications. |
| Figure 2.5 | Crystal structures of spinel Li$_4$Ti$_5$O$_{12}$. |
| Figure 2.6 | Structures of TiO$_2$: (a) anatase; (b) rutile; (c) TiO$_2$ (B). |
| Figure 2.7 | Schematics of single layer MoS$_2$ and graphene: (a) cross-section view; (b) top view. |
| Figure 3.1 | The overall experimental procedure and techniques. |
| Figure 3.2 | Schematic illustration of experimental set-up for electrospinning. |
| Figure 3.3 | Schematic diagram of set-up for refluxing chemical reaction. |
| Figure 3.4 | Schematic illustration of experimental set-up for titanium anodization. |
| Figure 3.5 | Schematic illustration of experimental set-up for spray pyrolysis. |
| Figure 3.6 | Component stacking sequence in a coin cell. |
| Figure 4.1 | Schematic model of synthetic procedure: (a) mixed raw |
materials; (b) solid molten salts and SnO$_2$; (c) porous and nanosized SnO$_2$.

**Figure 4.2** TGA curve of raw material consisting of SnCl$_2$·2H$_2$O mixed with LiOH and LiNO$_3$ (molar ratio 1 : 1).

**Figure 4.3** X-ray diffraction patterns of the as-prepared (a) SnO$_2$/C nanopowder and (b) SnO$_2$ nanocomposite.

**Figure 4.4** TEM images (a, b) of the as-prepared nano-SnO$_2$; (c, d) SnO$_2$/C nanocomposite prepared by molten salt method. Indexed diffraction pattern (inset in (d)) confirms the presence of SnO$_2$ nanoparticles and that the nanoparticles embedded in an amorphous carbon matrix.

**Figure 4.5** Electrochemical performance: (a) initial charge/discharge curves of as-prepared SnO$_2$ and SnO$_2$/C composite cycled between 0.01 and 3V; (b) cycling performance at 100 mA g$^{-1}$ in different voltage ranges.

**Figure 5.1** FESEM images of (a) MWCNTs, (b) bare SnO$_2$, (c) L-SnO$_2$/CNT composite, and (d) H-SnO$_2$/CNT composite.

**Figure 5.2** X-ray diffraction patterns of MWCNTs, SnO$_2$/CNT composites, and bare SnO$_2$ powder.

**Figure 5.3** TEM images of L-SnO$_2$/CNT (a, b), and H-SnO$_2$/CNT (c, d). The inset of (d) shows the lattice spacings of the composite.

**Figure 5.4** Cyclic voltammograms for the first 5 cycles of (a) MWCNTs, (b) bare SnO$_2$, (c) L-SnO$_2$/CNT, and (d) H-SnO$_2$/CNT at a scan rate of 0.1mV s$^{-1}$.

**Figure 5.5** Electrochemical performance: (a) specific discharge capacity
with cycle number of MWCNTs, bare SnO$_2$, and L-SnO$_2$/CNT and H-SnO$_2$/CNT composites (current density 100mA g$^{-1}$); (b) charge/discharge efficiency of bare SnO$_2$, and of L-SnO$_2$/CNT and H-SnO$_2$/CNT composites; (c) rate capability of bare SnO$_2$ and H-SnO$_2$/CNT.

**Figure 5.6** TGA curves of PAN in air (a) and in argon (b).

**Figure 5.7** FESEM images of as-collected tin composite/PAN nanofibers, as-pyrolyzed SnO$_2$ and SnO$_2$/Carbon nanofibers: (a) tin composite/PAN nanofibers, (b) high magnification FE-SEM image of tin composite/PAN nanofibers, (c) as pyrolyzed SnO$_2$ nanofibers in air at 500 °C for 2h, (d) high magnification images of SnO$_2$ nanofibers and single SnO$_2$ nanofiber (insert), (e) as-pyrolyzed SnO$_2$/carbon nanofibers in air at 360°C for 1h and further heat-treated in argon at 500 °C for 2h, (f) as-pyrolyzed SnO$_2$/carbon nanofibers prepared in air at 360°C for 1 h and further in argon at 500°C for 2h, with image of single nanofiber of SnO$_2$/carbon(insert), both at high magnification.

**Figure 5.8** X-ray diffraction patterns of as-prepared SnO$_2$ nanofibers and SnO$_2$/Carbon nanofibers. The diffraction peaks are characteristic of tetragonal rutile structure SnO$_2$ (JCPDS 41-1445), as indexed in the patterns.

**Figure 5.9** (a) TEM image and SAED pattern (inset) of a SnO$_2$ nanofiber, (b) low-magnification TEM image of SnO$_2$ nanofibers (with many hole/void interspaces between the bound SnO$_2$
nanoparticles in the nanofibers), (c) HRTEM image of a section of a SnO$_2$ nanofiber.

**Figure 5.10**  
(a) TEM image and SAED patterns (inset) of a SnO$_2$/Carbon nanofiber, (b) Low-magnification TEM image of SnO$_2$/Carbon nanofibers (with many hole/void nanopores between the bound SnO$_2$ nanoparticles in the nanofibers), (c) HRTEM image of a section of a SnO$_2$/Carbon nanofiber.

**Figure 5.11**  
XPS high-resolution spectra of (a) C1s, (b) O1s and (c) Sn3d regions of as-prepared SnO$_2$/Carbon nanofibers.

**Figure 5.12**  
(a) Cyclic voltammograms of SnO$_2$ nanofibers and (b) SnO$_2$/Carbon nanofiber electrodes from the first cycle to the fifth cycle at a scan rate of 0.1 mV s$^{-1}$ in the voltage range of 0.05-2.5 V, (c) The cycling performance from the first cycle to the 100$^{th}$ cycle of the SnO$_2$/Carbon nanofibers and SnO$_2$ nanofibers (58 cycles) at the same current density, 100 mA g$^{-1}$, (d) cycling performance from the first cycle to the 100$^{th}$ cycle of the SnO$_2$/carbon nanofibers and SnO$_2$ nanofibers at different discharge rates (0.5, 1, 2 C).

**Figure 5.13**  
Schematic diagram showing formation of SnO$_2$ nanofibers and their electrochemical reaction.

**Figure 6.1**  
Crystal structures of MoS$_2$ polytypes: (a) 1T, (b) 2H, (c) 3R (left: unit cell; right: 2a$\times$2a polyhedral supercell), (d) the 2H polytype, consisting of Mo and S layers.

**Figure 6.2**  
Specially designed electrochemical cells for *in-situ* neutron diffraction studies. (a) Cylindrical cell where A are brass
List of Figures

Figure 6.3  Schematic of a section through the “roll-over” cell for \textit{in-situ} neutron diffraction studies. Sheets of Celgard\textsuperscript{®} (white), MoS\textsubscript{2} electrode on Cu (red), Celgard\textsuperscript{®}, and Li (blue), are rolled and sealed inside a vanadium can (green). The can is sealed in an argon-filled glovebox.

Figure 6.4  (a) A multi-phase Rietveld refinement plot using a 5 minute ND pattern collected on Wombat with the custom-designed MoS\textsubscript{2} anode battery at $\lambda = 2.406(2)$ Å. Structural models for Li, Cu, and MoS\textsubscript{2} are used. The calculated pattern is shown in black, observed data in red, and the difference between the observed and calculated in purple. Reflection markers are shown as vertical bars. (b) A 5 minute ND pattern collected on Wombat with our custom-designed Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} anode battery at $\lambda = 1.535(1)$ Å. Intense reflections from Li, Cu, and Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} are indicated by reflection markers shown as vertical bars.

Figure 6.5  Selected regions ($20.8^\circ \leq 2\theta \leq 25.9^\circ$ and $62^\circ \leq 2\theta \leq 68^\circ$) of the \textit{in-situ} ND data obtained from the MoS\textsubscript{2} cell as a function of time showing discharge evolution of: (a) (002) peak with a
reference line (guide to the eye) showing the \(2\theta\) shift. (b) Rietveld-refined \(a\) (black squares) and \(c\) (red circles) lattice parameters of MoS\(_2\). (c) (103) MoS\(_2\) peak. (d) Measured voltage (black line) and applied current (red) correlated to the ND data. The reflections intensities are scaled.

**Figure 6.6** Transmission electron microscope (TEM) images of raw and restacked MoS\(_2\): (a) raw MoS\(_2\), with the inset showing the corresponding SAED pattern; (b) restacked MoS\(_2\), with the top inset showing a direct comparison of the layer spacing of raw and restacked MoS\(_2\) by a comparison of 9 layers, while the bottom inset indicates the particle source of the images enlarged in (b) and (c); (c) restacked MoS\(_2\), with the inset showing the corresponding SAED pattern; (d) turbostratically restacked MoS\(_2\).

**Figure 6.7** Rietveld refinement of XRD patterns of raw (top) and restacked (bottom) MoS\(_2\). The observed pattern, the calculated peak positions, and the difference between the observed and the calculated patterns are shown in black, red and green, respectively, from top to bottom.

**Figure 6.8** Raman spectra of raw and restacked MoS\(_2\).

**Figure 6.9** Electrochemical properties of raw and restacked MoS\(_2\): cyclic voltammograms for the first 5 cycles of (a) raw and (b) restacked MoS\(_2\) at a scanning rate of 0.2 mV s\(^{-1}\); (c) cycling performances at a current density of 50 mA g\(^{-1}\); (d) rate capabilities at different current densities (discharge current
density kept at 50 mA g$^{-1}$).

**Figure 6.10** Magnetic hysteresis curves recorded at room temperature from raw and restacked MoS$_2$.

**Figure 6.11** Characterization of cycled restacked MoS$_2$: (a) TEM image with the inset showing the corresponding SAED pattern, and (b) XRD patterns.

**Figure 6.12** EIS spectra for the cells made of (a, c) raw and (b, d) restacked MoS$_2$ at (a, b) 1.6 V and (c, d) 0.9 V at different temperatures.

**Figure 6.13** Equivalent circuit for the electrochemical impedance spectra.

**Figure 6.14** Arrhenius plots of ln($i_0$) versus 1/T for the electrodes containing raw (triangles) and restacked (rectangles) MoS$_2$ at (a) 1.6 V and (b) 0.9 V.

**Figure 6.15** X-ray diffraction patterns: (a) a comparison of raw MoS$_2$, Sample (I), and Sample (II); (b) enlarged pattern of Sample (I) and Sample (II).

**Figure 6.16** TEM images of Sample (I): (a) typical area of the composite, (b) SAED patterns of selected areas marked with 1 and 2 in (a), (c) high resolution image of right edge area marked with 3 in (a), (d) high resolution image from another area; high resolution TEM images of Sample (II): (e) and (f), with the inset in (f) showing the corresponding SAED pattern.

**Figure 6.17** Magnetic hysteresis curves recorded at room temperature from raw MoS$_2$, SnO$_2$ nanopowder, and as-prepared Samples (I) and (II).

**Figure 6.18** Schematic diagram of typical synthesis.
Figure 6.19  Room temperature Raman spectra: raw MoS$_2$ powder, as-prepared SnO$_2$ nanoparticles, Sample (I), Sample (II).

Figure 6.20  XPS high resolution spectra of Mo3d for (a) Sample (I) and (b) Sample (II).

Figure 6.21  Cyclic voltammetry curves for the first 5 cycles of (a) Sample (I) and (b) Sample (II).

Figure 6.22  Cycling performance of the two composites cycled in different voltage ranges.

Figure 6.23  Electrochemical performance of MoS$_2$: (a) voltage vs. capacity curves for selected cycles in the voltage range of 0.05 - 1.5 V and (b) cycling performance.

Figure 6.24  FESEM images of cycled electrodes for (a) Sample (I) and (b) Sample (II) in the voltage range of 0.05 - 1.5 V.

Figure 7.1  FESEM images of as-synthesized anatase@TiO$_2$(B) nanowires (a) and (b), (c) X-ray diffraction (XRD) pattern and Rietveld analysis, where the symbols in the top spectrum represent the data, and the solid line the calculated fit. The upper and lower vertical lines are the lines in the TiO$_2$(B) and anatase standards, respectively. The difference spectrum is shown below. The insets in (a) and (b) are the EDX spectrum and a higher resolution image, respectively. (Gold nanoparticles with a grain size of ~5-10nm were evaporated on the surface of the anatase@TiO$_2$(B) nanowire samples to reduce electrostatic charging during SEM imaging.)

Figure 7.2  (a) TEM image and SAED pattern (inset) of single
anatase@TiO$_2$(B) nanowire, (b) low-magnification TEM image and SAED pattern (inset) of anatase@TiO$_2$(B) nanowires, (c) high resolution TEM image of a section of an anatase@TiO$_2$(B) nanowire, (d) proposed carrier transfer mechanism during formation of the nanowire heterojunction (left) and charge diffusion mechanism of nanowires during charge/discharge processes (right). (Subscripts ‘A’ and ‘B’ represent ‘Anatase’ and ‘TiO$_2$(B)’, respectively.)

Figure 7.3 Electrochemical performance of anatase@TiO$_2$(B) nanowire electrode cycled between 1.0 and 3.0 V vs. Li$^+$/Li: (a) cyclic voltammograms from the first cycle to the fifth cycle at a scan rate of 0.1 mV s$^{-1}$ in the voltage range of 1.0-3.0 V, (b) capacity–cycle number curves from the first cycle to the 100$^{th}$ cycle at the current density of 30 mA g$^{-1}$, (c) voltage profiles at the different cycling rates of 30, 150, 300, 750, 1500, 3000, and 4500 mA g$^{-1}$, (d) discharge capacity as a function of the discharge rate (30, 150, 300, 750, 1500, 3000, 4500 mA g$^{-1}$); the inset is the discharge capacity vs. rate capability curve.

Figure 7.4 X-ray diffraction (XRD) patterns of samples: as-prepared and annealed at 250 °C, 350 °C, 500 °C, and 600 °C.

Figure 7.5 FESEM images of (a) as-prepared TiO$_2$ and samples annealed at (b) 250°C, (c) 350°C, (d) 500°C, and (e) 600°C, (f) high resolution image of sample annealed at 600 °C.

Figure 7.6 Cyclic voltammograms of the samples at a scan rate of 0.1 mV s$^{-1}$. 
List of Figures

**Figure 7.7** Electrochemical performance of the as-prepared and annealed samples: (a) charge-discharge curves; (b) discharge capacity vs. cycle number at a current density of 20 μA cm⁻².

**Figure 7.8** Electrochemical impedance spectroscopy of samples over a range of frequency from 0.01Hz to 100 kHz: (a) fresh cells, (b) cells charged to 3.0 V after 5 cycles. The insets show enlargements of the high frequency region.

**Figure 7.9** FESEM images of samples after 50 charge-discharge cycles: (a) as-prepared and annealed at (b) 250°C, (c) 350°C, (d) 500°C, and (e) 600°C; (f) typical EDS spectrum of the TiO₂ nanotube electrode annealed at 350 °C after 50 charge/discharge cycles.

**Figure 7.10** FESEM images of: (a) TiO₂ nano-array substrate, SnO₂/TiO₂ samples with different SnCl₂ precursor concentrations: (b) 0.001 M, (c) 0.005 M and (d) 0.02 M.

**Figure 7.11** FESEM images at different magnifications: TiO₂ substrate (a,b), with the inset in (a) showing a cross-sectional image, results of solvothermal reaction at 150°C with 0.005 M SnCl₂ for different reaction times: 0.5 h (c,d) and 10 h (e,f).

**Figure 7.12** X-ray diffraction patterns of the TiO₂ substrate and of the 0.5 h and 10 h SnO₂/TiO₂ samples.

**Figure 7.13** EDS results on 0.5 h SnO₂/TiO₂ sample: (a) Ti distribution, (b) Sn distribution, (c) EDS spectrum of sample.

**Figure 7.14** TEM cross-sectional images of 0.5 h SnO₂/TiO₂ sample: (a) image of array of tubes, (b) and (c) HRTEM images of a TiO₂
tube and of its SnO$_2$ nanocrystals, with the inset in (c) showing lattice fringes of one SnO$_2$ nanocrystal.

**Figure 7.15** EDS spectra corresponding to TEM images in Figure 7.14: (a) whole area of Figure 7.14 (a), (b) region 1, (c) region 2, and (d) region 3. Platinum and gallium were used for the holder to prepare the TEM sample for the cross-sectional images, so their peaks are present. The C and Cu peaks are from the copper grid.

**Figure 7.16** Electrode performances of SnO$_2$/TiO$_2$ samples: (a) cyclic voltammograms of 0.5 h SnO$_2$/TiO$_2$ sample, (b) cycling performance of 200 nm TiO$_2$ and 0.5 h SnO$_2$/TiO$_2$ samples at current density of 20 $\mu$A cm$^{-2}$ with different voltage ranges, (c) galvanostatic curves during the 10 first cycles of 0.5 h SnO$_2$/TiO$_2$ sample, (d) rate capability of 0.5 h SnO$_2$/TiO$_2$ sample at different current densities.

**Figure 7.17** (a) Cycling performance of 10 h SnO$_2$/200 nm or 2000 nm TiO$_2$ samples in different voltage ranges at current density of 20 $\mu$A cm$^{-2}$, (b) galvanostatic curves of 0.5 h SnO$_2$/TiO$_2$ sample at different current densities.

**Figure 7.18** (a) Reaction scheme, FESEM images after charge/discharge cycles (insets: higher magnification): (b) TiO$_2$ and (c) SnO$_2$/TiO$_2$ (after 5 cycles), (d) TiO$_2$ and (e) SnO$_2$/TiO$_2$ (after 50 cycles).

**Figure 7.19** (a) TEM image of 0.5 h SnO$_2$/TiO$_2$ electrode after 5 cycles, (b) high resolution image.
| Figure 8.1 | TEM images of raw Li$_4$Ti$_5$O$_{12}$: (a) low resolution, (b) and (c) high resolution image with the inset in (b) showing the corresponding selected area electron diffraction (SAED) pattern and (d) XRD pattern. |
| Figure 8.2 | TEM images: (a) LTO-N, with the inset showing the SAED pattern, and (b) a high resolution image, (c) LTO-A, with the inset showing the hollow spheres, and (d) a high resolution image. |
| Figure 8.3 | (a) Raman spectra of LTO samples annealed in N$_2$ and air, (b) high resolution TEM image of the LTO-N sample, and (c) schematic diagram of carbon distribution on grain boundaries. |
| Figure 8.4 | EDS mapping of sample LTO-N: (a) SEM image, (b) carbon distribution, with the inset showing the EDS spectrum, (c) titanium distribution, (d) oxygen distribution. |
| Figure 8.5 | XPS Ti 2p core level spectra of the LTO-N sample: (a) outer surface layer and (b) after Ar ion etching. |
| Figure 8.6 | Rietveld refinements of the Li$_4$Ti$_5$O$_{12}$ structural model based on XRD data for (a) LTO-N and (b) LTO-A. Crosses (×) indicate the collected data, the solid line through the data is the calculated model, the purple line below is the difference between observed and calculated, and the vertical lines indicate Bragg reflections. The insets contain digital photographs of the powder samples, respectively. |
| Figure 8.7 | Electrochemical performance: (a) cyclability of LTO-N and LTO-A at 0.5 C, (b) rate capability of LTO-N and LTO-A |
samples from 0.5 C to 30 C (with charge and discharge processes at the same C-rate), (c) Galvanostatic charge/discharge curves of Li₄Ti₅O₁₂ annealed in N₂ at different C-rates.

Figure 8.8  Li₄Ti₅O₁₂ anode and Li(Co₀.₁₆Mn₁.₈₄)O₄ cathode full battery tests: (a) galvanostatic charge/discharge curves for the first cycle, and (b) cycling performance.

Figure 8.9  Galvanostatic charge/discharge curves of Li(Co₀.₁₆Mn₁.₈₄)O₄ vs. Li⁺/Li at current densities of 87.5 mA g⁻¹ and 175 mA g⁻¹.

Figure 8.10  Cyclic performance of Li₄Ti₅O₁₂₋ₓBrₓ (x = 0.05, 0.10, 0.20, and 0.30) at the 0.5 C rate.

Figure 8.11  Rietveld plots using SXRD data of the sample with the chemical synthetic input composition of Li₄Ti₅O₁₁.₉₅Br₀.₀₅, showing (a) the fit of the Rietveld-refined Li₄Ti₅O₁₁.₉₇Br₀.₀₃ model with rutile TiO₂, and (b) an expanded region of the fit between 14 ≤ 2θ ≤ 44 °. Crosses (×) are the data, the Rietveld model is the line through the crosses, and the difference between the calculated model and the data is shown by the line below. Vertical lines indicate reflection markers for TiO₂ (red) and Li₄Ti₅O₁₁.₉₇Br₀.₀₃ (black).

Figure 8.12  Rietveld plots using SXRD data of the sample with the chemical synthetic input composition of Li₄Ti₅O₁₁.₉Br₀.₁, showing (a) the Rietveld-refined Li₄Ti₅O₁₁.₈₈Br₀.₁₂ model with rutile TiO₂, and (b) an expanded region of the fit between 26 ≤ 2θ ≤ 45 °. Crosses (×) are data, the Rietveld model is the line
through the crosses, and the difference between the calculated model and the data is shown by the line below. Vertical lines are reflection markers for TiO$_2$ (red) and Li$_4$Ti$_5$O$_{11.88}$Br$_{0.12}$ (black).

**Figure 8.13** Rietveld plots using SXRD data of the sample with the chemical synthetic input composition of Li$_4$Ti$_5$O$_{11.8}$Br$_{0.2}$, showing (a) the Rietveld-refined Li$_4$Ti$_5$O$_{11.90}$Br$_{0.10}$ model with rutile TiO$_2$, and (b) an expanded region of the fit between $20 \leq \theta \leq 45^\circ$. Crosses (×) are data, the Rietveld model is the line through the crosses, and the difference between the calculated model and the data is shown by the line below. Vertical lines are reflection markers for TiO$_2$ (red) and Li$_4$Ti$_5$O$_{11.90}$Br$_{0.10}$ (black). The arrow indicates the third phase in this sample with the inset in (b) showing detail.

**Figure 8.14** Rietveld plots using SXRD data of the sample with the chemical synthetic input composition of Li$_4$Ti$_5$O$_{11.7}$Br$_{0.3}$, showing (a) the Rietveld-refined Li$_4$Ti$_5$O$_{11.89}$Br$_{0.11}$ model with rutile TiO$_2$, and (b) an expanded region of the fit between $14 \leq \theta \leq 25^\circ$. Crosses (×) are data, the Rietveld model is the line through the crosses, and the difference between the calculated model and data is shown by the line below. Vertical lines are reflection markers for TiO$_2$ (red) and Li$_4$Ti$_5$O$_{11.89}$Br$_{0.11}$ (black). The arrows indicate the third phase and the inset in (b) shows detail.

**Figure 8.15** The charge-discharge behavior of our custom-designed cell
containing the composite TiO\textsubscript{2}/Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} electrode with the first 1.7 and 1.5 V discharge plateau regions indicated.

**Figure 8.16** Fit of the Rietveld model containing Li, Cu, anatase TiO\textsubscript{2}, and Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} to *in-situ* ND data at $\lambda = 2.406(2)$ Å. Crosses (×) are the data, the Rietveld model is the line through the crosses, the difference between the calculated model and the data is shown by the line below, and the vertical lines are reflection markers for Li, Cu, Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}, and TiO\textsubscript{2} (from top to bottom, respectively).

**Figure 8.17** The time evolution of voltage (black) and the $a$ (black) and $c$ (red) TiO\textsubscript{2} lattice parameters. The region shaded in green (between 786 and 902 minutes) may contain both the TiO\textsubscript{2} and Li$_x$TiO\textsubscript{2} phases, but could not be accurately modelled. The region shaded in blue corresponds to the *in-situ* ND patterns shown in Figure 8.18.

**Figure 8.18** Selected region of *in-situ* ND data highlighting the Li insertion process in ~80 mg of TiO\textsubscript{2} observed by the increase in 2θ value of the (112) reflection indicated by the arrow. Scaled peak intensities are shown.

**Figure 8.19** Parameters from the charge-discharge cycles between 1.6 and 3 V of the composite Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}/TiO\textsubscript{2} anode, determined from two sets of sequential multi-phase Rietveld refinements. Variations in the $a$ (a) and $c$ (b) TiO\textsubscript{2} lattice parameters were determined with a model containing only a TiO\textsubscript{2} phase. The phase fractions of TiO\textsubscript{2} (c) and lithiated TiO\textsubscript{2} (d) were
determined with a model containing both TiO$_2$ and lithiated TiO$_2$ phases with fixed lattice parameters. The measured voltage (e) and applied current (f) are also shown. The upper-most section of the figure is a section of the *in-situ* ND data showing Li$_4$Ti$_5$O$_{12}$, TiO$_2$, and lithiated TiO$_2$ reflections. Scaled peak intensities are shown.
LIST OF TABLES

Table 3.1  Chemicals used in the present work.  44
Table 4.1  Results of specific surface area measurements using low temperature liquid nitrogen absorption.  68
Table 6.1  Charge transfer resistance (R_{ct}), exchange current (i_0), and apparent activation energies (E_a) of raw and restacked MoS_2 measured at different discharge stages and temperatures.  128
Table 6.2  Raman peaks of the samples and the corresponding symmetry assignment.  136
Table 8.1  The fractions of Li_4Ti_5O_{12-x}Br_x and TiO_2 phases, input chemical compositions, Rietveld-refined compositions, lattice parameters, and figures of merit of the Rietveld model fits shown in Figures 8.11 - 8.14. The profile factor is R_p, the weighted profile factor is R_{wp} and goodness-of-fit term is \chi^2.  207
CHAPTER 1 INTRODUCTION

Energy was listed as the first of humanity’s top ten problems for the next 50 years by Nobel Laureate Professor Richard E. Smalley in 2003 and environment was the fourth on the list. Limited supplies of fossil fuels and greenhouse gas emissions are the key issues relevant to these two of the biggest problems facing humanity. Increasing energy demand worldwide and mandates to minimize greenhouse gas emissions require the production of energy in a sustainable manner and efficient usage. Therefore, the development of renewable energy sources is ongoing. Among the alternative power sources, lithium ion batteries have played a key role in portable electronics, and are being used for power tools and electric vehicles (EV) or hybrid electric vehicles (HEV), which would minimize the greenhouse gas emissions from exhausts in transportation. After several years’ research effort, it is expected that lithium-ion battery powered electric vehicles could penetrate the market from this year. Lithium ion batteries are also a good choice to store energy from other renewable sources in a green smart grid, especially in the case of intermittent sources of clean energy, such as wind, solar, and tidal energy.

Lithium ion batteries show several advantages compared with other batteries, such as high energy density, high power density, long cycle life, low self-discharge rate, lack of a memory effect, etc. Amongst the energy storage systems, these batteries have shown the greatest success in the portable electronics market for the past two decades. As the power source for transportation applications, lithium ion batteries are the only alternative that has well-developed technology in the new energy storage systems, in contrast to fuel cells or supercapacitors at the moment. However, compared with
traditional combustion engines and gas turbines, lithium ion batteries still exhibit much lower power. The specific requirements of lithium ion batteries in future applications are also very different. For example, next generation portable electronic devices demand higher energy density and must be more flexible and thinner. However, the most important requirements on lithium ion batteries for EVs or HEVs are safety and low cost. Energy storage systems require batteries with stable cycling performance and long cycle life. Electrode materials play the most important role in lithium ion batteries, having the most influence on the battery performance. Moreover, electrode materials account for most of the cost of a battery. For example, in a 18650 cell, cathode materials account for 40-50% of the overall battery cost, whereas the anode and electrolyte take up about 20-40%. In order to reduce the battery cost, it is necessary to develop and employ cost-effective electrode materials for sustainable development.

The recent research effort that has been put into electrode materials for lithium ion batteries could be described in terms of the following directions: (1) explore new electrode materials, (2) investigate intrinsic properties from structural chemistry and the reaction mechanism, either by experiments or by theoretical calculations, to obtain in-depth understanding of the electrochemical behaviour, (3) improve the electrochemical performance of the existing materials by employment of different synthesis techniques, formation of various morphologies, doping with different elements, making composites, etc. The overall objective of this doctoral work is to synthesize nanostructured materials, investigate their electrochemical performance as anode materials for lithium ion cells and extend our understanding of the dependence of the electrochemical properties on the materials’ morphology and structure. The
main scope of this study is outlined as follows: (1) synthesis of nanostructured electrode materials with different morphology, such as mesoporous SnO₂, one-dimensional TiO₂, nanocrystalline Li₄Ti₅O₁₂, etc., and composite materials, such as SnO₂-carbon, and MoS₂-SnO₂ and Li₄Ti₅O₁₂-TiO₂ composites; (2) employment of different synthesis techniques, such as the molten salt method, the hydrothermal technique, electrospinning, spray pyrolysis, etc.; (3) application of many physical and electrochemical characterization techniques for electrode materials, such as in-situ neutron diffraction, X-ray diffraction (XRD), synchrotron XRD, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, cyclic voltammetry, electrochemical impedance spectroscopy, etc.

Chapter 2 presents an extensive review on lithium ion batteries, including general background, a brief history, the working mechanism, fundamental considerations, chances, and challenges, and a review of recent literature on anode materials.

Chapter 3 presents the overall experimental procedures, all the chemicals used in this study, details of the electrode material synthesis techniques, and physical and electrochemical characterization methods.

Chapter 4 discusses the synthesis of ultra-fine porous SnO₂ and SnO₂/carbon composite by a simple, easily scaled-up, and low temperature molten salt method. The as-prepared porous nano-SnO₂ showed capacity retention of 64.8% after 100 cycles in the voltage range of 0.05-1.5 V. It is believed that the pores could accommodate the volume change during charge/discharge. Furthermore, the good interface affinity between the carbon matrix and the SnO₂ particles in the SnO₂/C
composite and the effective buffer presented by the carbon resulted in significant improvement in the electrochemical performance, with better capacity retention of 85.3%.

Chapter 5 discusses one-dimensional SnO$_2$ anode composed of nanocrystals less than 5 nm in size. In the first part, SnO$_2$ nanocrystals were deposited onto multi-walled carbon nanotubes, which could serve as an electron conductive core and prevent tin agglomeration because the SnO$_2$ crystals were pinned on the CNTs by a high pressure solvothermal process. In the second part, one-dimensional SnO$_2$ and SnO$_2$/C nanofibres were synthesized by electrospinning. The orderly bounded SnO$_2$ nanocrystals and their porous nature are favourable for electrochemical behaviour. The uniformly distributed carbon in the composite could further improve the cyclability and rate capability.

Chapter 6 investigates the electrochemical performance of MoS$_2$ as an anode material. In the first part, a novel characterization technique, \textit{in-situ} neutron diffraction, was achieved by the use of a custom roll-over design cell. The technique was first applied to investigate the structural change of MoS$_2$ with electrochemically driven lithium intercalation. In the second part, restacked MoS$_2$ with an increased $c$ lattice parameter was obtained by exfoliation and restacking in a hydrothermal process and exhibited superior electrochemical performance. MoS$_2$/SnO$_2$ composites were synthesized by a similar process with the addition of a tin source in the restacking process by reflux reaction.
Chapter 7 discusses one dimensional TiO$_2$ based anode materials. First, TiO$_2$(B)/anatase hybrid nanowire was prepared by the hydrothermal technique and exhibited excellent lithium storage capacity and rate capability, which are partially attributed to the bi-phase interaction. Three-dimensional TiO$_2$ nanotube arrays were then synthesized by anodization, and SnO$_2$ nanocrystal/TiO$_2$ nanotube array composites were prepared, with SnO$_2$ nanocrystals 5 nm in size deposited onto the TiO$_2$ nanotube arrays.

Chapter 8 discusses advanced Li$_4$Ti$_5$O$_{12}$ anode materials. In the first part, Li$_4$Ti$_5$O$_{12}$ nanocrystal anode with a carbon conductive network was prepared by spray pyrolysis, which is a continuously operating and industrially scalable technique. The well mixed precursor allowed shorter high temperature annealing time and saved considerable energy. The preservation of the carbon from the organic precursor under N$_2$ treatment improved the cyclability and rate capability. Structural analysis of Br-doped Li$_4$Ti$_5$O$_{12}$ was achieved by high intensity synchrotron X-ray powder diffraction to exactly determine the effects of doping level and impurity on electrochemical performance. Finally, in-situ neutron diffraction was applied to investigate Li$_4$Ti$_5$O$_{12}$/TiO$_2$ composite anode.

In Chapter 9, general conclusions are summarized, and the outlook for further investigations is also discussed.
CHAPTER 2 LITERATURE REVIEW

2.1 Lithium ion batteries

In order to maintain fast economic growth all over the world, increasing energy consumption is a necessity. Electricity is the dominant form of energy used, and the demand for electricity is increasing at an ever faster pace. At the same time, oil and natural gas production, as the main energy sources for electricity, is predicted to peak over the next few decades. Moreover, due to the excessive consumption of fossil fuels, environmental pollution and global warming have attracted the general attention of humanity. A worldwide effort to reduce CO$_2$ emissions and preserve the environment has promoted the development of alternative clean energy sources, especially nuclear energy, solar energy, and wind power. However, solar and wind are not constant and reliable sources of power; these systems require energy storage units due to intermittent energy generation. Vehicles are one of the largest sources of greenhouse gas emissions and fossil fuel consumption, so clean power transportation systems, such as electric vehicles (EVs) or hybrid electric vehicles (HEVs) are being developed.

Figure 2.1 compares different electrochemical energy conversion systems with conventional fossil fuel engines and turbines [1]. Fuel cells can be regarded as high-energy systems, whereas supercapacitors are the high-power systems. Batteries have intermediate power and energy characteristics, and they have better developed technology than the other two energy storage systems, so much effort has been put into increasing the power density and energy density of batteries to meet the vast new requirements.
Figure 2.1 Comparison of various electrochemical energy conversion systems with the internal combustion engine and turbine in terms of specific power and energy [1].

Lithium, with an atomic number of three and located in the top left corner of the periodic table, is the most electropositive (-3.04 V versus the standard hydrogen electrode (SHE), the lightest (Mw = 6.94 g mol⁻¹) and the least dense (ρ = 0.53 g cm⁻³) metal, so lithium ion batteries deliver the highest energy density among all the existing batteries (Figure 2.2) [2].

Since the commercialization of lithium ion batteries in the early 1990s, they have gained great success for portable electronics, such as laptop computers, cell phones, cameras, etc., and account for more than 60% of worldwide sales value in portable batteries. However, consumers are demanding a longer life in a smaller package and at a lower cost, with minimal if any wired connection. Moreover, the usage of lithium ion batteries has been expanded into both large units, such as EVs/HEVs,
robots, power tools, and electrical-energy storage systems, and small units known as microelectromechanical systems (MEMS). All these potential uses call for the development of high energy density, long cycle life, low cost, and high safety in the next-generation lithium ion batteries.

**Figure 2.2.** Comparison of the different battery technologies in terms of volumetric and gravimetric energy density [2].

### 2.1.1 Brief History

The first modern electrochemical cell was developed in the 1790s by Galvani [3]. From then on, many types of primary or rechargeable batteries were developed in the following centuries, such as the zinc-carbon battery, lead acid battery, nickel cadmium battery, zinc air battery, alkaline battery, etc.. Before 1970, commercial batteries used aqueous electrolytes. Because of the redox reaction of H₂O, these batteries have a small electrochemical window, with a cell potential less than 2 V [4].
Chapter 2 Literature review

The discovery of fast Na\textsuperscript{+}-ion conduction in the beta-aluminas [5] and the invention of the Na/S battery at the Ford Motor Company in 1967 [6] stimulated a worldwide interest in the development of rechargeable alkali-ion batteries operating with a non-aqueous electrolyte. Since lithium has the lightest weight, highest voltage, and greatest energy density, it attracted research attention in the alkali battery study.

Actually, the first published interest in lithium batteries began with the work of Harris in 1958 [7]. After many scientists’ and engineers’ efforts on the many lithium battery couples during the early days, it eventually led to the development and commercialization of a variety of primary lithium cells during the 1970s. The prominent systems include lithium/sulfur dioxide (Li/SO\textsubscript{2}), lithium/thionyl chloride (Li/SOCl\textsubscript{2}), lithium/sulfuryl chloride (Li/SOCl\textsubscript{2}), lithium/polycarbonate monofluoride (Li/(CF\textsubscript{x})\textsubscript{n}), lithium/manganese dioxide (Li/MnO\textsubscript{2}), and lithium/iodine (Li/Poly-2-vinyl pyridine)\textsubscript{In}, etc. [8].

A number of groups, with the first led by Whittingham (first at Stanford and then at Exxon), proposed and investigated the use of TiS\textsubscript{2} as a cathode in lithium batteries. Exxon and Moli Energy tried to commercialize the Li/TiS\textsubscript{2} and Li/MoS\textsubscript{2} systems, respectively, with the voltage systems operating near 2 V [9]. However, due to the safety problem involving lithium metal, the commercialization eventually failed.

The concept of a lithium-ion cell was tested in the laboratory with two insertion electrodes and lithium ions cycling between them, thus eliminating the use of a metallic lithium anode and enhancing the safety. Although Steele and Armand considered insertion compounds as battery electrodes and suggested graphite and
layered TiS$_2$ as potential candidates for the electrodes of a lithium-ion battery based on a non-aqueous liquid electrolyte in 1973 [10, 11], the electrochemical properties of lithium intercalation in graphite were first reported in a patent of Sanyo in 1981 [12]. At the same time, Goodenough’s group proposed the lithium insertion oxide LiCoO$_2$ for the cathode, which delivers higher voltage than sulfides [13]. Eventually, in 1991, Sony introduced the first commercial lithium-ion cell based on graphite/LiCoO$_2$, which had an open circuit potential of 4.2 V and an operational voltage of 3.6 V [2]. Since then, many electrode materials have been explored, such as spinel LiMn$_2$O$_4$, polyanion LiFePO$_4$ for cathode, and Si, Sn, and transition metal oxides for anode. Therefore, there has been an extraordinary amount of work on all aspects of lithium-ion chemistry, battery design, manufacture, and application.

2.1.2 Working mechanism

Components
A battery is one or more electrically connected electrochemical cells, either in series or in parallel. The lithium ion battery is a device converting chemical energy to electrical energy, which can be recharged through an external circuit. It is basically composed of anode, cathode, electrolyte with lithium salt, and separator [1]. The anode, also called the negative electrode, releases electrons into the external circuit during the discharge process, which is associated with oxidative chemical reactions. The cathode, also called the positive electrode, gains electrons from the external circuit during the discharge process, which is associated with reductive chemical reactions. An electrolyte is a material that acts as a charge carrier to provide pure ionic conductivity between the anode and cathode in a cell. A separator is a physical barrier between the positive and negative electrodes to prevent an electrical short circuit. The separator can be a gelled electrolyte, or a microporous plastic film or
other porous inert material filled with electrolyte. Separators must be permeable to the ions and inert in the battery environment.

The battery works by means of lithium ions shuttling from one electrode to the other through the electrolyte solution, while chemical energy is released or replenished inside the cell. Taking the commonly used materials LiCoO$_2$ and graphite, for example, as shown in Figure 2.3, initially, for the discharge process, Li ions move from the anode (graphite) to the cathode (LiCoO$_2$) via the electrolyte, which contains Li ions, while electrons spontaneously go through the external circuit, giving up the energy stored. During the recharge process, we spend energy from external power sources in relocating those ions back in the place where they don’t like to be, in the graphite electrode, and the electrical energy is stored as chemical energy. The reaction mechanisms are shown as follows:

\[ \text{LiCoO}_2 \leftrightarrow \text{Li}_{x-} \text{CoO}_2 + x\text{Li}^+ + x\text{e}^- \] (cathodic reaction) \hspace{1cm} (2.1)

\[ C + x\text{Li}^+ + x\text{e}^- \leftrightarrow \text{Li}_x C \] (anodic reaction) \hspace{1cm} (2.2)

**Figure 2.3.** Schematic of reaction mechanism in a rechargeable lithium ion battery.
Basic concepts

In order to describe the battery system and evaluate the performance of the electrochemical reaction, some basic concepts are discussed below:

Voltage

The open-circuit voltage $V_{oc}$ (V) is the voltage across the terminals of a cell without external current flow. It is determined by the difference between the electrochemical potential of the anode (negative) and the cathode (positive).

$$V_{oc} = (\mu_A - \mu_C)/(nF)$$  \hspace{1cm} (2.3)

where $\mu_A - \mu_C$ is the difference between the electrochemical potential of the anode and the cathode, $n$ is the number of electrons involved in the chemical reaction of the cell, and $F$ is the Faraday constant.

The operating voltage of the cell is determined by:

$$V = V_{oc} - IR$$  \hspace{1cm} (2.4)

where $I$ is the working current in the circuit and $R$ is the internal resistance of the cell.

Capacity

Capacity $Q$ (Ah) is the total amount of charge on the electrode in the cell for the redox reaction during the charge/discharge process.

$$Q = \int_{t_1}^{t_2} I(t)dt = nzF$$  \hspace{1cm} (2.5)

where $I(t)$ is the current, $t$ is the time, $n$ is the number of ions (mol), $z$ is the valence of the ions, $F = 96485 \text{ C mol}^{-1}$ is the Faraday constant.
Specific capacity

The specific capacity $Q_s$ (Ah kg$^{-1}$) for the charge ($Q_{sc}$) or the discharge ($Q_{sd}$) process is calculated based on both the capacity and the material’s weight, namely, the capacity per unit weight (kg) of the active material.

Irreversible capacity

Irreversible capacity results from irreversible lithium reactions which do not result in insertion into or extraction from the active materials. It equals the difference between the charge capacity and the discharge capacity for the $n^{th}$ cycle.

Irreversible capacity = $n^{th}Q_c - n^{th}Q_d$

Coulombic efficiency

Coulombic efficiency ($\eta_c$), always used to evaluate the cycling stability, is the ratio of the charge capacity to the discharge capacity for the $n^{th}$ cycle.

$$\eta_c = \frac{n^{th}Q_c}{n^{th}Q_d}$$ (2.6)

Energy

The terms specific energy, expressed in watt-hours per kilogram (Wh kg$^{-1}$), and energy density, expressed in watt-hours per liter (Wh L$^{-1}$), are used to compare the energy content of a cell.

Power

The terms specific power, expressed in watts per kilogram (W kg$^{-1}$) and power density, expressed in watts per liter (W L$^{-1}$), are used to evaluate the rate capability.

Charge/Discharge Rate

The term charge/discharge rate or C-rate is employed to estimate how fast lithium can be transferred. C denotes either the theoretical charge capacity of a cell or the
nominal capacity of a cell. For example, C/5 means a current allowing a full charge/discharge in 5 h.

2.1.3 Electrochemical Principles

Thermodynamics

Thermodynamics describes reactions at equilibrium and the maximum energy release for a given reaction. The reaction in an electrochemical cell is known as a redox reaction, where there is electron transfer between active species. The reactions on electrodes when the cell is releasing energy can be described by two half-cell reactions, i.e., the reduction reaction on the cathode (Equation 2.1) and the oxidation reaction on the anode (Equation 2.2) [14, 15].

At the cathode: \[ aA + ne^- + nLi^+ \rightarrow cC \] (2.7)

At the anode: \[ bB - ne^- - nLi^+ \rightarrow +dD \] (2.8)

Overall reaction: \[ aA + bB \rightarrow cC + dD \] (2.9)

The basic thermodynamic equations for the overall reversible electrochemical transformation are given as:

\[ \Delta G = \Delta H - T\Delta S \] (2.10)

where \( \Delta G \) is the Gibbs free energy, \( \Delta H \) is the enthalpy, \( T \) is the absolute temperature, and \( \Delta S \) is the entropy. When the reaction is under equilibrium conditions, the equation is described by standard condition variables:

\[ \Delta G^o = \Delta H^o - T\Delta S^o \] (2.11)

If the released Gibbs energy is all transferred to electrical work, then

\[ \Delta G = W = -nFE \] (2.12)

and under standard conditions:

\[ \Delta G^o = -nFE^o \] (2.13)
where \( E^o \) is the standard electrode potential. The Gibbs free energy of the reversible reaction is also related to the activity of the reactants and products:

\[
\Delta G = \Delta G^o + RT \ln \left( \frac{\gamma C^c \gamma D^d}{\gamma A^a \gamma B^b} \right)
\]  \hspace{1cm} (2.14)

where \( R \) is the gas constant, \( \gamma \) is the activity factor, and \( a, b, c \) and \( d \) are the number of active species involved in the reaction.

From equations (2.12) to (2.14), the Nernst equation for the electrochemical cell could be obtained as follows:

\[
E = E^o - \frac{RT}{nF} \ln \left( \frac{\gamma C^c \gamma D^d}{\gamma A^a \gamma B^b} \right)
\]  \hspace{1cm} (2.15)

**Kinetics**

The thermodynamics reflects the feasibility under equilibrium conditions, however, in the actual situation where current flows, the voltage decreases the non-equilibrium and kinetics limitations during operation, which is known as electrode polarization \((\eta)\). The three different kinetics effects related to polarization can be classified into three types [1]:

1. Activation polarization arises from the kinetics of the charge-transfer reaction taking place at the electrode/electrolyte interfaces. Activation polarization follows the Tafel equation:

\[
\eta_a = a - b \log(I/I_o)
\]  \hspace{1cm} (2.16)

where \( a \) and \( b \) are constants, \( I \) is the reaction current flow, and \( I_0 \) is the exchange current density.
(2) Ohmic polarization arises from the resistance of the system, including the electrolyte, electrode surfaces, active materials, current collector, etc. It follows the linear Ohm’s Law:

\[ \eta_o = IR \]  \hspace{1cm} (2.17)

(3) Concentration polarization arises from limited active species transport capabilities. It can be describe as follows:

\[ \eta_c = (RT/n) \ln(C/C_0) \]  \hspace{1cm} (2.18)

where \( C \) is the concentration at the electrode surface and \( C_0 \) is the concentration in the bulk of the solution.

\[ \textbf{2.1.4 Opportunities and challenges} \]

\[ \textbf{Advantages} \]

Compared with other batteries, lithium ion batteries show distinct advantages: (a) high open circuit potential compared with aqueous batteries (such as lead acid, nickel-cadmium, and nickel metal hydride), allowing higher energy density; (b) low self-discharge rate; (c) no memory effect; (d) components are environmentally safe compared with the lithium battery; (e) wide variety of shapes and sizes efficiently fitting the devices. Based on the successful technology for portable devices, the lithium ion battery has better-developed technology than fuel cells and supercapacitors for real applications. Moreover, supercapacitors should be combined with batteries when used in power systems. Although lithium based Li-S or Li-air batteries are also promising future battery technologies, they are still in the laboratory research stage and have a long way to go before real applications are possible. Therefore, lithium ion batteries are the best choice for future power sources.
Nanotechnology

Recent progress in advanced nanoscience and nanotechnology has presented the opportunity to design a series of novel nanostructured electrode materials for next-generation high-performance rechargeable lithium ion batteries [16-19], mainly because lithium ion batteries involve the transfer of Li$^+$ and electrons within the electrode materials and electrolyte, and across electrode-electrolyte interface. The diffusion time is given by $t = \frac{L^2}{D}$, where $L$ is the diffusion length and $D$ is the diffusion constant. The time $t$ decreases with the square of the particle size, so the reduced dimensions in nanosized electrode materials could significantly increase the rate of lithium insertion/extraction due to the short transport distance within the particles. Electron transfer is also enhanced in nanosized particles. Therefore, high power could be generated by increasing the charge/discharge rate. This is very important for the electrode materials with poor electronic and ionic conductivities, such as semiconductor oxide anodes, olivine polyanion cathodes, etc., which are especially designated for high power batteries. The high surface area of nanomaterials permits a high contact area with the electrolyte and ensures a high lithium ion flux across the interface. The nanosize could also change structural properties relating to intercalation, such as the solid-solution region, strain, or electrode potential, which could benefit the performance. Note that there are also disadvantages that come along with nanomaterials, such as complex and expensive synthesis, low packing density, or acceleration of side reactions.

Market

Lithium ion batteries have shown great success in the past decades in portable devices in our daily lives. However, in today’s information-rich, mobile society, the
use of information technology (IT) devices has become popular. As the revolution in portable devices as well as wireless communications has continued and new products are being explored, the need for the development of safe and longer lasting rechargeable batteries is still increasing. Most of the mobile IT device companies are focusing on next-generation smart phones and tablet personal computers (PCs) with new functions and fancy designs, and accordingly, there are increasing demands for new types of batteries, such as flexible and thin film batteries with high energy density [20]. At the same time, EV/HEV technologies are expected to penetrate the market from this year, with pure EV and plug-in hybrid electric vehicles (PHEV) sales reaching 2.5 and 5 million vehicles per year by 2020 [20], respectively, so the demand for Li-ion batteries for PHEVs and EVs is expected to increase rapidly, because there no alternatives in terms of the energy density and technology. Furthermore, the market for power storage applications is also expected to grow, although it is still at the initial stage and is worth approximately 2 billion dollars so far. In the long term, it is expected to grow explosively up to 35 billion dollars by 2020 with an expansion of renewable energy supplies and the smart grid system [21]. It is believed that all these new applications will open up a wider market for lithium ion batteries in the future.

**Challenges**

Despite the impressive growth in sales of batteries worldwide, the science underlying battery technology is often criticized for its slow advancement. It is well known that the real performance of lithium ion batteries falls far behind the power required from them, and unfortunately the gap between them is increasing. We have shown in Figure 2.1 that both the power density and the energy density of batteries are much lower than for fossil fuel combustion in vehicles. Moreover, the specific demands on
a battery in a particular application are different, as shown in Figure 2.4 [20]. The hexagonal diagrams indicate that the importance of each factor is more critical the further away from the center it is. The key requirements of batteries for portable electronic devices are high energy density, safety, and moderately high cycle life, while for power tools, high power is the most important factor, as well as safety. Although safety is always a very important factor, but the other requirements are different, for example, in pure battery electric vehicles (BEVs), high energy density is preferred, but for plug-in hybrid electric vehicles (PHEVs), cycle life is also very important, while in hybrid electric vehicles (HEV), only moderately high power and low cost are needed. However, in a stationary electrical power storage system, cost and cycle life are the most important requirements. Generally, the demands for next-generation lithium ion batteries are to increase energy density and power density, increase safety, enhance cycle life, reduce cost, and achieve sustainable and greener Li-ion batteries.

As the electrode materials play the key role in a battery, for example, in 18650 cells, cathode materials account for 40-50% of the overall battery cost, whereas the anode and electrolyte take up 20-40% [22]. Therefore, in order to improve the electrochemical performance and reduce the cost to meet the requirements for future applications, the main task for lithium ion batteries is to design and develop better electrode materials.
Figure 2.4. Requirements of lithium ion batteries for the three most important types of applications [20].
2.2 Anode materials

As mentioned above, a lithium ion battery is always composed of anode, cathode, electrolyte and separator. All these components could affect the battery performance. To meet the requirements for lithium ion batteries in potential applications, ideas for the improvement of each component have been advanced, such as the development of higher voltage, safety, and high rate cathode materials, new electrolytes with larger electrochemical windows and non-flammability, or new separators with good conductivity and safety, etc. As this doctoral work is concerned with nanostructured anode materials, the following review is only focused on anodes.

2.2.1 Carbonaceous anode

Graphite anode is the first commercial anode materials for lithium ion batteries and still the most widely used in the market. Lithium can be reversibly intercalated into and de-intercalated from its graphene interlayers with a low Li\(^+\) insertion voltage plateau of about 0.1 V (vs. Li\(^+\)/Li), which is close to that of metallic lithium, but greatly improves the safety compared with lithium batteries. It delivers a theoretical capacity of 372 mAh g\(^{-1}\) for the end compound LiC\(_6\) [23]. Many kinds of carbonaceous materials, from crystalline to strongly disordered carbon, have been tested as anodes in lithium ion batteries (LIBs) over the past decade, and the electrochemical lithium intercalation properties of such carbonaceous materials greatly depend on their crystallinity, morphology, surface area, orientation of crystallites, etc. As a result, graphite is now the most widely used as an anode in commercially available LIBs because of its relatively high specific capacity, small theoretical irreversible capacity, high initial coulombic efficiency and good cyclability. As a result of numerous chemical or physical modifications, carbon
negative electrodes display electrochemical performances that are improving continuously. Reversible capacities of about 450 mAh g\(^{-1}\) are now being reached [2]. However, the rapid development of electronic devices today demands much higher energy density for carbon anodes, as well as higher power density and smaller irreversible capacity.

As new allotropes of carbon have been discovered recently and are being used as energy storage materials, more functional carbonaceous materials or composites are being explored as electrode materials for lithium ion batteries. Among them, carbon nanotubes (CNTs) and graphene have been widely investigated and have advanced the science and engineering of carbon materials. CNTs can be categorized as single-wall (SWCNT), double-wall (DWCNT), and multi-wall types (MWCNT), with tube diameter less than 100 nm. It was found that CNTs can offer Li intercalation between their pseudo-graphitic layers and/or inside the central tubes [24]. The small diameters of CNTs can impose strain on the planar bonds of the hexagon. This strain causes de-localization of electrons and makes the structure more electronegative than regular graphitic sheets, which in turn, increases the degree of Li intercalation. Therefore, the reversible capacity of anodes made from CNTs can exceed 460 mAh g\(^{-1}\) and reach up to 1116 mAh g\(^{-1}\) [25].

Graphene, defined as a two-dimensional (2D) crystal, is composed of monolayers of carbon atoms arranged in a honeycomb network with six-member rings [26]. It can be considered as a basic building block for all the other dimensionalities of carbon materials, including the wrapped 0D buckyballs (fullerenes), the rolled 1D nanotubes, and the stacked 3D graphite. Therefore it can be obtained by unzipping single-wall
carbon nanotubes or exfoliation of graphite through chemical or mechanical methods [27]. Experiments show that graphene has remarkably high electron mobility, even at low temperatures, with reported values as high as 20000 cm$^2$ V$^{-1}$s$^{-1}$, and the mobilities for holes and electrons are nearly the same [28]. Graphene has been investigated as anode for lithium ion batteries due to its unique properties, such as ultra-high surface area, unique pore structure, superior electrical properties, good mechanical and thermal stability, etc. [29-32]. In addition, considerable Li storage capacity is expected, since Li can be bound not only on both sides of graphene sheets, but also on the edges, defects, disorder, and covalent sites of graphene nanoplatelets. However, low initial coulombic efficiency and large irreversible capacity handicap its real application. However, graphene is an ideal component when designed into composite electrode materials as an electrically conductive support for other high capacity materials, and its high mechanical resilience and open tubular network make it a good support for active materials [33-36]. It can also be used for freestanding design without the employment of the metal current collector to increase the specific energy of the whole battery package.

2.2.2 Lithium-Alloy anode

Lithium can be electrochemically alloyed with a number of metallic and semi-metallic elements, such as Si, Sn, Ge, Pb, P, As, Sb, Bi, Al, Au, In, Ga, Zn, Cd, Ag, and Mg [25, 37]. However, only a few elements (Si, Sn, Al, Sb, and P) have been widely investigated because they are cheap, abundant, and environmentally friendly. Among them, Sn and Si have been intensively focused on and are the most promising anodes for the replacement of graphite due to their high lithium storage
specific capacities (993 mAh g\(^{-1}\) for Li\(_{4.4}\)Sn and 4200 mAh g\(^{-1}\) for Li\(_{4.4}\)Si) and moderate operating potentials (Sn: 0.5-0.6 V and Si: 0.1 V vs. Li\(^+/Li\)).

However, the main challenge for lithium-alloy materials is the significant volume expansion and contraction during lithium intercalation and de-intercalation [38-41]. This causes cracking and crumbling, resulting in “dead volume”, which is electrically disconnected from the bulk material or the current collector. The mechanically inactive “dead volume” results in subsequent degradation of electrode performance during cycling. Therefore, many strategies have been developed to alleviate this mechanical strain and accommodate the volume change. These strategies can be mainly described in three categories, or combinations of them [25]:

(a) Minimization of particle size. When the particle size decreases, the absolute volume change of the anode material during lithium alloying/de-alloying will decrease, thus reducing the cracking. (b) Introducing a second component. Another component could be reaction inert or active (but not having the same reaction potential as lithium), forming a composite or alloy, in order to accommodate the anode material’s volume change and prevent aggregation. (c) Hollow nanostructure. The small space in the hollow area could accommodate the volume change, so as to reduce the chance that active materials will peel off.

In 1997, Fuji announced amorphous tin composite oxide (TCO) anode [42] and since then, the development of tin based anodes has been accelerating, but they were not commercialized because of the low initial coulombic efficiency. In 2005, Sony first commercialized its Nexelion battery with the anode composed of a Sn/Co/C composite with Ti metal [43]. Electrochemical lithiation of tin at elevated
temperatures showed that Sn reacts with lithium to yield seven different Li-Sn line phases within the Li-Sn diagram: \( \text{Li}_2\text{Sn}_5 \), \( \text{LiSn} \), \( \text{Li}_7\text{Sn}_3 \), \( \text{Li}_5\text{Sn}_2 \), \( \text{Li}_{13}\text{Sn}_5 \), \( \text{Li}_7\text{Sn}_2 \), and \( \text{Li}_{22}\text{Sn}_5 \) [44]. Lithium reversibly reacts with Sn, experiencing this series of Li-Sn alloys during the charge and discharge processes. Silicon shows a similar reaction mechanism with tin and lithiation at elevated temperatures has demonstrated the formation of intermetallic compounds, such as \( \text{Li}_{12}\text{Si}_7 \), \( \text{Li}_7\text{Si}_3 \), \( \text{Li}_{13}\text{Si}_4 \), and \( \text{Li}_{22}\text{Si}_5 \), in the reactions [45]. Although Si anode exhibits much high capacity than Sn and has attracted much attention for anode research recently, some technical issues remain that hinder commercialization [20].

**2.2.3 Metal oxide**

Various metal oxides have been extensively investigated as anode for lithium ion batteries. They always deliver much higher capacity than commercial graphite anode. Metal oxide anodes can be classified into three groups depending on their reaction mechanisms with lithium [25, 46-48]: (a) lithium alloy reaction (SnO\(_2\)); (b) insertion/extraction reaction (TiO\(_2\), Li\(_4\)Ti\(_5\)O\(_{12}\)); (c) conversion reaction (Fe\(_2\)O\(_3\), Co\(_3\)O\(_4\), NiO, CuO, etc.). In this doctoral work, nanostructured SnO\(_2\), TiO\(_2\), and Li\(_4\)Ti\(_5\)O\(_{12}\) are extensively investigated, so the following parts mainly focus on these three materials.

SnO\(_2\) is the most important metal oxide anode in the Li-alloy reaction category for lithium ion batteries. The reaction mechanism of SnO\(_2\) with lithium is as follows [49]:

\[
\text{SnO}_2 + \text{Li} \rightarrow \text{Sn}^+ + \text{Li}_2\text{O} \quad (2.19)
\]

\[
\text{Sn} + 4.4\text{Li} \leftrightarrow \text{Li}_{4.4}\text{Sn} \quad (2.20)
\]
In the first lithiation process, lithium ions are irreversibly introduced, forming metallic Sn and inactive Li$_2$O. Then for the second step, Sn reversibly reacts with lithium and undergoes the same process mentioned above. Because of the presence of inactive oxygen, SnO$_2$ shows less capacity (theoretical specific capacity: 783 mAh g$^{-1}$) and smaller initial coulombic efficiency than metallic Sn. However, as Sn shows very low melting point and trends to be oxidized when nanostructured, SnO$_2$ is more easily handled and stored. Moreover, the electrochemically induced Li$_2$O that is produced when SnO$_2$ reacts with lithium can work as a matrix to prevent tin aggregation. Although Fujifilm failed to commercialize their tin-based composite oxide anode, SnO$_2$ is still attracting research interest in combination with the concept of “nano”, and many nanostructures have been introduced to facilitate lithium alloying and improve cycling stability. Due to the same alloy mechanism, the large volume expansion of tin, and the destruction of the Li$_2$O matrix with cycling [50-52], strategies to alleviate the mechanical strain and volume change for Sn and Si will also work for SnO$_2$ to improve the cycling stability, mainly the use of nanostructures such as nanowires and nanorods, nanotubes, nanocomposites, and porous and hollow structures.

Owing to the advantages of high surface-to-volume ratios and excellent surface activities for one-dimensional (1D) nanostructured materials, SnO$_2$ nanowires and nanorods were investigated as anode for lithium ion batteries. Such 1D geometry can also offer direct channels for efficient electron transport while sharing the same advantages as other nanostructures, so good electrochemical performance is expected from such electrodes. SnO$_2$ nanowires synthesized by thermal evaporation combined with a self-catalyzed growth procedure [53] showed improved electrochemical
performance compared with SnO\textsubscript{2} powder and nanowires prepared by Au-assisted growth [54]. SnO\textsubscript{2} nanorods with high specific capacity were reported via a molten salt method at moderate temperatures and atmospheric pressure [55]. Later, SnO\textsubscript{2} nanorod arrays were reported, grown directly on a large-area flexible metallic substrate under the hydrothermal process, and tested as a binder-free electrode [56].

Carbon is an ideal component in SnO\textsubscript{2} based composite anodes because it could prevent the agglomeration of tin, accommodate the volume expansion, and also improve the electronic conductivity, so SnO\textsubscript{2}/carbon composites with various morphologies have been synthesized [25]. Moreover, carbon coating is always introduced in other SnO\textsubscript{2}-based nanostructured anodes, such as SnO\textsubscript{2}/carbon nanocolloids [57], SnO\textsubscript{2}/carbon nanoparticles [58], SnO\textsubscript{2}/carbon hollow nanospheres [59], etc. Besides these, SnO\textsubscript{2}-metal oxide composites have been deposited into thin films with unique porous structure by the electrospray method, such as Li\textsubscript{2}O-CuO-SnO\textsubscript{2} composite with a spherical, multideck/cage morphology [60] and SnO\textsubscript{2}-Co\textsubscript{3}O\textsubscript{4} composite with 3D reticular structure [61].

Porous and hollow structured SnO\textsubscript{2} has always been synthesized with the assistance of soft or hard templates, such as ordered mesoporous structures, hollow spheres, and nanotubes. The space in the pores or hollow structures could act as a buffer for the large volume change of tin compared with solid SnO\textsubscript{2} particles. Cho et al. prepared mesoporous SnO\textsubscript{2} anode using mesoporous silica template that delivered a reversible capacity of 800 mAh g\textsuperscript{-1} at 0.2 C [62]. Lou et al. reported a simple one-pot template-free synthesis of SnO\textsubscript{2} hollow nanostructures by the hydrothermal technique based on an inside-out Ostwald ripening mechanism involving an
ethanol-water mixed solvent and potassium stannate precursor [63]. Wang et al. reported the synthesis of polycrystalline hollow SnO$_2$ spheres in the presence of a secondary hollow carbon sphere template that had first been prepared from a primary silica template [64]. They also reported preparation of SnO$_2$-C composite consisting of porous SnO$_{24}$ nanotubes with coaxially grown CNT overlayers by the chemical vapor deposition (CVD) method in an anodized aluminum oxide AAO template [65].

Notably, although many SnO$_2$-based anode materials have been synthesized, it is still intellectually stimulating and technologically important to fabricate higher-order nanostructures and to explore their properties in applications, while keeping the methods of preparation relatively simple, low-cost, and scalable. Moreover, the large irreversible capacity resulting from the large surface areas for various SnO$_2$ nanostructures is still a big problem.

In contrast to from the Li-alloy mechanism with large volume expansion, the anode materials with the lithium intercalation reaction (TiO$_2$ and Li$_4$Ti$_5$O$_{12}$) show very small or negligible volume change when lithium ions enter the interstices of the lattice. Ti-based oxide anode materials have attracted much attention due to their advantages, which include excellent stability, low cost, and environmental friendliness [66]. In particular, Li$_4$Ti$_5$O$_{12}$ has been seriously considered as a promising anode for tomorrow’s high power lithium-ion batteries in EVs or HEVs. In spinel Li$_4$Ti$_5$O$_{12}$, as shown in Fig. 2.5, a fraction (1/6) of the Ti on the 16d sites is replaced by Li, and the electrochemically active Li ions fully occupy the tetrahedral 8a sites, i.e., (Li$_3$)$_{8a}$[LiTi$_5$]$_{16d}$O$_{12}$. Lithiation leads to 16c occupation and causes Li ions to move from 8a towards 16c positions, most likely because of Coulomb
repulsion between nearest neighbor Li ions occupying the 8a–16c positions (separated by 1.81 Å). Finally, at $x = 3$ all the electrochemically active Li ions occupy the octahedral 16c sites [67].

![Figure 2.5. Crystal structures of spinel Li$_4$Ti$_5$O$_{12}$ [68].](image)

Because the two end members, Li$_4$Ti$_5$O$_{12}$ and Li$_7$Ti$_5$O$_{12}$ have similar lattice parameters, the two-phase reaction during lithium intercalation/de-intercalation leads to negligible structural strain. This so-called “zero strain” process is favorable for very long cycle life [69]. Although the higher lithium insertion potential (1.56 V vs. Li$^+$/Li) as anode would reduce the battery voltage compared to industrially used graphite, thus decreasing the energy density, the enhanced safety arising from the elimination of solid electrolyte interphase (SEI) formation or lithium plating [67] is more important for high power batteries in EVs or HEVs. However, Li$_4$Ti$_5$O$_{12}$ delivers low capacity (theoretical specific capacity of 175 mAh g$^{-1}$) along with high working potential, both of which result in low energy density. Li$_4$Ti$_5$O$_{12}$ also suffers from quite low electronic conductivity and a moderate Li$^+$ diffusion coefficient [70-73], which would handicap its real application. So, techniques such as minimization of particle size or coatings of conductive materials have been applied.
to overcome such disadvantages [74-80]. In industry, Toshiba first commercialized high-rate lithium ion batteries, marketed as SCiB (Super Charge ion Batteries), employing Li$_4$Ti$_5$O$_{12}$ anode which can deliver charging of more than 90% of the battery capacity within 5 minutes and cycle up to 3000 charge/discharge cycles with only 10% capacity loss [81].

With similar lithium insertion properties to Li$_4$Ti$_5$O$_{12}$, TiO$_2$ has been attractive as an alternative to Li$_4$Ti$_5$O$_{12}$ with a high theoretical specific capacity at 335 mAh g$^{-1}$ or 1 lithium per TiO$_2$. Many polymorphs of TiO$_2$ have been reported so far, such rutile, anatase, brookite, TiO$_2$(B) (bronze), ramsdellite, hollandite, columbite, and baddeleyite. Anatase, rutile and TiO$_2$(B) are the most investigated for electrochemical activity with lithium [82].

Anatase TiO$_2$ has a tetragonal body-centered structure with space group $I4_1/amd$, and consists of strongly distorted TiO$_6$ octahedra sharing two adjacent edges with two other octahedral, so that planar double chains are formed which can be considered as a 1D zigzag chain. The stacking of these chains in anatase TiO$_2$ leads to empty zigzag channels in the anatase framework [83]. Figure 2.6(a) depicts the possible positions of lithium ions in anatase. Diffusion of Li ions in an anatase framework occurs along a reaction path connecting the octahedral interstitial sites [84-86]. Wagemaker et al. [87] reported that anatase undergoes spontaneous phase separation into Li$_{0.01}$TiO$_2$ and Li$_{0.6}$TiO$_2$ domains during Li insertion on a scale of several tens of nanometers. With Li insertion the symmetry of the anatase unit cell decreases up to $x = 0.5$ (Li$_{0.5}$TiO$_2$), where its original $I4_1/amd$ space group transforms into the orthorhombic $Pmn2_1$ space group due to loss of symmetry in the $y$ direction [88],
accompanied by a decrease of the unit cell along the c-axis and an increase along the b-axis [82]. Therefore, $x = 0.5$ is consistently reported as the maximum lithium content insertion into bulk anatase [89]. However, recent reports show increased specific capacity from anatase nanostructures with high surface area. Results reported by Zhou et al. on TiO$_2$ nanotubes with mesoporous walls within AAO membranes showed a Li-storage capacity of 303 mAh g$^{-1}$ (Li$_{0.9}$TiO$_2$) at a charge/discharge current density of 1 A g$^{-1}$ [90]. Kim and Cho [91] reported that anatase TiO$_2$ nanotubes prepared by annealing mixed H$_2$Ti$_2$O$_5$·H$_2$O and anatase TiO$_2$ nanotubes at 300 °C exhibited first discharge capacities of 296 mAh g$^{-1}$ (Li$_{0.88}$TiO$_2$).

Rutile is the most thermodynamically stable polymorph of TiO$_2$ under standard conditions. It has a tetragonal $P42/mnm$ space group, consisting of TiO$_6$ octahedra sharing edges in the c-direction and corners in the ab-plane. The preferential site for lithium insertion is the oxygen octahedral vacancy, as shown in Figure 2.6(b) [66]. It is believed that Li$^+$ diffusion in rutile is highly anisotropic. Experimental and simulation results have shown that the Li$^+$ diffusion coefficient along the c-direction is approximately $10^{-6}$ cm$^2$ s$^{-1}$, while it is only $10^{-15}$ cm$^2$ s$^{-1}$ in the ab-plane, indicating that Li diffusion is nearly one dimensional along c-axis channels [92-94]. Li insertion into bulk rutile is usually reported to be negligible at room temperature. However, nanometer-sized rutile shows a much higher electroactivity towards Li intercalation compared to its micrometer-sized counterparts. Hu et al. reported that up to 0.8 mol of lithium could be inserted into nanometer-sized rutile (Li$_{0.8}$TiO$_2$) with resulting excellent high rate performance as well [95].
Like anatase and rutile, TiO$_2$(B) is composed of corrugated sheets of edge and corner sharing TiO$_6$ octahedra [96], as shown in Figure 2.6(c). TiO$_2$(B) shows a system of one-dimensional infinite channels in molecular sheets which follow the [001] direction, in which transport and exchange of small cations can occur. Lithium ions can thus be inserted into these channels, where they are expected to be very mobile, making TiO$_2$(B) a superior lithium intercalation host compared with anatase and rutile. The structure of TiO$_2$(B) is more open than for the other polymorphs which may also enhance Li$^+$ transport. TiO$_2$(B) is the least dense polymorph of TiO$_2$, with a density of 3.73 g cm$^{-3}$ compared with 3.89 and 4.25 g cm$^{-3}$ for anatase and rutile, respectively [82, 83]. TiO$_2$(B) nanowires prepared by Armstrong et al. via the hydrothermal technique could intercalate lithium up to a capacity of 305 mAh g$^{-1}$ (Li$_{0.91}$TiO$_2$) [97]. There was excellent reversibility after the 1$^{st}$ cycle, 99.8%. A further study exhibited full cells constructed with a TiO$_2$(B) nanowire anode and either a LiFePO$_4$ or a LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode. Average cell potentials of approximately 2 and 3 V were obtained, respectively. Cycling stability was very good, as was rate capability, with 80% of the low-rate capacity being retained at 5 C [98].
2.2.4 Sulfides

Layered structured transition-metal dichalcogenides were investigated as cathode hosts for lithium intercalation. In this family, MoS$_2$ or TiS$_2$ were commercialized by Moli Energy and Exxon Mobile in the 1970s in lithium batteries [9]. However, due to the safety problem arising from the lithium metal anode in the lithium battery, it was replaced by lithium-ion batteries. These 2 V (vs. Li$^+/\text{Li}$) sulfide materials also motivated a search for a Li-insertion cathode material having a lower Fermi energy. As higher voltage cathodes were explored, sulfides such as MoS$_2$ [99-101], WS$_2$ [102-103], and SnS$_2$ [104] were investigated as cathode hosts for lithium-ion batteries.
[102], CoS8 [103], ZnS [104], and Al2S3 [105] have been recently investigated as anode materials. MoS2 shows similarity to graphite with its sandwiched S-Mo-S layers bonded by van der Waals forces. In analogy to carbon nanotubes, MoS2 nanotube was synthesized, and lithium could be intercalated. Recently, two-dimensional graphene has been a hot research topic and shows different lithium storage performance as anode from the other allotropes. MoS2 was prepared as 2D graphene-like nanosheets [106] and showed unique photo-illumiance [107] and transistor properties [108].

![Figure 2.7. Schematics of single layer MoS2 and graphene: (a) cross-sectional view; (b) top view.](image)

2.2.5 Nitrides/Phosphides/Fluorides

Besides sulfides, transition metal nitrides, phosphides, and fluorides have also been reported as anode materials for lithium ion batteries [109], such as M-X compounds (M = Co, Fe, Ni, Mn, etc.; X = N, P, F), delivering high capacities ranging from 400 mAh g⁻¹ to 1400 mAh g⁻¹ [18]. The reaction mechanism in such binary M-X systems during lithium charge/discharge processes is the same as for transition metal oxides.
and sulfides, i.e., reversible conversion reactions. Although such materials exhibit high lithium storage capacity, due to the conversion reaction mechanism, their industrial application is still handicapped because of some disadvantages in thermodynamics, for example, high surface energy, large interfacial area, high overpotential, large voltage hysteresis, and so on.

In summary, to date, the usual anode materials for commercial lithium-ion batteries are still carbon based materials, which are the same as for the first generation lithium-ion battery developed two decades ago for portable electronics, such as mobile phones, laptop computers, cameras, etc. Carbon anode can not meet all the requirements for present and future large-scale energy sources in various applications, such as electric vehicles and hybrid electric vehicles. Batteries with different operating voltage ranges, long, stable cycling life, high energy density, and high power density are needed to meet the requirements of energy-hungry devices. In order to achieve these critical targets, next generation anode materials should be explored. Amongst all the above anode candidates, metal oxides are stable under ambient conditions and easy to handle, as well as having the potential for use in large-scale applications. In this study, two types of metal oxide anode materials were systematically investigated, i.e., SnO₂ and Ti-based oxides (TiO₂ and Li₄Ti₅O₁₂). The former features high capacity and high energy, while the latter feature high operating voltage, stable cycling, and high rate performance. Various nano-structures and their carbon composites were fabricated to increase reaction sites, decrease the ion diffusion length, and increase electronic conductivity, thus improving electrochemical performance. Moreover, MoS₂ and its composites were also investigated in this doctoral work. This is because recently, two dimensional
graphene exfoliated from layered graphite has shown unique electronic and electrochemical properties, so that it is now widely studied, generating many new research topics. In analogy to graphite, layered, sandwich structured MoS₂ could also be exfoliated into single layers. Such new features could result in superior electrochemical performance if it is used as anode material for lithium ion batteries.

References


CHAPTER 3 EXPERIMENT

3.1 General procedure

The overall experimental procedures are described in Figure 3.1. Nanostructured electrode materials were prepared through various synthesis methods and characterized by different physical techniques. Electrochemical measurements were conducted involving the application of these materials as the electrodes in coin-type lithium ion batteries. Structure and morphology of the materials after electrochemical cycling were also investigated.

![Figure 3.1 The overall experimental procedure and techniques.](image-url)
3.2 Chemicals

Detailed information on the chemicals used in this study is summarized in Table 3.1.

Table 3.1 Chemicals used in the present work.

<table>
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<th>Formula</th>
<th>Grade</th>
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### 3.3 Fabrication procedure

The electrode nanomaterials investigated in this work were synthesized via various different chemical reactions. In this section, these techniques are explained in sequence, and the detailed experimental parameters will be discussed in the following chapters.

#### 3.3.1 Molten Salt Reaction

Molten salt method, also known as the flux method, is achieved at a temperature high enough that the salts are melted. The employed salts are simple, usually ionic and
stable compounds. In the case of one salt, it would only melt into a liquid when the temperature is above its melting point under normal pressure. However, a mixture of two or more salts could form a eutectic system that preserves the liquid phase at temperatures lower than the melting point of any component. Such molten salts function like a fluid and can serve as solvents for a chemical reaction with good heat transfer characteristics. In comparison with the conventional solid-state reaction, the molten salt method shows an accelerated reaction rate and controllable particle morphology, because the salt melt exhibits higher ion diffusion rates and strong dissolving capability.

3.3.2 Hydrothermal synthesis

The hydrothermal method is a typical wet-chemical treatment which is well known in the fields of mineralogy and geology for the formation of minerals. The term hydrothermal was first used to describe the action of water at elevated temperature and pressure in bringing about changes in the Earth’s crust leading to the formation of various rocks and minerals. Today, the hydrothermal technique has profound effects in several branches of science and technology, and has led to the appearance of several related techniques, such as synthesis of new phases or stabilization of new complexes, crystal growth of several inorganic compounds, preparation of finely divided materials and microcrystallites with well-defined size and morphology for specific applications, etc. Hydrothermal reaction can be defined as any heterogeneous chemical reaction in the presence of a solvent (whether aqueous or non-aqueous) above room temperature and at pressure greater than 1 atm in a closed system. The factors in a hydrothermal reaction, involving solvent species, the degree of solvent filling in the liner, the concentration of the precursors, temperature, pH value, and the use of a surfactant, could affect the final products in terms of purity,
phase, and crystal structure and morphology. The hydrothermal reactions in this doctoral work have taken place in Teflon liners sealed in stainless steel autoclaves.

### 3.3.3 Electrospinning

Electrospinning, as a relatively simple and versatile method for preparing fibrous mesostructure, originates from the fabrication of polymer fibers and has been extended to the preparation of many advanced functional ceramics and composites. This technique shares characteristics of both electrospraying and conventional solution drying spinning of fibers, applying an electrical charge to draw very fine (typically on the micro- and nanoscale) fibres from a liquid. The basic experimental set-up for electrospinning in the present work is illustrated in Figure 3.2. It consists of collector (usually a metal plate and connected to the ground), a metallic needle acting as spray nozzle, along with a syringe to host the polymer solution, and a high voltage direct current power supply connecting the collector and the needle. In the experiment, pendent polymer solution drops at the nozzle could be highly electrified after the application of a high voltage, and the induced charges are evenly distributed over the surface, causing electrostatic repulsion between the surface charges. At the same time, the electrified drops also experience the electrostatic force from the external electric field between the needle and the collector. The electrified polymer drops then undergo a stretching and whipping process, leading to the formation of a long and thin thread and deposition onto the collector. The polymer solution can be fed at a constant and controllable rate from a solution container with the use of a syringe pump.
3.3.4 Chemical Solution Reaction

Two chemical solution reactions were involved in this doctoral work. One is chemical lithiation of commercial MoS$_2$ powder by soaking it in butyllithium (1.6 M in hexane) to obtain Li$_x$MoS$_2$ for further product preparation. Another is the refluxing process, the experimental set-up for which shown as Figure 3.3. The reactants are placed in a round bottom flask connecting to a condenser open only at the top. The reaction is conducted at an elevated temperature that is above the solvent’s boiling point. The solvent vapours condensate with the aid of cooling water and return to the flask. The fluxing technique is used to supply energy to reactions over a long time in chemistry and to accelerate the reaction. The advantage of this technique is that the refluxing can be left for a long period of time without the need for adding more solvent.
3.3.5 Anodization

Anodization is an electrolytic passivation process used to increase the thickness of the oxide layer on the surface of a metal. Here, anodization was employed to prepare TiO$_2$ nanotube arrays. A schematic diagram of the experimental set-up is shown as Figure 3.4. A titanium plate was placed at the positive end of a 20 V direct current power supply, while platinum foil served as the counter electrode. With the application of the voltage, Ti was anodized to form TiO$_2$ on the Ti plate surface, and the reaction is expressed as equation (3.1). At the same time, this oxide would dissolve in the acidic 5% HF electrolyte by equation (3.2). By balancing the electrochemical TiO$_2$ formation reaction and the chemical TiO$_2$ dissolution reaction by controlling system factors such as temperature, acidity, ion flux, reaction time, etc., the tip area could be more active than the wall area and thus form a nanotube.

\[
\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ \quad (3.1)
\]

\[
\text{TiO}_2 + 6\text{HF} \rightarrow [\text{TiF}_6]^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+ \quad (3.2)
\]
3.3.6 Solid State Reaction

Conventional solid state reaction involves heating two or more solids (usually mixed by hand in a mortar or by ball milling) to obtain solid products in the absence of a solvent. The limiting factor for solid state reaction is the solid diffusion, governed by Fick’s Law:

\[ J = -D \frac{dc}{dx} \]  

where \( J \) is the flux of diffusing species, \( D \) is the diffusion coefficient, and \( \frac{dc}{dx} \) is the concentration gradient. \( D \) increases with temperature. Because of the low diffusion in solids, high treatment temperature and long heating time are always required for solid state reactions. In order to facilitate diffusion, the powder is usually pressed into pellets at high pressure before sintering. For some reactions, grinding, pressing and sintering may need to be repeated several times to obtain pure phase products.

3.3.7 Spray Pyrolysis

The spray pyrolysis experimental set-up is illustrated in Figure 3.5. Well mixed precursor solution was fed to a nozzle by a peristaltic pump at a constant and
controllable rate. It was then sprayed into a vertically placed three-zone tube furnace with the aid of a carrier gas through a compressor. The solution droplets pass through the furnace quickly (could be less than one second) where they are pyrolyzed under high temperature and turned into a fine product powder, which is subsequently sucked into the sample collector via the suction system. A well mixed precursor is favourable for high purity product, and the solution droplets sprayed under the force of gravity make it easy to obtain products with spherical and hollow nanostructures. Moreover, the continuous operation means that this spray technique is suitable for industrial application.

![Diagram of spray pyrolysis](image)

**Figure 3.5** Schematic illustration of experimental set-up for spray pyrolysis.

3.4 Techniques for characterization

The techniques for characterization of the as-prepared materials will be introduced in detail in the following section. Most of the characterizations were achieved in our institute and the Intelligent Polymer Research Institute (IPRI) under the Australian Institute of Innovative Materials (AIIM), with the exception of those at the
Australian Nuclear Science and Technology Organisation (ANSTO) and the Australian Synchrotron (AS).

### 3.4.1 X-ray powder diffraction

**Laboratory X-ray diffraction**

X-ray diffraction (XRD) is non-destructive analytical X-ray scattering technique revealing information about the crystallographic structure, chemical composition, and physical properties of materials. X-ray radiation is a type of electromagnetic wave with wavelengths on the order of angstroms (~1 Å), in the same order as the atomic plane $d$-spacing in crystals. So, interference occurs at a certain angle from the sets of atomic planes, and the scattering is unique to the crystal structure. The resultant pattern could be used to analyse the sample structure by scanning the sample through a range of angles ($2\theta$), as then all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to $d$-spacing allows identification of a mineral because each mineral has a set of unique $d$-spacing. The constructive interference between incident rays and the elastic scattering of X-rays from the electron clouds of the individual atoms of the crystal follow Bragg’s Law:

$$n\lambda = 2d \sin \theta \quad (3.4)$$

where $n$ is an integer, $\lambda$ is the wavelength of the incident X-ray beam, $d$ is the distance between atomic planes in a crystal, and $\theta$ is the angle of incidence. X-ray powder diffraction is commonly available in laboratories to characterise the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples. In this study, all the XRD measurements were performed in the step-scanning mode $\theta$ - $2\theta$ with a Cu Ka radiation source ($\lambda = 1.5406$ Å).
Synchrotron X-ray powder diffraction (SXRD)

Laboratory-based X-ray powder diffraction techniques are inherently resolution-limited in the range of observations (d-space range), the signal-to-noise ratio, and the shape and width of observed reflections. Synchrotron-based instruments could overcome such limitations and give the resolution required to determine and refine accurate structures of even moderately complex materials from powder samples. A synchrotron light source uses particle accelerators to produce a beam of high energy electrons which are then circulated in a storage ring to create synchrotron light. The advantages of synchrotron X-ray powder diffraction are higher flux with improved signal to noise ratio and good time resolution; high angular and energy resolution with a large and accessible dynamic d-space range; narrower peak width and simpler shape; and tunable and monochromatic X-rays with the ability to penetrate bulky sample cells while avoiding or exploiting absorption edges. SXRD measurements were conducted at the Australian Synchrotron (AS) powder diffraction beamline.

3.4.2 Neutron powder diffraction

Neutron diffraction, in the application of neutron scattering, follows the same diffraction law as X-ray diffraction. However, it exhibits advantages compared to X-ray from the following aspects due to the characteristics of neutrons compared to X-rays. Neutron scattering involves particle waves and interacts with the nucleus, so the neighbouring atoms or isotopes in a crystal can be discriminated. Neutron diffraction exhibits lower absorption than X-ray because the space in a nucleus is much smaller than in its electron cloud. Neutron scattering power is independent of $2\theta$, and the scattering lengths over elements are fairly constant, so therefore, light elements can be seen in the neutron beam, such as hydrogen, lithium, oxygen, etc.
Especially for a material with light elements in the presence of heavy ones, neutron diffraction is powerful technique for the measurements. Neutron diffraction can also detect magnetic materials owing to its magnetic dipole moment. High intensity neutron powder diffraction measurements in this study were conducted on the Wombat beamline at the Australian Nuclear Science and Technology Organisation (ANSTO) with optimized wavelength.

### 3.4.3 Raman spectroscopy

Raman spectroscopy is an important technique to investigate vibrational, rotational, and other low frequency modes in a structure. Based on a light scattering technique, Raman measurement can be considered as a process where a photon of light interacts with the molecule or lattice (phonons) in a sample to produce scattered radiation of different wavelengths. In the measurement, the incident monochromatic radiation (usually from a laser) interacts with the sample, which could result in both elastic scattering (Rayleigh scattering) and inelastic scattering (Stokes and anti-Stokes Raman scattering), which shows an energy shift from the incident radiation, unlike Rayleigh scattering. This energy shift (in the form of frequency or wavelength) is detected and recorded, providing chemical and structural information on materials due to the interaction between the incident electromagnetic waves and the molecular rotations and vibrations, or electronic level transitions. In this study, Raman spectroscopy was conducted on a JOBIN Yvon Horiba Raman Spectrometer HR800 with a laser at 632.8 nm.

### 3.4.4 Scanning electron microscopy and Energy-dispersive X-ray spectroscopy

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons, and
collects and analyses the signals from the specimen generated electrons, which contain the information about the sample’s surface topography, composition, and other properties. Signals in a SEM include secondary electrons, back-scattered electrons, characteristic X-rays, light, specimen current, and transmitted electrons. Secondary electron detectors are common in all SEMs. Secondary electrons are produced on the specimen surface and are detected by a suitable detector. The amplitude of the secondary electron signal varies with time according to the topography of the specimen surface. Then, the signal is amplified and used to display the corresponding specimen surface information. Secondary electron imaging can produce very high resolution images revealing details less than 1 nm in size. Energy-dispersive X-ray spectroscopy (EDS) is one of the variants of X-ray fluorescence spectroscopy for the elemental analysis or chemical characterization of a sample. Because each element has a unique atomic structure, allowing X-rays to identify them from one another, the EDS technique analyses the information from X-rays emitted from a specimen as it is hit by electrons, giving elemental information. In this work, SEM (JEOL JSM 6460A) and field-emission SEM (FE-SEM, JEOL 7500), and the EDS system supplied with the microscopes were all used.

3.4.5 Transmission electron microscopy

Transmission electron microscopy (TEM) is a microscopic surface analysis technique to identify the atomic structure of a material. By exposure of an ultra-thin specimen to a high energy electron beam (e-beam), the internal structure of a specimen can be imaged from the collected transmitted electrons after the interaction with the specimen. TEMs are capable of imaging at very high resolution, owing to
the small de Broglie wavelength of electrons. Selected area electron diffraction (SAED) can also be performed inside a transmission electron microscope, revealing crystallographic information on the samples. In this technique, atoms in a specimen act as a diffraction grating to the high-energy electrons from the electron gun. According to the crystal structure of the sample, some fraction of the electrons are scattered to particular angles, while others directly pass through the sample. As a result, there will be a series of spots on the image, with each spot corresponding to a satisfied diffraction condition of the sample’s crystal structure. In this work, TEM images were collected using a JEOL 2011 200 keV transmission electron microscope.

### 3.4.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface chemical analysis technique that works by irradiating a beam of monochromatic X-ray on a material while simultaneously measuring the kinetic energy and number of electrons that escape from the surface of the materials being analysed. XPS can probe the elemental composition, chemical state, or electronic state of the elements. It is able to detect all elements except for hydrogen and helium and usually analyses the top atomic layers of a sample (top 1-10 nm), with detection limits for most of the elements in the parts per thousand range. XPS instruments mainly consist of an ultra-high vacuum chamber, sample holder, X-ray source, and photoelectron energy analyser and detector. The electron binding energy \( E_{binding} \) in certain chemical species and bonding conditions can be determined by the following equation:

\[
E_{binding} = h\nu - (E_{kinetic} + E_{sof}) \tag{3.5}
\]
where \( h \nu \) is the energy of the X-ray photons, \( E_{\text{kinetic}} \) is the kinetic energy of the photoelectrons, and \( E_{\text{wf}} \) is the work function of the spectrometer.

### 3.4.7 Surface area measurement

Based on the Langmuir theory, with the hypothesis of monolayer gas adsorption on solid surfaces, Brunauer, Emmett, and Teller (BET) extended the theory to absorption of multilayer gas molecules, and the BET theory was developed as an important analysis technique for the measurement of the specific surface area of a material. The BET equation is expressed as:

\[
\frac{1}{W[(P_0/P) - 1]} = \frac{C - 1}{W_m C} \left( \frac{P}{P_0} \right) + \frac{1}{W_m C}
\]

(3.6)

in which \( W \) is the weight of gas absorbed at a relative pressure \( P/P_0 \) and \( W_m \) is the weight of adsorbate constituting a monolayer of surface coverage. The term \( C \) is the BET constant. In BET analysis, \( 1/W[(P_0/P) - 1] \) is plotted as a function of \( P/P_0 \). Within the range of \( 0.05 < P/P_0 < 0.35 \), the function remains linear. \( W_m \) can be obtained from the slope and the intercept. The specific surface area \( (S_{\text{BET}}) \) is expressed as:

\[
S_{\text{BET}} = \frac{W_n N_s}{aV}
\]

(3.7)

Where \( N \) is Avogadro’s number, \( s \) is the adsorption cross section of the adsorbing species, \( V \) is the molar volume of the adsorbate, gas and \( a \) is the mass of adsorbent.

In this study, the BET measurements were conducted on a Quantachrome Nova 1000 nitrogen gas analyser in 15-points mode at 77 K.
3.4.8 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a weight analysis technique to determine the weight changes in a material in relation to temperature changes. In this study, TGA was applied to determine the carbon contents in metal oxides/carbon electrode composites by heating samples to high temperature (up to 800 °C) in air atmosphere. Carbon contents were calculated based on the weight difference as the weight loss corresponds to the burn-off of carbon.

3.4.9 Magnetic measurements

Magnetic measurement is a fundamental technique to characterize various types of magnetic materials. The nanosize effect in some materials with small dimensions, especially at the edge areas of the structure, could result in a magnetic signal due to the abnormal behaviour of electrons. In this study, magnetic hysteresis loops of restacked MoS\textsubscript{2} were collected using a conventional physical properties measurement system (PPMS) at room temperature with fields up to 1 T.

3.5 Electrode preparation and coin-cell assembly

The working electrodes were prepared by mixing the as-prepared electrode materials, carbon black (conductive agent) and polyvinylidene difluoride (PVDF, a binder, dissolved in N-methyl-2-pyrrolidinone) at a typical weight ratio of 8:1:1 and pasting onto copper foil (18 microns in thickness) with an area of 1 cm\textsuperscript{2} for each electrode. The electrodes were dried in a vacuum oven at 80 to 110 °C for at least 6 hours. After pressing at a pressure of about 20 MPa, the electrodes were then transferred into an argon-filled glove box for coin cell assembly. The weight of each electrode was
calculated from the weight difference of the copper foil before and after application of the electrode material paste.

The coin cells were assembled in a glove box (Mbraun, Unilab, Germany) with H₂O and O₂ levels less than 1 ppm. CR2032 coin type cells were employed in the battery tests, with lithium foil serving as counter electrode and a porous Celgard polypropylene membrane as separator. The electrolyte consisted of a solution of 1 M LiPF₆ dissolved in a mixture of the solvents ethylene carbonate (EC) and dimethyl carbonate (DMC), in a volume ratio of 1:1, or EC and diethyl carbonate (DEC) in a volume ratio of 1:2, respectively. The coin cell component stacking sequence is shown in Figure 3.6.

Figure 3.6 Component stacking sequence in a coin cell.
3.6 Electrochemical measurements

Electrochemical measurements to investigate the materials were conducted on the coin cells, including galvanostatic charge/discharge testing, cyclic voltammetry, and electrochemical impedance spectroscopy.

3.6.1 Galvanostatic charge-discharge

The capacity and cycling performance of the materials were investigated by galvanostatic charge/discharge tests using constant current density mode. The charge or discharge capacity \( Q \) equals the total electron charge in each process and can be calculated from the recording current and the time \( Q = I \times t \). The coin cells were tested on Land C T2001A battery testers (Wuhan Kingnuo, China).

3.6.2 Cyclic voltammetry

Cyclic voltammetry (CV) is a widely used technique to investigate the thermodynamics and kinetics of electron transfer in an electrochemical reaction in the working electrode. The working electrode potential is ramped linearly versus time, and the corresponding current is recorded, so the data is plotted of current as a function of potential. The working electrode’s potential ramp is inverted after reaching a set end. The current will increase and form a peak when the potential reaches the point where a reaction occurs. In a redox reaction, pairs of oxidation and reduction peaks appear when potential is ramped in different directions. The change of potential as a function of time is called the scan rate. The relationship between the peak current \( i_p \) and scan rate follows the Randles-Sevcik equation:

\[
i_p = (2.69 \times 10^5)n^{3/2}ACD^{1/2}v^{1/2}
\]  

(3.8)
where $n$ is the number of moles of electrons transferred in the reaction, $A$ is the area of the electrode, $C$ is the analyte concentration, $D$ is the diffusion coefficient, and $v$ is the scan rate. In this work, the CV data were collected on a CHI660 electrochemical workstation.

### 3.6.3 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a technique to examine electrochemical processes, such as electron transfer, mass transport, and chemical reactions. EIS can be performed in potentiostatic (PEIS) or galvanostatic (GEIS) mode. In PEIS, impedance measurements are conducted by applying a sine wave around a potential $E$ that can be set to a fixed value or a value that is relative to the working electrode equilibrium potential over a range of frequencies. A typical impedance spectrum consists of a low frequency semicircle resulting from the kinetic processes and a high frequency tail corresponding to the diffusion processes. The GEIS technique is very similar to PEIS, except that the current is controlled instead of the potential. In this study, potentiostatic mode was employed, and all the EIS data were collected via CHI660 or Ametek PARSTAT 2273 electrochemical workstations.
CHAPTER 4 Ultra-fine Porous SnO₂ and SnO₂/Carbon Composite

4.1 Introduction

Since the successful synthesis of mesoporous silica by using a molecular self-assembly template in 1992, much work has been performed on metal oxides by the same approach, with wide application as catalysts, electronic materials and battery electrodes [1]. In lithium ion battery application, the porous structure always shows a large specific surface area and small particle size or wall size, which could provide a large electrolyte/electrode interface, while the nanostructure decreases the diffusion length, so both of these aspects will benefit the electrochemical performance. Because the electrode reaction in a rechargeable lithium battery relies on the simultaneous intercalation of Li⁺ and e⁻ into the active intercalation host, the rate of intercalation thus influences the power of the battery.

Although SnO₂ is considered as a promising anode material, exhibiting higher theoretical specific capacity (781 mAh g⁻¹) compared with conventional graphite electrode (372 mAh g⁻¹) [2-4], the significant volume expansion and contraction during lithium intercalation and de-intercalation [5, 6] prohibits its commercial application. Porous structure has been employed to effectively improve the electrochemical performance of SnO₂ because the pores can accommodate the volume change, thus improving the cycling stability. Carbon coating is another conventional method to improve the SnO₂ electrochemical performance, because carbon can inhibit the agglomeration of tin during charge/discharge cycles and also enhance the electronic conductivity. However, most types of porous SnO₂ have been
prepared through hard template or soft template synthesis, which are expensive or not easy to control [7-9].

In this chapter, a simple, easily scaled-up and low temperature molten salt method was applied to synthesize ultra-fine porous SnO$_2$ nanostructures and SnO$_2$/carbon composite by adding malic acid. The molten salt method can result in very fine morphology due to the large viscosity and dielectric behaviour of the eutectic system. 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. This technique could also be used to produce other metal oxides, such as nanosized magnetic or electrode materials. Moreover, in-situ carbon incorporation could give better results than subsequent carbon coating and leads to complete amalgamation and good interface affinity between the SnO$_2$ and the carbon, thereby ensuring structural stability of the composite during discharge-charge cycling.

4.2 Experimental

4.2.1 Sample Preparation

Porous SnO$_2$ nanopowder was synthesized by a molten salt method. 100 mmol of lithium nitrate (Aldrich), 100 mmol of lithium hydroxide monohydrate (Aldrich), and 10 mmol of tin(II) chloride dehydrate (Sigma-Aldrich) were mixed in an agate mortar to obtain a homogeneous mixture. The SnO$_2$/C composite was prepared in the presence of 10 mmol malic acid. Then, 50 mmol hydrogen peroxide (Sigma-Aldrich) was added into the mixture, which was stirred for 24 hrs. The mixture was then given
a heat-treatment at 120 °C for 4 h in a vacuum oven, followed by further heat treatment in air at 300 °C for 3 h in a muffle furnace. After cooling down, the product was separated from the eutectic mixture by washing with a large amount of de-ionized water and by centrifugation, and then the product was dried under vacuum at 60 °C for 24 h.

4.2.2 Electrochemical Characterization

The electrode was prepared by mixing 80 wt% as-prepared SnO₂ or SnO₂/C composite as active material with 10 wt% carbon black (Super P, MMM, Belgium) and 10 wt% polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidinone (NMP) solvent to form a homogeneous slurry, which was then spread on copper foil. The coated electrodes (average thickness of ~50 μm) were dried in a vacuum oven at 110 °C for 24 h and then pressed. Electrochemical measurements were carried out using CR 2032 coin-type cells that were assembled in an argon-filled glove box (Mbraun, Unilab, Germany) by stacking a porous polypropylene separator containing liquid electrolyte between the composite electrode and a lithium foil counter electrode. The electrolyte used was 1M LiPF₆ in a 50:50 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC), provided by MERCK KgaA, Germany. The cells were galvanostatically charged and discharged in different voltage ranges at a constant current density of 100 mA g⁻¹. All the electrochemical tests were carried out at room temperature (25 °C).

4.3 Physical Characterization

The overall synthetic procedure is described in Figure 4.1. 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 [10].
Furthermore, the melted salts with their low melting point are helpful in hindering the growth of SnO₂ particles. When cooled down, the SnO₂ particles were surrounded by the salts, which were then washed away by de-ionized water, leaving pores behind, thus generating ultra-fine porous nanostructures.

Figure 4.1 Schematic model of synthetic procedure: (a) mixed raw materials; (b) solid molten salts and SnO₂; (c) porous and nanosized SnO₂.

Temperature is a crucial parameter for crystal growth, so the temperature option is the first consideration. Figure 4.2 shows the thermogravimetric analysis (TGA) result on the mixed raw materials. No weight losses above 250 °C can be observed from the curve. Since low temperatures are typically favourable for the synthesis of nanostructures and porous structures, 300 °C was chosen in the experiment to ensure that the reaction occurred in the liquid phase.
**Figure 4.2** TGA curve of raw material consisting of SnCl₂·2H₂O mixed with LiOH and LiNO₃ (molar ratio 1:1).

**Figure 4.3** X-ray diffraction patterns of the as-prepared (a) SnO₂/C nanocomposite and (b) SnO₂ nanopowder.

The structure of the as-prepared SnO₂ nanopowder and SnO₂/C composite were characterized using X-ray diffraction, as shown in Figure 4.3. All reflections for both samples are in good agreement with a tetragonal rutile structure (JCPDS 41-1445) belonging to the space group P4₂/mnm (136). There is no notable peak shifting or
significant intensity variation between the bare SnO$_2$ sample and the SnO$_2$/C composite. The highly broadened peaks indicate that the as-prepared SnO$_2$ and SnO$_2$/C composite are composed of SnO$_2$ crystallites of very small size. The calculated mean crystallite size of SnO$_2$ estimated from Scherrer’s formula are 3.6 and 4.1 nm for the bare SnO$_2$ and SnO$_2$/C nanocomposite, respectively, based on the (110), (101), and (211) peaks.

The morphology images are displayed in Figure 4.4. The transmission electron microscope (TEM) images show that the crystal size of the as-prepared SnO$_2$ is around 5 nm, and lattice fringes are present with $d$ spacing values of 0.318 nm, corresponding to the (110) planes of SnO$_2$. There are also a great many pores among the nanoparticles, and the average pore width calculated from Brunauer-Emmett-Teller (BET) measurements is 2.015 nm. The TEM images show that the SnO$_2$ nanoparticles in the SnO$_2$/C nanocomposite are dispersed in an amorphous carbon matrix. High-resolution TEM images (Figure 4.4(d)) clearly show lattice fringes with spacings of about 0.32 and 0.27 nm, corresponding to the (110) and (101) planes of SnO$_2$, respectively. The corresponding indexed ring patterns in the inset are consistent with the X-ray diffraction pattern, and the blurred ring patterns can be derived from the amorphous carbon phase. BET analysis shows that the SnO$_2$/C nanocomposite possesses a slightly larger pore size and volume, as illustrated in Table 1. These pores provide void space to accommodate the volume expansion during Li$^+$ insertion [11, 12]. According to the TGA results, the weight percentage of amorphous carbon in the as-prepared composite is about 12 wt%.
Figure 4.4 TEM images (a, b) of the as-prepared nano-SnO$_2$; (c, d) SnO$_2$/C nanocomposite prepared by molten salt method. Indexed diffraction pattern (inset in (d)) confirms the presence of SnO$_2$ nanoparticles and that the nanoparticles are embedded in an amorphous carbon matrix.

Table 4.1 Results of specific surface area measurements using low temperature liquid nitrogen absorption.

<table>
<thead>
<tr>
<th></th>
<th>SnO$_2$</th>
<th>SnO$_2$/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m$^2$ g$^{-1}$)</td>
<td>158.4017</td>
<td>125.7393</td>
</tr>
<tr>
<td>Pore volume (cm$^3$ g$^{-1}$)</td>
<td>0.079797</td>
<td>0.103043</td>
</tr>
<tr>
<td>Average pore width (nm)</td>
<td>2.01506</td>
<td>3.27798</td>
</tr>
</tbody>
</table>
4.4 Electrochemical performance

The first discharge (Li insertion)-charge (Li extraction) curves of the SnO\textsubscript{2}/C nanocomposite and the bare SnO\textsubscript{2} electrodes were obtained in the voltage range of 0.01-3 V at a current density of 100 mA g\textsuperscript{-1} (Figure 4.5(a)). The SnO\textsubscript{2}/C nanocomposite shows a much higher reversible capacity (848 mAh g\textsuperscript{-1}) than the bare nano-SnO\textsubscript{2} (643 mAh g\textsuperscript{-1}), where the specific capacities are calculated with respect to the weight of active materials. Furthermore, the SnO\textsubscript{2}/C nanocomposite electrode exhibits an initial coulombic efficiency of about 50%, which is remarkably higher than that of the bare nano-SnO\textsubscript{2} (43.2%).

The cycling performance (Figure 4.5(b)) of the as-prepared samples was characterized by charge/discharge cycling over different voltage ranges and compared with the performance of commercial SnO\textsubscript{2} nanoparticles and of SnO\textsubscript{2} nanowires prepared in our laboratory [13]. The open symbols show the cycling performance of the as-prepared and the commercial SnO\textsubscript{2} in the voltage range of 0.01-3 V. Both the materials show a decrease in discharge capacity with time. However, obviously, the as-prepared ultra-fine porous nanopowder shows a much higher discharge capacity than the commercial powder. The solid symbols compare the cycling performance of the as-prepared SnO\textsubscript{2} nanoparticles and SnO\textsubscript{2}/C composite with that of SnO\textsubscript{2} nanowires when the voltage is limited to the 0.05-1.5 V range. Both the as-prepared samples exhibit significantly better cycling performance than the SnO\textsubscript{2} nanowires, with a reversible capacity of 410.1 and 449.7 mAh g\textsuperscript{-1} after 100 cycles for bare SnO\textsubscript{2} and SnO\textsubscript{2}/C composite, respectively. Moreover, the composite has a good initial coulombic efficiency of 70.6% and better capacity
retention (85.3%) than the bare nano-SnO$_2$ (64.8%). It is believed that the improved initial coulombic efficiency of the SnO$_2$/C nanocomposite can be attributed to fewer non-bonding terminations of Sn atoms or O atoms on the surface of the SnO$_2$, as well as to the enhanced charge transport induced by the carbon component [14].

Figure 4.5 Electrochemical performance: (a) initial charge/discharge curves of as-prepared SnO$_2$ and SnO$_2$/C composite cycled between 0.01 and 3 V; (b) cycling performance at 100 mA g$^{-1}$ in different voltage ranges.
The promising electrochemical performance of the as-prepared SnO\(_2\) nanoparticles could be attributed to: (1) the pores, which provides further buffering against the local volume change during the Li-Sn alloying/de-alloying reactions; (2) the ability of the pores to promote liquid electrolyte diffusion into the bulk of the anode and provide fast transport channels for the Li ions; (3) the lower absolute volume changes during the Li-Sn alloying/de-alloying reactions due to the nanosized oxide crystals (around 5 nm); and (4) the shorter diffusion length for Li insertion due to the ultra-fine nanosized particles, with benefits in retaining the structural stability, thereby leading to good cycling performance. The superior electrochemical performance of SnO\(_2\)/C composite could also be ascribed to the following reasons other than the above: (1) the high distribution of oxide particles within the carbon matrix and the good interface affinity between oxide and carbon particles, which resulted from the in situ preparation of the oxide and carbon; (2) the carbon matrix, which not only improves the conductivity of the SnO\(_2\) anode, but also effectively buffers the volume expansion of Sn during lithium intercalation and hinders tin aggregation during cycling.

4.5 Summary

A simple molten salt method has been developed for synthesis of ultra-fine porous SnO\(_2\) nanopowder and in-situ preparation of SnO\(_2\)/C composite. The nanosized (around 5 nm) porous SnO\(_2\) delivered a higher capacity and more stable cyclability compared to SnO\(_2\) nanowires due to the pores between particles. The reversible capacity was 410 mAh g\(^{-1}\) after 100 cycles in the voltage range of 0.05-1.5 V. As for the porous SnO\(_2\)/C composite, the good interface affinity between the carbon matrix and the SnO\(_2\) particles and the effective buffer provided by the carbon resulted in
significant improvement of the electrochemical performance as an anode material for lithium-ion batteries. The SnO$_2$/C nanocomposite has a good initial coulombic efficiency of 70.6% when the electrodes are cycled in the voltage range of 0.05-1.5 V. Moreover, the nanocomposite shows better capacity retention (85.3%) than the bare nano-SnO$_2$ (64.8%) after 100 cycles. The as-prepared SnO$_2$/C nanocomposite could be a good anode material for commercial lithium-ion batteries. In addition, the simple molten salt synthesis method used in this study involves no templates or surfactants, and has the added advantage of a shorter synthesis time.

References


CHAPTER 5 One Dimensional SnO₂/CNT Composites and SnO₂ Nanofibre

5.1 Introduction

One-dimensional nanostructured electrode materials have attracted a great deal of research interest for lithium ion batteries due to the high surface to volume ratios and excellent surface activities. One-dimensional structures such as nanowires [1-4], nanotubes [5, 6], and nanorods [7, 8] have been synthesized for high capacity SnO₂ anode. However, because of the volume expansion during lithium intercalation, the electrode SnO₂ crystallites should be as small as possible to minimize the absolute volume change. Moreover, carbonaceous materials can be the most effective candidates among the “buffering” matrices because of their good conductivity, Li⁺ permeability, chemical stability, and compatibility with other electrode materials. From this point of view, composites consisting of nanosized SnO₂ crystals decorated on one-dimensional carbon cores could be suggested as promising anode materials.

SnO₂/carbon nanotube (CNT) composites have attracted considerable attention because CNTs have a high theoretical electrical conductivity, high aspect ratio, remarkable thermal conductivity, and good mechanical properties, which could improve electrodes’ reversible capacity, rate capability, strength, flexibility, and safety [9]. SnO₂ deposited onto single-walled carbon nanotubes (SWCNT) or multi-walled carbon nanotubes (MWCNT) to form composites have generally been prepared by the chemical solution route, the sol-gel method, chemical vapour deposition, or the supercritical fluid method [10-15]. In first part of this chapter, the solvothermal method was applied to synthesize SnO₂ nanoparticle decorated
Chapter 5 One dimensional SnO$_2$/CNT composites and SnO$_2$ nanofibre

multi-wall carbon nanotube composites, from which high SnO$_2$ loading as well as good affinity of SnO$_2$ to the CNTs was expected.

Uniform SnO$_2$ distribution in carbon matrix was expected to be achievable by *in-situ* preparation techniques, so in the second part of this chapter, one-dimensional SnO$_2$/C fibre was synthesized by electrospinning to obtain uniform spun nanofibres with large surface area. Electrospinning is a simple and versatile method to form continuous one-dimensional nanofibres under the electrostatic force of the charges on the surface of a liquid droplet in a sufficiently high electric field, which is applied between the capillary nozzle and the metal collector [16, 17]. This technique has been extended to prepare many advanced functional ceramics and composites, including carbon nanotube [18, 19], TiO$_2$ [20], WO$_3$ [21], manganese oxide [22], ZnO [23], and some carbon and inorganic oxide composites. By mixing a polymer carbon source and tin precursor, uniform SnO$_2$ particles dispersed in carbon were easily achieved by this in-situ preparation.

5.2 SnO$_2$/CNT composite

5.2.1 Experimental

*Synthesis*

SnCl$_2$·2H$_2$O (98%, Sigma-Aldrich) was first dissolved in ethanol, and then multi-walled carbon nanotubes (Sigma-Aldrich, carbon > 90%, trace metal basis) were added without any pretreatment. Two composites were prepared with molar ratios Sn:C of 0.1:1 and 0.3:1, respectively. (The samples were marked as L-SnO$_2$/CNT and H-SnO$_2$/CNT, respectively.) The suspensions were further
dispersed by ultrasonication for 30 min, and then transferred into autoclaves and kept at 150 °C for 10 h. The resulting products were washed with de-ionized water, dried, and then heat-treated in a tube furnace at 360 °C for 10 min with natural cooling. The bare SnO₂ sample was prepared in the absence of carbon nanotubes.

Electrochemical Measurements

The electrochemical performances of the as-prepared samples were tested via CR2032 coin-type cells. The working electrodes were prepared by mixing 80 wt% as-prepared materials with 10 wt% carbon black and 10 wt% polyvinylidene difluoride (PVDF). The electrolyte was 1 M LiPF₆ in a 1:2 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The cells were galvanostatically charged and discharged in the voltage range of 0.01-3 V at a constant current density of 100 mA g⁻¹, based on the weight of the composite, on a Land CT2001A cycler. Cyclic voltammetry (CV) was conducted on a CHI660C electrochemical workstation at a scan rate of 0.1 mV s⁻¹.

5.2.2 Physical Characterization

The scanning electron microscope (SEM) observations give a general view of the SnO₂/CNT composites compared with bare carbon nanotube and SnO₂ powder. Figure 5.1(a) shows the smooth outer walls of the carbon nanotubes with diameters of approximately 20-30 nm and lengths of several micrometers in field emission SEM (FESEM) images. The impurities in the bare CNTs can be ignored, based on the energy dispersive X-ray spectroscopy (EDS) results (not displayed here).
Figure 5.1 FESEM images of (a) MWCNTs, (b) bare SnO₂, (c) L-SnO₂/CNT composite, and (d) H-SnO₂/CNT composite.

From the reported results, SnO₂ with different morphologies can be obtained by hydrothermal methods in different solvents, such as distilled water, ethanol, methanol, or 2-propanol [24, 25]. The surface tensions of these solvents are very different from each other, so the final morphology is easily changed by changing the solvent, owing to the different surface tension of the solution. On the other hand, pH also has a great influence on the final product. In the present study, ethanol was used as the solvent. Figure 5.1(b) shows an agglomeration of SnO₂ particles with a particle size of around 10 nm. As shown in Figure 5.1(c), for the L-SnO₂/CNT sample, very fine SnO₂ nanoparticles were deposited on some selected sites on the surface of the CNTs, while in the H-SnO₂/CNT sample, shown in Figure 5.1(d), the deposited SnO₂ nanoparticles form a uniform layer on the surface of the CNTs, causing a small
increase in the diameter of the nanotubes. It is obvious that the loading of SnO$_2$ is significantly affected by the concentration of SnCl$_2$. The higher the concentration of SnCl$_2$, the higher the amount of SnO$_2$ deposited on the CNTs.

Figure 5.2 X-ray diffraction patterns of MWCNTs, SnO$_2$/CNT composites, and bare SnO$_2$ powder.

Structural features were confirmed by X-ray diffraction (XRD) patterns, as shown in Figure 5.2. The MWCNTs present characteristic peaks at about 26° and 43°, corresponding to the (002) and (101) reflections. For the bare SnO$_2$ powder, all the reflections are in good agreement with a tetragonal structure (JCPDS No. 41-1445), which belongs to space group (SG) $P4_{2}/mnm$ (SG No. 136, with lattice parameters $a = b = 4.738$ Å, $c = 3.187$ Å). For both the L-SnO$_2$/CNT and the H-SnO$_2$/CNT samples, peaks at 26.6°, 33.8°, 37.9°, and 51.8° correspond to the (110), (101), (200), and (211) reflections of SnO$_2$. 
Figure 5.3 TEM images of L-SnO₂/CNT (a, b), and H-SnO₂/CNT (c, d). The inset of (d) shows the lattice spacings of the composite.

The distribution and morphology of the L-SnO₂/CNT and H-SnO₂/CNT samples were further analyzed by transmission electron microscopy (TEM). The lower magnification images in Figure 5.3 (a) and (c) show general views of the L-SnO₂/CNT with a small amount of SnO₂ and of the H-SnO₂/CNT with a large amount of SnO₂. In the Figure 5.3(b) and (d) images at higher magnification, the distributions of SnO₂ on the surfaces of single carbon nanotubes are different. It is found that the SnO₂ nanocrystals are first deposited onto the knots or the defects of the CNTs, and then deposited onto the normal surfaces of CNTs when the amount of SnO₂ is increased. Both samples show that the crystal size of the deposited SnO₂ is about 5 - 10 nm. The crystal size of SnO₂ in H-SnO₂/CNT is a little bit smaller than
that in L-SnO$_2$/CNT, which corresponds to the lower XRD intensity of H-SnO$_2$/CNT compared to L-SnO$_2$/CNT. The inset of Fig. 5(d) clearly shows the lattice fringes of the CNTs and the SnO$_2$ nanoparticles. The interlayer spacings of approximate 0.32 nm and 0.26 nm, respectively, correspond to the (110) and (101) planes of tetragonal SnO$_2$.

5.2.3 Electrochemical Performance

![Cyclic voltammograms for the first 5 cycles of (a) MWCNTs, (b) bare SnO$_2$, (c) L-SnO$_2$/CNT, and (d) H-SnO$_2$/CNT at a scan rate of 0.1 mV s$^{-1}$.](image)

*Figure 5.4* Cyclic voltammograms for the first 5 cycles of (a) MWCNTs, (b) bare SnO$_2$, (c) L-SnO$_2$/CNT, and (d) H-SnO$_2$/CNT at a scan rate of 0.1 mV s$^{-1}$.

The results of cyclic voltammetry (CV) measurements of the four samples are displayed in Figure 5.4. There is a strong peak at about 0.62 V for the MWCNTs during the first discharge process, but it disappears in the following cycles. This peak
is caused by the electrolyte decomposition on the pristine surfaces of the carbon material and the solid electrolyte interface (SEI) formation [26]. During the first scan of the bare SnO$_2$ powder electrode, characteristic peaks at about 1.12 V, 0.76 V, and 0.12 V appear in the cathodic sweep process, while two peaks at about 0.57 V and 1.30 V appear in the anodic sweep process. The reduction peaks around 1.12 V and 0.76 V correspond to electrolyte decomposition and Li$_2$O formation, as described in equation (5.1) [27]:

$$SnO_2 + 4Li^+ + 4e^- \rightarrow 2Li_2O + Sn \quad (5.1)$$

The cathodic peak at about 0.12 V and the two anodic peaks, as well as the new peaks in the following cycles, correspond to the reversible reaction in equation (5.2) [27]:

$$Sn + xLi^+ + xe^- \xrightarrow{\, \, \Box\, \,} Li_xSn (0 \leq x \leq 4.4) \quad (5.2)$$

There is an obvious increase in the anodic peak at 0.57 V in the second cycle and little further increase until the 4$^{th}$ cycle, indicating an activation process in the material. Peaks at 0.27 V and 0.55 V that appear from the 4$^{th}$ cycle are due to the formation of $\beta$ phase tin during the reaction process. They may begin to appear only after several cycles because of the aggregation to some extent of tin particles in the Li$_2$O matrix. As for the L-SnO$_2$/CNT electrode, there are a small peak at 0.76 V and an obvious peak at 0.62 V, which respectively correspond to the reaction of lithium with SnO$_2$ and MWCNTs in the first discharge process, with the former peak being small because of the small amount of deposited SnO$_2$, while for the H-SnO$_2$/CNT electrode, which was deposited with a greater amount of SnO$_2$, the peak at 0.76 V is very noticeable, and the peak at 0.62 V is inconspicuous. Both samples show reasonably well repeated curves in the following cycles, revealing the good cycling
stability. Nonetheless, the anodic peak at 0.57 V of both samples is different from that of the SnO$_2$ sample. The peak decreases with cycling, indicating that there is no activation process. This is probably because the SnO$_2$ nanocrystals are deposited on the walls of the CNTs and all the active materials are involved in the reaction from the first cycle.

The cycling performances of the samples over the potential range of 0.01 V to 3.0 V were investigated up to 100 cycles (Figure 5.5(a)). The initial discharge capacities are 1034 mAh g$^{-1}$, 1665 mAh g$^{-1}$, 1415 mAh g$^{-1}$, and 1466 mAh g$^{-1}$ for MWCNTs, SnO$_2$ powder, L-SnO$_2$/CNT, and H-SnO$_2$/CNT, respectively. The initial efficiencies of these samples are 29.4%, 56.7%, 41.5%, and 46.2%, respectively. The discharge capacity of SnO$_2$ powder decreases gradually until the 60$^{th}$ cycle (130 mAh g$^{-1}$), corresponding to an efficiency increase of up to 98%. The nanosize particles of SnO$_2$ are favourable for cycling stability, because the absolute volume change decreases when the particle size of tin decreases. However, with charge/discharge cycling, tin nanocrystals will aggregate, and that will affect cycling performance.
Figure 5.5 Electrochemical performance: (a) specific discharge capacity with cycle number of MWCNTs, bare SnO$_2$, and L-SnO$_2$/CNT and H-SnO$_2$/CNT composites (current density 100 mA g$^{-1}$); (b) charge/discharge efficiency of bare SnO$_2$, and of L-SnO$_2$/CNT and H-SnO$_2$/CNT composites; (c) rate capability of bare SnO$_2$ and H-SnO$_2$/CNT.

Both SnO$_2$/CNT composites show stable retention, with the H-SnO$_2$/CNT sample also delivering higher capacity. According to the result of thermogravimetric analysis (TGA), the weight percentage of SnO$_2$ in the H-SnO$_2$/CNT sample is about 54%. Although loaded with a high level of SnO$_2$, it still demonstrates excellent electrochemical performance. An initial reversible capacity of 709.9 mAh g$^{-1}$ is
obtained, and capacity retention reaches as high as 402 mAh g⁻¹ up to the 100th cycle. We note that in reference [11], although TEM images showed a high SnO₂ loading in the SnO₂/CNT sample, this sample exhibited obvious capacity fading, which is probably due to the incompact deposition of SnO₂ on the CNTs by the wet chemical method. However, in our experiment, the affinity of SnO₂ to CNTs was improved by the solvothermal method, owing to the higher pressure and because the SnO₂ crystals were pinned on the surface of the CNTs, which could effectively prevent SnO₂ agglomeration, so that the cycling stability of our SnO₂/CNT was better than the data published in reference [11]. It can be observed from Figure 5.5(b) that the bare SnO₂ sample has efficiency below 94% for the first 20 cycles, while both the composite samples have higher efficiency than the SnO₂ powder from the 10th cycle. Rate capability test results are shown in Figure 5.5(c). Although the H-SnO₂/CNT sample shows a slightly lower specific capacity than the SnO₂ powder in the beginning, it shows a more stable cycling performance at each current density. It also shows larger capacity at the high current density of 2 C, in which the CNTs contribute to maintaining the electronic conduction, as well as preventing tin aggregation and accommodating the volume variation [28]. When the current density changes back to 0.1 C, the H-SnO₂/CNT sample delivers a specific capacity above 500 mAh g⁻¹, which is much higher than that of the bare SnO₂ powder electrode. This loss in capacity is almost reversible on lowering the current density again for the H-SnO₂/CNT sample, which indicates that this capacity loss is not due to breaking of the electrical contact of the active material as a result of volume changes and reveals the effects of CNTs in the composite.
5.3 \textbf{SnO}_2 \textbf{and SnO}_2/C \textbf{nanofibres}

5.3.1 \textbf{Synthesis}

Based on a number of preliminary experiments, a polyacrylonitrile (PAN, MW=150,000, Aldrich) solution with a concentration of 7 wt\% was selected for the electrospinning process. Typically, 0.7 g PAN was dissolved in 6.3 g N,N-dimethylformamide (DMF, 99.8\%, Aldrich) to form a transparent solution at 80 °C with the aid of vigorous stirring for 2 h. This solution was marked as No. 1. Then, 0.5 g tin(II) 2-ethylhexanoate (95\%, Aldrich) was mixed with 2.5 g anhydrous ethanol with stirring for 1 h to form a homogenous solution. The latter solution was marked as No. 2. Afterwards, the No. 2 solution was added drop by drop to the No. 1 solution at 80 °C with vigorous stirring, followed by continuous stirring at room temperature for 3 h again. The polymer solution was transferred into a 10 ml syringe with a capillary tip (0.8 mm diameter). For spinning, the set-up is similar to that described previously [21]. Typically, the collector was placed 8 cm from the spinneret to collect the nanofibres. A high voltage of 13 kV was supplied at the spinneret by a direct-current power supply (DW-P303-5ACCD, Tianjin Dongwen High Voltage Power Supply Co., China). The solution was pushed out of the spinneret by a syringe pump (TS2-60, Baoding Lange Constant Flux Pump Co., China) at the rate of 0.5 ml h\(^{-1}\). The collector was kept at 180 °C during electrospinning to evaporate the solvent. After spinning for more than six hours, the nanofibre films were easily peeled off. Different subsequent heat treatments were employed to obtain SnO\(_2\) nanofibres and SnO\(_2\)/carbon composite nanofibres. For SnO\(_2\) nanofibres, the as-fabricated polymer nanofibres were heated in air at 500 °C for 2 h (heating rate: less than 1 °C min\(^{-1}\)), and a white film (pure SnO\(_2\) nanofibres)
was then obtained. As for the SnO$_2$/carbon composite nanofibres, the electrospun nanofibres were first partly pyrolyzed and carbonized in an air environment at 360 °C for 1 h (heating rate: less than 1 °C/min), and then fully carbonized at 500 °C for 2 h in argon atmosphere (heating rate: 2 °C/min). Finally, a black film (SnO$_2$/carbon nanofibres) was obtained.

5.3.2 Physical Characterization

![TGA curves of PAN in air (a) and in argon (b).](image)

**Figure 5.6** TGA curves of PAN in air (a) and in argon (b).

The treatment temperature for the nanofibres can be decided from the TGA curves of PAN treated in air and argon, shown as Figure 5.6. During the whole pyrolysis process in air, with increasing temperature, the tin composite/PAN nanofibres would experience two weight loss regions which correspond to pyrolysis and carbonization (when T = 300–400 °C), followed by oxidization at higher temperature, and finally form SnO$_2$ nanofibres consisting of orderly bonded nanoparticles. However, the carbon will be preserved in argon above 500 °C.

The FESEM images (Figure 5.7(a) and (b)) clearly show a general view of the uniform tin composite/PAN nanofibres with diameters of 100-150 nm and lengths
extending to several tens of millimeters. After calcination in air at 500 °C for 2 h, the nanofibrous morphology has been retained, while the diameters of the nanofibres are reduced. The tin composite/PAN nanofibres have been transformed to SnO₂ nanofibres with diameters of 50-80 nm, consisting of orderly bonded nanoparticles with an average size of ~10 nm, as shown in Figure 5.7(d) and its inset. In addition, many holes/voids have been left between the bonded SnO₂ particles in the nanofibres, possibly arising from the pyrolysis of PAN. Some mesoporosities between nanofibres are also revealed. Figure 5.7(e) and (f) show SnO₂/carbon nanofibres with diameters of 60-100 nm, consisting of SnO₂ nanoparticles encapsulated in carbon matrices. The SnO₂/carbon nanofibres can be seen as an intermediate product in the preparation of pure SnO₂ nanofibres, but with carbon filling in between the SnO₂ particles. However, the average size of the SnO₂ nanoparticles in the SnO₂/carbon nanofibres may differ from that in the pure SnO₂ nanofibres. Additionally, there are some fine SnO₂ nanoparticles on the outside of the SnO₂/carbon nanofibres, and mesopores in the nanofibre films can also be observed in high-magnification images of the nanofibres, as shown in the inset of Figure 5.7(f).
Figure 5.7 FESEM images of as-collected tin composite/PAN nanofibres, as-pyrolyzed SnO$_2$, and SnO$_2$/carbon nanofibres: (a) tin composite/PAN nanofibres, (b) high magnification image of tin composite/PAN nanofibres, (c) as pyrolyzed SnO$_2$ nanofibres prepared in air at 500 °C for 2 h, (d) high magnification images of SnO$_2$ nanofibres and single SnO$_2$ nanofibre (inset), (e) as-pyrolyzed SnO$_2$/carbon nanofibres prepared in air at 360 °C for 1 h and further heat-treated in argon at 500 °C for 2 h, (f) as-pyrolyzed SnO$_2$/carbon nanofibres prepared in air at 360 °C for 1 h and further in argon at 500 °C for 2 h, with image of single nanofibre of SnO$_2$/carbon (inset), both at high magnification.
Figure 5.8 X-ray diffraction patterns of as-prepared SnO$_2$ nanofibres and SnO$_2$/carbon nanofibres. The diffraction peaks are characteristic of tetragonal rutile structure SnO$_2$ (JCPDS 41-1445), as indexed in the patterns.

X-ray diffraction analysis of the as-pyrolyzed SnO$_2$ and SnO$_2$/carbon nanofibres clearly reveals the diffraction pattern of a tetragonal rutile structure (JCPDS 41-1445) belonging to the space group $P4_2/mnm$ (136) with lattice parameters $a = b = 4.7386$ Å and $c = 3.1872$ Å (Figure 5.8). According to previous reports, carbothermal reduction of SnO$_2$ becomes feasible only when the carbonization temperature reaches around 600 °C [29, 30]. The XRD analysis confirms that carbothermal reduction of SnO$_2$ does not take place during carbonization at 500 °C because no other peaks corresponding to tin or tin monoxide were observed.

TEM was employed to determine useful structural and chemical information on the samples, and the images are shown as Figures 5.9 and 5.10 for SnO$_2$ nanofibres and SnO$_2$/carbon nanofibres, respectively. Figure 5.9(a) shows a bright-field TEM image...
of a single SnO$_2$ nanofibre and its corresponding selected-area electron diffraction (SAED) pattern (inset). The SAED pattern rings indicate that the SnO$_2$ nanofibres are polycrystalline. The spotted diffraction rings from inside to outside can be indexed to the (110), (101), (200), (211), and (301) planes of rutile SnO$_2$, respectively. These indexed patterns are in good accordance with the XRD reflections described above. Figure 5.9(b) similarly reveals many hole/void nanopores between the bound SnO$_2$ nanoparticles in the nanofibres. As marked in Figure 5.9(c), the high resolution TEM (HRTEM) image confirms this crystal structure, with an interplanar spacing of approximately 0.336 nm between neighbouring (110) planes of tetragonal SnO$_2$, as those planes were parallel to the electron beam. Only a few crystals have revealed clear lattice fringes in the HRTEM image, while other areas without lattice fringes are present. These areas could be nanopores or crystals whose orientations are not parallel to the electron beam. The crystal size of the SnO$_2$ in the nanofibres is about 10 nm, approximately the same as the average size of the SnO$_2$ nanoparticles shown in the FESEM images. The TEM images for the SnO$_2$/carbon nanofibres shown in Figure 5.10 are very similar in morphology to the SnO$_2$ nanofibres. The SAED pattern rings shown as the inset to Figure 5.10(a) also correspond to the XRD results. Notably, the crystal size of SnO$_2$ in Figure 5.10(c) is about 5-10 nm, which is smaller than that in the bare SnO$_2$ nanofibres. The formation of this specific structure may be understood as follows: the SnO$_2$ nanoparticles originate from the decomposition and oxidation of tin(II) 2-ethylhexanoate in the tin composite/PAN nanofibres, followed by the further diffusion and crystal growth of tin dioxide in the nanofibres, similar to what was reported in Ref. [21]. Because of the low diffusion capability of tin oxide in the nanofibres at that pyrolysis temperature, which is far below its melting point, only small SnO$_2$ crystals form during PAN burn-off, but as a whole, the nanofibres
are polycrystalline. The hole/void nanopores in the nanofibres probably are voids resulting from the pyrolysis and oxidation of PAN. When heated in argon, the residual carbon matrix could further prevent SnO$_2$ crystal growth, so that smaller SnO$_2$ crystals are formed in the SnO$_2$/carbon composite nanofibres.

Figure 5.9 (a) TEM image and SAED pattern (inset) of a SnO$_2$ nanofibre, (b) low-magnification TEM image of SnO$_2$ nanofibres (with many hole/void interspaces between the bound SnO$_2$ nanoparticles in the nanofibres), (c) HRTEM image of a section of a SnO$_2$ nanofibre.
Figure 5.10 (a) TEM image and SAED pattern (inset) of a SnO$_2$/carbon nanofibre; (b) low-magnification TEM image of SnO$_2$/carbon nanofibres (with many hole/void nanopores between the bound SnO$_2$ nanoparticles in the nanofibres), (c) HRTEM image of a section of a SnO$_2$/carbon nanofibre.
Figure 5.11 XPS high-resolution spectra of (a) C1s, (b) O1s, and (c) Sn3d regions of as-prepared SnO$_2$/carbon nanofibres.
To reveal the presence and oxidation states of tin and carbon in the SnO$_2$/carbon nanofibres, X-ray photoelectron spectroscopy (XPS) analysis has been conducted from 0 to 1100 eV. Obvious C1s, O1s, and Sn3d peaks were detected, and their high-resolution spectra are shown in Figure 5.11. Figure 5.11(a) displays the high-resolution spectrum of the C1s region of the as-prepared SnO$_2$/carbon nanofibres fitted to five peaks, including un-oxidized graphitic (sp$^2$) carbon. The two large peaks at 284.45 and 284.98 eV are possibly attributable to graphitic carbon containing a polyaromatic layered structure [31, 32], while the peak at 285.6 eV should probably be assigned to disordered carbon [31]. Some oxidized carbon functions are also found from the higher binding energy (BE) peaks at 286.68 and 288.5 eV, assigned to oxidized carbon present in alcohol and carbonyl, respectively. As shown in Figure 5.11(b), a pronounced O1s response occurred from 530-532 eV. A portion could come from unreduced SnO$_2$, as evidenced by the O1s BE peak at $\sim$530.7 eV [31], while the peak at 531.3 eV may be the result of the OH$^-$ radical, adsorbed oxygen, or the carbonyl [31]. As for the high BE peak at 532.2 eV, it is possibly attributable to the alcohol, which is in good accordance with the fitted C1s peaks in Figure 5.11(a). The Sn3d spectrum (Figure 5.11(c)) for SnO$_2$/carbon comprises two symmetrical peaks with BEs at 487.07 and 495.46 eV, which are attributable to Sn3d5/2 and Sn3d3/2, respectively. The separation between these two peaks is 8.39 eV, in good agreement with the energy splitting reported for SnO$_2$ [33-35]. In all, the XPS results confirm that the as-prepared SnO$_2$/carbon nanofibres are composed of pure SnO$_2$ and carbon, except for some adsorbed water or OH$^-$ on their surfaces. Additionally, part of the carbon binds with the SnO$_2$ by means of C-O or C=O to form this particular structure, i.e., one-dimensional SnO$_2$/carbon nanofibres consisting of SnO$_2$ particles encapsulated in carbon matrices.
5.3.3 Electrochemical Performance

Figure 5.12 (a) Cyclic voltammograms of SnO₂ nanofibre and (b) SnO₂/carbon nanofibre electrodes from the first cycle to the fifth cycle at a scan rate of 0.1 mV s⁻¹ in the voltage range of 0.05-2.5 V; (c) cycling performance from the first cycle to the 100th cycle of the SnO₂/carbon nanofibres and SnO₂ nanofibres (58 cycles) at the same current density, 100 mA g⁻¹; (d) cycling performance from the first cycle to the 100th cycle of the SnO₂/carbon nanofibres and SnO₂ nanofibres at different discharge rates (0.5, 1, 2 C).

Figure 5.12(a) and (b) compares cyclic voltammograms of the as-prepared SnO₂ and SnO₂/carbon nanofibres. The CV curves for the first five cycles for the two samples are very similar, but show some differences from each other. The first CV profile for the SnO₂ nanofibres shows two apparent reduction peaks at around 0.78 V and 0.11 V. The 0.78 V peak would be derived from Li₂O formation according to equation
(5.1). This peak does not appear in subsequent CV cycles. The 0.11 V peak can be attributed to the alloying of tin with lithium. Hence, after the first CV cycle, the electrode demonstrates quite reversible behaviour in terms of the reaction in equation (5.2). In the following CV cycles, three pairs of reduction and oxidation peaks at 0.58 and 0.65 V, 0.29 and 0.535 V, and 0.113 and 0.120 V can be ascribed to the process of LiₓSn formation according to the reaction in equation (5.2), which is considered reversible to a large extent. The formation of SnO₂ fibre and the electrochemical reaction schematic are shown as Figure 5.13. For the SnO₂/carbon nanofibre electrode, the 0.873 V peak should be ascribed to Li₂O formation and the peak at about 0.12 V during the first discharge is attributed to the alloying of tin with lithium. In the following CV cycles, three main pairs of reduction and oxidation peaks at 0.586 and 0.74 V, 0.337 and 0.638 V, and 0.136 and 0.161 V can be ascribed to the process of LiₓSn formation.

The cycling performance of the as-prepared pure SnO₂ and SnO₂/carbon nanofibre electrode is shown in Figure 5.12(c) at a constant current of 100 mA g⁻¹ with a cut-off voltage window of 0.05 to 1.5 V (versus Li⁺/Li). The SnO₂ nanofibres exhibit improved cyclic performance and a higher reversible specific capacity of over 446 mAh g⁻¹ up to the 50th cycle compared to SnO₂ nanowire [1]. However, the SnO₂/carbon nanofibres deliver much higher Li⁺ storage and a larger initial reversible capacity of 964 mAh g⁻¹ for the first cycle, and 555 mAh g⁻¹ for the 50th cycle. Additionally, the SnO₂/carbon nanofibres display an initial coulombic efficiency of approximately 55.43%, which is obviously higher than that of the pure SnO₂ nanofibres (49.96%). To further investigate the effect of the carbon matrix on the electrochemical behaviour of the SnO₂/carbon nanofibre electrode, the cycling
performance for the SnO$_2$/carbon nanofibres and the pure SnO$_2$ nanofibres at
different charge/discharge rates (0.5, 1, 2 C) has been displayed in Figure 5.12(d).
The SnO$_2$/carbon nanofibre electrode delivers a rate capacity of about 226 mAh g$^{-1}$ at
0.5 C up to 100 cycles, and 236 mAh g$^{-1}$ at 2 C at 100 cycles, respectively, while
these values for the pure SnO$_2$ nanofibre electrode are only 55.8 mAh g$^{-1}$ at 0.5 C
and 10.5 mAh g$^{-1}$ at 2 C after 100 cycles.

The highly improved electrochemical behavior of the SnO$_2$/carbon nanofibre
electrode is probably attributable to its special structure with one-dimensional
nanofibres consisting of SnO$_2$ nanoparticles encapsulated in carbon matrices. The
carbon matrix could not only improve electronic conduction, but also increase Li$^+$
transport between the active phases [33, 36]. Additionally, the carbon matrix
encapsulating the SnO$_2$ nanoparticles acts as a “buffer zone” to accommodate the
large volume changes and prevent the agglomeration of the tin nanocrystals during
charge/discharge cycling. Moreover, the nanostructured SnO$_2$ particles in the
SnO$_2$/carbon nanofibres shorten the transport lengths for both electrons and lithium
ions to a large extent, and the mesopores in the SnO$_2$/carbon nanofibres ensure a high
electrode-electrolyte contact area. All these factors finally lead to not only improved
reversible capacity, initial coulombic efficiency, and cyclic retention, but also to
great enhancement of the rate capacity.
Figure 5.13 Schematic diagram showing formation of SnO$_2$ nanofibres and their electrochemical reaction.

5.4 Summary

SnO$_2$/MWCNT composites have been prepared by a simple solvothermal method. The distribution of SnO$_2$ nanocrystals can be controlled by changing the molar ratio of Sn$^{2+}$ and CNTs in the precursor. In the higher SnO$_2$ content sample, a uniform layer of SnO$_2$ nanocrystals with crystal size of about 5 nm was deposited on the surface of the MWCNTs. This composite shows very stable cyclic retention up to 100 cycles because the active material is nanosize and the carbon nanotubes prevent
tin agglomeration. Moreover, it delivers reasonable capacity when the current density is changed back from a high to a smaller value.

A simple and low-cost technique consisting of a combination of electrospinning and subsequent thermal treatments in air and then in argon was applied to synthesize SnO$_2$ and SnO$_2$/carbon composite nanofibres. The as-prepared one-dimensional SnO$_2$ nanofibres are characterized by many mesoporosities in the nanofibres and nanopores between the bound SnO$_2$ nanoparticles. The SnO$_2$/carbon nanofibres consist of SnO$_2$ nanoparticles encapsulated in carbon matrices. SnO$_2$ nanofibre electrode exhibits discharge capacity of 446 mAh g$^{-1}$ after 50 cycles at a current density of 100 mA g$^{-1}$, while the SnO$_2$/carbon composite nanofibre electrode exhibit highly improved electrochemical performance owing to both the high conductivity pathways for electrons and lithium ions and the buffering effect provided by the carbon matrices in the nanofibres during the charge/discharge cycling. This composite nanofibre electrode delivers reversible capacity of 555 mAh g$^{-1}$ at the 50$^{th}$ cycle. It also exhibits strong enhancement of the reversible discharge capacity at higher rates, such as 0.5, 1, and 2 C, compared with the performance of the pure SnO$_2$ nanofibres. The electrochemical behaviour of SnO$_2$/carbon nanofibre electrode makes it a promising anode material for lithium ion batteries.

References


CHAPTER 6 Superior Restacked MoS₂ Anode and MoS₂/SnO₂ Composites

6.1 Introduction

Layered transition-metal dichalcogenides MX₂ (M = Ti, Nb, Mo, Ta; X = S, Se, Te) are of great research interest as electrode materials for lithium ion batteries, because they act as host lattices by reacting with a variety of guest atoms or molecules to yield intercalation compounds, in which the guest is inserted between the host layers. In layered MX₂, atoms within a layer are bound by strong ionic/covalent forces, while the individual layers are bound by weak van der Waals interactions, forming a sandwich structure. MoS₂ is one of the most stable and versatile members of this family of layered materials. Three polytype crystal structures of MoS₂ have been reported so far [1], as shown in Figure 6.1. The lattice parameter c values for the 1T, 2H, and 3R polytypes are 6.147 Å, 12.294 Å, and 18.37 Å, respectively [2-4].

Recently, it was reported that MoS₂ demonstrated reasonably reversible capacity (∼400 mAh g⁻¹) and good cycling stability when used as anode material [5]. When a lithium ion first intercalates into these layered materials, it enters the S layer and forms Li–S bonds, resulting in volume changes. It was observed for TiS₂ that lattice parameter c suffers approximately 10% expansion, while the value of lattice parameter a remains almost the same regardless of the intercalation process [6, 7]. For MoS₂, an increment to the c parameter of 0.25 Å was also reported for one mole of lithium intercalation [8].
Figure 6.1 Crystal structures of MoS<sub>2</sub> polytypes: (a) 1T, (b) 2H, (c) 3R (left: unit cell; right: 2a×2a polyhedral supercell), (d) the 2H polytype, consisting of Mo and S layers.

In order to achieve high cycling stability, the stress induced by lithium intercalation/de-intercalation cycling must be properly accommodated or relieved. It can be imagined that the increase in the c lattice constant of MoS<sub>2</sub> can provide a
larger space for Li ion intercalation, which also reduces the barriers to Li ion mobility, thereby facilitating lithium ion diffusion.

In the first part of this chapter, the *in-situ* neutron technique was applied to investigate commercial MoS$_2$ anode in a custom roll-over design cell. Because MoS$_2$ had been previously used as cathode material in lithium batteries with an operating voltage around 2 V, and a lower voltage limit will applied as anode material, different structural change would be expected during the charge/discharge process, and this is ideal for *in-situ* neutron investigation. In the second part of this chapter, exfoliation and restacking of layered MoS$_2$ with enlarged $c$-axis spacing were achieved by a chemical solution process and the hydrothermal technique, and the restacked MoS$_2$ was tested as anode material for lithium ion batteries. In the third part of this chapter, MoS$_2$/SnO$_2$ composites were synthesized as anode materials.

### 6.2 *In-situ* neutron diffraction

#### 6.2.1 Experimental setup

Two types of electrochemical cells previously designed for *in-situ* diffraction studies of Li-ion batteries are shown in Figure 6.2. The first cell [9, 10] (Figure 6.2(a)), used to investigate LiMn$_2$O$_4$, has a cylindrical geometry, containing approximately 5 g of cathode mixture, and it uses a stainless steel current collector. Neutron diffraction (ND) patterns were collected using this cell at specific voltages during a slow discharge. Although the background in the ND patterns is significant, some structural peaks were able to be resolved. Using these data, the authors were able to model and refine Li occupancies at selected potentials, however, no observation of two-phase
behaviour at high potentials was made, a result attributed to the slow rate of charge used [10]. The second cell [11, 12] (Figure 6.2(b)), used to investigate LiNiO$_2$ and Li$_4$Ti$_5$O$_{12}$, has a coin cell geometry, but the relatively thick electrode used results in an over-potential of approximately 120 mV. Some of the challenges associated with *in-situ* experimentation, *e.g.* effects of the separator and electrolyte solution, are highlighted in this work [11]. Li$_4$Ti$_5$O$_{12}$ was the first anode material to be examined with such an *in-situ* cell custom-built for ND experiments. This work demonstrated that subtle changes in Li positions can be determined at specific voltages.

In this work, electrochemical cells were constructed using MoS$_2$ (Sigma Aldrich, 99%, particle size < 2 μm) mixed with carbon black and polyvinylidene fluoride (PVDF) to form a paste, which was applied to a Cu sheet, followed by drying overnight under vacuum. Layers of materials were arranged in the following order: Celgard® (insulator), Cu with MoS$_2$ electrode, Celgard® (separator), and Li metal. Cu wires were placed in contact with both electrodes.
Figure 6.2 Specially designed electrochemical cells for in-situ neutron diffraction studies: (a) Cylindrical cell [9, 10], where A indicates brass plugs, B is a Pyrex® tube lined with Li foil, C is the separator soaked in hydrogen-containing electrolyte, D is the stainless steel current collector, and E is the active material mixed with carbon black and binder. Reproduced from ref. [10] with permission from Elsevier. (b) Coin cell design [11, 12] where 1 is the cell top, 2 is a spring, 3 and 6 are the current collectors, 4 is the cell body consisting of electrodes with glass fibers and Celgard® separator, and 5 is the active material compartment. Reproduced [11] with permission of the International Union of Crystallography.

The electrolyte was added dropwise and was composed of 1 M LiPF₆ dissolved in a 1:1 vol% mixture of deuterated ethylene carbonate (CDN, isotopic purity 99%) and deuterated dimethyl carbonate (Cambridge Isotopes, isotopic purity 99%). This assembly was rolled (using the outer Celgard® layer) and inserted into a vanadium can with an inner diameter of 9 mm, which was then sealed. These procedures were
carried out in an Ar-filled glove box. Figure 6.3 illustrates this electrochemical cell for use during in-situ ND studies, which we term the roll-over design.

![Figure 6.3](image)

**Figure 6.3** Schematic of a section through the “roll-over” cell for in-situ neutron diffraction studies. Sheets of Celgard® (white), MoS$_2$ electrode on Cu (red), Celgard®, and Li (blue), are rolled and sealed inside a vanadium can (green). The can is sealed in an argon-filled glove box.

The size and geometry of cylindrical batteries is ideal for in-situ ND experiments, and a roll-over cylindrical type cell is used to collect real-time data during electrochemical cycling, unlike the two previous cell designs (the cylindrical and the coin cell types) where cells were charged ex-situ (without continuous data acquisition) and data collected with the cell contents in an equilibrium or quasi-equilibrium state. As with previous cylindrical cells [9, 10] used for in-situ ND, the cell design mimics the commonly available commercial 18650-type [13] battery.

*In-situ* ND data were collected on the high-intensity powder diffractometer, Wombat, at the Open Pool Australian Lightwater (OPAL) reactor facility at the Australian
Chapter 6 Superior restacked MoS2 anode and MoS2/SnO2 composites

Nuclear Science and Technology Organisation (ANSTO) [14]. The electrochemical cell was placed in a neutron beam with wavelength ($\lambda = 2.406(2) \, \text{Å}$), and diffraction patterns were collected every 5 minutes for 36 hours in the two-theta (2$\theta$) range $16 \leq 2\theta \leq 136^\circ$. Wombat features an area detector covering $120^\circ$ in 2$\theta$, enabling diffraction data to be continuously collected rather than through a 20-step-scan type acquisition. The combination of Wombat’s relatively intense neutron beam and its area detector make Wombat an ideal instrument for in-situ ND studies of this type. Data correction, reduction, and visualisation were undertaken within the program LAMP [15]. The electrochemical cell was simultaneously electrochemically cycled in galvanostatic (constant current) mode, with applied currents ranging from ± 1 to 30 mA using a Neware battery testing device. Rietveld refinements were carried out using the GSAS [16] suite of programs with the EXPGUI [17] interface.

6.2.2 Electrochemical performance

Galvanostatic charge/discharge procedures were performed offline to ensure that the electrochemical performance of the roll-over electrochemical cell was acceptable. From these data, the first cycle capacity of the in-situ ND MoS2 cell is estimated to be $670 \, \text{mA h g}^{-1}$, which is within reported capacity ranges for coin cell experiments [18-20], but there is a significant decrease in the maximum current rate that can be applied for stable battery performance. Hence, the roll-over electrochemical cell used here required that relatively small currents be used during the first discharge (1 - 10 mA), despite the presence of 200 - 500 mg of active electrode material. Larger currents are able to be applied during charging, although their application was noted to cause some voltage spikes, presumably due to the higher internal resistance of this electrochemical cell relative to the coin-cell type. Some of these differences in the
electrochemical performance of the *in-situ* ND cell compared to a coin cell may arise due to isotope effects (using deuterated electrolyte solution) or the reduced quantity of electrolyte used. The electrodes used for these experiments had a maximum of 500 mg of active material, MoS$_2$, which is less than in the previous *in-situ* experiments [9, 10]. ND data is able to be obtained from these small amounts of MoS$_2$, relative to other studies, a result arising due to the capacity of Wombat to measure smaller samples, combined with the enhanced signal-to-noise ratio obtained from this specialist roll-over cell design. The signal-to-noise ratio of the data is limited by the components within the battery itself, and the custom-made battery maximizes this ratio. ND data were collected for 5 minutes, as no worthwhile gain in neutron signal statistics was obtained with longer collection times.

ND patterns collected using this cell clearly show powder diffraction features from MoS$_2$, as shown in Figure 6.4(a). A second roll-over cell was constructed using 500 mg of Li$_4$Ti$_5$O$_{12}$, another anode material which is more crystalline and thus gives a larger diffraction signal than MoS$_2$. The details of this material will be discussed in Chapter 8. The purpose of the Li$_4$Ti$_5$O$_{12}$ battery was to allow comparison of the signal-to-noise ratio relative to other cells used for *in-situ* ND [12] using the same electrode. Using the roll-over cell design, comparable signal-to-noise ratios are observed for Li$_4$Ti$_5$O$_{12}$ collected for 5 minutes on Wombat to those obtained using a coin cell-type configuration [12]. A key difference between these data is the collection time, which was 5 minutes on Wombat and up to 9 hours for the previous [12] work. The present cell design was intentionally tailored for use on Wombat, taking advantage of its fast data collection capability. Furthermore, the design overcomes some electrochemical issues faced in previous designs [9-12], in
particular, the quantity of electrode material and its contact with the current collector and separator. Previous designs use thick electrodes, while in this design the electrode is spread over a current collector with a large surface area, which is then rolled over. Therefore, the need for thin electrodes with good contact to current collector and separator can be satisfied, and to some extent, control the quantity of electrode material by introducing more rolls or reducing the number of rolls. The electrodes are thin, so polarization effects (differences between the voltage under equilibrium and that with a current flow) are minimized and applied currents are higher than previously applied to in-situ cells [9-12].

**Figure 6.4** (a) A multi-phase Rietveld refinement plot using a 5 minute ND pattern collected on Wombat with the custom-designed MoS$_2$ anode battery at $\lambda = 2.406(2)$ Å. Structural models for Li, Cu, and MoS$_2$ are used. The calculated pattern is shown in black, observed data in red, and the difference between the observed and calculated in purple. Reflection markers are shown as vertical bars. (b) A 5 minute ND pattern collected on Wombat with the custom-designed Li$_4$Ti$_5$O$_{12}$ anode battery at $\lambda = 1.535(1)$ Å. Intense reflections from Li, Cu, and Li$_4$Ti$_5$O$_{12}$ are indicated by reflection markers shown as vertical bars.
Figure 6.4(a) shows the multi-phase Rietveld refinement using a 5 minute ND pattern collected on Wombat of an un-cycled MoS\(_2\) cell. For the Rietveld refinement, structural models of MoS\(_2\) [21], Cu [22], and Li [23] were used, while a broad peak shape approximation was used for the carbon black peak centred at 2\(\theta\) = 38°. The refined cell parameters for MoS\(_2\) were \(a = 3.149(5)\), \(c = 12.250(26)\); the \(z\) atomic position for the S atom is 0.618(9), and atomic displacement parameters for Mo and S are 0.08(3) and 0.22(8) Å\(^2\), respectively. The figures of merit for the refinement were the profile factor (\(R_p\)) = 2.36\%, weighted profile factor (\(wR_p\)) = 3.09\%, and goodness-of-fit term (\(\chi^2\)) = 3.741. Using \(\lambda = 2.406(2)\) Å the two MoS\(_2\) reflections were able to be better resolved that are of particular interest, the (002) reflection at 2\(\theta\) = 23.7° and (103) at 2\(\theta\) = 65.3°.

\textit{In-situ} ND patterns were collected during the first stages of discharge of the MoS\(_2\) cell. The observed (002) and (103) reflections of MoS\(_2\) are shown in Figure 6.5 and are correlated with the discharge curve and lattice parameters. Variation in the 2\(\theta\) value of the (002) reflection (due to the inter-plane spacing or \(d\)-spacing) corresponds to Li insertion into MoS\(_2\), producing Li\(_x\)MoS\(_2\). Li insertion into MoS\(_2\) occurs during the 1.1 V plateau, highlighted by the gradual shift to lower 2\(\theta\) values (increase in the \(d\)-spacing of the (002) reflection), a step to higher \(d\)-spacings at 900 minutes (indicated by the arrowhead in Figure 6.5(a)), followed by further increases in the \(d\)-spacing. Overall, the (002) reflection shifts from 2\(\theta\) = 23.7° to 2\(\theta\) = 22.5° and then disappears during the 0.5 V plateau. A part of the transition is complete, as shown by the disappearance of the (103) reflection during the course of the 1.1 V plateau, possibly initiating the drop in voltage to the next plateau region.
Figure 6.5 Selected regions (20.8° ≤ 2θ ≤ 25.9° and 62° ≤ 2θ ≤ 68°) of the *in-situ* ND data obtained from the MoS$_2$ cell as a function of time, showing discharge evolution: (a) (002) peak with a reference line (guide to the eye) showing the 2θ shift. (b) Rietveld-refined $a$ (black squares) and $c$ (red circles) lattice parameters of MoS$_2$. (c) (103) MoS$_2$ peak. (d) Measured voltage (black line) and applied current (red) correlated to the ND data. The reflection intensities are scaled.
This behaviour is quantitatively reflected in the Rietveld refined cell parameters (Figure 6.5(b)). Sequential Rietveld-refinements were undertaken using 5 minute datasets, with fixed atomic parameters, where the figures of merit varied from $2.49 \% \leq R_p \leq 3.22 \%$, $3.14 \% \leq wR_p \leq 4.13 \%$, and $3.39 \leq \chi^2 \leq 5.07$. An increase in the $c$ lattice parameter is observed, followed by a step and further increase until 1500 minutes, as shown by the changes in the $2\theta$ value or $d$-spacing of the (002) reflection. In the case of the $a$ lattice parameter the step is evident, but there is no noticeable fluctuation, as expected, since the (103) reflection disappears. Following the step, the spread in the $a$ lattice parameter is larger, a consequence of the fact that the reflection is disappearing, and the reliability of the determination of the parameter diminishes. For both lattice parameters, a prominent second step appears after 1500 minutes, indicating that subsequent changes cannot be determined using the ND data. The (103) reflection disappears, and the intensity of the (002) reflection begins to decrease from its maximum around this point in the discharge.

The reduction in reflection intensity is due to the formation of LiMoS$_2$ [24], a material that shows short-range structural coherence (~50 Å) and lack of long-range structural order, and has been structurally characterized by atomic pair distribution techniques [21]. The MoS$_2$ to LiMoS$_2$ transformation during the 1.1 V plateau is observed, which is completed during the 0.5 V plateau and corresponds to a loss of long-range order. The (002) reflection remains visible in the 0.5 V plateau region before disappearing at a time close to 2000 minutes, highlighting the transformation of long-range ordered MoS$_2$ to short-range ordered LiMoS$_2$. The MoS$_2$ (002) reflection is the most intense reflection of the relatively short-range ordered LiMoS$_2$, as determined by atomic pair distribution analysis [21], and the slow disappearance
of the (002) reflection, relative to the (103) reflection, is consistent with the transformation to the short-range ordered end member. Note that once LiMoS$_2$ is formed, as shown by the transformation to a product without long-range order in the ND data, the crystallinity of the anode material does not recover. *In-situ* ND data were collected on offline cycled MoS$_2$ cells, and there were no features corresponding to MoS$_2$ or MoS$_2$-derived compounds. By using *in-situ* ND data on an un-cycled MoS$_2$ cell, it is demonstrated that the electrochemically driven overall transformation from crystalline MoS$_2$ to a short-range ordered material, most likely LiMoS$_2$.

Figure 6.5 reveals a linear increase in the $c$ lattice parameter and a step around 900 minutes. The initial insertion of Li into MoS$_2$ results in the linear increase of the $c$ lattice parameter, as Li inserts itself between adjacent MoS$_2$ layers. Li insertion into MoS$_2$ with some degree of lithiation (*i.e.* Li$_x$MoS$_2$ where $x > 0$) results in a non-linear increase in the lattice parameters (a step). This non-linear step in the lattice parameters suggests the formation of an intermediate phase, Li$_x$MoS$_2$, with $a \approx 3.11$ and $c \approx 12.43$ Å, which is linked to a change in the oxidation state of Mo. The structure of this phase is likely to express features similar to those of the end-member lithiated product, short-range ordered LiMoS$_2$ and thus unable to be precisely determined using this method, which is limited to the measurement of long-range structural information. *In-situ* ND using even custom-designed cells such as the one presented here presents significant difficulties for the determination of short-range order, such as analysis using the pair-distribution function (PDF), due to the amount of material contributing to the diffraction data and the complexity in resolving the contributions arising from the phase of interest. Re-design of the electrochemical-cell...
to allow diffraction data only from the material of interest, in this case the anode, to be collected, may overcome this major roadblock to \textit{in-situ} PDF investigations. \textit{In-situ} ND investigation does show the real-time evolution of lattice parameters and the presence of new intermediate phases.

\section*{6.3 Restacked MoS$_2$}

\subsection*{6.3.1 Experimental}

Commercial raw MoS$_2$ was soaked in 1.5 equivalents butyllithium (n-BuLi, 1.6 M in hexane) and kept in argon atmosphere for a week. Then, 0.1 g LiMoS$_2$ product was exfoliated in water by stirring through the redox reaction. The reactions are described as follows [25]:

\begin{equation}
\text{MoS}_2 + n\text{-BuLi} \rightarrow \text{LiMoS}_2 + \frac{1}{2}\text{C}_8\text{H}_{18} \tag{6.1}
\end{equation}

\begin{equation}
\text{LiMoS}_2 + \text{H}_2\text{O} \rightarrow (\text{MoS}_2)_{\text{exfoliated layers}} + \text{LiOH} + \frac{1}{2}\text{H}_2 \tag{6.2}
\end{equation}

The exfoliated MoS$_2$ is very sensitive to temperature. It will restack turbostratically when dried, and it undergoes an irreversible phase transition to disordered 2H-MoS$_2$ at temperatures above 98 °C, with an ordered stacking appearing at higher temperature [26]. Here, the restacking process was achieved via a hydrothermal procedure at 160 °C for 48 h.

The samples were characterized by transmission electron microscopy (TEM, JEOL 2011, 200 keV), X-ray diffraction (XRD, Philips PW1730 diffractometer with Cu K\textalpha radiation, $\lambda = 1.54056$ Å), and Raman spectroscopy (Jobin Yvon HR800). The XRD profiles were refined by the program Fullprof. Specific surface area was determined.
by gas adsorption on a NOVA 1000 (Quantachrome). Magnetic measurements were performed using a conventional physical properties measurement system (PPMS). Magnetic hysteresis loops were collected at room temperature in fields up to 1 T.

### 6.3.2 Characterization

The morphologies of the raw and the as-prepared restacked MoS$_2$ are shown in Figure 6.6. The estimated $c$-axis parameter of the raw material is 0.620 nm and 0.635 nm for restacked MoS$_2$. The zone axis of the selected area electron diffraction (SAED) pattern of the inset in (a) is close to [100]. The normal of the stacked layers is parallel to [001]. In a direct comparison of raw and restacked MoS$_2$ in the top inset to (b), which shows nine layers, an obviously enlarged spacing for the restacked material can be seen. Figure 6.6(c) shows the basal plane (001) of the restacked MoS$_2$, and the estimated plane spacing $d_{100}$ is about 0.30 nm. The zone axis of the SAED pattern is [001], which shows a typical hexagonal structure. Figure 6.6(d) shows a very clear $c$ axis ordering with distortion and dislocations, indicating that the restacking of MoS$_2$ layers is turbostratic.
Both raw and restacked MoS₂ samples are single phase, as determined by the X-ray diffraction (XRD) patterns shown in Figure 6.7. All reflections are in good agreement with a hexagonal structure (JCPDS No. 37-1492) which belongs to the space group P63/mmc (No. 194). The raw material shows very sharp peaks with very high intensity, indicating good crystallization. The strong (002) peak (14.4°) signifies a well-stacked layered structure [27]. The restacked sample shows broadened peaks and a shortened (002) peak, which is consistent with previously reported restacked or
partially exfoliated MoS$_2$ [28, 29], suggesting that the mean crystallite size of the restacked MoS$_2$ is much smaller than that of the raw MoS$_2$. The broadened (00$l$) and (10$l$) peaks also indicate a reduced number of layers along the $c$-axis perpendicular to the atomic layers in Figure 6.1(d). The Rietveld refinement of the XRD pattern fits the experimental data well. The lattice parameters of the raw material can be determined to be $a = b = 3.159(1)$ Å, $c = 12.291(2)$ Å, which are in good agreement with the standard values cited previously. The corresponding parameters of the restacked MoS$_2$ are $a = b = 3.129(6)$ Å, $c = 12.526(8)$ Å (Bragg R-factor = 7.15, Rf-factor = 7.93). The great increase in the $c$-axis parameter of restacked MoS$_2$, by as much as 0.235 Å, indicates a larger space for lithium ions entering the S slab. On the other hand, the smaller lattice $a$ of the restacked MoS$_2$ compared to that of the raw material, might result in relaxation of the $d$-spacing enlargement effect, resulting in improvement in the electrochemical stability of MoS$_2$. The Raman spectrum of the restacked MoS$_2$ (Figure 6.8) is almost the same as that of the raw MoS$_2$ in the frequency range of 200 to 1000 cm$^{-1}$, confirming that the single layers of MoS$_2$ have been restacked during the hydrothermal process.
Figure 6.7 Rietveld refinement of XRD patterns of raw (top) and restacked (bottom) MoS$_2$. The observed pattern, the calculated peak positions, and the difference between the observed and the calculated patterns are shown in black, red, and green, respectively, from top to bottom.

Figure 6.8 Raman spectra of raw and restacked MoS$_2$. 
6.3.3 Electrochemical performance

Figure 6.9 Electrochemical properties of raw and restacked MoS$_2$: cyclic voltammograms for the first 5 cycles of (a) raw and (b) restacked MoS$_2$ at a scanning rate of 0.2 mV s$^{-1}$; (c) cycling performances at a current density of 50 mA g$^{-1}$; (d) rate capabilities at different current densities (discharge current density kept at 50 mA g$^{-1}$).

In spite of their attractive capacity, none of the MoS$_2$ electrodes previously reported shows both high lithium storage and good capacity retention over the studied voltage range (0.01–3.0 V) [5, 20, 30]. When MoS$_2$ is cycled between 3.0 and 0.01 V as an anode material, two step reactions occur. First, lithium intercalates into the S slab, and the van der Waals S–S bonds must be broken to be replaced by Li–S bonds. MoS$_2$ then decomposes into Mo nanoparticles embedded in a Li$_2$S matrix,
corresponding to two cathodic peaks at about 1.0 V and 0.4 V in the first cathodic segment in the cyclic voltammograms (CVs), as shown in Figure 6.9(a) and (b). Both the raw and the restacked samples show these two peaks. In the following cycles, an extra peak at about 2.0 V appears. This change can be explained by the formation of a gel-like polymeric layer [5]. *In-situ* X-ray diffraction patterns have indicated that lithium intercalation at about 1.0 V corresponds to a phase change [31], which is also confirmed by *in-situ* neutron diffraction investigation. When lithium ions enter the S layers, the MoS$_2$ structure changes from 2H to 1T, namely, from trigonal prismatic to octahedral, as illustrated in Figure 6.1. The following MoS$_2$ decomposition reaction applies:

\[
\text{MoS}_2 + 4\text{Li} \rightarrow \text{Mo} + 2\text{Li}_2\text{S} \quad (6.3)
\]

For raw MoS$_2$, the current at all the peaks decreases with cycling. However, for the restacked sample, the peak at 0.4 V decreases, while the current at the 2.0 V peak increases with cycling, and as a result, a much better cycling performance can be obtained. The cyclic performance curves are in good agreement with the results shown in Figure 6.9(c). For raw MoS$_2$, the charge capacity obviously decreases with the cycle number, from over 800 mAh g$^{-1}$ for the first three cycles to 226 mAh g$^{-1}$ at the 50th cycle. However, the restacked MoS$_2$ shows much better cycling stability, with a slight decrease after the 40th cycle, which may be caused by electrochemically driven electrolyte degradation over long cycling. After 50 cycles, it still can sustain a high capacity above 750 mAh g$^{-1}$. The first cycle coulombic efficiency of the raw MoS$_2$ is 83.5%, and it increases with cycle number, reaching 98% by the 40th cycle. For the restacked MoS$_2$, the coulombic efficiency of the first cycle is 87.9%, but it is over 98% from the 4th cycle. The rate capability of the restacked MoS$_2$ electrode was also evaluated at different charge/discharge rates. The
restacked MoS₂ displayed extraordinarily high charge storage capacities. The capacities only slightly decrease as the current density increases. The restacked MoS₂ electrodes exhibit a reversible specific capacity as high as 710 mA h g⁻¹ at a current density of 1000 mA g⁻¹. It has been reported that for layered structure LiNi₀.₅Mn₀.₅O₂ cathode material, a small increase in the spacing between Li layers can significantly reduce the activation energy for Li⁺ motion [32]. It is believed that a similar assumption can also be made for MoS₂ electrodes. The much enlarged c parameter, as revealed from Rietveld refinement of the XRD results, relaxes the strain, lowers the barrier for lithium intercalation, and is favourable for Li⁺ diffusion. Compared to the raw MoS₂ electrodes, the restacked MoS₂ possesses faster ionic conductivity and electrochemical reaction speed under charge/discharge, and therefore, shows significantly improved rate capability. The specific surface areas of raw and restacked MoS₂ are 4.89 m² g⁻¹ and 9.83 m² g⁻¹, respectively, so another possible reason for the improved electrochemical performance of restacked MoS₂ is the increase in the surface area, particularly at edges, which would facilitate interfacial reactions. This is also supported by the magnetic measurement results (Figure 6.10). The restacked MoS₂ shows much higher magnetization than the raw MoS₂ due to higher density of edge terminations, in which the different Mo:S coordination generates magnetism [33].
Figure 6.10 Magnetic hysteresis curves recorded at room temperature from raw and restacked MoS$_2$.

The restacked MoS$_2$ electrode after cycling was characterized by TEM and XRD, as shown in Figure 6.11. The reduction of crystallite size of the restacked MoS$_2$ after cycling, down to about 10 nm, is believed to be due to the electrochemically driven grinding and size-reduction of the initial particles. The SAED pattern comprises a diffuse set of rings/diffuse bright spots, indicating the very small size of crystallites and lattice defects. No obvious peaks can be observed from 10° to 40° in the ex-situ XRD pattern, consistent with the nanoparticle nature of the electrochemically formed species [24].
Figure 6.11 Characterization of cycled restacked MoS$_2$: (a) TEM image with the inset showing the corresponding SAED pattern, and (b) XRD patterns.

In order to evaluate the effects of the enlarged $c$ parameter on reducing the activation energy for Li$^+$ motion and to understand the electrode kinetics, the apparent activation energies of the raw and restacked MoS$_2$ were calculated from electrochemical impedance spectra [34, 35]. The relevant results are shown in Figure 6.12. It can be seen that the impedance curves consist of two partially overlapping semicircles in the high and medium frequency regions and an approximately 45$^\circ$ inclined line in the low frequency region. The compressed semicircles can be assigned to the combination of electrode/electrolyte interface film resistance ($R_f$)
and charge transfer resistance \( (R_{ct}) \), respectively, while the line is assigned to the Warburg impedance \( (W) \). The equivalent circuit for the electrochemical impedance spectra is presented in Figure 6.13. The exchange current \( (i_0) \) and activation energy \( (E_a) \) can be calculated from the following equations:

\[
i_0 = \frac{RT}{nFR_{ct}} \tag{6.4}
\]

\[
i_0 = A \exp(-E_a / RT) \tag{6.5}
\]

where \( A \) is a temperature independent coefficient, \( R \) is the gas constant, \( T \) is the absolute temperature, \( n \) is the number of transferred electrons, and \( F \) is the Faraday constant.

Figure 6.12 EIS spectra for the cells made of (a, c) raw and (b, d) restacked MoS\(_2\) at (a, b) 1.6 V and (c, d) 0.9 V at different temperatures.
The simulated parameters are shown in Table 6.1, and the activation energies of the raw and restacked MoS$_2$ at 1.6 V are calculated to be 68.3 and 63.3 kJ mol$^{-1}$, respectively. When discharged to 0.9 V, the activation energies are 63.5 and 41.5 kJ mol$^{-1}$, respectively. The activation energy of the restacked MoS$_2$ is slightly smaller than that of the raw material at 1.6 V, which means faster Li diffusion. However at 0.9 V, there is a phase transition from the pristine 2H form to the 1T form when Li intercalates into the S slabs, and the molybdenum atoms change from trigonal prismatic coordination to octahedral coordination. The activation energy for the restacked MoS$_2$ is much smaller than that of the raw materials. This is quite consistent with the previous analysis that the energy barrier to Li$^+$ motion is reduced when the space around Li increases and the diffusion length for lithium ions are shortened due to the decrease in the crystallite size, especially for the high current charge process.
Figure 6.14 Arrhenius plots of ln(i₀) versus 1/T for the electrodes containing raw (triangles) and restacked (rectangles) MoS₂ at (a) 1.6 V and (b) 0.9 V.

Table 6.1 Charge transfer resistance (Rₜ), exchange current (i₀), and apparent activation energies (Eₐ) of raw and restacked MoS₂ measured at different discharge stages and temperatures.

<table>
<thead>
<tr>
<th>Samples</th>
<th>T (°C)</th>
<th>1000/T (K⁻¹)</th>
<th>Rₜ (Ω)</th>
<th>i₀ (A)</th>
<th>ln(i₀(A))</th>
<th>Eₐ (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
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Chapter 6 Superior restacked MoS2 anode and MoS2/SnO2 composites

0.9V

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6.4 MoS2/SnO2 composites

6.4.1 Synthesis

0.75 g commercial MoS2 (< 2 μm) was soaked in 11.7 mL n-Butyllithium (1.6 M in hexane) for a week to prepare LiₓMoS₂, which was then washed with hexane several times and dried in a vacuum oven at 60 °C. In a typical synthesis, 0.113 g SnCl₂·2H₂O was dissolved in 20 mL ethanol in a round flask, and then 0.167 g LiₓMoS₂ was added to 30 mL de-ionized (DI) water, stirred for 10 min, and then poured into the first ethanol solution. The mixed solution was stirred and refluxed at 120 °C for 1 hour. The product was separated by centrifugation and washed 5 times with ethanol. Then, the precipitate was heated to 300 °C for 1 hour under argon gas in a tube furnace to obtain the final MoS2/SnO2 composite. Two samples were
prepared with nominal MoS₂ and SnO₂ molar ratios of 2:1 and 1:2, and labelled as Sample (I) and Sample (II), respectively. As a comparison, bare SnO₂ nanoparticles were prepared by refluxing SnCl₂ in ethanol and water at 120 °C and then annealing at 450 °C for 1 hour in air. The field emission scanning electron microscope (FESEM) image of this SnO₂ nanopowder sample shows uniform particles with sizes of less than 10 nm.

6.4.2 Characterization

![Figure 6.15 X-ray diffraction patterns: (a) a comparison of raw MoS₂, Sample (I), and Sample (II); (b) enlarged patterns of Sample (I) and Sample (II).](image)

Figure 6.15 X-ray diffraction patterns: (a) a comparison of raw MoS₂, Sample (I), and Sample (II); (b) enlarged patterns of Sample (I) and Sample (II).

Figure 6.15(a) shows the X-ray diffraction patterns of Sample (I) and Sample (II) compared with that of the raw MoS₂. Both composites show much a weaker and more broadened (002) reflection corresponding to MoS₂ than the raw material, indicating decreased stacking of Mo-S layers along the c axis after exfoliation [27]. Moreover, this peak is weaker in Sample (II) than in Sample (I), revealing thinner average stacking, which is probably due to the larger deposited amount of SnO₂ in the composite. The enlarged XRD patterns of Samples (I) and (II) in Figure 6.15(b)
clearly show peaks corresponding to the (110), (101), and (211) reflections of SnO$_2$. No other impurity peaks are observed in either composite from the XRD results.

TEM images of Sample (I) are shown in Figure 6.16(a)-(d). Two different areas marked as 1 and 2 were selected from Figure 6.16(a) for selected area electron diffraction (SAED) patterns, as shown in (b). Both of them show hexagonal patterns corresponding to the MoS$_2$ basal plane with zone axis along [001] and diffraction rings corresponding to SnO$_2$, indicating its polycrystalline nature. Different contrast of spots and rings reveals the different ratios between MoS$_2$ and SnO$_2$ in the two samples. Other areas and particles were also selected for SAED, and all of them show similar patterns, as in Figure 6.16(b), indicating the uniformity on a large scale. A high magnification image of the edge area marked as 3 in Figure 6.16(a) is shown in (c), in which the graphene-like stacking of a few exfoliated MoS$_2$ layers can be clearly seen. A high resolution image from another particle is shown in Figure 6.16(d). It can be observed that SnO$_2$ nanocrystals with sizes of about 5 nm were deposited onto the MoS$_2$ layers, which is responsible for the diffraction rings shown in (b).
Figure 6.16 TEM images of Sample (I): (a) typical area of the composite, (b) SAED patterns of selected areas marked with 1 and 2 in (a), (c) high resolution image of right edge area marked with 3 in (a), (d) high resolution image from another area; high resolution TEM images of Sample (II): (e) and (f), with the inset in (f) showing the corresponding SAED pattern.

Analogous to Sample (I), TEM images of Sample (II) at lower magnification show a similarity to Figure 6.16(a), and the electron diffraction pattern also contains both MoS₂ hexagonal spots and SnO₂ rings. Figure 6.16(e) is a typical high resolution image of sample (II) with exfoliated MoS₂ layers and SnO₂ nanocrystals deposited onto them, while a four-layer MoS₂ sheet shows the cross-section. In contrast with
sample (I), SnO$_2$ agglomeration was found in sample (II), as shown in Figure 6.16(f). The inset diffraction pattern rings indicate the existence of bare SnO$_2$, which is probably present because a larger amount of tin source was used in the precursor, resulting in some tin crystal seeds that grew without adhesion to the exfoliated MoS$_2$ layers.

It has been found that the magnetic properties of MoS$_2$ are related to the edge surface area [33]. In the as-prepared composites, it is easy for the exfoliated MoS$_2$ to form exposed edge areas, and therefore, the magnetization was investigated. As a comparison, raw MoS$_2$ and the SnO$_2$ nanoparticles were also measured. It can be seen from Figure 6.17 that the SnO$_2$ nanoparticles show the lowest magnetization, followed by the raw MoS$_2$, and then Sample (I). Sample (II) shows the highest magnetization. Note that although the magnetization of the bare SnO$_2$ is low and the weight ratio of SnO$_2$ in Sample (II) is higher than in Sample (I), Sample (II) still shows the highest magnetization. The results are likely to be due to the higher density of MoS$_2$ edge terminations in this composite, in which the different Mo:S coordination generates magnetism.
The typical reaction scheme for the exfoliation and reassembly route is shown in Figure 6.18. In the layer-structured raw MoS$_2$, S-Mo-S sandwich-like molecular slabs are stacked by weak van der Waals forces along the $c$ axis. During the first chemical lithiation process, Li ions enter the S slabs between two S-Mo-S layers, and then break the S-S covalent bonds and form Li-S bonds, forming the Li$_x$MoS$_2$ precursor. When the lithiated product reacts with water, the H$_2$ gas that is formed repels and exfoliates the MoS$_2$, as in equation (6.2). During the following reflux process, exfoliated MoS$_2$ layers are reassembled in the presence of Sn(OH)$_2$, and Sn(OH)$_2$ is deposited on the exfoliated MoS$_2$ layers. The final MoS$_2$/SnO$_2$ composites were obtained by annealing.
Figure 6.18 Schematic diagram of typical synthesis.

Further evidence on the quality and composition were obtained from Raman and XPS spectra of the products, as shown in Figure 6.19 and Figure 6.20, respectively. The Raman peaks for Sample (I) and Sample (II) are almost same in Figure 6.19. Both samples show new peaks at about 280 cm\(^{-1}\), 334 cm\(^{-1}\), 665 cm\(^{-1}\), 820 cm\(^{-1}\), and 993 cm\(^{-1}\), which are different from those characteristic of commercial MoS\(_2\) and SnO\(_2\), while these new peaks are very consistent with o-MoO\(_3\) peaks. The peak positions and the corresponding symmetry assignment are summarized in Table 2. Figure 6.20 shows Mo3d high-resolution XPS spectra of the two composites. Characteristic doublets of the Mo 3d5/2 peak located at 228.8 eV and the Mo 3d3/2 peak at 232 eV could be attributed to Mo\(^{4+}\) atoms [36]. In the whole survey spectrum, the S2p spectrum is primarily dominated by the XPS peak at 162 eV, which was ascribed to [S\(^{2-}\)] [37]. These further indicate the existence of MoS\(_2\). Moreover, the peaks of Mo 3d3/2 at 235.7 eV and 3d5/2 at 232.6 eV show that Mo is in the VI oxidation state [38], which is attributed to the Mo-O interaction. Both the Raman and XPS results reveal that there are interactions of molybdenum with sulphur and
oxygen atoms at the surface, but MoO₃ crystals were not be detected in the XRD patterns and TEM, probably due to the very tiny amount of MoO₃.

![Room temperature Raman spectra: raw MoS₂ powder, as-prepared SnO₂ nanoparticles, Sample (I), Sample (II).](image)

**Figure 6.19** Room temperature Raman spectra: raw MoS₂ powder, as-prepared SnO₂ nanoparticles, Sample (I), Sample (II).

**Table 6.2** Raman peaks of the samples and the corresponding symmetry assignments.

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**Figure 6.20** XPS high resolution spectra of Mo3d for (a) Sample (I) and (b) Sample (II).

### 6.4.3 Electrochemical performance

Electrochemical properties were investigated by preparation of the composites as electrodes in coin-type lithium cells. Figure 6.21 shows cyclic voltammograms of the two samples for the first 5 cycles. In the first discharge process, the peak at 1.0 V corresponds to the MoS$_2$ phase change from 2H hexagonal to 1T octahedral when lithium is intercalated, and the peak at 0.35 V corresponds to the formation of Mo and Li$_2$S when lithium is further intercalated [5]. The peak at 0.1 V corresponds to the formation of Li$_x$Sn [45]. In the charge process, peaks at 0.58 V and 1.26 V correspond to the Li de-intercalation from Li$_x$Sn, and the peak at 2.2 V corresponds to the reversible reaction related to MoS$_2$. The two composites show different peak intensities due to the different molar ratios of MoS$_2$ to SnO$_2$. Sample (I) shows highly repeatable curves of the reactions involving SnO$_2$ and a decreased peak intensity corresponding to reactions of MoS$_2$, while for Sample (II), the current density obviously decreases with cycling.
Figure 6.21 Cyclic voltammetry curves for the first 5 cycles of (a) Sample (I) and (b) Sample (II).

The cycling performance is displayed in Figure 6.22. From the energy dispersive X-ray spectroscopy spectra, the percentage of SnO\textsubscript{2} in Sample (I) is about 39.6 wt\%, and about 65.4 wt\% in Sample (II). The reversible capacity of sample (I) could be sustained at a fairly high value, above 1000 mAh g\textsuperscript{-1}, for the initial 15 cycles in the voltage range of 0.01 - 3 V, but it suffers fast decay afterwards. However, Sample (II) exhibits capacity decrease from the beginning. This could be due to the large volume change of SnO\textsubscript{2} in the large voltage range and because sample (II) contains more SnO\textsubscript{2}. When cycled in the voltage range of 0.05 - 1.5 V, MoS\textsubscript{2} shows low reversible capacity, below 200 mAh g\textsuperscript{-1}, so the main contribution is from SnO\textsubscript{2} in this voltage range, while MoS\textsubscript{2} could act as a buffer to block tin agglomeration during cycling. When cells were tested in the voltage range of 0.05 - 1.5 V, the capacity is displayed for SnO\textsubscript{2} only after subtraction of the contribution of MoS\textsubscript{2}, based on the weight ratios for the two composites. The electrochemical performance of MoS\textsubscript{2} is shown in Figure 6.23. The calculation process is similar to that reported for Sn@C composite [46]. Sample (I) delivers a relatively stable capacity of 525 mAh g\textsuperscript{-1} in the 30\textsuperscript{th} cycle, while the equivalent capacity for Sample (II) is only 416 mAh g\textsuperscript{-1}. These results can
be attributed to the well dispersed SnO$_2$ in the MoS$_2$ in Sample (I), with MoS$_2$ working as a matrix to prevent tin aggregation, while there are SnO$_2$ agglomerations in Sample (II).

**Figure 6.22** Cycling performances of the two composites cycled in different voltage ranges.

**Figure 6.23** Electrochemical performance of MoS$_2$: (a) voltage vs. capacity curves for selected cycles in the voltage range of 0.05 - 1.5 V and (b) cycling performance.
Chapter 6 Superior restacked MoS$_2$ anode and MoS$_2$/SnO$_2$ composites

Figure 6.24 FESEM images of cycled electrodes for (a) Sample (I) and (b) Sample (II) in the voltage range of 0.05 - 1.5 V.

To confirm the effects of MoS$_2$ mentioned above, FESEM images of the electrodes cycled in the voltage range of 0.05 – 1.5 V were collected, as shown in Figure 6.24. In Figure 6.2 (a) for Sample (I), a film has partially covered the surface, and small cracks can be observed on the film, probably due to the good distribution of SnO$_2$ between the MoS$_2$ sheets, while in Figure 6.24(b), Sample (II) shows the opposite situation. Large aggregations and cracks can be clearly observed from the FESEM image, due to the higher amount of SnO$_2$ in the composite, which causes large volume change during lithium intercalation/de-intercalation. This morphology is believed to be responsible for the poorer electrochemical cycling performance.
6.5 Summary

Roll-over cell design is practical for in-situ neutron diffraction studies, with only a slight perturbation in the electrochemistry relative to the more commonly-used coin-type cell. The roll-over cell design is sensitive to weakly diffracting materials, and its use is anticipated to further the understanding of the mechanisms of Li insertion or extraction from a variety of electrode materials and to characterize the phases and their transitions with electrochemical cycling.

Restacked MoS$_2$ with an enlarged $c$-axis parameter was prepared by exfoliation and then restacking by a simple hydrothermal method. The enlarged $c$ parameter and the increased surface area are favourable to the intercalation reaction, which can also be proven by electrochemical kinetic analysis. The restacked MoS$_2$ electrodes exhibit a large capacity of 800 mAh g$^{-1}$ and extraordinarily high cycling stability, even at high charge current density. The results suggest that the restacked MoS$_2$ is a promising anode material for lithium ion batteries. This strategy, i.e. enlarging the space between layers and increasing the surface area (especially the edge area) for electrode materials with layered structures, could be a common way to improve the intercalation kinetics in terms of rechargeable batteries.

Exfoliated MoS$_2$ and SnO$_2$ nanocrystal composites were prepared by exfoliation of commercial MoS$_2$, and SnO$_2$ nanocrystals with a size of 5 nm were deposited onto the exfoliated MoS$_2$ layers by a reflux process. The weight ratio of MoS$_2$ to SnO$_2$ in the products can be controlled by changing the ratio of the tin source to MoS$_2$ in the precursor, and the ratio of MoS$_2$ to SnO$_2$ could significantly affect the distribution of
SnO$_2$ nanocrystals in the composites, thus affecting their electrochemical performance as anode materials for lithium ion batteries and the magnetization which arises from the edge area of the MoS$_2$ layers

References


CHAPTER 7 One Dimensional TiO₂ Nanowire and Three Dimensional Nanotube Array

7.1 Introduction

More and more attention has been paid to one-dimensional titanium oxide nanomaterials because of their broad applications in photocatalysts [1, 2], microelectronics [3], electron field emission [4], photovoltaic cells [5, 6], rechargeable lithium ion batteries [7, 8], chemical sensors [9, 10], etc. Several synthesis methods, such as the hydrothermal method [4, 11], the chemical-solution route [12, 13], electrochemical deposition [9, 14], and the molten salt method [15], have been developed to form many kinds of one-dimensional TiO₂ nanomaterials such as nanorods [15-17], nanowires [18] and nanotubes [9]. Among all those synthesis methods above, the hydrothermal method is a relatively facile way to prepare one-dimensional TiO₂ nanomaterials [19].

Generally, there are four common polymorphs of TiO₂ [19, 20]: rutile, anatase, brookite, and TiO₂(B). Among these TiO₂ polymorphs, hydrothermal anatase TiO₂ nanotubes or nanowires were generally considered to be the most promising anode materials in lithium-ion battery applications [16] due to their good electrochemical properties [21]. However, their low lithium-ion diffusion capability and electronic conductivity are still the main obstacles for their practical applications. Recently, metastable TiO₂(B) nanotubes or nanowires, prepared by hydrothermal or other methods, have attracted great interest as anode materials for lithium-ion batteries because they have a relatively open structure with significant voids and continuous
channels, and further possess lower density (3.73 g/cm$^3$) than the other polymorphs [7, 22], which all favour lithium-ion diffusion during charge/discharge cycling. Thus, one possible way to improve the electrochemical lithium storage properties of one-dimensional TiO$_2$ nanomaterials is to enhance electronic conductivity and lithium-ion diffusion capability via the introduction of mixed phases TiO$_2$ anatase/TiO$_2$(B) nanotubes or nanowires because of the special properties of heterojunction in their interfaces [1, 23-25] and the continuous channel structures of TiO$_2$(B) [7, 22].

Currently, lithium ion batteries are used as power sources for a wide range of applications, such as laptops, mobile phones, cameras, and other portable electronics, and are beginning to be used for power tools and hybrid electric vehicles [26, 27]. However, another massive market is expected to be developed over the next decade in the area generally known as microelectromechanical systems (MEMS), which grew out of the integrated circuits industry [28, 29]. This field demands a high energy and high power unit on a small footprint area, which requires the use of special nanostructured architectures in the form of three-dimensional (3D) microbatteries. Microbatteries can also be used in hearing aids, medical implants, radio frequency transmitters, memory chips, and many other devices. There are only a few experimental examples of 3D electrodes, which are mainly designed as nanorod current collectors with deposited active materials [30-35]. Difficulties associated with this design include the requirement for template assisted fabrication and the fact that the nanorods are so easy to displace. Recently, self-organized TiO$_2$ nanotube arrays created by anodization have been reported for use as anode material in microbatteries [36]. There are also reports that researchers have succeeded in
preparing other metal or metal oxide compositions deposited onto the surface of TiO2 nanotube arrays for use as photocatalysts, drug delivery systems, and solar cells [37-41]. As an anode material, TiO2 has a very low capacity, with a volume change of less than 4% when forming Li_xTiO2 (0 ≤ x ≤ 1) [42-47]. However, SnO2 has a theoretical capacity (781 mA h g⁻¹) more than twice as large as that of the commercially used graphite, and it is considered as one of the most promising anode candidates [48-56]. The main drawback is nevertheless that the volume expansion when forming Li_xSn during lithium intercalation is more than 250%, so various structures have been designed to accommodate the volume expansion of tin. It can be imagined that using the 3D structure of a TiO2 nanotube array as support, with SnO2 nanocrystals used to decorate the TiO2 nanotube array, could be an even better strategy to accommodate the volume expansion of tin oxide, thus improving its cycling performance and suitability for 3D electrodes for microbatteries. The SnO2 in the 3D electrode can make a great contribution by enhancing the capacity, while the 3D TiO2 nanotube array can accommodate the volume expansion and maintain the structural integrity of the electrode.

In the first part of this chapter, novel bi-crystalline anatase@TiO2(B) hybrid nanowires are reported that have been prepared readily by a hydrothermal reaction between NaOH and TiO2 powder, followed by consecutive partial phase transition processes of H₂Ti₃O₇ nanowires [1]. The anatase@TiO2(B) hybrid nanowires have more unique advantages [1], such as high electronic conductivity and lithium-ion diffusion because of this special TiO2 anatase/TiO2(B) configuration. The possible carrier transfer mechanism during the formation of heterojunctions and the mechanisms of further charge diffusion and conduction during Lithium intercalation/deintercalation have been proposed in detail. The electrochemical
properties, such as the high discharge performance and good cyclability of TiO$_2$ anatase@TiO$_2$(B) nanowire electrodes reveal their potential application in the lithium ion battery. In the second part of this chapter, 3D TiO$_2$ nanotube arrays are reported that were prepared by the anodization process. The effect of annealing on morphology, structure, and electrochemical performance was systematically investigated. The third part of this chapter reports SnO$_2$ nanocrystals that were deposited on a TiO$_2$ nanotube array substrate via the solvothermal method to form SnO$_2$/TiO$_2$ composites for use as 3D anode and demonstrate that the electrochemical performance of this electrode is promising for application in lithium ion microbatteries. The 3D anodes reported here possess the following advantages: (1) Unlike other porous SnO$_2$ anodes fabricated using template assisted methods, there is no need to remove the TiO$_2$ substrate, since it is also a kind of anode material. (2) TiO$_2$ can make a contribution to the capacity, so it is better than introducing an inactive composition into SnO$_2$ anode. (3) Aligned TiO$_2$ nanotubes with a self-organized and self-supported array structure will lead to high physical stability, which contributes to the cycling stability of the anode. Moreover, the intratubal space of a TiO$_2$ nanotube is large enough to accommodate the volume expansion of SnO$_2$ during Li$^+$ intercalation, which helps to maintain the integrity of the anode during cycling. (4) The capacity of the 3D electrode is controlled by the TiO$_2$ tube length, as well as by the amount of SnO$_2$ loading. (5) Finally, the anodes fabricated in this way are conductive carbon and binder free, which will drastically increase the energy density and power density of the whole battery.
7.2 TiO$_2$(B)

7.2.1 Synthesis

Synthesis of anatase@TiO$_2$(B) hybrid nanowires was performed by the facile hydrothermal process and post treatments, similar to the synthesis process described in the literature [1, 10, 18, 19]. Typically, the precursors, titanate nanowires, were synthesized by adding 4.5 g TiO$_2$-anatase (powder, 99.8%, Aldrich) to a 15 M aqueous solution of NaOH. After stirring for 1 h, the resulting suspension was transferred to a Teflon-lined autoclave and heated to 150 °C for 72 h. The product was subjected to acid washing, which involved stirring the sample in 0.1 M HCl solution for 1 h twice to prepare precursor H$_2$Ti$_3$O$_7$ nanowires [1, 23-25]. The material was then filtered, washed with distilled water until pH ≈ 7 (each time stirring the sample in 500 ml distilled water for 1 h), and dried at 80 °C for 20 h. Anatase@TiO$_2$(B) hybrid nanowires were obtained by heating the acid-washed titanate nanowires at 400 °C for 4 h in air.

7.2.2 Characterization

The field-emission scanning electron microscope (FE-SEM) images clearly show a general view of randomly aligned TiO$_2$ nanowires with diameters of 30-80 nm and lengths extending to a few micrometers (Figure 7.1(a–b)). Some TiO$_2$ nanowires have become attached together to form a single thicker belt (Figure 7.1(b)). Initial Rietveld analysis was based on the structural models of TiO$_2$ anatase (JCPDS 21-1272) and TiO$_2$(B) (JCPDS 74-1940) with narrow peak widths. All observed reflections were found to match these two phases. Peak shapes for X-ray diffraction (XRD) data were modelled prior to the refinements, using single peak fits to the (110) peak of TiO$_2$(B) and the (200) peak of anatase. The Rietveld refined fit of the structural model using XRD data is shown in Figure 7.1(c). Refined
cell parameters for TiO$_2$(B) are $a = 12.635(6)$ Å, $b = 3.743(1)$ Å, $c = 6.473(2)$ Å, and $\beta = 107.45(4)^\circ$, adopting C2/m symmetry, and for anatase with XRD cell parameters, $a = 3.756$ Å and $c = 9.500$ Å, adopting I41/amd symmetry. These values agree with the literature, but non-stoichiometry cannot be ruled out of any anatase containing TiO$_2$ phases [57, 58]. The anatase showed some preferred orientation along the [200] direction, which was modelled using a March-Dollase function, which has been shown not to skew the phase fraction analysis [59]. The phase fractions by weight were determined to be 92.8(5)% TiO$_2$(B) and 7.2(1)% anatase. These phase fractions support the postulation of the motif formed by this combination, that is, a majority phase of TiO$_2$(B), covered by a minority anatase TiO$_2$ phase. Generally, the experimental acid environment should be more favourable to the TiO$_2$ anatase phase transformation [60], and therefore, more TiO$_2$ anatase in the outer layer of the nanowire should form and propagate inwards owing to the higher H$^+$ concentration in the outer layers of nanowires during the Na$^+ \rightarrow$ H$^+$ ion exchange. Figure 7.2(a) shows a bright-field transmission electron microscope (TEM) image of a single TiO$_2$ nanowire, combined with the corresponding selected area electron diffraction (SAED) pattern in the inset, which shows that this hybrid nanowire extends along the [010]B direction in TiO$_2$(B) [22, 1, 25] to form continuous channels along its axis direction [7, 22]. The (001) plane of anatase connects with the (100) plane of TiO$_2$(B) to form the heterojunction interface [1]. However, for random nanowires, two obvious spotted diffraction rings from the inside to the outside were indexed to the (200) and (110) planes of TiO$_2$(B) (see Figure 7.2(b) and its inset). Figure 7.2(c) further confirms that the hybrid nanowire extends along the [010]B direction, with an interplanar spacing of ~0.536 nm between neighbouring (200) planes of TiO$_2$(B) and ~0.35 nm between (110) planes. The combination of the FE-SEM, energy dispersive
X-ray spectroscopy (EDX), XRD, and TEM results verify that the parent H$_2$Ti$_3$O$_7$ nanowire [1] is converted into TiO$_2$(B)@anatase hybrid nanowire, consisting of a major TiO$_2$(B) crystal core inside a shell of minor anatase nanocrystals. Therefore, a carrier transfer mechanism during the formation of heterojunctions is proposed in Figure 7.2(d) (left). The differences in band edges of the entangled phases promote one way charge migration from anatase to TiO$_2$(B), much as in a one way valve [1, 25]. In the hybrid nanowire, both the high conductivity layer or belt and the good Li$^+$ diffusion channel along the length direction are described in Figure 7.2(d) (right).

**Figure 7.1** FESEM images of as-synthesized anatase@TiO$_2$(B) nanowires (a) and (b), (c) X-ray diffraction (XRD) pattern and Rietveld analysis, where the symbols in the top spectrum represent the data, and the solid line the calculated fit. The upper and lower vertical lines are the lines in the TiO$_2$(B) and anatase standards, respectively. The difference spectrum is shown below. The insets in (a) and (b) are the EDX spectrum and a higher resolution image, respectively. (Gold nanoparticles with a grain size of ~5-10 nm were evaporated on the surface of the anatase@TiO$_2$(B) nanowire samples to reduce electrostatic charging during SEM imaging.)
**Figure 7.2** (a) TEM image and SAED pattern (inset) of single anatase@TiO$_2$(B) nanowire, (b) low-magnification TEM image and SAED pattern (inset) of anatase@TiO$_2$(B) nanowires, (c) high resolution TEM image of a section of an anatase@TiO$_2$(B) nanowire, (d) proposed carrier transfer mechanism during formation of the nanowire heterojunction (left) and charge diffusion mechanism of nanowires during charge/discharge processes (right). (Subscripts ‘A’ and ‘B’ represent ‘Anatase’ and ‘TiO$_2$(B)’, respectively.)

### 7.2.3 Electrochemical performance

Cyclic voltammograms (CV) of hybrid nanowires from the first to the fifth cycle at a scan rate of 0.1 mV s$^{-1}$ in the voltage range of 1.0-3.0 V are presented in Figure 7.3(a). The voltammogram is dominated by two pairs of peaks denoted S1 and S2, which are assigned to TiO$_2$(B) [11, 61]. Additionally, a pair of small redox peaks at 1.73 V and 1.96 V, the A-peaks, is likely to have originated from the minor anatase in the sample [8]. The cycling performance of the hybrid nanowire electrode from
the 1st to the 100th cycle was obtained at a constant current of ~30 mA g⁻¹ or 0.1 C, with a cut-off voltage window of 1.0 V to 3.0 V (vs. Li⁺/Li). The intensity ratio of the A-peaks to the S-peaks is in good agreement with the molar ratio of anatase to TiO₂(B) in the mixed phase. Therefore, the electrochemical behaviour of TiO₂(B) dominates in the TiO₂(B)@anatase hybrid nanowires, as evidenced by the dominant S-peaks in the CV results. Figure 7.3(b) shows the discharge/charge capacity curves and the coulombic efficiency versus cycle number. The composite electrode exhibits a highly reversible initial specific discharge and charge capacity of over 256.5 mAh g⁻¹ and 232 mAh g⁻¹, respectively, in the first cycle. It maintains a high capacity of ~196 mAh g⁻¹ after 100 cycles. The low initial coulombic efficiency (90.45%) may be ascribed to the Li being inserted into irreversible sites, either in TiO₂(B) and/or in anatase. However, the irreversible capacity decreases, and the coulombic efficiency increases in the subsequent cycles and stabilizes at above 99% from the third cycle onwards. Figure 7.3(c) shows the plot of voltage vs. capacity at different current densities from 0.1 C to 15 C, where each step lasts six cycles, except for the last recovery step, which lasts for 10 cycles. As the current rate increases, the charging voltages increase, while the discharging voltages decrease. This can be attributed to variation in the specific charge transport mechanism in the hybrid nanowires. The rate capabilities of the anatase/TiO₂(B) composite electrode are shown in Figure 7.3(d). The hybrid nanowire electrode delivers a capacity of about 230.7 mAh g⁻¹ at 0.1 C after 6 cycles. This value decreases to 206 mAh g⁻¹ at 0.5 C, 187.3 mAh g⁻¹ at 1 C, 163.6 mAh g⁻¹ at 2.5 C, 144.4 mAh g⁻¹ at 5 C, 130.8 mAh g⁻¹ at 10 C, 125 mAh g⁻¹ at 15 C, and after the application of 15 C, recovers to 219.3 mAh g⁻¹ at 0.1 C. The electrochemical performance of TiO₂(B)@anatase composite electrode is comparable
or even superior to the latest promising research results on anatase TiO$_2$ [62, 63] and TiO$_2$ nanowires [64].

**Figure 7.3** Electrochemical performance of anatase@TiO$_2$(B) nanowire electrode cycled between 1.0 and 3.0 V vs. Li$^+$/Li: (a) cyclic voltammograms from the first cycle to the fifth cycle at a scan rate of 0.1 mV s$^{-1}$ in the voltage range of 1.0-3.0 V, (b) capacity–cycle number curves from the first cycle to the 100$^{th}$ cycle at the current density of 30 mA g$^{-1}$, (c) voltage profiles at the different cycling rates of 30, 150, 300, 750, 1500, 3000, and 4500 mA g$^{-1}$, (d) discharge capacity as a function of the discharge rate (30, 150, 300, 750, 1500, 3000, 4500 mA g$^{-1}$); the inset is the discharge capacity vs. rate capability curve.

Superior cyclability and rate capability of the anatase/TiO$_2$(B) composite electrode might be due to the arrangement of TiO$_2$(B) and anatase in the hybrid nanowire consisting of a major TiO$_2$(B) core encapsulated in a minor anatase matrix. Reasons for its excellent electrochemical performance include a shorter diffusion length for
both electrons and Li ions, and the proposed high conductivity column layer (Figure 7.2(d)) or belt formed around the heterojunction interface. All these factors finally lead to excellent reversible capacity, high coulombic efficiency, and high cyclic retention and rate capability.

7.3 TiO$_2$ nanotube array

7.3.1 Synthesis

The preparation procedure has been described previously [65]. In a typical process, two electrode anodization at ambient temperature was applied to prepare a TiO$_2$ nanotube array. Commercial titanium foils (purity >99.7%) with dimensions of 30 × 60 × 0.1 mm were used as working electrodes, and a platinum foil with the same area was used as the counter electrode. The titanium foils were first polished with 800 grit sandpaper, rinsed with de-ionized (DI) water, and then cleaned by ultrasonication in acetone and dried. A typical anodization was carried out in 0.5wt% HF electrolyte with direct current power for 20 min at 20 V. The resultant nanotube length is about 2 µm. Annealing treatments were carried out at 250 °C, 350 °C, 500 °C, and 600 °C in air for 1 hour with a heating rate of 5° min$^{-1}$ and natural cooling.
7.3.2 Characterization

Figure 7.4 X-ray diffraction (XRD) patterns of samples: as-prepared and annealed at 250 °C, 350 °C, 500 °C, and 600 °C.

Annealing treatments at 250 °C, 350 °C, 500 °C, and 600 °C were selected. The X-ray diffraction patterns of these samples together with that of the as-prepared TiO₂ are shown in Figure 7.4. The as-prepared TiO₂ nanotubes are amorphous, and there is no peak in the XRD pattern except for peaks belonging to the titanium substrate. After annealing at 250 °C, there are still no obvious extra peaks. However, when the annealing temperature increases to 350 °C, new peaks at about 25.3° and 48° are detected, which correspond respectively to the (101) and (200) reflections of the anatase phase. On increasing the annealing temperature to 500 °C, two more small peaks at about 27.4° and 54.3° appear, corresponding respectively to the (110) and (211) reflections of the rutile phase, which indicates a mixture of phases, but one
mainly composed of anatase. When annealed at 600 °C, the mixed phases mainly change to rutile.

Top-view FE-SEM images of samples are shown in Figure 7.5(a)-(e). All the samples show tubular structures, and the average diameter of the nanotubes is about 100 nm. Annealing treatments at different temperatures do not change the morphology too much except at 600 °C, at which the tube walls show a slight amount of breakage. A typical high resolution FE-SEM image of the sample annealed at 600 °C is shown in Figure 7.5(f). Note that there is structure that appears flocculated in Figure 7.5(b) and (d). This could be ascribed to non-uniform dissolution on the surface of the as-prepared TiO$_2$ during the preparation in an acid medium.
Figure 7.5 FESEM images of (a) as-prepared TiO$_2$ and samples annealed at (b) 250°C, (c) 350°C, (d) 500°C, and (e) 600°C; (f) high resolution image of sample annealed at 600 °C.

7.3.3 Electrochemical performance

Figure 7.6 shows the cyclic voltammetry (CV) curves of all the samples. There is no obvious peak for the as-prepared amorphous TiO$_2$ in its cyclic voltammogram, but
only a very broad band from 1.8 V to 2.3 V, and almost the same is the case for the sample annealed at 250 °C. However, the samples annealed at higher temperatures show sharp peaks at about 1.72 V for the cathodic scan and at 2.1 V for the anodic scan. The difference in voltage between the redox peaks, $\Delta E_p$, becomes larger as the annealing temperature increases. The $\Delta E_p$ of the sample annealed at 250 °C is larger than that of the as-prepared sample, which may indicate that the amorphous phase changes to crystalline to some extent.

![Cyclic voltammograms of the samples at a scan rate of 0.1 mV s⁻¹.](image)

**Figure 7.6** Cyclic voltammograms of the samples at a scan rate of 0.1 mV s⁻¹.

Figure 7.7(a) shows the second cycle galvanostatic charge/discharge curves from 1.0-3.0 V. For the as-prepared sample and the one annealed at 250 °C, there is no plateau, while for the samples annealed at 350 °C, 500 °C, and 600 °C, there are plateaus at 1.7 V for discharge and 2.0 V for charge, corresponding to lithium intercalation into and de-intercalation out of crystalline TiO₂, in good agreement with the CV curves in Figure 7.6. The cycling performance over 50 cycles is presented in Figure 7.7(b). The sample annealed at 250 °C shows the highest discharge capacity.
of about 67-69 μAh cm\(^{-2}\). The discharge capacity of the as-prepared sample is about 64-66 μAh cm\(^{-2}\), with a small increase at the end of the cycling compared to the 250 °C annealed sample. The value for the sample annealed at 350 °C is about 55 μAh cm\(^{-2}\), which is almost the same as that for the sample annealed at 500 °C. For the sample annealed at 600 °C, the discharge capacity is about 41 μAh cm\(^{-2}\). All the samples show quite good cycling stability. Although the XRD results show no obvious changes for the sample annealed at 250 °C compared to the as-prepared one, the reason for higher lithium storage capacity is still unclear. It is believed that there is some degree of change from amorphous to ordered phase on annealing.

**Figure 7.7** Electrochemical performance of the as-prepared and annealed samples: (a) charge-discharge curves; (b) discharge capacity vs. cycle number at a current density of 20 μA cm\(^{-2}\).

Typical Nyquist plots collected from fresh cells at the open circuit potential of 1.8 V and from the same cells at a charged potential of 3 V after five charge-discharge cycles are presented in Figure 7.8(a) and (b). The semicircle related to the high to medium frequencies can be assigned to the combination of the electrode/electrolyte
interphase film resistance \( (R_f) \) and the charge transfer impedance \( (R_{ct}) \). The impedance spectra of both the fresh cells and the cells after cycling show the same trend, i.e., the resistance of the sample annealed at 250 °C is smallest, then that of the as-prepared sample, followed in order by those of the samples annealed at 350 °C, 500 °C, and 600 °C.

**Figure 7.8** Electrochemical impedance spectroscopy of samples over a range of frequencies from 0.01 Hz to 100 kHz: (a) fresh cells, (b) cells charged to 3.0 V after 5 cycles. The insets show enlargements of the high frequency region.

To demonstrate how the structure is maintained after cycling, FESEM images of the electrodes after 50 cycles are presented in Figure 7.9(a)-(e). They show that all the samples maintain the tubular structure. Although the cycled electrodes were first soaked in DEC for one day and then in acetone for one day, and finally carefully washed, there is still a thin film on the surface of the electrodes. This thin film is unstable under the high resolution FESEM electron beam and can be melted if the energy is high enough, allowing the real TiO\(_2\) tubular morphology underneath to reappear. The energy dispersive X-ray (EDS) spectrum is shown in Figure 7.9(f). The film contains F and P, which formed from the reaction with the electrolyte.
Figure 7.9 FESEM images of samples after 50 charge-discharge cycles: (a) as-prepared and annealed at (b) 250 °C, (c) 350 °C, (d) 500 °C, and (e) 600 °C; (f) typical EDS spectrum of the TiO\textsubscript{2} nanotube electrode annealed at 350 °C after 50 charge/discharge cycles.

7.4 SnO\textsubscript{2} nanocrystal/TiO\textsubscript{2} nanotube composites

7.4.1 Synthesis

TiO\textsubscript{2} nanotubes were prepared by a potentiostatic anodization process. Commercial titanium foil (30 mm × 60 mm × 0.1 mm) was used as the working electrode, and Pt foil with the same area as the titanium was used as the counter electrode. The titanium foil was first polished with sandpaper (1000 #) and washed with de-ionized water. It was then washed with acetone for 30 min with ultrasonication and dried before use. The titanium foil was anodized in 0.5 wt% HF solution with applied DC
voltage of 20 V for 20 min to prepare 200 nm length TiO$_2$ tubes, and longer tubes were prepared in 0.5 wt% HF + 1 M NH$_4$H$_2$PO$_4$ solution at a voltage of 20 V for about 15 h. The TiO$_2$/Ti substrate was annealed in air at 500 °C for 1 h. The solvothermal method was used to synthesize the SnO$_2$/substrate composite. In a typical synthesis, 0.005 M SnCl$_2$·2H$_2$O in ethanol was sealed in a Teflon autoclave with a 1 cm × 1 cm substrate and ultrasonicated for 30 min, and then heated at 150 °C for 0.5 h. All the samples were then heat-treated at 450 °C in air for 1 h, with a heating rate of 5 °C/min.

### 7.4.2 Characterization

The solvothermal treatment was carried out at 150 °C for 10 h with different SnCl$_2$ concentrations of 0.001 M, 0.005 M, and 0.02 M. The FESEM images are shown as Figure 7.10. The 0.001 M sample is a very dense film without obvious holes on the surface, while the 0.005 M and 0.02 M samples show a porous structure with a decreased tube diameter, although the surface of the 0.02 M sample is more compact. The reason why a dense film formed in the 0.001 M sample is not clear, but repeated experiments show the same results. This may be because the lower Sn$^{2+}$ concentration affects the solution wettability to the TiO$_2$ substrate surface, so the equilibrium between the nucleation speed and the crystal growth speed is different from the case with higher Sn$^{2+}$ concentrations, with corresponding effects on the morphology. The Sn$^{2+}$ concentration was chosen to be 0.005 M SnCl$_2$, using different reaction times according to this concentration dependent experimental result, so the different samples are designated by the reaction time. In Figure 7.11(a), FESEM images of the TiO$_2$ substrate show uniform tubes with diameters of about 60-80 nm, and the inset cross-sectional image shows a well aligned array of tubes. The high resolution image in Figure 7.11(b) shows the smooth surface of the tube
walls. Figure 7.11(c) - (f) contains general views of SnO$_2$/TiO$_2$ samples created with different reaction times of 0.5 h and 10 h. The tubular morphology of these two samples is similar to that of the TiO$_2$ substrate. The same morphology can be obtained for samples with reaction times of 2 h and 5 h (not shown here). The thickness of the tube wall increases and the inner diameter of the nanotubes decreases as the reaction time increases, which indicates increased loading of SnO$_2$. The higher magnification images of Figure 7.11(d) and (f) clearly show that fine SnO$_2$ nanocrystals with crystal size less than 10 nm are deposited uniformly on the surface of the TiO$_2$ nanotube array.

Figure 7.10 FESEM images of: (a) TiO$_2$ nano-array substrate; SnO$_2$/TiO$_2$ samples with different SnCl$_2$ precursor concentrations: (b) 0.001 M, (c) 0.005 M, and (d) 0.02 M.
Figure 7.11 FESEM images at different magnifications: TiO$_2$ substrate (a,b), with the inset in (a) showing a cross-sectional image; results of solvothermal reaction at 150 °C with 0.005 M SnCl$_2$ for different reaction times: 0.5 h (c,d) and 10 h (e,f).

XRD was carried out to confirm the structures of the samples, as shown in Figure 7.12. The titanium oxide substrate is a mixture of anatase and rutile phases, as determined from the Joint Committee on Powder Diffraction Standards (JCPDS) database. The peaks at about 25.3°, 48.1°, 54° and 55.1° correspond to the (101), (200), (105), and (211) reflections of the anatase phase (JCPDS No. 21-1272), while
the peaks at 27.5° and 54.3° can be indexed as the (110) and (211) reflections of the rutile phase (JCPDS No. 21-1276). For the 0.5 h SnO$_2$/TiO$_2$ sample, peaks at 26.6° and 33.8° correspond to the (110) and (101) planes of the tetragonal rutile structure of SnO$_2$ (JCPDS No. 41-1445). The peaks corresponding to SnO$_2$ are not very strong because of the small amount of deposited SnO$_2$. For the 10 h sample, more SnO$_2$ was deposited, and the peaks are much stronger. In addition, a peak at 52° corresponding to the (211) reflection can be clearly observed. The energy dispersive X-ray spectroscopy (EDS) mapping of the 0.5 h sample in Figure 7.13 also confirms the presence of tin, which is consistent with the XRD results.

Figure 7.12 X-ray diffraction patterns of the TiO$_2$ substrate and of the 0.5 h and 10 h SnO$_2$/TiO$_2$ samples.
Figure 7.13 EDS results on 0.5 h SnO$_2$/TiO$_2$ sample: (a) Ti distribution, (b) Sn distribution, (c) EDS spectrum of sample.

TEM images of thin sample sections are shown in Figure 7.14. These sections through the tubes, going down from the top surface into the substrate, were prepared by focused ion beam (FIB) milling of the sample. Regions marked as 1, 2, and 3 are associated with a single TiO$_2$ nanotube, while the black area (top left) is a Pt protective layer. The thin layer directly underneath is rich in Au, deposited to allow direct SEM viewing during the dual electron beam-FIB preparation procedure. The tube lengths are about 200 nm with a bamboo-like structure, while the tube widths of around 40-60 nm match those in the SEM images.
Figure 7.14 TEM cross-sectional images of 0.5 h SnO$_2$/TiO$_2$ sample: (a) image of array of tubes, (b) and (c) HRTEM images of a TiO$_2$ tube and of its SnO$_2$ nanocrystals, with the inset in (c) showing lattice fringes of one SnO$_2$ nanocrystal.

The combination of TEM and EDS (Figure 7.15) results for the selected areas 1, 2, and 3 provided evidence that SnO$_2$ nanocrystals are located deep inside the tubes. Some tubes are filled with SnO$_2$ nanocrystals, as shown in Figure 7.14(b), and the
high resolution TEM (HRTEM) image in Figure 7.14 (c) clearly shows the lattice fringes on one nanocrystal, with an interplanar spacing of an estimated 0.243 nm, corresponding to the (200) planes of tetragonal SnO$_2$. The particle size is less than 5 nm.

**Figure 7.15** EDS spectra corresponding to TEM images in Figure 7.14: (a) whole area of Figure 7.14(a), (b) region 1, (c) region 2, and (d) region 3. Platinum and gallium were used for the holder to prepare the TEM sample for the cross-sectional images, so their peaks are present. The C and Cu peaks are from the copper grid.
7.4.3 Electrochemical performance

Figure 7.16 Electrode performances of SnO₂/TiO₂ samples: (a) cyclic voltammograms of 0.5 h SnO₂/TiO₂ sample, (b) cycling performance of 200 nm TiO₂ and 0.5 h SnO₂/TiO₂ samples at current density of 20 µA cm⁻² over different voltage ranges, (c) galvanostatic curves for the 10 first cycles of 0.5 h SnO₂/TiO₂ sample, (d) rate capability of 0.5 h SnO₂/TiO₂ sample at different current densities.

Cyclic voltammograms (CV curves) of a SnO₂/TiO₂ sample are shown in Figure 7.16(a). The reduction/oxidation peaks at 1.69 V and 2.08 V vs. Li⁺/Li correspond to lithium ion intercalation/de-intercalation in the TiO₂, according to the reaction below [47]:

\[ x\text{Li}^+ + \text{TiO}_2 + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2 \quad (0 \leq x \leq 1) \] (7.1)
The reduction peaks at around 1.25 V and 0.90 V in the first cycle are related to
electrolyte decomposition and Li$_2$O formation, respectively, when SnO$_2$ reacts with
Li$^+$, as described below [48, 52]:

$$\text{SnO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow 2\text{Li}_2\text{O} + \text{Sn} \quad (7.2)$$

The reduction peaks at 0.20 V, 0.60 V, and 0.92 V, and the oxidation peaks at 0.50 V,
0.63 V, and 1.20 V can be attributed to the formation of a series of Li-Sn alloys [48,
52]:

$$\text{Sn} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{Sn} \quad (0 \leq x \leq 4.4) \quad (7.3)$$

The results of cycling stability testing at a charge/discharge current density of 20 $\mu$A
cm$^{-2}$ are shown in Figure 7.16(b). Because TiO$_2$ and SnO$_2$ exhibit different voltage
plateaus, electrochemical performance over different voltage ranges is displayed. The
samples show good cycling stability when cycled in the voltage range of 1 to 3 V,
and deliver almost the same capacities because TiO$_2$ makes a large contribution. In
the voltage range of 0.05 to 2.5 V, the SnO$_2$/TiO$_2$ sample exhibits much higher areal
capacity, more than twice that of the bare TiO$_2$ sample. The capacity retention of the
SnO$_2$/TiO$_2$ sample for the 100$^{th}$ cycle is 70.8% of the capacity of the first cycle,
which is higher than that of the TiO$_2$ sample (65.7%). Figure 7.16(c) shows the
galvanostatic curves of voltage vs. capacity for a SnO$_2$/TiO$_2$ sample. The plateaus at
about 1.75 V for discharging and 2.08 V for charging correspond to the Li$^+$ reaction
with TiO$_2$, and the plateaus at less than 1 V correspond to the reaction of SnO$_2$, both
of which are consistent with the CV curves. For microbattery application, Ortiz et al.
[36] recently reported that TiO$_2$ nanotubes, grown by anodization with a length of
920 nm, delivered a reversible capacity of 50 mAh cm$^{-2}$ at a current density of 20
mA cm$^{-2}$. Cheah et al. reported a capacity of about 10 mAh cm$^{-2}$ for a TiO$_2$ thin layer
deposited onto Al nanorods at a current density of C/5 [33]. Note that the capacity of this kind of 3D electrode is driven by the length of the active material pillars. In this work, TiO$_2$ nanotubes with different lengths were tested, and different SnO$_2$ loadings were prepared by controlling the solvothermal reaction time. The cycling performances are shown in Figure 7.17(a). Apparently, the 200 nm TiO$_2$/SnO$_2$ sample shows increased capacity if the reaction time is increased from 0.5 h to 10 h due to the higher content of SnO$_2$. When cycled in the voltage range of 0.05 to 2.5 V, the reversible capacity is 115 mAh cm$^{-2}$, which is much higher than that of the sample in Figure 7.16(b), 40 mAh cm$^{-2}$. The 2000 nm TiO$_2$/10 h SnO$_2$ sample exhibits the highest reversible capacity, which is about 300 mAh cm$^{-2}$ over the voltage range of 0.05 V to 2.5 V for the first cycle. These results reveal that the capacity can be controlled by varying the TiO$_2$ length and the SnO$_2$ loading. The initial efficiency of the SnO$_2$/TiO$_2$ nanotube array electrodes is 69.4%, which is much higher than that of the bare SnO$_2$ powder electrodes (always less than 50%). Rate capability tests conducted with multiple current densities of 10 mA cm$^{-2}$, 20 mA cm$^{-2}$, 40 mA cm$^{-2}$, 80 mA cm$^{-2}$, 100 mA cm$^{-2}$, and 150 mA cm$^{-2}$ are displayed in Figure 7.16(d). The areal capacity of the SnO$_2$/TiO$_2$ sample is more than twice that of the TiO$_2$ substrate at each current density. The SnO$_2$/TiO$_2$ anodes exhibit excellent cycling stability, even at a current density of 150 mA cm$^{-2}$, while it is well known that the capacity of conventional SnO$_2$ nanopowder anodes always decreases with cycling. Voltage vs. capacity curves for rate capability tests are shown in Figure 7.17(b). At high charge/discharge current densities, the plateau for the TiO$_2$ reaction is inconspicuous. The superior electrochemical performance may result from the transport and physical advantages of the 3D nanotube array structure, which provides shorter transport lengths, one-dimensional transport of electrons along nanotubes,
higher electrode–electrolyte contact areas, and enough space to accommodate SnO₂ volume expansion. The electrochemical performance, especially the rate capability of the 3D SnO₂/TiO₂ anodes, could be further enhanced by introducing another component with good electrical conductivity (such as carbon or silver), considering the semiconducting natures of both SnO₂ and TiO₂.

**Figure 7.17** (a) Cycling performance of 10 h SnO₂/200 nm and 2000 nm TiO₂ samples in different voltage ranges at current density of 20 µA cm⁻², (b) galvanostatic curves of 0.5 h SnO₂/TiO₂ sample at different current densities.

The reactions of lithium ions with TiO₂ and SnO₂ occur at different voltages, as revealed in the CV curves, so the TiO₂ nanotubes can act as a stable framework for deposited SnO₂ nanocrystals. The reaction scheme is displayed in Figure 7.18(a). In the first discharge process, Li⁺ reacts with the TiO₂ nanotubes and forms LiₓTiO₂, and then the SnO₂ reacts with Li⁺, forming Sn and Li₂O. As the discharge process goes deeper, LiₓSn alloy is formed, while in the following charge process, Li⁺ is first extracted from LiₓSn, and the alloy changes back to Sn. Then, Li⁺ is extracted from LiₓTiO₂ at higher voltage, and the TiO₂ reappears. The following cycles repeat the discharge and charge processes according to the reversible equations (7.1) and (7.3).
To investigate the structural stability after charge/discharge cycling, *ex-situ* FESEM images were obtained after the end of different charging cycles at 2.5 V, which are shown in Figure 7.18(b)-(e). It can be seen that the nanotube wall after 5 cycles is quite smooth for the TiO$_2$ substrate. Although tiny “thorns” can be seen on the tube wall after 50 cycles in the high magnification image, the nanotube structure still looks very good in the lower magnification images. For the SnO$_2$/TiO$_2$ samples, there is also no obvious change after 5 cycles. However, the inner diameter of the nanotubes clearly decreases after 50 cycles, and the wall becomes thicker, owing to the reaction involving SnO$_2$ and aggregation changes with cycling. Most tubes still can be seen, although some tubes are filled with tin. There is also no cracking, which always occurs for bare SnO$_2$ samples after only a few cycles. TEM cross-sectional images of the SnO$_2$/TiO$_2$ electrode after 5 cycles are shown in Figure 7.19. It can be observed that the tubular structure is well maintained after charge/discharge cycles. The electron microscope images after cycling reveal that the tubular structure can effectively accommodate SnO$_2$ volume expansion. The lower magnification images demonstrate that there is no collapse of the structure, but only a decrease in the space in the tubes, so they verify that this structure is more physically stable than some other hollow structures and explain the high cycling stability.
Figure 7.18 (a) Reaction scheme; FESEM images after charge/discharge cycles (insets: higher magnification): (b) TiO$_2$ and (c) SnO$_2$/TiO$_2$ (after 5 cycles), (d) TiO$_2$ and (e) SnO$_2$/TiO$_2$ (after 50 cycles).
7.5 Summary

Novel TiO$_2$(B)/anatase hybrid nanowires have been successfully synthesized by the facile hydrothermal method, followed by acid-washing and heat treatment. The hybrid nanowire electrode delivered a highly reversible capacity of 196 mAh g$^{-1}$ after 100 cycles at 30 mA g$^{-1}$ (0.1 C). It also exhibited a reversible discharge capacity as high as 125 mAh g$^{-1}$, when cycled at 4500 mA g$^{-1}$ (15 C). This composite is a promising candidate anode material for lithium-ion batteries. There is still scope to improve the composition and structure of these materials via optimizing the preparation process parameters.

Three dimensional TiO$_2$ nanotube arrays were synthesized by the anodization process. The effects of annealing on the morphology, structure and electrochemical performance were systematically investigated. Furthermore, three-dimensional SnO$_2$/TiO$_2$ electrodes with SnO$_2$ nanocrystal size of less than 5 nm were prepared via a simple solvothermal technique. SnO$_2$/TiO$_2$ samples made with a reaction time of
0.5 h deliver an areal capacity more than twice that of TiO$_2$ when used as anode for lithium ion batteries. This composite also shows very good cycling stability, even at multiple charge/discharge current densities. The capacity is controlled by both the length of the TiO$_2$ tubes and by the SnO$_2$ loading. The space in the TiO$_2$ tubes can accommodate the volume changes of SnO$_2$ during Li$^+$ charge/discharge processes, thus improving the electrochemical performance. The excellent electrochemical performance of the as-prepared 3D composite anodes and the lack of any need for binders make it a very promising anode material for lithium ion microbatteries. It is also believed that this strategy can be applied to synthesize other functional materials, such as electrocatalytic or photocatalytic materials.

**References**


CHAPTER 8 Efficient Preparation of Li₄Ti₅O₁₂ Anode and Structure

Investigation of Bromine Doping Effect

8.1 Introduction

Lithium ion batteries have been recently developed to provide power for electric vehicles (EVs) or hybrid electric vehicles (HEVs) in order to reduce environmental pollution [1-3]. However, the performance of the conventional carbon anode in lithium ion batteries can not meet all the requirements of modern EVs, such as the need for high-rate cycling or fast charging. Moreover, safety issues with the use of commercial carbon are not well addressed, which include its low working voltage and lithium dendritic growth under high current if the battery is overcharged [4]. Therefore, cost-effective anode materials with high power densities that are safe and feature long cycle lives are required.

As an alternative, spinel Li₄Ti₅O₁₂ is under serious consideration as an anode in high power cells [5, 6] owing to its following advantages: a working potential of 1.5 V vs. Li⁺/Li, high thermal stability, especially at elevated temperatures, and enhanced safety. Since a solid electrolyte interphase (SEI) layer forms below 1 V vs. Li⁺/Li, in part due to the reduction of the organic electrolyte, having a working voltage above 1 V, as in Li₄Ti₅O₁₂ anode, can avoid the SEI formation and may also avoid lithium plating under high current conditions [7, 8]. Li₄Ti₅O₁₂ can accommodate three further lithium cations in its structure and shows very flat charge/discharge curves during electrochemical cycling. Moreover, Li₄Ti₅O₁₂ is referred to as a “zero strain” material during the transition between the two end members, Li₄Ti₅O₁₂ and Li₇Ti₅O₁₂,
with lithium intercalation and de-intercalation, resulting in stable cycling due to the negligible volume change [9-11]. However, the low electronic conductivity and moderate Li\(^+\) diffusion coefficient hinder its high rate performance and applicability for Li-ion batteries [12-14]. The conventional methods to improve rate capability are by minimizing the particle size to decrease the Li\(^+\) diffusion length, carbon coating to improve the conductivity, and element doping to change the electrochemical behaviour [15-22]. For the first two strategies, the practical problems imply that it is not easy to prepare \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) nanostructures, and it is also difficult to control the uniformity of the carbon coating if extra organic carbon sources are used. As for the doping synthesis, impurities are always concomitant.

Above all, for industrial application, the laboratory-based synthesis procedure should be low-cost, energy non-intensive, and facile and feasible for scaled up production. Commonly for most titanium salts, the starting precursors are easily hydrolyzed to form TiO\(_2\). Once TiO\(_2\) is formed, it is necessary to heat it with lithium salts at high temperatures for extended periods of time in order to obtain well-crystallized \(\text{Li}_4\text{Ti}_5\text{O}_{12}\), which is an energy consuming process [15]. Furthermore, due to the time-consuming heat treatment at high temperatures, the \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) particle sizes grow to several hundred nanometers or even several microns, which, in turn, increase the lithium diffusion path within isolated particles and thereby decrease electrode performance. Spray pyrolysis is a well-known cost effective and industrially scalable technique, providing the capability to manufacture large varieties of nanostructured ceramics and composites with promising applications in energy storage devices [23-27]. Precursor salts are dissolved in a solution that allows uniform mixing of each component at the atomic level, leading to high chemical purity in the products.
Spray pyrolysis with appropriately chosen precursor salts is expected to save on heat treatment times, and thus save energy and cost in large-scale production.

In the first part of this work, Li$_4$Ti$_5$O$_{12}$ was prepared by an in-situ spray pyrolysis technique in the form of nanocrystallites. Both the uniformity of the precursor components and the pre-formed crystallites allowed subsequent short annealing times, which are required to save energy in large-scale production. Meanwhile, the heat treatment under N$_2$ atmosphere preserves carbon from the decomposed organic precursors, forming in-situ carbon-containing samples, thus improving the conductivity and allowing favorable electrochemical performance. In the second part of this work, the crystallographic cause of the reported electrochemical behavior of Li$_4$Ti$_3$O$_{12-x}$Br$_x$ was investigated using high-resolution synchrotron X-ray diffraction (SXRD). The findings suggest that the conventional solid-state synthesis of Li$_4$Ti$_3$O$_{12-x}$Br$_x$ results in the formation of TiO$_2$ as a second phase. These findings are complemented with an in-situ neutron diffraction (ND) study of a composite Li$_4$Ti$_3$O$_{12}$/TiO$_2$ anode to determine the Li insertion/extraction mechanism in the composite Li$_4$Ti$_5$O$_{12}$/TiO$_2$ electrode using a purpose-built electrochemical cell.

8.2 Spray Pyrolysis Preparation of Li$_4$Ti$_5$O$_{12}$

8.2.1 Synthesis

A clear transparent precursor solution was prepared by dissolving a stoichiometric ratio of lithium acetate and titanium butoxide (Sigma) in ethanol to obtain a 0.5 M solution. The solution was sprayed into the pyrolysis furnace at a temperature of 800 °C using a two-fluid spray nozzle and air as a carrier gas at a flow rate of 6.5 mL
min$^{-1}$ to obtain raw Li$_4$Ti$_5$O$_{12}$ (designated as raw LTO). Then, the raw LTO sample was post-annealed in N$_2$ (designated as LTO-N) and air (designated as LTO-A) at 800 °C for 1 h with a ramping speed of 5° min$^{-1}$.

8.2.2 Characterization

The morphology and structure of the sprayed raw Li$_4$Ti$_5$O$_{12}$ (raw LTO) are shown in Figure 8.1. The low magnification transmission electron microscope (TEM) image (Figure 8.1(a)) shows micron-size hollow spheres and sheet-like fractured particles, both of which are the typical features of materials prepared by the spray pyrolysis technique. The higher magnification image (b) shows a mesoporous structure with a high specific surface area of 74.5 m$^2$ g$^{-1}$. The selected area electron diffraction (SAED) pattern of raw LTO (inset) shows very diffuse diffraction rings, indicating that the sample is not well crystallized, but the high resolution image (c) shows that the sample is in a semicrystalline and semi–amorphous state with crystal sizes of about 5 nm, which is consistent with the broad and weak intensities observed in the X-ray diffraction (XRD) pattern (Figure 8.1(d)) and the poorly developed fringes in some areas. The unique morphology and structure of the raw LTO can be attributed to the mixing of the precursor solution on the atomic level and the ultra-fast spray pyrolysis process (around 0.5 s) in the furnace at 800 °C. Thus, the crystallites are formed but not well developed, and the subsequent evaporation process involving the escape of the solvent results in a mesoporous sample.
Figure 8.1 TEM images of raw Li$_4$Ti$_5$O$_{12}$: (a) low resolution, (b) and (c) high resolution, with the inset in (b) showing the corresponding selected area electron diffraction (SAED) pattern; and (d) XRD pattern.
Figure 8.2 TEM images: (a) LTO-N, with the inset showing the SAED pattern, and (b) a high resolution image; (c) LTO-A, with the inset showing the hollow spheres, and (d) a high resolution image.

TEM images of Li$_4$Ti$_5$O$_{12}$ annealed in N$_2$ (LTO-N) and in air (LTO-A) are presented in Figure 8.2. Both samples show the same morphology as the raw LTO, with micron-size hollow spheres and sheet-like fractured particles. Note that there is a very dark contrast for the large spheres in Figure 8.2(c), not because they are solid particles, but because of the large contrast difference between the spheres and the fractured sphere sheets in the image. If the contrast is altered, the hollow nature of the spheres is revealed, as presented in the inset. For the LTO-N sample, the inset in Figure 8.2 (a) shows bright and sharp diffraction rings, indicating a well crystallized
sample. The particles within the polycrystalline sample were of the order of 10 - 30 nm in size, a size range which is difficult to synthesize by conventional solid state reaction, as the long heating times required tend to form micron-size particles. Notably, the LTO-A sample shows non-uniform crystal sizes (Figure 8.2(d)), with a significant fraction of crystallites around 100 nm and numerous microtwins.

The high resolution TEM images of LTO-N show amorphous features in some areas, which indicate the presence of carbon produced by the decomposition of the organic precursor salts under the final heat treatment in inert atmosphere. To verify the presence of residual carbon, Raman spectra were conducted and are shown in Figure 8.3(a). The Raman spectrum of the LTO-N sample shows two peaks at about 1340 and 1590 cm$^{-1}$, corresponding to the D and G bands of carbonaceous materials, confirming the presence of carbon. Furthermore, these peaks are absent for the LTO-A sample, suggesting that the residual carbon is removed when annealing takes place in air. The energy dispersive X-ray spectroscopy (EDS) mapping (Figure 8.4(b)) also confirms the uniform distribution of carbon in the LTO-N sample. The EDS spectrum, as shown in the inset in Figure 8.4(b), clearly shows the carbon peak, and the estimated carbon content from EDS is less than 5 wt%. To determine where the carbon is located in this sample, high resolution TEM was performed (Figure 8.3(b)). The image shows that the carbon is mainly on the Li$_4$Ti$_5$O$_{12}$ grain boundaries, as described in the schematic (Figure 8.3(c)). Thus, it is believed that the carbon on grain boundaries also acts to inhibit growth of the primary particles for the LTO-N sample, for which the TEM images indicate smaller crystal sizes relative to the LTO-A sample.
Figure 8.3 (a) Raman spectra of LTO samples annealed in N₂ and air, (b) high resolution TEM image of the LTO-N sample, and (c) schematic diagram of carbon distribution on grain boundaries.
Figure 8.4 EDS mapping of LTO-N sample: (a) SEM image, (b) carbon distribution, with the inset showing the EDS spectrum, (c) titanium distribution, (d) oxygen distribution.

Carbon coating or addition has been a traditional way to improve the conductivity of electrode materials, and it is very common to use extra carbon sources (such as pitch, organic ionic liquid, polyaniline, or citric acid [17-20]) for carbon addition. In this work, Ti(OCH₂CH₂CH₂CH₃)₄ and CH₃COOLi are used as starting materials, with the –(OCH₂CH₂CH₂CH₃)₄ and –COOCH₃ groups acting as atomic level carbon sources. In this way, uniform carbon distribution is achieved, and the carbon is located along the grain boundaries for LTO-N. It is highly likely that the affinity created between carbon and Li₄Ti₅O₁₂ during the synthetic procedures would be better than with post-synthetic carbon coating through the use of additional carbon sources. As shown in Figure 8.3(c), the LTO-N nanoparticles are agglomerated, with
a thin layer of carbon between them, and such a well-formed carbon-Li$_4$Ti$_5$O$_{12}$ network will effectively facilitate both electron and lithium ion transport. This would therefore significantly improve the electrochemical performance of the electrodes.

![Figure 8.5 XPS Ti 2p core level spectra of the LTO-N sample: (a) outer surface layer and (b) after Ar ion etching.](image)

For LTO-N, the heat treatment atmosphere was slightly reductive, which presumably reduced the tetravalent Ti in Li$_4$Ti$_5$O$_{12}$ to trivalent Ti to some extent. Jung et al. [17] recently reported a change in Ti valence in carbon-coated Li$_4$Ti$_5$O$_{12}$ samples annealed in argon. Thus, to determine the Ti valence, X-ray photoelectron spectroscopy (XPS) was conducted on the spray pyrolyzed LTO-N sample, and the results are shown as Figure 8.5. The sample was stored in ambient atmosphere, and the outer surface is composed of tetravalent Ti (Figure 8.5(a)). The two peaks located at 458.5 and 464.1 eV can be assigned to the core levels of Ti$^{4+}$ 2p$_{3/2}$ and Ti$^{4+}$ 2p$_{1/2}$, respectively. However, after Ar ion etching, two additional peaks located at 456.5 and 461.8 eV, ascribed to the Ti$^{3+}$ 2p$_{3/2}$ and Ti$^{3+}$ 2p$_{1/2}$ peaks, could be identified, suggesting the presence of Ti$^{3+}$ species [17, 28].
Figure 8.6 Rietveld refinements of the Li$_4$Ti$_5$O$_{12}$ structural model based on XRD data for (a) LTO-N and (b) LTO-A. Crosses (×) indicate the collected data, the solid line through the data is the calculated model, the purple line below is the difference between observed and calculated, and the vertical lines indicate Bragg reflections. The insets contain digital photographs of the powder samples, respectively.

Rietveld refinement of Li$_4$Ti$_5$O$_{12}$ modelled from XRD data (shown in Figure 8.6) demonstrates a larger lattice parameter for LTO annealed in N$_2$ ($a = 8.3692(3)$ Å) compared to LTO annealed in air ($a = 8.3607(1)$ Å). The lattice parameter is expected to increase if some Ti$^{4+}$ is transformed to Ti$^{3+}$, because of the larger ionic
radius of Ti$^{3+}$ (0.67 Å) compared to Ti$^{4+}$ (0.605 Å) [29]. Digital photographs of the two powder samples are also shown as insets in Figure 8.6, and clearly, the sample annealed in air is white, while the sample annealed in N$_2$ is grey. The colour change from white to grey may not be entirely due to the presence of carbon, but also due to the partial formation of Ti$^{3+}$ [17]. The difference in crystallite sizes between LTO-N and LTO-A is demonstrated by the peak shapes in the XRD patterns, with LTO-N featuring broader peaks characteristic of smaller crystallites, relative to LTO-A with sharper peaks characteristic of larger crystallites. If particle size is considered as the major contributor to the broadening of the peak shapes and use peak-profile functions (particle-size broadening effect) in the Rietveld analysis to investigate average crystallite sizes, the ratio of average crystallite sizes, LTO-A : LTO-N, is 2:1.
8.2.3 Electrochemical performance

**Figure 8.7** Electrochemical performance: (a) cyclability of LTO-N and LTO-A at 0.5 C, (b) rate capability of LTO-N and LTO-A samples from 0.5 C to 30 C (with charge and discharge processes at the same C-rate), (c) galvanostatic charge/discharge curves of Li$_4$Ti$_5$O$_{12}$ annealed in N$_2$ at different C-rates.
Figure 8.7(a) compares the cycling performances of both annealed samples at a current rate of 0.5 C (87.5 mA g\(^{-1}\)). The initial reversible capacities are 165 mAh g\(^{-1}\) and 162 mAh g\(^{-1}\) for LTO-N and LTO-A, respectively, and both show good capacity retention of 90.9\% and 89.5\%, respectively, for up to 500 cycles. Rate capabilities of LTO-N and LTO-A samples from 0.5 C to 30 C are shown in Figure 8.7(b). Both samples show stable cycling performance at each applied current density, but LTO-N shows a higher discharge capacity than LTO-A, especially at high rates. LTO-N exhibits discharge capacities of 160 mAh g\(^{-1}\), 148 mAh g\(^{-1}\), 132 mAh g\(^{-1}\), and 112 mAh g\(^{-1}\) for 1 C (175 mA g\(^{-1}\)), 4 C (0.7 A g\(^{-1}\)), 10 C (1.75 A g\(^{-1}\)), and 20 C (3.5 A g\(^{-1}\)), respectively, and a discharge capacity of 96 mAh g\(^{-1}\) is also achieved at 30 C (5.25 A g\(^{-1}\)). Moreover, the discharge capacity increases to 157 mAh g\(^{-1}\) when the discharge rate returns back to 1 C. The corresponding galvanostatic charge-discharge curves at different C-rates are shown in Figure 8.7(c). It shows that the difference between the charge and discharge voltage plateaus tends to increase with increasing current density. The outstanding rate capability of the LTO-N sample can be attributed to the following factors: (i) carbon located on grain boundaries, enhancing the conductivity; (ii) carbon inhibiting crystal growth during annealing, resulting in nanoparticles which feature the shorter lithium diffusion lengths that are favourable for high rate performance; and (iii) the presence of Ti\(^{3+}\) in LTO-N, which enhances electronic conductivity and thus improves performance. Tetravalent Ti exhibits insulating properties arising from empty Ti 3d states \([30, 31]\), and the conductivity enhancement with trivalent Ti is due to the presence of one extra electron in Ti\(^{3+}\) compared to Ti\(^{4+}\).
A full battery test was also undertaken using Li(Co$_{0.16}$Mn$_{1.84}$)O$_4$ (LCMO) as the cathode and LTO-N as the anode. The voltage vs. capacity curves of the LCMO half cell are shown in Figure 8.9. Two discharge voltage plateaus are exhibited at about 4.1 and 4.0 V vs. Li$^+$/Li. The discharge capacities of the cathode material are 103 and 99 mAh g$^{-1}$ when cycled at the current densities of 87.5 (0.5 C for LTO) and 175 mA g$^{-1}$ (1 C for LTO), respectively. The weight ratio of the LTO-N electrode to the LCMO electrode in the full battery was designed such that the electrode capacity ratio is 1:1. The testing conditions employed involved a constant current charge step at the rate of 0.5 C, followed by a constant voltage (CV) step until the current decreased to 0.01 C. The discharge process was at the rate of 1 C (175 mA g$^{-1}$), except for the first three cycles, where activation was performed at a current rate of 0.1 C. Figure 8.8(a) shows the galvanostatic charge/discharge curves, with discharge cell voltage plateaus of about 2.5 and 2.4 V, and a discharge capacity of about 140 mAh g$^{-1}$ (calculated based on Li$_4$Ti$_5$O$_{12}$). Note that the capacity of the constant voltage charge mode only accounts for about 2.5% of the whole charge capacity. Due to the various engineering factors, such as electrode fabrication, geometric effects, and load balancing with two distinctly different single electrodes integrated via a laboratory scale fabrication procedure into a full cell, the electrochemical performance of the Li$_4$Ti$_5$O$_{12}$ electrode in the full battery is not as good as that in a half cell. Nonetheless, the full battery exhibits good capacity retention, as shown in Figure 8.8(b). The capacity at the 40th cycle retains 96.8% of the discharge capacity for the first cycle.
Figure 8.8 Li₄Ti₅O₁₂ anode and Li(Co₀.₁₆Mn₁.₈₄)O₄ cathode full battery tests: (a) galvanostatic charge/discharge curves for the first cycle, and (b) cycling performance.

Figure 8.9 Galvanostatic charge/discharge curves of Li(Co₀.₁₆Mn₁.₈₄)O₄ vs. Li⁺/Li at current densities of 87.5 mA g⁻¹ and 175 mA g⁻¹.
8.3 Br doping of Li$_4$Ti$_5$O$_{12}$

8.3.1 Experimental

Synthesis

Li$_4$Ti$_5$O$_{12-x}$Br$_x$ ($x = 0.05, 0.1, 0.2$ and $0.3$) samples were prepared by conventional high temperature solid state reaction using LiOH·H$_2$O, LiBr·H$_2$O, and TiO$_2$ in a Li:Ti molar ratio of 4.35:5. Excess Li (8 mol. %) was provided to compensate for lithium volatilization during the high temperature of synthesis. The reagents were mixed in an agate mortar and ground with a pestle for 1 h to prepare the Li$_4$Ti$_5$O$_{12-x}$Br$_x$ ($x = 0.05, 0.1, 0.2,$ and $0.3$) precursor powders. The mixed reactant mixtures were heated in a muffle furnace at 900 °C for 12 h in air, followed by natural cooling to room temperature. The synthesized samples were reground before powder characterization and electrode preparation.

Characterization

High-resolution synchrotron X-ray diffraction (SXRD) data were collected on the Powder Diffraction beamline (10-BM-1) [32] at the Australian Synchrotron at the wavelength, $\lambda = 0.82398(1)$ Å, determined using the NIST 660a LaB$_6$ standard reference material. Powder samples were packed in 0.3 mm glass capillaries, and data were collected for 6 minutes at ambient temperature using the Debye-Scherrer geometry. In-situ neutron diffraction (ND) data were collected on the high intensity powder diffractometer, Wombat, at the Open Pool Australian Lightwater (OPAL) reactor facility at the Australian Nuclear Science and Technology Organisation (ANSTO) [33]. ND data were collected at 2.406(2) Å, determined using the NIST 676 Al$_2$O$_3$ standard reference material, every 5 minutes for ~ 24 hours in the two
Chapter 8 Efficient preparation of \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) anode and structure investigation of bromine doping effect

theta (20) range \( 16^\circ \leq 2\theta \leq 136^\circ \). Wombat has an area detector covering 120° in 20 mode, enabling diffraction data to be continuously collected. Data correction, reduction, and visualization were undertaken using the program LAMP [34]. During ND data collection, the electrochemical cell was charged-discharged in galvanostatic (constant current) mode with applied currents ranging from \( \pm 1 \) to 15 mA using a Neware battery tester. Rietveld refinements using the SXRD and ND data were carried out using the GSAS [35] suite of programs with the EXPGUI [36] interface.

Composite electrodes used for \textit{in-situ} ND were made by first heating \( \text{TiO}_2 \) (Sigma Aldrich, anatase, \( \geq 99 \% \)) and \( \text{Li}_2\text{CO}_3 \) (Sigma Aldrich, 99 %) at 900 °C for 12 h to yield \( \text{Li}_4\text{Ti}_5\text{O}_{12} \). The product was then mixed with 20 wt. % \( \text{TiO}_2 \) and heated at 500 °C for 5 h to form the \( \text{TiO}_2/\text{Li}_4\text{Ti}_5\text{O}_{12} \) composite. The electrode for the electrochemical cell was made from the \( \text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2 \) composite, which was mixed with carbon black and polyvinyl difluoride (PVDF) to form a paste. The paste was applied to a Cu sheet and dried overnight. The electrochemical cell was assembled with layers of materials arranged in the following order: Celgard® (insulator), Cu with composite \( \text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2 \) electrode, Celgard® (separator), and Li metal electrode. Cu wires were placed in contact with both electrodes, and the assembly was rolled using the outer Celgard layer and inserted into a 9 mm inner diameter vanadium can. The electrolyte was made from 1 M LiPF\(_6\) dissolved in a 1:1 vol.% mixture of deuterated ethylene carbonate (CDN, chemical purity 99.3 % and isotopic purity 99 %) and deuterated dimethyl carbonate (Cambridge Isotopes, chemical purity 98 % and isotopic purity 99 %). The electrolyte was added dropwise to the can, which was then sealed with wax. All procedures to make the electrochemical cell were carried out in an Ar-filled glove box.
8.3.2 Characterization

8.3.2.1 Li$_4$Ti$_5$O$_{12-x}$Br$_x$

Electrochemical performance testing demonstrated that the discharge capacity of Li$_4$Ti$_5$O$_{12}$ is improved through Br inclusion, as illustrated in Figure 8.10 [22]. The maximum discharge capacity in Li$_4$Ti$_5$O$_{12-x}$Br$_x$ is found at $x = 0.20$, where $x$ is the chemical input amount of Br in the starting synthesis mixture. $x'$ denotes the actual amount of Br incorporated into the crystal structure of Li$_4$Ti$_5$O$_{12-x}$Br$_x$. Notably, at higher synthetic chemical Br concentrations ($x > 0.20$), the discharge capacity is reduced, and the performance advantage is lost [22]. In order to determine the possible structural cause of the variation in discharge capacity, high-resolution SXRD experiments were used to characterize Li$_4$Ti$_5$O$_{12-x}$Br$_x$ with $x = 0.05$, 0.10, 0.20,
and 0.30. Rutile TiO$_2$ is observed as a second phase in all samples, ranging from 2.1(2) to 9(4) wt. %. The relatively small quantity of rutile is difficult to detect using conventional laboratory-based diffractometers and was not observed in previous work that focused on the electrochemical properties of Li$_4$Ti$_5$O$_{12-x}$Br$_x$, including discharge capacity, rate capability, and conductivity [22]. In this study the crystal structure of Li$_4$Ti$_5$O$_{12-x}$Br$_x$ was refined using whole-pattern data modelling, and the fits to the SXRD data are presented in Figures 8.11 - 14 for samples with $x = 0.05$, 0.10, 0.20, and 0.30, respectively. The figures of merit of the fits, refined composition, phase fractions, and lattice parameters, are presented in Table 8.1. From the refined site occupancy results, the maximum substitution of Br on the O site in Li$_4$Ti$_5$O$_{12-x}$Br$_x$ is $x' = 0.12$. Attempted higher Br substitution led to the formation of a structurally unidentified third phase, shown in the inset of Figures 8.13(b) and 8.14(b). The Li$_4$Ti$_5$O$_{12-x}$Br$_x$ lattice parameters of $x = 0.10$, 0.20, and 0.30 were strikingly similar and correspond to the similar refined Br concentration of $x' \approx 0.10$. As expected, a slight decrease in the lattice parameters is observed for the $x = 0.05$ sample relative to the others due to the lower Br substitution.
Figure 8.11 Rietveld plots using SXRD data for the sample with the chemical synthetic input composition of Li$_4$Ti$_5$O$_{11.95}$Br$_{0.05}$, showing (a) the fit of the Rietveld-refined Li$_4$Ti$_5$O$_{11.97}$Br$_{0.03}$ model with rutile TiO$_2$, and (b) an expanded region of the fit between $14^\circ \leq 2\theta \leq 44^\circ$. Crosses ($\times$) are the data, the Rietveld model is the line through the crosses, and the difference between the calculated model and the data is shown by the line below. Vertical lines indicate reflection markers for TiO$_2$ (red) and Li$_4$Ti$_5$O$_{11.97}$Br$_{0.03}$ (black).
Figure 8.12 Rietveld plots using SXRD data for the sample with the chemical synthetic input composition of Li$_4$Ti$_5$O$_{11.9}$Br$_{0.1}$, showing (a) the Rietveld-refined Li$_4$Ti$_5$O$_{11.88}$Br$_{0.12}$ model with rutile TiO$_2$, and (b) an expanded region of the fit between $26^\circ \leq 2\theta \leq 45^\circ$. Crosses ($\times$) are data, the Rietveld model is the line through the crosses, and the difference between the calculated model and the data is shown by the line below. Vertical lines are reflection markers for TiO$_2$ (red) and Li$_4$Ti$_5$O$_{11.88}$Br$_{0.12}$ (black).
Figure 8.13 Rietveld plots using SXRD data for the sample with the chemical synthetic input composition of Li$_4$Ti$_5$O$_{11.8}$Br$_{0.2}$, showing (a) the Rietveld-refined Li$_4$Ti$_5$O$_{11.90}$Br$_{0.10}$ model with rutile TiO$_2$, and (b) an expanded region of the fit between $26^\circ \leq 2\theta \leq 45^\circ$. Crosses ($\times$) are data, the Rietveld model is the line through the crosses, and the difference between the calculated model and the data is shown by the line below. Vertical lines are reflection markers for TiO$_2$ (red) and Li$_4$Ti$_5$O$_{11.90}$Br$_{0.10}$ (black). The arrow indicates the third phase in this sample with the inset in (b) showing detail.
Figure 8.14 Rietveld plots using SXRD data of the sample with the chemical synthetic input composition of Li$_4$Ti$_5$O$_{11.7}$Br$_{0.3}$, showing (a) the Rietveld-refined Li$_4$Ti$_5$O$_{11.89}$Br$_{0.11}$ model with rutile TiO$_2$, and (b) an expanded region of the fit between 14° ≤ 2θ ≤ 25°. Crosses (×) are data, the Rietveld model is the line through the crosses, and the difference between the calculated model and data is shown by the line below. Vertical lines are reflection markers for TiO$_2$ (red) and Li$_4$Ti$_5$O$_{11.89}$Br$_{0.11}$ (black). The arrows indicate the third phase and the inset in (b) shows detail.
Table 8.1 The fractions of Li$_4$Ti$_5$O$_{12-x}$Br$_x$ and TiO$_2$ phases, input chemical compositions, Rietveld-refined compositions, lattice parameters, and figures of merit of the Rietveld model fits shown in Figures 8.11 - 8.14. The profile factor is $R_p$, the weighted profile factor is $R_{wp}$, and the goodness-of-fit term is $\chi^2$.

<table>
<thead>
<tr>
<th>Synthetic chemical input amount of $x$ in Li$_4$Ti$<em>5$O$</em>{12-x}$Br$_x$</th>
<th>Refined $x'$ in Li$_4$Ti$<em>5$O$</em>{12-x}$Br$_x$</th>
<th>Relative phase fraction</th>
<th>Lattice parameters [Å]</th>
<th>$R_p$ [%]</th>
<th>$R_{wp}$ [%]</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Li$_4$Ti$<em>5$O$</em>{12-x}$Br$_x$</td>
<td>$a$ of TiO$_2$</td>
<td>$c$ of TiO$_2$</td>
<td>$a$ of Li$_4$Ti$<em>5$O$</em>{12-x}$Br$_x$</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>0.03</td>
<td>0.021(2)</td>
<td>0.9786(4)</td>
<td>4.58960(5)</td>
<td>2.95655(7)</td>
<td>8.351699(9)</td>
</tr>
<tr>
<td>0.10</td>
<td>0.12</td>
<td>0.023(3)</td>
<td>0.9770(2)</td>
<td>4.58959(5)</td>
<td>2.95645(7)</td>
<td>8.351797(8)</td>
</tr>
<tr>
<td>0.20</td>
<td>0.10 [a]</td>
<td>0.06(2)</td>
<td>0.93(2)</td>
<td>4.58949(2)</td>
<td>2.95616(3)</td>
<td>8.351740(7)</td>
</tr>
<tr>
<td>0.30</td>
<td>0.11 [a]</td>
<td>0.09(4)</td>
<td>0.91(4)</td>
<td>4.58960(2)</td>
<td>2.95632(2)</td>
<td>8.351767(8)</td>
</tr>
</tbody>
</table>

[a] Contains a third, structurally unidentified phase

The structurally unidentified third phase is observed in the $x = 0.20$ and 0.30 samples with a quantity that increases with $x$. Since the lattice parameter of TiO$_2$ is virtually constant and independent of $x$, minimal Br-doping into TiO$_2$ is indicated, and the third phase is therefore likely to be Br-containing. Hypothesize that the third phase accounts for the remaining Br that does not substitute into Li$_4$Ti$_5$O$_{12-x}$Br$_x$. In conjunction with the electrochemical data presented in Figure 8.10 [22], it is likely that the concentration of the third phase in the $x = 0.20$ and 0.30 samples is, in part, responsible for the electrochemical performance degradation in samples with synthetic chemical Br composition of $x > 0.20$.

The best electrochemically performing composition is reported with synthetic chemical Br input of $x = 0.20$ [22], which produces a three phase composite material containing approximately 93(2) % Li$_4$Ti$_5$O$_{11.89}$Br$_{0.11}$, 6(2) % rutile TiO$_2$, and a trace amount of a structurally unidentified and presumably Br-rich, third phase. Note that
the uncertainties in the phase fraction determinations increase with increasing amounts of the unknown third phase. Overall, the increase in discharge capacity in samples with synthetic chemical Br inputs of $x = 0.05$ to $x = 0.10$ is directly correlated with increasing Br substitution. From $x = 0.10$ to $x = 0.20$, an increasing amount of the TiO$_2$ (second) phase forms and that Br substitution in Li$_4$Ti$_5$O$_{12-x}$Br$_x$ saturates crystallographically at $x' \approx 0.1$, with the remaining Br incorporated into the structurally unknown (third) phase. Therefore, the increase in discharge capacity shown in Figure 8.10 [22] for samples with synthetic chemical Br input of $x = 0.10$ to $x = 0.20$ is predominantly due to the increasing amount of the TiO$_2$ (second) phase and/or the structurally unknown (third) phase that is formed in the material. At $x = 0.30$, the composite is composed of Li$_4$Ti$_5$O$_{11.89}$Br$_{0.11}$, with amounts of the TiO$_2$ (second) and structurally unknown (third) phases that increase with $x$. Hypothesize that the decrease in discharge capacity reported from synthetic chemical Br inputs of $x = 0.20$ to $x = 0.30$ [22] is predominantly due to the increasing quantity of the third phase, since the crystallographic concentration of Br is $x' \approx 0.1$ for both samples. It is worthwhile to note that the quantity of the parent Li$_4$Ti$_5$O$_{12}$ phase decreases in samples formed with synthetic chemical Br inputs of $x = 0.10$ to 0.30, which may contribute to some of the loss in discharge capacity. Nonetheless, improvement in performance gained through the increased crystallographic concentration of Br in Li$_4$Ti$_5$O$_{12-x}$Br$_x$ is an intraparticle effect, where Br is substituted for O within a particle, which influences the discharge capacity. Similarly, enhanced performance through the presence of TiO$_2$ and/or structurally unknown phases is an interparticle effect, where the changes in discharge capacity are related to electron or Li$^+$ transport between particles.
8.3.2.2 Composite Li$_4$Ti$_5$O$_{12}$/TiO$_2$ Anode

From the crystallographic results, the presence of TiO$_2$ and/or a compositionally and structurally unidentified phase, which may act as conducting media, allow faster electron transport through the composite electrode. These phases may also participate electrochemically, so as to enhance electrode functionality. To investigate the effects of TiO$_2$ on the electrochemical performance of the composite electrode, including on the Li insertion and extraction processes, \textit{in-situ} neutron diffraction (ND) on a TiO$_2$-rich composite electrode is performed. The sample was composed of 20 wt.% anatase TiO$_2$ and Li$_4$Ti$_5$O$_{12}$ in a custom-designed cell. In total ~ 400 mg of the active composite electrode was used for \textit{in-situ} ND. In order to obtain a good signal from the TiO$_2$, a higher concentration of TiO$_2$, relative to that found in the SXRD data on Li$_4$Ti$_5$O$_{12-x}$Br$_x$ samples, was used. The TiO$_2$ quantity used in the \textit{in-situ} ND study (~80 mg) was smaller than for any previously reported \textit{in-situ} ND work on an active electrode material [37-39] and in some cases, smaller than for active electrode components in \textit{in-situ} SXRD cells [40, 41]. The charge-discharge behaviour of the electrochemical cell is shown in Figure 8.15, highlighting two plateau-like regions in the first discharge, one at 1.7 V and the other at 1.5 V, corresponding to Li insertion into TiO$_2$ and Li$_4$Ti$_5$O$_{12}$, respectively. The first discharge was performed at -2 mA over the course of 600 minutes, while later charge-discharge cycles were successfully performed at higher applied currents, ~15 mA.
The fit of the Rietveld-refined Li [42], Cu [43], TiO$_2$ [44], and Li$_4$Ti$_5$O$_{12}$ [45] models to an *in-situ* ND dataset is shown in Figure 8.16. The figures of merit of this fit are the profile factors, $R_p = 2.55 \%$ and $R_{wp} = 3.25 \%$, and the goodness-of-fit term, $\chi^2 = 2.08$, found for a model containing 20 refinable parameters. Data collected at $\lambda = 2.406(2)$ Å enabled separation of the constituent Bragg reflections, but only relatively few TiO$_2$ and Li$_4$Ti$_5$O$_{12}$ reflections were observed, limiting the accuracy and reliability of the atomic parameter refinement, including Li occupation. Unfortunately, the use of shorter wavelengths (*e.g.* $\lambda \approx 1.5$ Å) did not afford sufficient angular resolution to separate sufficiently the Bragg reflections corresponding to Li, Li$_4$Ti$_5$O$_{12}$, and TiO$_2$. Thus, for sequential Rietveld refinements, all refinable parameters of the Li, Cu, TiO$_2$, and Li$_4$Ti$_5$O$_{12}$ models were fixed, with the exception of the TiO$_2$ and Li$_4$Ti$_5$O$_{12}$ lattice parameters and the scale factors (phase fractions). Figures of merit of the sequential refinements were in the ranges of $3.13 \% \leq R_p \leq 4.36 \%$, $3.74 \% \leq R_{wp} \leq 5.89 \%$, and $1.78 \leq \chi^2 \leq 4.56$. 

*Figure 8.15* The charge-discharge behaviour of the custom-designed cell containing the composite TiO$_2$/Li$_4$Ti$_5$O$_{12}$ electrode, with the first 1.7 and 1.5 V discharge plateau regions indicated.
Chapter 8 Efficient preparation of Li$_4$Ti$_5$O$_12$ anode and structure investigation of bromine doping effect

Figure 8.16 Fit of the Rietveld model containing Li, Cu, anataseTiO$_2$, and Li$_4$Ti$_5$O$_12$ to in-situ ND data at $\lambda = 2.406(2)$ Å. Crosses ($\times$) are the data, the Rietveld model is the line through the crosses, the difference between the calculated model and the data is shown by the line below, and the vertical lines are reflection markers for Li, Cu, Li$_4$Ti$_5$O$_12$, and TiO$_2$ (from top to bottom, respectively).

No significant change in the Li$_4$Ti$_5$O$_12$ lattice parameters was observed with charge-discharge, in agreement with other in-situ ND work [37]. The time evolution of the TiO$_2$ lattice parameters (Figure 8.17) reveals two TiO$_2$-containing phases, the first being anatase with lattice parameters $a \approx 3.80$ and $c \approx 9.45$ Å, the other a lithiated TiO$_2$ phase, Li$_x$TiO$_2$, with lattice parameters $a \approx 3.90$ and $c \approx 9.30$ Å. The transition between TiO$_2$ and the lithiated TiO$_2$ phase occurs in approximately 15 minutes with applied currents of 2 mA, as shown in Figure 8.18, where this transition corresponds to the region identified by the shaded blue box in Figure 8.17. Anatase TiO$_2$ transforms into lithiated TiO$_2$ via a two-phase mechanism: the reflections associated with TiO$_2$ decrease in intensity, while the reflections associated with lithiated TiO$_2$ increase in intensity (Figure 8.18). Li insertion into TiO$_2$ occurs during
the initial stages of the 1.7 V discharge plateau, and Li extraction occurs at the final stages of charging. The extraction of Li from lithiated TiO$_2$ is demonstrated by the increase in the 20 value of the characteristic (112) TiO$_2$ reflection (Figure 8.18), corresponding to the contraction and expansion of the $a$ and $c$ lattice parameters, respectively. Between 786 and 902 minutes both phases may co-exist as the two-phase reaction proceeds, but it is unable to model this region accurately. Nonetheless, this work shows that TiO$_2$ is an active component of the composite electrode.

**Figure 8.17** The time evolution of voltage (black), and the $a$ (black) and $c$ (red) TiO$_2$ lattice parameters. The region shaded in green (between 786 and 902 minutes) may contain both the TiO$_2$ and Li$_x$TiO$_2$ phases, but could not be accurately modelled. The region shaded in blue corresponds to the *in-situ* ND patterns shown in Figure 8.18.
Figure 8.18 Selected region of \textit{in-situ} ND data highlighting the Li insertion process in $\sim$80 mg of TiO$_2$, observed by the increase in the 20 value of the (112) reflection indicated by the arrow. Scaled peak intensities are shown.

In the last region of the collected \textit{in-situ} ND data, $> 900$ minutes, the battery was cycled between 1.6 and 3 V, revealing Li insertion into and extraction from only the TiO$_2$ component. In this region two different sets of Rietveld refinements were performed. The first set is the same as those described earlier, and the TiO$_2$ and Li$_4$Ti$_5$O$_{12}$ lattice parameters are shown in Figure 8.19(a) and (b), respectively. In the second set a new phase, lithiated TiO$_2$ with $a = 3.91$ and $c = 9.29$ Å, was introduced into the Rietveld model, along with anatase TiO$_2$, Li$_4$Ti$_5$O$_{12}$, Li, and Cu. In this model the lattice parameters were fixed and only the background and scale factors (phase fractions) were refined, and the results are shown in Figure 8.19(c) and (d) for TiO$_2$ and lithiated TiO$_2$, respectively. Figure 8.19(e) and (f) show the measured voltage and applied current, respectively. The top section of Figure 8.19 shows a selected region of the \textit{in-situ} ND data, highlighting the relative intensities of the Li$_4$Ti$_5$O$_{12}$ and TiO$_2$ reflections.
Figure 8.19 Parameters from the charge-discharge cycles between 1.6 and 3 V of the composite Li$_4$Ti$_5$O$_{12}$/TiO$_2$ anode, determined from two sets of sequential multi-phase Rietveld refinements. Variations in the $a$ (a) and $c$ (b) TiO$_2$ lattice parameters were determined with a model containing only a TiO$_2$ phase. The phase fractions of TiO$_2$ (c) and lithiated TiO$_2$ (d) were determined with a model containing both TiO$_2$ and lithiated TiO$_2$ phases with fixed lattice parameters. The measured voltage (e) and applied current (f) are also shown. The uppermost section of the figure is a section of the in-situ ND data showing Li$_4$Ti$_5$O$_{12}$, TiO$_2$, and lithiated TiO$_2$ reflections. Scaled peak intensities are shown.
The Rietveld-refined lattice parameters indicate a correlation between the increase in voltage to 2.5 V and the lithiation of TiO₂, and also with the delithiation process occurring during the 1.7 V plateau. The use of higher current rates in the charging process increases the rate of Li insertion into TiO₂ and reduces the time of the (two-phase) transition. For example, sharp increases in the phase fraction of lithiated TiO₂ are noted between 970 - 990 and 1070 - 1090 minutes at applied currents of 15 mA, relative to the more gradual decrease in the phase fraction of lithiated TiO₂ between 990 - 1070 and 1090 - 1160 minutes at applied currents of -5 mA. Unlike anode materials such as MoS₂, both TiO₂ and Li₄Ti₅O₁₂ maintain their crystallinity during the charge/discharge processes. Furthermore, the transition from anatase to lithiated TiO₂ occurs quickly relative to the MoS₂ anode.

The composite TiO₂/Li₄Ti₅O₁₂ anode undergoes Li insertion into TiO₂ during discharge at 1.7 V, transforming Ti⁴⁺ to Ti³⁺ and forming the lithiated TiO₂ compound, LiₓTiO₂. The data suggest that the TiO₂ to LiₓTiO₂ transition is a two-phase reaction, i.e., the phase fraction of TiO₂ decreases while that of LiₓTiO₂ increases. Below 1.7 V the composite anode is composed of LiₓTiO₂ and Li₄Ti₅O₁₂, where the Ti³⁺ in LiₓTiO₂ is expected to enhance the overall conductivity of the electrode. Discharge to lower voltages allows Li insertion into the Li₄Ti₅O₁₂ component. In the completely discharged state the composite anode is composed of LiₓTiO₂ and Li₄₋ₓTi₅O₁₂. During charge, Li is extracted from Li₄₋ₓTi₅O₁₂ at 1.5 V, followed by extraction from LiₓTiO₂ at 2.5 V. Since the TiO₂ component can enhance conduction in a composite Li₄Ti₅O₁₂/TiO₂ electrode, the performance of Li₄₋ₓTi₅O₁₂ₓBrₓ will be influenced by the concentration of the TiO₂-type phases. Thus, it can be inferred that the TiO₂ found in the SXRD data is likely to have a role in
improving the electrochemical performance. Other factors can also contribute to the improved performance of $\text{Li}_4\text{Ti}_5\text{O}_{12-x}\text{Br}_x$, including the distribution of $\text{Ti}^{3+}/\text{Ti}^{4+}$ in $\text{Li}_4\text{Ti}_5\text{O}_{12-x}\text{Br}_x$ and the formation of additional phases on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ grain boundaries, as proposed for nanosized metal phosphides found in $\text{Li}_M\text{PO}_4$ (where $M = \text{Fe and Ni}$) cathodes [46].

The findings suggest that composite electrodes can be tailored for specific applications, e.g. a fast charging option for electric-vehicle applications, where one component provides peak performance at higher current rates and a second component provides peak performance at lower current rates. The ratio between the components may be controlled via the ratio of input materials used to form the composite electrode. This part of work shows that ideal, model composites can be used to elucidate the active voltage range for each component. Exploring a range of composites is necessary to further understand such systems and will lead to a greater understanding of the mechanisms involved in performance optimization of such composite materials.

### 8.4 Summary

A promising anode candidate based on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for high power lithium ion battery applications was synthesized by the spray pyrolysis technique, which is highly feasible for industrial use. Spray pyrolyzed $\text{Li}_4\text{Ti}_5\text{O}_{12}$ annealed in $\text{N}_2$ for short periods of time features carbon on the grain boundaries, which originates from the decomposition of the organic synthetic precursors. The carbon acts to inhibit growth of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles and improves conductivity, both of which are favorable for electrochemical performance. The as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibited outstanding electrochemical behavior, even at a high C-rate. Moreover, in full battery tests, the
material also shows excellent performance, demonstrating its applicability as a good anode candidate for lithium ion batteries.

The crystallographic reasons behind the improved discharge capacities of Li$_4$Ti$_5$O$_{12-x}$Br$_x$ electrodes were explored. A crystallographic maximum of Br of $x' = 0.12$ in Li$_4$Ti$_5$O$_{12-x}$Br$_x$ is found, with a structurally unknown impurity phase forming when Br in excess of this amount is used to synthesise the electrode material. Residual rutile TiO$_2$ is found in the solid-state synthesis of Li$_4$Ti$_5$O$_{12-x}$Br$_x$, regardless of the amount of Br used in the synthesis (within the lower limit of the tested nominal input concentration of $x = 0.05$). TiO$_2$ and the structurally unknown phase are found in relatively small quantities, and therefore were undetected using the conventional XRD methods of previous work [22]. There exists an optimal crystallographic concentration of Br in Li$_4$Ti$_5$O$_{12-x}$Br$_x$ at $x' \approx 0.1$, and also of the other phases – of the rutile TiO$_2$ at approximately 6 wt. % and the Br-rich third phase, all of which leads to the best discharge performance in the composite material. This composition is produced by using the synthetic chemical Br input concentration of $x = 0.20$. This optimum in performance is related to both intraparticle (crystallographic Br-doping) and interparticle (the TiO$_2$ and Br-rich phases) effects, both of which produce a ratio of mixed Ti$^{3+}$/Ti$^{4+}$ that enhances conduction.

Composite electrodes may facilitate the widespread use of Li-ion batteries in electric vehicles, by providing a fast charging-discharging component in conjunction with a second component that is electrochemically more active at lower current rates. *In-situ* ND experiments with a composite anatase Li$_4$Ti$_5$O$_{12}$/TiO$_2$ electrode were used to demonstrate that anatase TiO$_2$ is electrochemically active, where Li can be
selectively intercalated at 1.7 V to form Li<sub>x</sub>TiO<sub>2</sub>. Li insertion/extraction in anatase TiO<sub>2</sub>/Li<sub>x</sub>TiO<sub>2</sub> occurs in approximately 15 minutes with applied current of 2 mA. This process is a two-phase reaction, with increasing quantities of lithiated TiO<sub>2</sub> forming during discharge. The electrochemically reduced Li<sub>x</sub>TiO<sub>2</sub> is likely to enhance conduction during the Li insertion/extraction of the Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>.

**References**


9.1 General Conclusions

This doctoral work investigated the synthesis, physical characterization, and electrochemical performance of various nanostructured anode materials for lithium ion batteries, including SnO$_2$, MoS$_2$, TiO$_2$, and Li$_4$Ti$_5$O$_12$ or their composites, to broaden the current understanding of their structural evolution and corresponding electrochemical behaviour. As electrode materials, the morphology, specific surface area, crystal size, crystalline phase, etc. are key factors that affect the electrochemical performance because they could influence the lithium absorption sites and the lithium diffusion pathways and time. Finally, as a powerful characterization technique, in-situ neutron diffraction was successfully applied to investigate electrode materials in custom designed cells.

Various nanostructured SnO$_2$ and SnO$_2$/C composites were prepared in this work, such as porous SnO$_2$ and SnO$_2$/C composite by the molten salt method, SnO$_2$/CNT composite by the solvothermal method, and one-dimensional porous SnO$_2$ and SnO$_2$/C nanofibres by electrospinning. The porous SnO$_2$ prepared by the molten salt method exhibits high surface area, giving more contact area between the active material and the electrolyte, and decreasing the lithium diffusion length. At the same time, the pores could accommodate the volume expansion. It delivers reversible capacity of 410 mAh g$^{-1}$ after 100 cycles in the voltage range of 0.05-1.5 V. The SnO$_2$/C nanocomposite that was prepared by the same method shows better capacity retention (85.3%) than bare nano-SnO$_2$ (64.8%) after 100 cycles. In the SnO$_2$/CNT
composite, SnO₂ nanocrystals about 5 nm in size were deposited and pinned onto CNTs which could serve as conductive cores. Very large surface area uniform SnO₂ and SnO₂/C composite nanofibres consisting of orderly bonded nanoparticles have been obtained by the electrospinning technique and thermal pyrolysis process under optimized synthesis conditions. The *in-situ* carbon incorporation from the well mixed precursor via the molten salt and electospinning methods is expected to give more uniform carbon distribution in the composites and good affinity of the carbon to the active material, which could improve the electrochemical performance.

Layer structured MoS₂ was first exfoliated and then restacked by a simple hydrothermal method, resulting in an enlarged \(c\)-axis parameter. The enlarged \(c\) parameter and the increase in the surface area are favourable to the intercalation reaction, which can also be proven by the much lower activation energy compared to the raw MoS₂, indicating the fast electrochemical reaction kinetics. The restacked MoS₂ electrodes exhibit a large capacity of 800 mAh g⁻¹ and extraordinarily high cycling stability, even at high charge current density. A similar strategy was applied to prepare MoS₂/SnO₂ composite by exfoliation and restacking of commercial MoS₂, with SnO₂ nanocrystals deposited between the MoS₂ layers.

Ti-based oxides, TiO₂ or Li₄Ti₅O₁₂, exhibit higher operating voltage, which could avoid electrolyte decomposition and SEI formation on the electrode, thus improving anode safety in lithium-ion batteries, which is very important for potential applications in electric vehicles. One-dimensional TiO₂(B)/anatase nanowires were synthesized by the hydrothermal method. The hybrid nanowire electrode delivered a
highly reversible capacity of 196 mAh g\(^{-1}\) after 100 cycles at 30 mA g\(^{-1}\) (0.1 C). It also exhibited a reversible discharge capacity as high as 125 mAh g\(^{-1}\), when cycled at 4500 mA g\(^{-1}\) (15 C). Three-dimensional TiO\(_2\) nanotube arrays were prepared by anodization, and then SnO\(_2\) nanocrystals were deposited into/onto the TiO\(_2\) nanotube arrays to create a composite anode in which the TiO\(_2\) could serve both as an electroactive material and as a buffer to accommodate SnO\(_2\) volume expansion during the charge/discharge process. As a promising anode candidate, Li\(_4\)Ti\(_5\)O\(_{12}\) was also investigated. This involved its synthesis by spray pyrolysis, which is energy saving and applicable in industry. The molecular level mixing of the precursor allows for shorter high temperature treatment and high purity in the products. Furthermore, the annealing in N\(_2\) atmosphere preserved the carbon from the organic precursor and distributed it uniformly, which could improve the conductivity. This material exhibits excellent rate capability (132 mAh g\(^{-1}\) at 10 C) and stable cycling in full battery tests. Br doped Li\(_4\)Ti\(_5\)O\(_{12}\) was investigated by synchrotron X-ray diffraction to clarify the effects of the structure and of impurities on the electrochemical behaviour. Finally, Li\(_4\)Ti\(_5\)O\(_{12}\)/TiO\(_2\) composite anode was investigated by \textit{in-situ} neutron diffraction to understand the electrochemical behaviour.

\textbf{9.2 Outlook}

This doctoral work was mainly focused on the synthesis and characterization of nanostructured anode materials. The techniques involved, such as the molten salt method, the hydrothermal method, electrospinning, spray pyrolysis, \textit{etc.}, are effective techniques to prepare nanomaterials and are also applicable to prepare other electrochemical materials, such as Si and transition metal (M) oxide anodes, or LiMPO\(_4\), LiMn\(_2\)O\(_4\), or Li\(_2\)MSiO\(_4\) cathodes.
Carbon could improve the electronic conductivity as an effective component in the composite electrode materials. However, the crystallinity of carbon has not been investigated in this work, such as differences in the performance of amorphous and graphitic phase, and the intrinsic nature of the carbon from different carbon sources that were utilized in the experiments. Moreover, the carbon content in the SnO$_2$/C composites could be optimized, and the amount could be controlled, as otherwise it would affect the energy density of the composites. The same problem would occur in other carbon-containing composite electrode materials, especially for materials with low tap density and low electronic conductivity, such as Li$_4$Ti$_5$O$_{12}$ and LiFePO$_4$.

Composite electrodes, especially composites with more than one active component, could benefit from the advantages of each individual component, because only one material can hardly satisfy all the requirements, such as enhancing capacity, buffering volume change, exhibiting different operating voltage plateaus, improving electronic and ionic conductivity, etc. However, the reaction mechanisms need to be further understood, especially the interactions between the active species.

The *in-situ* neutron diffraction technique is a powerful way to investigate structural changes in electrodes during charge/discharge process due to the sensitivity of neutrons to light elements, such as lithium, oxygen, etc. However, sometimes, during the conversion reaction, as the crystallinity of the active material decreases, it is impossible to see the structural change by more conventional techniques. So, this method would be ideal for lithium intercalation reaction materials, most of which are
cathode materials. To fully understand the mechanism, other *in-situ* techniques, such as *in-situ* TEM, *in-situ* Raman spectroscopy, or *in-situ* synchrotron X-ray diffraction should also be performed.

Although nanostructured polymorphs show better electrochemical performance than many other electrode materials, especially in terms of rate capability, due to the large surface area and shorter lithium diffusion length, there might also be some increase in side reactions due to the nanosize effect. In order to prevent this disadvantage, particle size selection or surface modifications should be investigated for different materials. Moreover, the nanomaterial fabrication process is always tedious and difficult to extend to large scale application, so efficient, easily scaled-up synthesis techniques should be explored.
APPENDIX: LIST OF PUBLICATIONS


8) **G. D. Du**, B. R. Winton, K. Konstantinov, Z. X. Chen and Z. P. Guo, “In-situ spray pyrolyzed Li$_4$Ti$_5$O$_{12}$ with conductive network as a long cycle life, high rate
anode material for lithium ion batteries”, *In Preparation.*


nanocomposite as anode material by molten salts method and its application in lithium ion batteries”, *Phys. Status Solid A*, 206, 2546, (2009).


