ADDRESSING IRREVERSIBLE ISSUES IN HIGH CAPACITY LITHIUM ION BATTERY ANODE MATERIALS

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2012
DECLARATION

I hereby declare that this thesis is my original work and it has been written by me in its entirety.

I have duly acknowledged all the sources of information which have been used in the thesis.

This thesis has also not been submitted for any degree in any university previously.

Ji Ge

14 February, 2013
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# TABLE OF CONTENT

- **ACKNOWLEDGEMENT** ............................................................................................................ I
- **TABLE OF CONTENT** ........................................................................................................... II
- **SUMMARY** VI
- **LIST OF TABLES** ................................................................................................................ IX
- **LIST OF FIGURES** ................................................................................................................ X
- **LIST OF ABBREVIATIONS** ............................................................................................... XV

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

1. 1 Background .................................................................................................................. 1

1. 2 Objectives and Scope ............................................................................................ 4

## CHAPTER 2 LITERATURE REVIEW ........................................................................... 7

2. 1 Lithium Ion Batteries ............................................................................................. 7

2. 2 Strategies for Capacity Retention and Rate Performance Improvements.... 11

2.2.1 Nanostructured Materials .................................................................................. 12

2.2.1.1 Solid Nanostructured Materials ........................................................................ 12

2.2.1.2 Hollow Nanostructured Materials ............................................................... 14

2.2.1.3 Porous Nanostructured Materials ............................................................... 15

2.2.1.4 Hierarchical Structured Materials ............................................................... 17

2.2.2 Composite Materials ............................................................................................ 18

2.2.2.1 Disordered Carbon....................................................................................... 19

2.2.2.2 CNT ............................................................................................................. 22

2.2.2.3 Graphene ................................................................................................... 24

2.2.2.4 Other Composites ....................................................................................... 26

2. 3 Origin of ICL and Strategies for ICL Mitigation .................................................. 28

2.3.1 The Origin of ICL ............................................................................................... 28
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.2</td>
<td>Strategies for ICL Mitigation</td>
<td>32</td>
</tr>
<tr>
<td>2.3.2.1</td>
<td>Compositing with Li$<em>{2.5}$Co$</em>{0.5}$N</td>
<td>32</td>
</tr>
<tr>
<td>2.3.2.2</td>
<td>Pre-lithiation</td>
<td>33</td>
</tr>
<tr>
<td>2.3.2.3</td>
<td>Artificial SEI</td>
<td>34</td>
</tr>
<tr>
<td>2.3.2.4</td>
<td>Carbon Coating</td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>SELF-ASSEMBLED 3D FLOWER-LIKE HIERARCHICAL TIN OXIDE NANOSTRUCTURES WITH DIFFERENT PACKING</td>
<td>38</td>
</tr>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>38</td>
</tr>
<tr>
<td>3.2</td>
<td>Experimental Section</td>
<td>40</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Material Synthesis and Characterization</td>
<td>40</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Electrochemical Measurements</td>
<td>41</td>
</tr>
<tr>
<td>3.3</td>
<td>Results and Discussion</td>
<td>41</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Morphology Control by Solution pH</td>
<td>41</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Morphology Control by Reactant Concentrations</td>
<td>46</td>
</tr>
<tr>
<td>3.3.3</td>
<td>The Morphology Evolution Process</td>
<td>48</td>
</tr>
<tr>
<td>3.3.4</td>
<td>Reversible Lithium Storage Properties</td>
<td>50</td>
</tr>
<tr>
<td>3.4</td>
<td>Conclusion</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>CONFORMAL GRAPHENE ENCAPSULATION OF TIN OXIDE NANOPARTICLE AGGREGATES FOR IMPROVED REVERSIBILITY OF LITHIUM ION STORAGE</td>
<td>56</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>56</td>
</tr>
<tr>
<td>4.2</td>
<td>Experimental Section</td>
<td>59</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Synthesis of Tin Oxide NP Aggregates</td>
<td>59</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Synthesis of SnO$_2$@GO Composites</td>
<td>60</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Synthesis of SnO$_2$@TRGO Composites</td>
<td>60</td>
</tr>
</tbody>
</table>
### Table of Content

4.2.4 Materials Characterization ................................................................. 60
4.2.5 Electrochemical Measurements .......................................................... 61
4.3 Results and Discussion ........................................................................... 62
  4.3.1 Structural Analysis ............................................................................. 62
  4.3.2 XRD/XPS Analysis ............................................................................ 67
  4.3.3 Reversible Lithium Storage Properties .............................................. 71
4.4 Conclusion .............................................................................................. 78

CHAPTER 5 LITHIUM TITANATE SURFACE COATING OF TIN-BASED HIGH CAPACITY Li ION ANODE MATERIALS ........................................ 80
  5.1 Introduction .......................................................................................... 80
  5.2 Experimental Section ............................................................................ 83
    5.2.1 Preparation of Hollow SnO$_2$/Li$_4$Ti$_5$O$_{12}$ Core-shell Composite Particles. 83
    5.2.2 Characterization ............................................................................. 84
    5.2.3 Electrochemical Measurements .................................................... 85
  5.3 Results and Discussion ........................................................................... 85
    5.3.1 Structure Analysis .......................................................................... 85
    5.3.2 EDX/XRD Analysis ........................................................................ 90
    5.3.3 Reversible Lithium Storage Properties ........................................... 91
  5.4 Conclusion ............................................................................................. 98

CHAPTER 6 ANODE MATERIALS FOR LITHIUM ION BATTERIES WHICH CAN BE USED WITHOUT CONDUCTIVE ADDITIVES ........... 100
  6.1 Introduction .......................................................................................... 100
  6.2 Experimental Section ............................................................................ 103
    6.2.1 Electrode Fabrication ..................................................................... 103
    6.2.2 Material Characterization .............................................................. 104
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>Results and Discussion</td>
<td>105</td>
</tr>
<tr>
<td>6.3.1</td>
<td>Structure Analysis</td>
<td>105</td>
</tr>
<tr>
<td>6.3.2</td>
<td>XRD/XPS Analysis</td>
<td>107</td>
</tr>
<tr>
<td>6.3.3</td>
<td>Reversible Lithium Storage Properties</td>
<td>110</td>
</tr>
<tr>
<td>6.4</td>
<td>Conclusion</td>
<td>118</td>
</tr>
<tr>
<td></td>
<td><strong>CHAPTER 7 CONCLUSIONS AND FUTURE WORK</strong></td>
<td>120</td>
</tr>
<tr>
<td>7.1</td>
<td>Conclusion</td>
<td>120</td>
</tr>
<tr>
<td>7.2</td>
<td>Future Work</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td><strong>REFERENCES</strong></td>
<td>128</td>
</tr>
<tr>
<td></td>
<td><strong>PUBLICATIONS</strong></td>
<td>147</td>
</tr>
</tbody>
</table>
SUMMARY

A significant improvement of the current lithium ion battery performance is needed to meet the needs of large-scale applications such as electric vehicle and distributed electrical energy storage. This is best accomplished through materials innovation. Anode materials such as those based on tin/tin dioxide have shown the potential to easily increase the current anode capacity by two to three folds (from 372 mAh/g for carbon anodes to 992 mAh/g for Sn and 782 mAh/g for SnO₂ anodes). Previous research has greatly improved the capacity retention of these ‘new’ materials in prolonged cycling but the issues of initial irreversible capacity loss (ICL) and rate performance remain outstanding. This thesis study is focused on the design and synthesis of tin-based anode materials with high capacity, low ICL, stable cycling performance and high rate capability. The emphasis is on the design and fabrication of 3D hierarchical structures and their optimization for battery applications. There are also efforts on using composites (composites of tin/tin oxide with graphene, spinel lithium titanate (Li₄Ti₅O₁₂), or TiO₂) to optimize the reversibility of the tin-based anodes.

Topically the thesis is divided into seven chapters. Chapter 1 outlines the motivation and the scope of work. Chapter 2 is a survey of the current literature related to this research. Major findings of this study are discussed in Chapters 3 through 6, with conclusions and suggestions for further work covered in Chapter 7.

A facile method to synthesize SnO₂ hierarchical structures with different packing densities is described in Chapter 3. Flower-like 3D hierarchical structures were assembled from tin oxide nanosheets in varying packing density. Electrochemical
measurements indicated that the ICL of hierarchical structures due to solid electrolyte interface (SEI) formation were all smaller than those of unassembled nanosheets or SnO\(_2\) nanoparticles. The hierarchical SnO\(_2\) structure with a moderate packing degree, in particular, showed the best overall capacity retention.

The capacity retention in flower-like tin oxide 3D hierarchical structures was however not satisfactory, most probably due to macro-scale volume changes of the anode material during discharging (Li insertion) and charging (Li extraction), where the induced stresses could eventually lead to electrode deconstruction. Hence, the composite approach was used in the rest of the research to moderate the volume changes. The compositing mediums, which included graphene (Chapter 4), lithium titanate (Chapter 5) and titania (Chapter 6), were used to simultaneously promote cycle stability, SEI quality and the transport (electronic and/or ionic) properties of the electrode. The composites were fabricated as core-shell systems to maximize the benefits of the storage host and the compositing medium. The core was tin oxide nanoparticle aggregates with sufficient internal porosity to cushion the volume changes but dense enough not to compromise the volumetric density of the active material. Electrochemical measurements of these core-shell composites confirmed the possibility of combining high capacity, low ICL for SEI formation, high rate capability and good cyclability.

Chapter 4 describes the preparation and performance of SnO\(_2\)/graphene composites for reversible Li ion storage. The composites were fabricated as SnO\(_2\) nanoparticle aggregates individually wrapped in thermally reduced graphene oxide shells of different thicknesses. Chapter 5 presents another composite design in the form of
SnO$_2$@Li$_4$Ti$_5$O$_{12}$ core-shell composite particles with different shell thicknesses. The conformal Li$_4$Ti$_5$O$_{12}$ coating was effective in reducing the ICL of SEI formation. It was applied as a thin layer and its conductivity for electron and Li ion transport also contributed to an elevated rate performance. A tin oxide based anode with good power density which could be used without any conductive carbon additive is described in Chapter 6. The composite anode was fabricated as a tin oxide@titania core-shell composite with excellent rate performance. It is believed that the titania layer was converted into a more conductive form (Li$_y$Ti$_{1-y}$O$_2$) during cycling which functioned as individual ‘current collector’ for each of the tin oxide nanoparticle aggregates.
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1</td>
<td>The ICL of tin-based anode materials tested at different current densities and in different voltage windows.</td>
<td>29</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>Matrix of experiment conditions.</td>
<td>40</td>
</tr>
<tr>
<td>Table 3.2</td>
<td>Summary of electrochemical properties of HS-A, HS-B, HS-C and HS-D.</td>
<td>52</td>
</tr>
<tr>
<td>Table 5.1</td>
<td>Summary of electrochemical performance of SO and SO/LTO composites.</td>
<td>93</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 2.1  Basic components and operation of a Li ions cell. ................................. 8

Figure 2.2  Voltage profiles of the SnO₂ NPs as a function of a) ~3 nm, b) ~4 nm, and c) ~8 nm in coin-type half cells. SnO₂ anodes were cycled at the rate of 60 mA/g for the first cycle and at the charge rate of 1800 mA/g and the discharge rate of 300 mA/g between 1.2 and 0 V for the remaining cycles. (Kim et al. 2005) ..................................................... 13

Figure 2.3  a) A high-resolution transition electron microscopy (HRTEM) image of the mesoporous SnO₂. b) Charge capacities as a function of cycle number at different discharge rates tested in coin-type half cells. The discharge rate was fixed at 0.2 C. (Kim et al. 2008) ............................ 17

Figure 2.4  a) FESEM image of chestnut-like Sn@carbon mesospheres. b) Plot of capacity vs. cycle number evaluated at 100 mA/g and 200 mA/g in the 0.005-2 V voltage window. (Deng et al. 2010) .................................... 22

Figure 2.5  Li insertion/extraction properties of the GNS families. a) discharge/charge profiles of (a) graphite, (b) GNS, (c) GNS+CNT, and (d) GNS+C₆₀ at a current density of 50 mA/g. b) Discharge/charge cycle performance of (a) graphite, (b) GNS, (c) GNS+CNT, and (d) GNS+C₆₀. (Yoo et al. 2008) ................................................................. 24

Figure 2.6  Illustrative relationship between the specific capacity of the full cell and the specific capacity of anode. (Basis: cathode with a specific capacity of 200 mAh/g). The blue line represents an anode material without ICL while the green line corresponds to an anode with a 30% ICL. ....... 30

Figure 2.7  a) TEM image of SnO₂/carbone composite hollow spheres. b) Discharge-charge voltage profiles of SnO₂/carbone composite hollow spheres for 1ˢᵗ and 2ⁿᵈ cycles at a current density of 100 mA/g. (Lou et al. 2008)...... 36

Figure 2.8  a) TEM micrograph of the pyrolyzed nanofibers obtained by calcining Sn@carbonencapsulated in carbon nanofibers in Ar/H₂ at 1000 °C for 5 h. b) Electrochemical performance of the Sn/C composite electrode cycled between 0.01 and 3 V (versus Li/Li⁺) at 50 mA/g. (Yu et al. 2009) ................................................................. 36

Figure 3.1  SEM images of a) HS-A precursor before hydrothermal reaction, b) HS-A, c) HS-B precursor before hydrothermal reaction, d) HS-B, e) XRD patterns of HS-A and HS-B precursors before hydrothermal reaction, and f) XRD patterns of HS-A, HS-B. ................................. 44
| Figure 3.2 | SEM images of a) HS-C at low magnification, b) HS-C at high magnification, c) TEM images of HS-C and d) XRD patterns of HS-C. |
| Figure 3.3 | Proposed formation mechanisms of HS-A, HS-B and HS-C. |
| Figure 3.4 | Morphology and XRD patterns of HS-D and HS-E. a) SEM image of HS-D at low magnification, b) SEM image of HS-D at high magnification, c) TEM image of HS-D, d) SEM image of HS-E at low magnification, e) SEM image of HS-E at high magnification, f) TEM image of HS-E, g) XRD patterns of HS-D and HS-E, h) proposed mechanism for the formation of hierarchical flower-like structures with different packing densities by changing the reactant concentrations. The inset in Figure d) shows a semi-spherical flower-like particle. |
| Figure 3.5 | SEM images of a) HS-H b) HS-G precursor before hydrothermal reaction, c) HS-G, d) XRD patterns of HS-H, HS-G precursor before the hydrothermal reaction and HS-G. |
| Figure 3.6 | Discharge and charge curves of a) HS-A, b) HS-C, c) HS-D and d) HS-E at 0.5 A/g and 1A/g in the 0.01-2 V (versus Li/Li⁺) voltage window. |
| Figure 3.7 | Cycling stability of a) HS-A, b) HS-C, c) HS-D and d) HS-E at 0.5 A/g and 1A/g in the 0.01-2 V (versus Li/Li⁺) voltage window. |
| Figure 4.1 | a) Preparation of SnO₂@TRGO core-shell composites. b) Schematic illustration showing the effect of structure on electrochemical performance. |
| Figure 4.2 | Morphology of intermediate and final products in the GO encapsulation of tin oxide NP aggregates. a, d, h) TEM, b, e, i) FESEM and c, f, g) STEM images of a-c) pristine tin oxide NP aggregates, d-f) SnO₂@GO-5 and h-g) SnO₂@TRGO-5. All scale bars are 100 nm in the figures. |
| Figure 4.3 | Linescan image of three representative SnO₂@TRGO-5 particles. |
| Figure 4.4 | Morphology of intermediate and final products in the graphene encapsulation of tin oxide NP aggregates. a, d) TEM, b, e) FESEM and c, f) STEM images of a-c) SnO₂@GO-10 and h-j) SnO₂@TRGO-10. All scale bars are 100 nm. |
| Figure 4.5 | C1s XPS spectra of GO, SnO₂@GO-5 and SnO₂@TRGO-5. |
| Figure 4.6 | a) XPS survey scan spectra of SnO₂@TRGO-5 and SnO₂@TRGO-10. b) C1s XPS spectrum of SnO₂@TRGO-10. |
| Figure 4.7 | a) XRD patterns of GO, tin oxide, SnO₂@GO-5, SnO₂@TRGO-5 and SnO₂@TRGO-10. b) TGA curves of SnO₂@TRGO-5 and SnO₂@TRGO-10. |
Figure 4.8  Discharge and charge curves of a) tin oxide, b) TRGO at 200 mA/g in the 0.005-2 V (versus Li/Li'). ................................................................. 70

Figure 4.9  a) 1st and 2nd cycle discharge and charge curves of SnO2@TRGO-5 and SnO2@TRGO-10 at 200 mA/g in the 0.005-2 V (versus Li/Li') voltage window.  b) Cycling performance of tin oxide, TRGO, SnO2@TRGO-5 and SnO2@TRGO-10. (Test conditions: 200 mA/g, 0.005-2 V versus Li/Li'). ................................................................. 70

Figure 4.10 a) TEM, b) FESEM and c) STEM images, d) C1s XPS spectrum and e) cycle stability of SnO2@CRGO-5. SnO2@CRGO-5 was prepared by the following procedure: 50 mg SnO2@GO-5 was dispersed in 10 mL hydrazine (N2H4, 53%) for 0.5 h with stirring. The recovered solid was washed by DI water for 3 times. ........................................................... 73

Figure 4.11 a) Rate performance of SnO2@TRGO-5 and SnO2@TRGO-10 electrodes at current densities from 100 to 1000 mA/g.  b) Nyquist plots of SnO2, SnO2@TRGO-5, SnO2@CRGO-5 and SnO2@TRGO-10 electrodes before cycling at a discharged potential of 1.6 V (versus Li/Li') in the 100 kHz to 0.1 Hz frequency region. ......................... 75

Figure 4.12 Nyquist plots of SnO2, SnO2@TRGO-5 after 50 discharge/charge cycles at a discharged potential of 1.6 V (versus Li/Li'). Frequency range: 100 kHz to 0.1 Hz. ................................................................. 78

Figure 5.1  Schematic illustration showing hollow tin oxide particles with and without the LTO coating. For the uncoated hollow tin oxide particles, an unstable SEI layer is formed in the 1st cycle resulting in a larger irreversible consumption of Li ions. With the LTO coating, a more stable SEI layer is formed in the 1st cycle; reducing the irreversible consumption of Li ions and also improving material cyclability. The high Li ions mobility in LTO could also facilitate Li ions transport to the core to increase rate performance. ........................................... 82

Figure 5.2  a) Evolution of the SnO2@Li4Ti5O12 core-shell composite, b-l) morphologies of intermediate and final products.  b, e-i) TEM, d) STEM and c, j-l) SEM micrographs of b, c) pristine hollow tin oxide nanoparticles, d) SO/TO-5, e) SO/TO-15, f) SO/TO-30, g, j) SO/LTO-5, h, k) SO/LTO-15, i, l) SO/LTO-30. The inset in figure i) shows the circled region at higher magnification. ........................................... 86

Figure 5.3  Line scan image of a SO/LTO-30 particle. .................................................. 87

Figure 5.4  Element mapping of a) SO/LTO-15, b) SO/LTO-30. ................................. 89

Figure 5.5  XRD patterns of SO, SO/LTO-5, SO/LTO-15 and SO/LTO-30. The vertical lines denote the standard XRD patterns corresponding to cassiterite SnO2 (JCPDS Card No. 41-1445) (grey line) and spinel lithium titanate (JCPDS Card No. 26-1198) (yellow line). .......................... 90
Figure 5.6  ICL due to SEI formation and discharge capacity in the 30th cycle of SO, SO/LTO-5, SO/LTO-15 and SO/LTO-30 .......................................................... 94

Figure 5.7  a) Voltage profiles of SO and SO/LTO-15 at 100 mA/g. b) Cycling performance of SO, SO/LTO-5, SO/LTO-15 and SO/LTO-30 at 100 mA/g. ........................................................................................................... 95

Figure 5.8  Cyclic voltammograms of SO a) and SO/LTO-15 b) at a scan rate of 0.2 mV/s. .................................................................................................. 96

Figure 5.9  Cycling performance of SO/LTO-15 at 200 and 1000 mA/g. .......... 97

Figure 5.10  Nyquist plot of SO/LTO-15 at the end of 3rd, 10th and 30th cycles. Impedance measurements were taken at the open circuit condition after the cell was rested for 5 h after cycling. ......................................................... 98

Figure 5.11  SEM micrographs of a) the as-prepared SO/LTO-15 electrode, b) a SO/LTO-15 electrode after 30 cycles................................. 98

Figure 6.1  Explanation for the excellent rate performance of the core-shell SnO2/TiO2 composite in this study. .......................................................... 103

Figure 6.2  SEM images of a) pristine SnO2, b) electrode fabricated by casting a mixture of SnO2, conductive carbon and PVDF. The inset in figure a) shows the TEM image of pristine SnO2.................................................. 105

Figure 6.3  a) TEM image, b) SEM image of SnO2/amorphous TiO2. .............. 105

Figure 6.4  a) FESEM image, b) STEM image, c) HRTEM image, d) corresponding FFT pattern of the region of interest and e) elemental maps of SO@TO. ......................................................................................... 109

Figure 6.5  a) XRD patterns of SO, SO@TO and SO@TO charged to 2 V after 10 cycles. b) Survey scan spectrum of SO@TO. The inset is the high-resolution Ti 2p XPS spectrum of SO@TO. ........................................... 110

Figure 6.6  CVs of SO/C and SO@TO at a scan rate of 0.2 mV/s in the 0-3 V range (versus Li/Li+). The solid lines are for SO/C and the dash lines are for SO@TO. ............................................................................................. 113

Figure 6.7  a) 1st cycle discharge and charge curves of SO@TO, SO and SO/C. b) Cycling performance of SO@TO, SO and SO/C. Test conditions: current density=200 mA/g, voltage range=0.005-2 V versus Li/Li+ . 113

Figure 6.8  a) Discharge and charge curves of SO@TO in the first two cycles. b) Cyclability of SO@TO at 1 A/g and 3 A/g. Test conditions: voltage range=0.005-2 V versus Li/Li+ ......................................................... 114

Figure 6.9  Nyquist plots of SO/C and SO@TO electrodes in different stages of discharge and charge. a) SO/C, b) SO@TO at open-circuit condition, 1st cycle discharge to 2 V, 1 V, 0.005 V and 1st cycle charge to 1 V at 200
mA/g, c) SO/C, d) SO@TO in the 10th cycle discharged to 2 V, 1 V, 0.005 V and then charged to 1 V at 1 A/g. ........................................ 116

**Figure 6.10** TEM image of SO@TO after 10 discharge and charge cycles......... 118
## LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Lithium</td>
</tr>
<tr>
<td>Sn</td>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>Germanium</td>
</tr>
<tr>
<td>NWs</td>
<td>Nanowires</td>
</tr>
<tr>
<td>RF</td>
<td>Resorcinol-formaldehyde</td>
</tr>
<tr>
<td>NSs</td>
<td>Nanosheets</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon NTs</td>
</tr>
<tr>
<td>CVD</td>
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</tr>
<tr>
<td>AAO</td>
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</tr>
<tr>
<td>CMC</td>
<td>Carboxymethylcellulose</td>
</tr>
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<td>Graphene oxide</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
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<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field-emission scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transition electron microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methylpyrrolidone</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethylene carbonate</td>
</tr>
<tr>
<td>TRGO</td>
<td>Thermally reduced graphene oxide</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>PAH</td>
<td>Poly(allylamine hydrochloride)</td>
</tr>
<tr>
<td>TTIP</td>
<td>Titanium isopropoxide</td>
</tr>
<tr>
<td>TBOT</td>
<td>Titanium tetrabutoxide</td>
</tr>
</tbody>
</table>
1. 1 Background

Highly efficient energy storage devices are indispensable in any energy system where mismatches between energy supply and demand are perennial and unavoidable. Rechargeable batteries, while not the largest energy storage option per se, are nonetheless the most versatile since the stored energy can be released on demand as electricity, the most useful form of energy. Rechargeable lithium ion batteries, with their high cell voltage and long cycle life, are the most advanced rechargeable battery on the market today, offering 2-3 times higher energy density and 5-6 times higher power densities than Ni–MH, Ni–Cd, and lead acid batteries. (Ji et al. 2011) Lithium ion batteries are the de-facto standard power source for portable electronic products and are now a strong contender as the energy storage system for electric vehicles and smart grids. (Manthiram 2011; Scrosati et al. 2011) A substantial improvement of the current performance of lithium ion batteries is needed to meet these large scale and more demanding applications.

The capacity of a lithium ion battery is determined by the properties of the active electrode materials. Despite the large number of studies to increase the capacity of the cathode (positive electrode) material, there is only a limited number of inorganic structures which can reversibly store and release Li ions at high potentials and provide capacities greater than 250 mAh/g. (Ellis et al. 2010; Fergus 2010; Goodenough et al. 2010; Wang et al. 2012) On the contrary, it is relatively easy to find anode (negative
electrode) materials with a high capacity. A high capacity anode material can therefore be used to release valuable internal cell volume for use by the cathode material. Anode materials such as those based on tin/tin dioxide have shown the potential to easily increase the current capacity of anode (almost exclusively carbon-based) by two to three folds (C: 372 mAh/g with stoichiometry of LiC₆; Sn: 992 mAh/g with stoichiometry of Li₄.₄Sn). (Courtney et al. 1997; Brousse et al. 1998; Lee et al. 2003) The use of these high-capacity anode materials however encounters three major issues: large initial irreversible capacity loss (ICL), poor capacity retention in prolonged cycling, and low rate performance. Large ICL is caused by irreversible side reactions such as the reductive decomposition of solvent and electrolyte salt. (Bridel et al. 2010; Xu et al. 2011) Poor capacity retention is due to the macroscopic volume changes of the anode material during discharging (Li insertion) and charging (Li extraction), where induced stresses can eventually lead to cracking and crumbling of the electrode. (Yang et al. 1996; Park et al. 2010) Low rate performance is caused by the low electronic conductivity and/or low Li ion conductivity of the active material. (Chen et al. 2008; Zhao et al. 2011)

The most common strategy for improving the cycling performance of non-carbonaceous anode materials is nanostructuring, where the Li ions diffusion length is reduced and the tolerance to the stress and strain from repetitive Li ions insertion/extraction is increased. The literature is replete with recipes for fabricating nanostructured anode materials. (Li et al. 2000; Li et al. 2001; Chan et al. 2010; Liu et al. 2012) Compositing is another effective means used to improve the cycling performance of non-carbonaceous anode materials. Carbon is the most commonly used compositing medium since it is electrically conductive and is sufficiently soft to
cushion the volume changes in discharging and charging. (Read et al. 2001; Fu et al. 2006; Derrien et al. 2007; Li et al. 2012; Li et al. 2012)

These two strategies have notably improved the capacity retention in prolonged cycling but the issue of ICL remains outstanding and the rate performance is still limited. It should be mentioned that nanostructuring may inadvertently increase the ICL because the large surface area of nanomaterials can promote unwanted side reactions which are mostly surface processes. ICL also increases with the disorder of the carbon used for compositing. While the ICL of natural graphite has been well studied, (Komaba et al. 2003; Zhang et al. 2004; Wang et al. 2005; Zhang 2006) the origin of ICL of non-carbonaceous materials and its rectification are lesser known. (Martin et al. 2008; Menkin et al. 2009; Bridel et al. 2010) In principle a surface coating, an electrolyte additive, or both, may be used to form a stable passivating film (the solid electrolyte interface, or SEI) on the anode. The consumption of Li ions must be low in the process in order to reduce the ICL. A systematic study of the effectiveness of these approaches for the non-carbonaceous anode materials is still lacking in the literature. While nanostructuring and compositing have demonstrated some improvements over the performance of pristine microstructured materials, the aggregation of nanoparticles (NPs) during cycling and the limited conductivity of some of these composites (even with carbon as the compositing medium) are still the problems to overcome. (Mattia et al. 2006; Deng et al. 2009; Deng et al. 2010) The simultaneous improvement of rate performance and cyclability of these alternative anode materials is still an on-going effort.
1.2 Objectives and Scope

This Ph.D study is aimed at improving the reversibility of high capacity lithium ion batteries anode materials. Hence, the design and preparation of anode materials with high capacity, low ICL, stable cycling performance and high rate performance are primary project objectives. Tin-based anode materials; which have a high Li ions storage capacity (Sn: 992 mAh/g, SnO₂: 784 mAh/g with stoichiometry of Li₄.₄Sn) and are relatively easy to synthesize by environmentally friendly methods from low cost resources; are the model anode materials in this study. The emphasis is on the design and fabrication of 3D hierarchical structures of tin-based anodes and the optimization of their structures for battery electrochemical performance. There are also efforts on using composite designs (composites of tin/tin oxide with graphene, spinel lithium titanate (Li₄Ti₅O₁₂), and TiO₂) to optimize the reversibility of tin-based anodes; and knowledge extraction from the experimental findings. The specific tasks in this thesis study include the following:

1. If NPs can be arranged into a hierarchical structure with the reduction of global surface area, there is a good opportunity that ICL may be proportionally reduced. The small dimension of NPs should enhance the anode rate performance and the pores between the primary NPs provide the space for cushioning the volume excursions in discharging and charging. Hence, the first part of this thesis study was concerned with the development of reliable methods for the formation of tin-based hierarchical structures where adjustments of shape and the extent of NP packaging were possible by tuning the synthesis environment, thereby enabling the study of some basic morphology-electrochemical performance relationships.
2. Graphene, an excellent carbon nanoform, was selected to form composite with the tin-based anode materials because its high electrical conductivity should lead to noticeable improvements of the anode rate performance. The composite structure has to be carefully crafted to also improve cycle stability and reduce ICL at the same time. Hence, active materials were first fabricated as porous ensembles of nanoscale particles and then individually wrapped by graphene sheets. The function of the graphene sheets was two folded: to provide electrical contact and to prevent the aggregation of the active materials. A method to fabricate this particular structure was developed. The effects of structure on electrochemical performance such as Li ions across-plane diffusivity were analyzed. The analysis resulted in some useful guidance on the design of composites of graphene with other active materials.

3. Spinel lithium titanate is as an alternative anode material with good reversibility (it incurs zero strain in Li insertion and extraction reactions) and excellent rate performance, and more importantly there is stable SEI formation on its surface in the 0-2.0 V voltage range with very low Li ion consumption. Experimental methods were developed for depositing a Li₄Ti₅O₁₂ layer on the exterior of tin/tin oxide NPs. The methods were fairly facile and could produce layers with variable thickness and strong adhesion to the core materials in various morphologies. Performance tests including cyclability and rate performance measurements were carried out with and without the Li₄Ti₅O₁₂ layer in order to establish the effects of the titanate coating. The relation between electrochemical performance and coating thickness was analyzed to provide guidance on material design.
4. A structure (SnO$_2$/TiO$_2$ core-shell particles) which could improve the rate performance without any conductive carbon was also designed and fabricated. Cyclability and rate performance were tested with and without the TiO$_2$ layer to quantify the contributions of the TiO$_2$ coating; and to suggest a rational approach to the design of electrodes with good reversibility without carbon additives.
CHAPTER 2 LITERATURE REVIEW

This chapter provides an up-to-date account of major topics relevant to this research in three sections. The first section introduces the lithium ion batteries, particularly the materials aspects. The second section discusses the improvements of the capacity retention and rate performance of anode materials by nanostructuring and nanocompositing. The third section discusses the origin of ICL and surveys the current methods for ICL reduction.

2.1 Lithium Ion Batteries

The lithium ion batteries were initially proposed as a solution to the dendrite growth of metallic Li in rechargeable Li metal batteries. (Murphy et al. 1978; Lazzari et al. 1980) Lithium ion batteries are inherently safer than Li metal batteries because Li is present in the ionic state rather than the (hazardous) metallic form. It, however, took nearly three decades of developmental efforts (from the sixties to the nineties) in order to find a suitable negative electrode to replace the metallic Li. The introduction of the C/LiCoO$_2$ rocking chair batteries by Sony Corporation in 1991 officially marked the advent of commercial lithium ion batteries.

A lithium ion battery cell is made up of a negative electrode (anode), a positive electrode (cathode), an electrolyte and a separator (see Figure 2.1). The electrolyte is a solution of inorganic lithium salt in a mixed organic solvent formulated to provide good ionic conductivity. The separator is an electrical insulator which is used to
prevent the internal short-circuiting of anode and cathode. It is a porous material with abundant channels to shuttle Li ions between the two electrodes during charge and discharge operations.

![Diagram of a Li-ion cell](image)

**Figure 2.1** Basic components and operation of a Li ions cell.

During discharge, electrons move from the anode to the cathode external circuit where electrical energy is harvested. At the same time Li ions move in the same direction through the electrolyte in the battery interior. The reverse occurs during recharge. The reactions in charging and discharging the C/LiCoO$_2$ cell may be written as follows (Wakihara 2001):

Cathode: \[ LiCoO_2 \xrightarrow{charging} Li_{1-x}CoO_2 + xLi^+ + xe^- \] (2-1)

Anode: \[ 6C + xLi^+ + xe^- \xrightarrow{charging} Li_xC_6 \] (2-2)

Overall reaction: \[ 6C + LiCoO_2 \xrightarrow{charging} Li_{1-x}CoO_2 + Li_xC_6 \] (2-3)

The most widely used cathode materials are LiCoO$_2$, LiMn$_2$O$_4$ and LiFePO$_4$. LiCoO$_2$ has reasonably good structural stability and can be produced in high quality relatively
easily. It is however expensive and somewhat toxic.(Amatucci et al. 1996) LiMn$_2$O$_4$ overcomes the cost and toxicity issues of LiCoO$_2$ but its cycle stability is relatively poor, showing severe capacity fading in cycling.(Takahashi et al. 2002) LiFePO$_4$ is the most talked about cathode material today. It has the most robust structure and can in principle be produced by environmentally benign methods from low cost raw materials. However, its low intrinsic electronic conductivity at room temperature makes it difficult to fully utilize its theoretical capacity. There have been many efforts to increase the electronic conductivity of LiFePO$_4$ by carbon coating, nanoscale construction and super-valence doping.(Li et al. 2009; Yuan et al. 2011; Zhang 2011; Wang et al. 2012) Kang and co-workers reported an off-stoichiometric LiFePO$_4$ with purportedly excellent rate performance by creating a fast ion-conducting surface phase.(Kang et al. 2009) Their results have however been disputed by others.(Zaghib et al. 2009)

The anode material is almost exclusively graphitic carbon, which can intercalate Li ions reversibly to a theoretical capacity of 372 mAh/g (or 818 mAh/cm$^3$) based on the LiC$_6$ stoichiometry. The practical capacity is lower (340mAh/g) because of various polarization effects. Graphitic carbon generally has good cyclability; and its rate performance can be improved by morphological modifications (e.g., the petroleum or coal-derived mesocarbon microbeads, or MCMB). On the other hand, the gravimetric and volumetric capacities of carbon-based anode materials are constrained by their relatively small theoretical limits. A more substantial increase of the anode capacity has to come from other Li storage materials. Li ion anode materials can be categorized into three major families by the Li storage mechanism into: intercalation anodes (e.g., carbon, titania and lithium titanate), conversion anodes (transition metal oxides) and
alloying anodes (Sn, Si, Ge, and their intermetallics). Storage by the intercalation mechanism incurs the least amount of structural changes. Cycle stability is generally very high although storage capacity could be low. LTO is another well-known intercalation anode material other than graphite. Thackeray and co-workers were among the first to use LTO for the anode of lithium ion batteries. (Ferg et al. 1994) Although its de-lithiation potential is relatively high (about 1.56 V vs. Li), it has some significant advantages such as good cyclability and high rate performance. (Nakahara et al. 2003; Hao et al. 2006; Jiang et al. 2007; Song et al. 2012). Very high storage capacities can be realized by storing Li ions in 3d transition metal oxides by the conversion reactions. A good example is Fe₃O₄ which has as a theoretical specific capacity of 927 mAh/g. (Yoon et al. 2011) The insertion/extraction potential is however relatively and slow electrode kinetics and low ionic and electronic conductivities are known disadvantages. (Chen et al. 2005) Li storage can also be based on alloy formation with group 4 elements. Among them tin/tin oxide anodes have drawn the most interest because they can be prepared easily in various customizable morphologies. (Li et al. 2000; Li et al. 2001; Li et al. 2011; Wu et al. 2011) The storage of Li by these different mechanisms may be represented by the following reactions:

Intercalation

\[
6C + xLi^+ + xe^- \xrightarrow{\text{charging}} Li_xC_6 \xleftarrow{\text{discharging}} \]

(2-2)

\[
Li_4Ti_5O_{12} + 3e^- + 3Li^+ \xrightarrow{\text{charging}} Li_4Ti_5O_{12} \xleftarrow{\text{discharging}} \]

(2-4)

Conversion

\[
Fe_3O_4 + 8Li^+ + 8e^- \leftrightarrow 4Li_2O + 3Fe
\]

(2-5)

Alloying and dealloying
\[ Sn + xLi^+ + xe^- \rightarrow Li_xSn(0 \leq x \leq 4.4) \quad (2-6) \]

Anode materials often determine the cyclability and safety of the lithium ion batteries in practice. While a low insertion potential is desirable from the energy density point of view, it may also cause dendritic Li formation and consequently internal short-circuiting at high rate charging. While many new anode materials have shown a higher initial capacity than carbon, their application performance is often undermined by three major material deficiencies: large ICL, poor capacity retention in prolonged cycling and low rate performance. The strategies that have been proposed to circumvent these three issues will be discussed in the following sections. In a nutshell while many of the studies focusing on the capacity retention problem have shown good progress and notable successes, the same cannot be said about the ICL issue which is indeed a more critical problem to solve. Anode materials which combine low ICL, good capacity retention and high rate performance are still rare today.

### 2.2 Strategies for Capacity Retention and Rate Performance Improvements

In general, the volume changes in the anode material caused by discharging (Li ions insertion) and charging (Li ions extraction) are an intrinsic material property that cannot be eliminated. Their adversarial effects can, however, be contained by downsizing the active material to the nanoscale or forming a composite material. This is because nanostructured materials can better accommodate the volume change without material disintegration by cracking and crumbling. A properly chosen co-compounding material(s) of the composite can likewise absorb the induced stress
caused by volume changes. Furthermore, the reduced dimensions of nanoscale materials support faster diffusion of Li ions in the active material, and together with the increase in surface area and hence more direct contact with the electrolyte, can result in significant improvements in cyclability and rate performance.

2.2.1 Nanostructured Materials

Many nanostructured materials have been studied as potential anode materials for the lithium ion batteries. These materials can be classified by their structural and morphological differences into solid nanostructured materials, hollow nanostructured materials, porous nanostructured materials and hierarchical nanostructured materials.

2.2.1.1 Solid Nanostructured Materials

Solid nanostructured materials are the easiest to synthesize. The reversible Li ions storage properties of solid SnO$_2$ NPs have been investigated by Kim et al. 3 nm, 4 nm and 8 nm SnO$_2$ NPs were prepared by changing the temperature of a hydrothermal synthesis(Figure 2.2).(Kim et al. 2005) The cycle life of the 3 nm SnO$_2$ NPs was the best, showing negligible capacity fading after the 1$^{st}$ cycle. On the contrary capacity fading was noticeable in the larger NPs and increased with increasing size. Unlike the larger NPs, the 3 nm NPs did not aggregate after cycling. The authors attributed this to the reversibility of the volume changes of NPs in cycling. However, the authors also reported a very substantial ICL. The same group also examined the critical size of Si NPs for lithium ion batteries recently.(Kim et al. 2010) 5 nm, 10 nm and 20 nm Si NPs were prepared by a high-pressure (>100 atm) process in the presence of different surfactants. Their results showed some decrease in the ICL with increasing particle size which confirmed the surface origin of ICL processes. However, different from the
SnO$_2$ NPs where the smallest size produced the best results, the medium sized 10 nm Si particles showed the highest overall capacity retention.

Another well studied solid nanostructure is nanowires (NWs), which are believed to facilitate the transport of electrons and Li ions, and have good mechanical stability. Fairly uniform SnO$_2$ NWs were prepared by combining thermal evaporation with self-catalyzed growth by Park and coworkers. (Park et al. 2007) The SnO$_2$ NWs showed higher Li ion storage capacity and better (but not excellent) capacity retention than pure SnO$_2$ powder. The improvement was attributed to the 1D NW architecture with short Li ions diffusion length and good electron conduction.

Figure 2.2   Voltage profiles of the SnO$_2$ NPs as a function of  a) ~3 nm,  b) ~4 nm, and  c) ~8 nm in coin-type half cells. SnO$_2$ anodes were cycled at the rate of 60 mA/g for the first cycle and at the charge rate of 1800 mA/g and the discharge rate of 300 mA/g between 1.2 and 0 V for the remaining cycles. (Kim et al. 2005)
2.2.1.2 Hollow Nanostructured Materials

Hollow nanostructured materials could also be used to buffer the volume changes in the anode material in cycling. Han and coworkers (Han et al. 2005) prepared hollow tin oxide microspheres by heat treating a tin precursor in a resorcinol-formaldehyde gel (RF gel). However, the product performance in terms of ICL and capacity retention was unsatisfactory. A notably simpler method to prepare hollow tin oxide NPs was reported by Lou and co-workers. (Lou et al. 2006) The authors claimed that the template-free synthesis was based on an inside-out Ostwald ripening mechanism. Lou also reported other creative methods to prepare hollow tin oxide NPs. For example, tin oxide hollow spheres were synthesized using mesoporous silica as ‘nanoreactors’ and uniform tin oxide nanoboxes were prepared by ‘template-engaged coordination etching’ of pre-grown Cu₂O nanocubes. (Ding et al. 2010; Wang et al. 2011). These interesting nanostructures however did not lead to any improvements of the electrochemical performance. Another interesting morphology is hollow core-shell tin oxide mesospheres synthesized by a self-templating method which showed some slight improvements over the electrochemical performance of hollow microspheres. (Deng et al. 2008) Besides SnO₂, hollow LTO, Sb, carbon and α-Fe₂O₃ were also fabricated as the anode materials for lithium ion batteries. Hollow LTO spheres were prepared by a sol–gel process using carbon spheres as the template. (Jiang et al. 2007) The rate performance of the hollow LTO spheres was significantly higher than that of densely agglomerated LTO particles. The hollow Sb NPs synthesized by Kim et al. (Kim et al. 2008) from SiO₂ templates also showed excellent rate performance and good capacity retention although there was severe cracking of the shell after template removal. However, the discharge capacity was not reported in that article. Interconnected hollow carbon nanospheres prepared by pressure-assisted reduction and graphitization of
sucrose in autoclaves also exhibited good capacity retention and high rate performance but the ICL was large. (Han et al. 2011) Polycrystalline $\alpha$-Fe$_2$O$_3$ nanotubes (NTs) with thin walls synthesized by chemical etching also showed significantly improved capacity retention compared to $\alpha$-Fe$_2$O$_3$ NPs. (Wang et al. 2011) In summary, hollow nanostructured materials with high surface area, shorter diffusion path length for Li ion transport, and an abundance of free space to cushion the volume changes, almost always show better capacity retention and higher rate performance than their all-solid counterparts. However, hollow materials also almost always show a larger ICL due to their increased contact area with the electrolyte. The abundant free space in hollow materials also contributed to a low volumetric capacity.

2.2.1.3 Porous Nanostructured Materials

The porous nanostructure has also been explored for both anode and cathode materials due to expectations of improved electrochemical properties such as high rate capacity and good capacity retention. (Jiao et al. 2005; Ren et al. 2010) The earlier generations of porous nanostructured anode materials were prepared with the help of surfactant templates. (Yu et al. 2002; Kim et al. 2005) For example, mesoporous tin oxide was synthesized by the Frech group, which showed good capacity retention and increased rate performance amidst a large ICL. (Yu et al. 2002) The porous SnO$_2$ nanofibers prepared by Li and coworkers using polycarbonate membrane templates, on the other hand, showed outstanding rate capabilities and excellent capacity retention (>700 mAh/g at 8 C). (Li et al. 2000; Li et al. 2001) There were also studies using carbon to template the synthesis of mesoporous tin dioxide microspheres. (Demir-Cakan et al. 2008) After calcination the SnO$_2$-containing carbon spheres became mesoporous tin dioxide microspheres of aggregated tin dioxide NPs. The ICL problem remained
unmitigated in all of these attempts. The hydrothermal process was used to prepare mesoporous spinel LTO microspheres without any template. (Tang et al. 2009) The proposed mechanism was based on the Kirkendall effect. The product exhibited superior rate performance even at the 20 C rate (discharge capacity of 125 mAh/g after 200 cycles).

Co$_3$O$_4$ is easy to form porous structures through the assembly of primary NPs. In Lou’s paper, the needle-like Co$_3$O$_4$ synthesized by a topotactic transformation had a porous structure which, in spite of the large ICL, showed some improvements in capacity retention. (Lou et al. 2008) Co$_3$O$_4$ nanocapsules have also been synthesized by a solvothermal method, showing almost the same electrochemical performance as that of mesoporous needle-like Co$_3$O$_4$ prepared by Lou and co-workers. (Liu et al. 2010) Recently, porous Co$_3$O$_4$ nanoneedle arrays grown on copper foils were reported where large specific capacity and high rate performance were shown (1176 mAh/g at 0.5 C). (Xue et al. 2011) The high rate performance was also attributed to the good electrical contact with the current collector, facilitating the electron flow from the substrate to Co$_3$O$_4$. Capacity retention of the nanoneedle arrays was worse; probably due to the omission of binder and conductive carbon in the electrode composite.

Many porous anode materials have also been made with the silica templates. (Kim et al. 2008; Kim et al. 2008; Kim et al. 2008; Shi et al. 2009; Shon et al. 2009; Shon et al. 2009; Park et al. 2010) In these efforts cubic KIT-6 or hexagonal SBA-15 silica templates were first impregnated with a tin or Si precursor. After the formation of active materials (SnO$_2$, Si) by calcination, the template was removed by NaOH etching. Many of such studies were carried out in the Cho group with reports of excellent
cyclability and rate performance. An example of mesoporous SnO$_2$ from this group is shown in Figure 2.3. (Kim et al. 2008) Both the cyclability and rate performance were very good although ICL was still very large. The good cyclability could be categorically attributed to the porous architecture of ordered pore arrays which not only accommodated the volume changes in discharge and charge reactions with ease; but also the rapid transport of electrons and Li ions.

Recently, monodisperse hollow porous Si NPs were fabricated in our group by the magnesiothermic reduction of hollow porous SiO$_2$ NPs prepared by a templating method, followed by treatment with Ag NPs to increase the electrical conductivity. The final Ag-treated nanoscale hollow porous Si particles displayed high specific reversible capacity, good cycling stability and rate performance. (Chen et al. 2012)

![Image of mesoporous SnO$_2$](image)

**Figure 2.3** a) A high-resolution transition electron microscopy (HRTEM) image of the mesoporous SnO$_2$. b) Charge capacities as a function of cycle number at different discharge rates tested in coin-type half cells. The discharge rate was fixed at 0.2 C. (Kim et al. 2008)

### 2.2.1.4 Hierarchical Structured Materials

In theory hierarchical structured nanomaterials combine the advantages of nanomaterials such as facile kinetics and fast dynamic response with the improved stability and handling of materials on the micron or sub-micron length scale.
Hierarchical nanostructured electrode materials could be prepared by self-assembly through the control of the reaction conditions in hydrothermal processes (Yin et al. 2010; Ding et al. 2011; Chen et al. 2012) and microemulsion-mediated preparations (Zhang et al. 2011). The crystal growth mechanism of hierarchical nanostructures is rather complex. Generally, the driving force for the aggregation of smaller units into hierarchical structures is the reduction of the high surface energy of nanocrystals. In one report, the decomposition rate of the intermediate product was adjusted by changing the amount of water injection. Different decomposition rates formed SnO nanosheets (NSs) of different sizes which aggregated differently into hierarchical SnO nanostructures of various morphologies. The electrochemical performance of the hierarchical SnO nanostructures was morphology dependent (Ning et al. 2009). On the other hand, a hierarchical SnO2 hollow nanostructure formed by self-assembly under hydrothermal conditions showed acceptable ICL and capacity retention (Yin et al. 2010). Hollow spheres of anatase TiO2 NSs with predominately exposed (001) facets were also fabricated by hydrothermal processing using polystyrene hollow spheres as the sacrificed template (Ding et al. 2011). These TiO2 hollow spheres exhibited excellent capacity retention especially at high current rates. These research studies indicated that hierarchical structured materials could be an effective way to decrease the ICL and to improve capacity retention and rate performance.

2.2.2 Composite Materials

The other strategy to improve capacity retention is by forming nanostructured composite materials where at least one component serves as the buffer for the volume changes in the active component. Disordered carbon, carbon NTs (CNT) and graphene
have been used this way and also for the simultaneous improvement of the electrode electrical conductivity. Composites can also be formed with two or more active materials. In these cases one of the components also serves as the buffer and the composites may perform better than either of the constituents alone.

2.2.2.1 Disordered Carbon

Due to the good cyclability of graphite, there have been numerous efforts to improve the capacity retention properties of high capacity anode materials by forming active material/carbon composites. A SnO$_2$-carbon composite was prepared by heat-treating a mixture of colloidal SnO$_2$ and sucrose by the Read group. The improvement of the electrochemical performance of SnO$_2$ was however not significant.(Read et al. 2001) The deposition of tin oxide on mesoporous carbon to form ordered tin-oxide/carbon composites also did not appear to be a good solution.(Fan et al. 2004) These attempts were not successful because carbon or carbon precursor was simply mixed with tin oxide NPs or their precursor without complete homogenization. In a further study, metallic tin was also encapsulated in hollow carbon spheres using micelles of cetyltrimethylammonium bromide as the soft template to form RF spheres loaded with a Sn precursor (tributylphenyltin).(Lee et al. 2003) Subsequent *in situ* calcination carbonized the RF polymer and formed hollow carbon spheres encapsulated with 24 wt% of Sn NPs. In another study, a tin precursor was infiltrated into a RF gel and calcined in argon to form metallic tin in a carbon matrix.(Derrien et al. 2007) The Sn-C composite formed as such showed excellent capacity retention even at the 5 C rate which the authors attributed to the small size of the Sn NPs and their uniform dispersion in the carbon matrix.
Later studies revealed that carbon coating of the active material exterior generally improved the cyclability of the active material at some loss of the capacity. The carbon source could be an aromatic oil (Zhou et al. 2009), benzene (Wang et al. 2006), acetylene (Deng et al. 2009; Kim et al. 2010; Ma et al. 2011), polyvinyl chloride (Yin et al. 2011) and glucose (Noh et al. 2005; Kim et al. 2006; Lou et al. 2008; Zhang et al. 2008; Deng et al. 2009; Lou et al. 2009; Lou et al. 2009). Glucose was the most commonly used among them. It has been reported that carbon spheres could be formed from the carbonization of glucose under hydrothermal conditions between 160 °C and 180 °C (Sun et al. 2004). Hence, the earlier generations of carbon coated active materials were prepared in two steps (Noh et al. 2005; Kim et al. 2006; Lou et al. 2008; Zhang et al. 2008; Lou et al. 2009; Chen et al. 2011): The first step was the preparation of the active material which was then added to a glucose solution followed by hydrothermal treatment. Later a one-pot synthesis of SnO₂@carbon core-shell composites was reported (Lou et al. 2009). Uniform carbon-coated SnO₂ nanocolloids were synthesized by using stannate and glucose as the precursors. The synthesis was a combination of hydrothermal synthesis and post-synthesis carbonization under an inert atmosphere. Further work based on this method showed that increasing the ratio of glucose in the precursor solution could lead to the formation of SnO₂@carbon core-shell nanochains (Yu et al. 2011). The core-shell nanochains could be calcined at higher temperatures to provide a higher graphitization degree of the carbon layer. The capacity retention and rate performance of the SnO₂@carbon core-shell nanochains were significant improvements of previously reported carbon-coated SnO₂ nanocolloids.
In situ reduction of SnO$_2$ to Sn in a carbon matrix has also been explored. (Deng et al. 2009; Deng et al. 2010) Here carbon mesospheres with dispersed SnO$_2$ NPs were prepared by the concurrent carbonization of glucose and the hydrolysis of SnCl$_4$ in situ. The graphitization degree of the carbon prepared as such was however rather low. High temperature chemical vapour deposition (CVD) treatment with an extraneous carbon source was then used to improve the graphitization of carbon spheres and to reduce the encapsulated SnO$_2$ to Sn. The Sn NPs formed as such were catalytic for the formation of CNTs on the carbon sphere surface. The low melting (232 °C) Sn was liquefied under the reaction conditions and siphoned into the interior of the CNTs forming an intriguing hair-like Sn@C core–shell structure on the carbon spheres. The as synthesized chestnut-like Sn@C composite and its electrochemical performance are shown in Figure 2.4. The graphitization degree of the carbon in the composite was still not high. Consequently, ICL remained substantial and rate performance was also not very high.

Yu and co-workers reported two interesting structures of Sn/carbon composites prepared from polyacrylonitrile and organometallic Sn precursors. (Yu et al. 2009; Yu et al. 2009) The first one was Sn@carbon encapsulated in bamboo-like hollow carbon nanofibers prepared from the pyrolysis of tributyltin (core)/ polyacrylonitrile (sheath) nanofibers formed by a coaxial electrospinning method. (Yu et al. 2009) This composite displayed a high reversible discharge capacity of 737 mAh/g after 200 cycles at 0.5 C. It also exhibited a reversible discharge capacity of 480 mAh/g when cycled at the 5 C rate. The other structure was metallic Sn NPs encapsulated in porous multichannel carbon microtubes, also formed by the electrospinning method. (Yu et al. 2009) The specific capacity was 570 mAh/g at 2 C and 295 mAh/g at 10 C after 50
cycles. The good capacity retention and rate performance of these materials were attributed to their unique structures. The electrospinning method was also used to fabricate a porous core-shell Sn@carbon anode on nickel foam substrate. (Li et al. 2012) Capacity retention was quite good but the rate performance was lower than the materials prepared by Yu and co-workers. This could be due to the larger size of the solid Sn particles in the porous core-shell Sn@carbon anode. These examples demonstrated that a low graphitization degree of the carbon in these composites is still limiting the performance of the composites, especially with regard to ICL and rate performance.

![FESEM image of chestnut-like Sn@carbon mesospheres](image1.png)

**Figure 2.4** a) FESEM image of chestnut-like Sn@carbon mesospheres. b) Plot of capacity vs. cycle number evaluated at 100 mA/g and 200 mA/g in the 0.005-2 V voltage window. (Deng et al. 2010)

### 2.2.2.2 CNT

CNTs, with their outstanding electrical conductivity and mechanical strength, should be an excellent form of carbon for compounding with the active materials. One possible arrangement is to encapsulate the active materials within the CNT interior. For example, CNT-encapsulated SnO₂ could be prepared by the CVD of CNTs on SnO₂ NTs. In this process polycrystalline SnO₂ NTs with uniform diameters were first produced by infiltrating tin oxide NPs into an anodic alumina oxide (AAO) membrane.
Subsequent CVD treatment of the SnO$_2$ NTs in AAO membrane using acetylene as the carbon source led to the encapsulation of the SnO$_2$ NTs by a thin layer of CNTs. (Wang et al. 2006) The products showed good capacity retention. By infiltrating tin precursors into the AAO membrane followed by CVD treatment, CNT-encapsulated Sn NPs could also be formed. (Wang et al. 2009) The yield of SnO$_2$/Sn core/ CNT shell was however low because of the loading limit imposed by the AAO template. Fe$_2$O$_3$ NP-filled CNTs were also prepared by the same method and reported to have quite good rate performance. (Yu et al. 2010)

The active component could also be formed on the outside of the CNTs if commercial CNTs are used as the nucleation sites. In a rather esoteric construction, Xia et al. dispersed Au NPs on an amorphous tin oxide overlayer formed uniformly on a coaxial CNT. (Chen et al. 2008) The authors hypothesized that the metallic Au could increase the conductivity within the electrode material as shown by the higher specific capacity and rate performance of the product with Au than the product without Au. CNT@TiO$_2$ core/porous sheath coaxial nanocables were also found to perform better than either of the constituents. (Cao et al. 2010) Si/CNT composites have also been extensively studied. Si nanoclusters on CNTs were fabricated by the CVD of Si on pre-formed vertically aligned CNTs, and good capacity retention was reported. (Wang et al. 2010) According to the authors, the CNTs were efficient electrically conducting channels which also worked as a flexible mechanical support for strain release. In another study, amorphous Si was deposited on porous sponge-like CNTs. (Hu et al. 2011) Capacity retention in this case was worse than Si on vertically aligned CNTs. This could be due to the lack of good electrical contact with the current collector compared with the case of Si on well-aligned CNTs.
Interestingly, CNTs have also been used as a conductive additive. (Chan et al. 2010; Wang et al. 2010) The composite electrode which was prepared with CNTs as a conductive additive showed better capacity retention than an electrode using a conventional conductive additive. The authors attributed the improvement to the good conductivity and connectivity of the network formed by Si NWs and CNTs.

**Figure 2.5** Li insertion/extraction properties of the GNS families. a) discharge/charge profiles of (a) graphite, (b) GNS, (c) GNS+CNT, and (d) GNS+C$_{60}$ at a current density of 50 mA/g. b) Discharge/charge cycle performance of (a) graphite, (b) GNS, (c) GNS+CNT, and (d) GNS+C$_{60}$. (Yoo et al. 2008)

### 2.2.2.3 Graphene

Graphene is exfoliated graphite and as such has the layered structure of the latter. It has large surface area and numerous edge sites for anchoring electroactive materials. Yoo and coworkers were among the first to investigate Li storage in graphene NSs (Figure 2.5). (Yoo et al. 2008) They attempted to increase the storage capacity by varying the distance between the graphene sheets with CNT and fullerene intercalation. However, there was no improvement on capacity retention. SnO$_2$ (Paek et al. 2009), TiO$_2$ (Wang et al. 2009) and Si (Chou et al. 2010; Lee et al. 2010) have also been
combined with graphene as a composite anode electrode. Capacity retention in these hybrid materials was much better than the active materials alone. The proposal to sandwich the active material between the graphene sheets is however difficult to realize. This is because during compositing, the graphene sheets tend to assemble among themselves leaving the active material to the outside surface of the graphene aggregates.

Graphene oxide (GO) prepared by the Hummers method (Hummers et al. 1958) was also used as the starting material to prepare graphene-based composites. The presence of carboxyl and epoxides groups enables the GO layers to be prepared as suspensions in polar and nonpolar solvents. Many active materials/graphene composites have been prepared by mixing the solutions of a metal precursor and GO followed by reduction. All kinds of active materials including intercalation hosts (carbon, TiO₂), alloying metals (Si, Sn, Sb) and 3d transitional metal oxides (Mn₆O₁₉, Co₃O₄, NiO, Fe₃O₄, Cu₂O) have been composited with graphene using GO as the starting material. For intercalation hosts where the main drawback is their low specific capacity, graphene compounding could only improve capacity retention and electrical conductivity. (Yang et al. 2011) On the other hand, some 3d transitional metal oxide-graphene composites have shown very good electrochemical performance. For example, the specific capacity of a graphene NSs/Fe₃O₄ composite was 520 mAh/g at 1750 mA/g after 70 cycles, which was 53% of the initial capacity. On the contrary, the capacities of commercial Fe₃O₄ decreased to only 10% of their respective initial capacities in the same number of cycles at this high charge rate. (Zhou et al. 2010) The voltage hysteresis indigenous to the transition metal oxides was still very large for the transitional metal oxide/graphene composites. (Chen et al. 2010; Wang et al. 2010; Wu
et al. 2010; Yang et al. 2010; Zhang et al. 2010; Zhou et al. 2010; Behera 2011; Chen et al. 2011; Guo et al. 2011; Li et al. 2011; Lu et al. 2011; Wang et al. 2011; Zhou et al. 2011; Zhu et al. 2011; Zou et al. 2011) For alloying metals where large volume changes were the cause of severe capacity fading, a Si NPs/graphene paper composite showed much better capacity retention compared with the active material alone. (Lee et al. 2010) In-plane vacancies are usually created in the graphene sheets to decrease the resistance of graphene to Li ions transport. For example, a Si/graphene composite with in-plane vacancies delivered a reversible capacity of around 1100 mAh/g at 8 A/g. (Zhao et al. 2011) The research showed that the electrochemical performance of the graphene composite is also determined by the Li ions conductivity of the graphene sheets. Recently, a strategy to improve the electrochemical performance through Ge@carbon core–shell nanostructures and a reduced GO network was also reported. (Xue et al. 2012) The rate performance was significantly improved.

Normally, the capacity fading of tin-based anodes is severe and their rate performance is limited. Blending with graphene has helped with capacity retention but stable performance can only be realized after some ‘conditioning’ by initial cycling (20 cycles typically). (Du et al. 2010; Kim et al. 2010; Li et al. 2010; Wang et al. 2010; Wang et al. 2010; Zhang et al. 2010; Ding et al. 2011; Huang et al. 2011; Liang et al. 2011; Liang et al. 2011; Wang et al. 2011; Zhang et al. 2011; Zhong et al. 2011; Li et al. 2012; Park et al. 2012) This may be indication that stable SEI layer on graphene takes longer to form.

2.2.2.4 Other Composites
In some studies, hybrids of two active materials have shown better electrochemical performance than the individual active materials alone. Previously we have mentioned the AAO template synthesis of SnO$_2$ NTs. A nanoscale coating of a Si layer on the pore walls of as-prepared SnO$_2$ NTs was reported in a subsequent study. (Lee et al. 2010) The authors claimed that the improved electrochemical performance was derived from the amorphous Si phase serving as a buffer layer for the Sn shell. As it is common with all templated syntheses, scalability of the preparation method is the greatest challenge. CVD was used to deposit a highly conductive Ge layer on Si NTs. The resulting composite showed lower capacity than Si NTs but rate performance was significantly improved by the presence of the conductive Ge layer. (Song et al. 2011)

In another study, an interesting $\alpha$-Fe$_2$O$_3$/SnO$_2$ branched composite with six-fold-symmetry was prepared by growing $\alpha$-Fe$_2$O$_3$ hydrothermally on preformed SnO$_2$ NWs. (Zhou et al. 2011) The composite showed much higher initial discharge/charge capacities than its constituents on their own at 1 A/g. The authors attributed the composite performance to more active surface sites for the Li ions access. However, this method was not effective for capacity retention. Indeed capacity fading was more severe in the composite than in the constituents alone. In a recent study, a SnO$_2$-SiC/graphene core-shell structure was prepared by ball-milling, in which SnO$_2$ NPs were uniformly dispersed on a supporting SiC substrate and the ensemble was encapsulated with a graphene coating. (Chen et al. 2012) The SnO$_2$-SiC/graphene core-shell structure showed good capacity retention. A reversible capacity of 810 mAh/g at 100 mA/g was possible in a narrow potential window (0.01-1.5 V), and $\approx$ 83% of the initial capacity was retained after 150 cycles. This method appears to be quite facile and scalable. However the explanation that nano-SiC acts as a rigid structural framework to accommodate the volume changes of the Sn–Li alloy is not plausible.
2.3 Origin of ICL and Strategies for ICL Mitigation

As a percentage of the reversible capacity basis, the ICL of tin-based anodes is amongst the highest in anode materials. Table 1 shows that the typical values are in the range of 29%-56%. The relationship between the specific capacity of the full cell and the anode specific capacity (with and without ICL) is shown in Figure 2.6. The specific full cell capacity is definitely lower in the case of a 30% ICL. This figure indicates clearly how the benefits of a high capacity anode can be compromised by a large ICL.

This section highlights the research progress on the mitigation of the ICL of high capacity non-carbonaceous anode materials. The origin of ICL in non-carbonaceous anode materials is introduced first. Since Sn, SnO₂ have attracted the most research interest, they are the focus of the discussion. This is followed by a survey of reported methods on mitigating the ICL of these materials. The literature on this subject matter is rather limited, and some of the methods have not been reproduced outside the original work.

2.3.1 The Origin of ICL

There are in general two principal causes for ICL: the conversion of the anode material from its pristine form to an active Li storage host, and the formation of SEI on the active electrode surface within the first few cycles of use. Both processes consume electrons and Li ions. Since a lithium ion battery has a limited supply of Li ions, many of the practical issues with ICL are associated with the depletion of the Li source derived from the more expensive cathode material. While the use of an active anode
(e.g., Sn instead of its oxides) can in principle eliminate the ICL due to the activation of the anode; the ICL associated with SEI formation presents a greater challenge.

**Table 2.1** The ICL of tin-based anode materials tested at different current densities and in different voltage windows

<table>
<thead>
<tr>
<th>Types of anode material</th>
<th>Current density (mA/g)</th>
<th>Voltage window (V)</th>
<th>ICL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT-encapsulated Sn–Sb nanorods (Wang et al. 2006)</td>
<td>180</td>
<td>0.1-1.2</td>
<td>36</td>
</tr>
<tr>
<td>Hollow SnO$_2$ NPs (Lou et al. 2006)</td>
<td>0.2C</td>
<td>0.005-2</td>
<td>54</td>
</tr>
<tr>
<td>SnO$_2$ NWs (Park et al. 2007)</td>
<td>100</td>
<td>0.05-1.5</td>
<td>53</td>
</tr>
<tr>
<td>Mesoporous SnO$_2$ microspheres (Demir-Cakan et al. 2008)</td>
<td>100</td>
<td>0.05-1</td>
<td>47</td>
</tr>
<tr>
<td>SnO$_2$/carbon composite hollow spheres (Lou et al. 2008)</td>
<td>100</td>
<td>0.005-2</td>
<td>56</td>
</tr>
<tr>
<td>Hollow core-shell mesospheres of SnO$_2$ nanoparticle aggregates (Deng et al. 2008)</td>
<td>50</td>
<td>0.05-2</td>
<td>45</td>
</tr>
<tr>
<td>Carbon-coated SnO$_2$ (Lou et al. 2009)</td>
<td>120</td>
<td>0.005-2</td>
<td>49</td>
</tr>
<tr>
<td>Carbon-coated Sn nanocolloids (Lou et al. 2009)</td>
<td>120</td>
<td>0.005-2</td>
<td>48</td>
</tr>
<tr>
<td>Sn@carbon NPs in bamboo-like hollow carbon nanofibers (Yu et al. 2009)</td>
<td>50</td>
<td>0.01-3</td>
<td>29</td>
</tr>
<tr>
<td>Sn particles encapsulated in porous multichannel carbon microtubes (Yu et al. 2009)</td>
<td>100</td>
<td>0.005-2</td>
<td>30</td>
</tr>
<tr>
<td>Sn@carbon composites (Deng et al. 2010)</td>
<td>100</td>
<td>0.005-2</td>
<td>42</td>
</tr>
<tr>
<td>Dense core–shell structured SnO$_2$/C composites (Liu et al. 2010)</td>
<td>100</td>
<td>0.01-2</td>
<td>33</td>
</tr>
<tr>
<td>SnO$_2$ NSs grown on graphene sheets (Ding et al. 2011)</td>
<td>160</td>
<td>0.01-1.2</td>
<td>63</td>
</tr>
<tr>
<td>SnO$_2$ nanoboxes (Wang et al. 2011)</td>
<td>0.2C</td>
<td>0.01-2</td>
<td>54</td>
</tr>
<tr>
<td>SnO$_2$–graphene composite (Park et al. 2012)</td>
<td>100</td>
<td>0.01-2</td>
<td>51</td>
</tr>
</tbody>
</table>
Figure 2.6  Illustrative relationship between the specific capacity of the full cell and the specific capacity of anode. (Basis: cathode with a specific capacity of 200 mAh/g). The blue line represents an anode material without ICL while the green line corresponds to an anode with a 30% ICL.

SEI formation is prevalent among the group 4 Li hosts (carbon, Sn, Si). It is caused by the catalytic reduction of the electrolyte components on the electrode surface. A previous study has pointed out that the mechanism of SEI formation and hence the composition of the SEI on the alloying electrodes can be different from the carbon electrodes.(Wagner et al. 2004) The following is an account of the current understanding of the ICL in Sn, SnO₂ electrodes. A detailed knowledge of the origin of the ICL is still not possible because of the complexity of a formulated anode system.

The presence of carbon conductivity enhancer and binder molecules in a formulated anode makes the investigation of the reactions at the electrode-electrolyte interface a difficult challenge. Hence, much of the information available today was obtained from idealized systems using e.g., thin film electrodeposited Sn electrodes. The Cyclic voltammetry (CV) of electrodeposited Sn films in a standard 1 M LiPF₆ in ethylene
carbonate (EC)/dimethyl carbonate (DMC) electrolyte revealed an irreversible reduction peak between 1.4-1.1 V vs. Li/Li\(^+\), which was assigned to electrolyte decomposition leading to SEI formation. (Li et al. 2007) Different from graphite, the volume changes in Li alloying/de-alloying reactions are significant; causing the SEI to be easily breached but at the same time allowing nascent SEI to form on the newly exposed surfaces. Such deconstruction and reconstruction process would continue until there is no more creation of new surfaces; resulting in the persistence of ICL in the first few cycles of use. There have been some disagreements regarding the composition of the SEI layer on Sn. The main products from electrolyte reduction are ROCO\(_2\)Li, according to Sun’s analysis by \textit{in situ} Fourier transform infrared reflection spectroscopy and microscope. (Li et al. 2007) However Song et al. claimed that the overlapping signals from the electrolyte would interfere with the \textit{in situ} analysis of the SEI layer on Sn anodes. Hence, they chose to use \textit{ex situ} attenuated total reflection FTIR spectroscopy for the identification of the surface species on tin films. (Baek et al. 2009; Song et al. 2009) They reported that the Sn surface contains mainly PF-containing inorganic species. The passivation of Sn surface by these PF-containing species during initial cycling was believed to be the principal cause for the ICL. However, these surface reactions are not well understood and there are disagreements about the SEI composition. The only certainty is that the SEI layer lacks the ability to withstand the volume swing in the electrode material during initial cycling; and hence most ICL formation requires a few cycles to stabilize.

Aside from metallic Sn, SnO\(_2\) has also been used as an anode material for reversible Li ions storage. The reactions between Li ions and SnO\(_2\) generally involve two discrete steps: the reduction of SnO\(_2\) to Sn and amorphous Li\(_2\)O (reaction 4); and the reversible
alloying/de-alloying reactions between Li and Sn (reaction 5) which is the Li storage mechanism proper. The ICL due to SEI formation is assumed to occur mostly on metallic Sn and as such, would have the same value as the SEI formation on Sn. It was initially assumed that the reduction of SnO₂ to Sn is totally irreversible. (Brousse et al. 1998) However, the ICL calculated as such would be 47.6% even before consideration for the SEI formation on the nascent Sn surface. This calculated value is even greater than many of the measured values in Table 1. The difference is particularly glaring in the case of Han’s study, where hollow SnO₂ microspheres cycled between 0.8-2.0 V (above the potential regime for the alloying-dealloying reactions) could still contribute to a discharge specific capacity of 120 mAh/g even after the tenth cycle. Hence, reaction (4) could not be totally irreversible. Indeed reaction (4) is similar to the reversible storage of Li ions in transition metal oxides; which is termed as the conversion reaction by the Tarascon group. (Poizot et al. 2000) However, the irreversibility of reaction (4) and its role in ICL has not been quantified and still needs further investigations.

2.3.2 Strategies for ICL Mitigation

Since ICL formation consumes Li ions, the first mitigation strategy is to supply additional Li resources such as combining the anode with Li-rich Li₂.₆Co₀.₄N or pre-lithiation. The other strategy is to coat the active anode material with a protective layer which can either be SEI-promoting or SEI-inhibiting. For example, forming an artificial SEI layer or using carbon coating to minimize the direct contact between the active material and the electrolyte.

2.3.2.1 Compositing with Li₂.₆Co₀.₄N
Li$_{2.6}$Co$_{0.4}$N is a Li-rich compound. It was added to an active anode material (e.g., SnO (Yang et al. 2000), SnSb alloy (Yang et al. 2000), Si (Liu et al. 2005; Liu et al. 2006)) as the Li source for SEI formation on the latter; thereby averting the extraction of precious Li ions from the cathode material. In the case of a metal oxide anode, the metal oxide was reduced to metal and Li$_2$O by Li$_{2.6}$Co$_{0.4}$N before cycling; and the structure of Li$_{2.6}$Co$_{0.4}$N changed from crystalline to amorphous after the first Li extraction. The first cycle efficiency can then be adjusted by varying the ratio of Li$_{2.6}$Co$_{0.4}$N to the Li host in the electrode. Li$_{2.6}$Co$_{0.4}$N can also cushion the electrode volume excursion during cycling and adds to the improvement of the cyclability of the composite electrode. However, if poor capacity retention is not caused mainly by volume excursion, the addition of Li$_{2.6}$Co$_{0.4}$N does not contribute to cyclability improvement (Yang et al. 2000). Since cobalt is expensive and has known environmental issues, the use of cobalt in lithium ion batteries does not appear to be a prudent resolution.

2.3.2.2 Pre-lithiation

Pre-lithiation is more often applied to Si-based anodes than to other anode materials. For example, Yoon and co-workers (Seong et al. 2009) pre-lithiated a carbon-coated SiO film by depositing Li powder right onto it; and then compacted the electrode in the presence of electrolyte for some time to invoke the reaction between metallic Li and carbon-coated SiO. Lithium silicate and lithium oxide were formed in this pre-lithiation process. This pre-lithiation method was able to reduce the ICL by 5% (the first cycle coulombic efficiency was improved from 67.7% for the pristine electrode to 72.8% for the pre-lithiated electrode). The authors attributed the small improvement to a low pre-lithiation efficiency. In a follow-up study, the authors inserted a copper mesh
between a Li-powder layer and a coated Si monoxide on a copper current electrode. (Seong et al. 2010) It was then discovered that the ICL in the first cycle was totally eliminated. However, the coulombic efficiency in the 2\textsuperscript{nd} cycle was only 70\% and was around 90\% thereafter. The authors attributed these observations to the depletion of Li supply in the first cycle; resulting in inadequate Li to sustain the SEI formation in the subsequent cycles. This could have been easily proven by adding more Li powder. As the first and second methods are based on the same pre-lithiation mechanism, the apparent effectiveness of the second method is not understood.

2.3.2.3 Artificial SEI

Previous research has shown that carboxymethylcellulose (CMC) is a stiff material which can withstand the significant deformation in the anode material (up to 400\%). (Lestrie et al. 2007) This has motivated Peled and coworkers to use CMC as the base material to form artificial SEI layers on the anode. (Menkin et al. 2009) A sodium CMC solution was vacuum-infiltrated into the structural voids of a copper-tin alloy anode. The ICL of the tin-copper alloy with the artificial SEI prepared as such was reduced from 50\% to 20\%. The detailed explanation for such improvement was not given in the article. It is likely that the artificial SEI selectively covers the active sites on the anode surface which are catalytic towards electrolyte decomposition; and hence the progress of the latter could be alleviated. These preliminary research results demonstrated the potential of decreasing ICL by an artificial SEI.

2.3.2.4 Carbon Coating

Since ICL is caused by irreversible reactions occurring on the electrode surface in the initial few cycles, an intuitive prevention method would be to insulate the anode from
the electrolyte with a Li conductor known for quality SEI formation. Carbon coating is a good candidate since SEI formation on carbonaceous materials has been extensively studied and optimized. It was found that the ICL in carbon-coated anodes is strongly dependent on the crystallinity of the carbon layer. For example, Lou et al. synthesized SnO$_2$ hollow spheres based on an inside-out Ostwald ripening mechanism, and deposited carbon layers onto both the interior and exterior surfaces of the shell as well as within the pores of the SnO$_2$ hollow spheres (Figure 2.7), (Lou et al. 2006; Lou et al. 2008) yet there was no noticeable improvement in ICL abatement: indeed the ICL nudged up slightly from 54% -56 % after the carbon layer construction. The large ICL was attributed to the irreversible reduction of SnO$_2$ to Sn and other possible unspecified processes. The irreversible losses associated with the first-cycle reduction of SnO$_2$ to Sn could in principle be addressed by using Sn@carbon composites, and yet ICL remains large in many of these composites. For example, ICL was 42% for a chestnut-like Sn@carbon composite (Deng et al. 2010) and 49% for carbon-coated Sn nanocolloids (Lou et al. 2009). The carbon layers in these composites were all derived from glucose carbonation followed by relatively low temperature calcination. As what we have mentioned previously, Sn@carbon NPs encapsulated in bamboo-like hollow carbon nanofibers prepared from the pyrolysis of coaxially electrospun nanofibers showed relatively low ICL and good cycling performance (Figure 2.8). With calcination under 1000 ºC, the carbon layer has high crystallinity and this may be the main reason for the lower ICL (29% when cycled between 0.01-3 V. The ICL calculated from Figure 2.8b for a more typical voltage window of 0.01-2 V is, however, 35%). These researches showed that the ICL can be alleviated to some degree by carbon coating, but the effectiveness of this method is largely dependent on the crystallinity of the coating layer. In this regard, graphite would be the most promising
coating layer for ICL mitigation ICL. However, graphite is only formed under extreme temperature and pressure conditions which would alter many of the anode materials that graphite intends to protect.

![Figure 2.7](image1.png)

**Figure 2.7** a) TEM image of SnO$_2$/carbon composite hollow spheres. b) Discharge-charge voltage profiles of SnO$_2$/carbon composite hollow spheres for 1$^{st}$ and 2$^{nd}$ cycles at a current density of 100 mA/g. (Lou et al. 2008)

![Figure 2.8](image2.png)

**Figure 2.8** a) TEM micrograph of the pyrolyzed nanofibers obtained by calcining Sn@carbonencapsulated in carbon nanofibers in Ar/H$_2$ at 1000 °C for 5 h. b) Electrochemical performance of the Sn/C composite electrode cycled between 0.01 and 3 V (versus Li/Li$^+$) at 50 mA/g. (Yu et al. 2009)

In conclusion, prior research has shown the possibility of mitigating the ICL but not the complete elimination of the latter while preserving good cycling performance.
Based on the current understanding, the ICL due to SEI formation could be reduced by either suppressing its formation, or by facilitating the formation of high quality SEI layers without \textit{in situ} Li ion consumption. These two opposite approaches then lead to different material designs and materials synthesis. For example, one can design hierarchical structured materials with a protective outside layer.
CHAPTER 3  SELF-ASSEMBLED 3D
FLOWER-LIKE HIERARCHICAL TIN OXIDE NANOSTRUCTURES WITH DIFFERENT PACKING

3.1 Introduction

The shorter electron and Li ion diffusion lengths in nanoscale materials are advantageous for a more facile electrode process. The large surface area of nanomaterials also increases the contact with the electrolyte and consequently the accessibility of the Li storage host. Hence, there have been numerous efforts in the past two decades on the preparation of nanoscale electrode materials for the lithium ion batteries. The structure of nanomaterials can be solid (Park et al. 2007; Wang et al. 2011), hollow (Lou et al. 2006; Deng et al. 2008; Ding et al. 2010; Wang et al. 2011), or porous (Demir-Cakan et al. 2008; Kim et al. 2008; Shon et al. 2009). In general most of the nanostructured materials would show improvements over the microscale materials in at least some performance areas (e.g., storage capacity and rate performance). However, nanomaterials are difficult to handle and the reactivity of their (large) surfaces can bring about undesirable side reactions.

Hierarchical structured materials which combine the nanometer and micrometer length scales can benefit from the advantages of both nanostructured (facile response) and
microstructured (compactness and ease of handling) materials if they are properly
designed. There are at least two length scales in a hierarchical structure – length scales
for the elements (building block) and length scale for the ensemble. The organization
of NPs/NTs/NSs into a dense compact structure can reduce the accessibility of the
surface for side reactions such as SEI formation. The pores in the building blocks can
provide the space for containing the volume changes in discharging and charging. The
building blocks can be NPs(Chen et al. 2012), NTs(Li et al. 2012), or NSs(Mo et al.
2005; Ding et al. 2011), while the ensemble may be microspheres(Mo et al. 2005;
Ding et al. 2011), cog-like structures(Zhang et al. 2011) or flower-like structures(Zhu
et al. 2009). Hierarchical structured materials can be prepared with the use of hard or
soft templates.(Hu et al. 2007; Kim et al. 2011; Sun et al. 2011) This method of
preparation is however often laborious and high cost. The alternative approach of self-
assembly(Cao et al. 2005; Mo et al. 2005; Yin et al. 2010; Wang et al. 2011; Wang et
al. 2011) is more facile and green chemistry compliant (less waste in the process – no
templates and hence no chemicals for template removal). Self-assembly, however,
requires careful selection of the synthesis process and careful control of the synthesis
conditions to achieve the desired outcome. Previous research has shown that
hierarchical structured SnO$_2$ nanomaterials with a hollow interior could be formed by
self-assembly.(Yin et al. 2010) The mechanism of self-assembly is complex and has
not been well understood. Consequently, the preparation of hierarchical structured
materials, especially those with controllable packing density, is still a challenge.

The ability to assemble hierarchical structured materials with different packing
densities is of interest not only because it provides a large sample space to examine the
many facets of the self-assembly process (thereby leading to potentially a better
understanding of the phenomenon) but also its potential for material performance improvements through structural optimizations. A facile method to synthesize SnO₂ hierarchical structures with different packing densities is presented in this chapter. It was found that simple controls such as pH of the reaction medium and reactant concentrations were sufficiently effective to create differently structured hierarchical materials. The electrochemical performance of hierarchical structured SnO₂ for reversible Li ions storage was then measured. The ICLs of hierarchical structures for SEI formation were all smaller than those of unassembled NPs or NSs of SnO₂. The hierarchical SnO₂ structure with a moderate packing density, in particular, showed the best overall capacity retention.

Table 3.1  Matrix of experiment conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Urea (mg)</th>
<th>Water (mL)</th>
<th>NaOH (mg)</th>
<th>SnCl₂ (mg)</th>
<th>Temperature (°C)</th>
<th>Reaction time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS-A</td>
<td>600</td>
<td>60</td>
<td>0</td>
<td>600</td>
<td>160</td>
<td>6</td>
</tr>
<tr>
<td>HS-B</td>
<td>600</td>
<td>60</td>
<td>400</td>
<td>600</td>
<td>160</td>
<td>6</td>
</tr>
<tr>
<td>HS-C</td>
<td>600</td>
<td>60</td>
<td>800</td>
<td>600</td>
<td>160</td>
<td>6</td>
</tr>
<tr>
<td>HS-D</td>
<td>300</td>
<td>60</td>
<td>400</td>
<td>300</td>
<td>160</td>
<td>6</td>
</tr>
<tr>
<td>HS-E</td>
<td>1200</td>
<td>60</td>
<td>1600</td>
<td>1200</td>
<td>160</td>
<td>6</td>
</tr>
<tr>
<td>HS-F</td>
<td>0</td>
<td>60</td>
<td>1600</td>
<td>1200</td>
<td>160</td>
<td>6</td>
</tr>
<tr>
<td>HS-G</td>
<td>Ammonia carbonate 960 mg</td>
<td>60</td>
<td>1600</td>
<td>1200</td>
<td>160</td>
<td>6</td>
</tr>
<tr>
<td>HS-H</td>
<td>600</td>
<td>60</td>
<td>800</td>
<td>600</td>
<td>160</td>
<td>0.5</td>
</tr>
</tbody>
</table>

3.2 Experimental Section

3.2.1 Material Synthesis and Characterization

Table 3.1 shows the matrix of experimental conditions investigated in this study. The preparation of HS-C is given below as an example. 600 mg urea and 800 mg NaOH were added to 60 mL DI water with stirring. Stirring was continued for 5 more min
after the end of addition, 600 mg SnCl$_2$·2H$_2$O was then introduced and stirred to form a transparent solution after 20 min (for HS-A and HS-B precipitates were formed). The solution was transferred to a 100 mL Teflon-lined stainless steel reactor and hydrothermally processed at 160 °C for 6 h. The yellow precipitate formed was separated by centrifugation, followed by washing with ethanol and deionized water, and then vacuum dried at 100 °C for 4 h.

The precipitates before (HS-A and HS-B only) and after the hydrothermal treatment were characterized by FESEM on a JEOL JSM-6700F operating at 5 kV, by transition electron microscopy (TEM) on a Philips FEG-CM300 operating at 200 kV; and by powder X-ray diffraction (XRD) on a Bruker D8 Advance spectrometer using Cu Kα radiation.

### 3.2.2 Electrochemical Measurements

The tin oxide anode material prepared above, and 10 wt% each of polyvinylidene fluoride (PVDF) binder and Super P (Timcal) were mixed into a homogenous slurry in N-methylpyrrolidone (NMP). The slurry was applied to a copper disc current collector and dried in vacuum at 120 °C overnight. Li test cells were assembled in an argon-filled glove box using a Li metal foil as the reference electrode and 1 M LiPF$_6$/ EC+diethylene carbonate (DEC) (1:1 w/w) as the electrolyte. The cells were discharged and charged on a Maccor Series 2000 battery tester at ambient conditions at different discharge and charge current densities in the 10 mV to 2 V voltage window.

### 3.3 Results and Discussion

#### 3.3.1 Morphology Control by Solution pH
Chapter 3

The morphology and crystalline structure of SnO$_2$ are known to vary with the rate of Sn(II) oxidation and the degree of super-saturation. (Uchiyama et al. 2006) In this study the pH of the reactant mixture and hydrothermal treatment were used to provide the conditions necessary for the formation of SnO$_2$ hierarchical structures. pH adjustments were based on sodium hydroxide addition. The morphologies of the precipitates formed by SnCl$_2$ addition and the products of hydrothermal treatment (HS-A, HS-B) are shown in Figure 3.1a-d. The XRD patterns of HS-A, HS-B precursors (the precipitates) and HS-A, HS-B are also shown in Figure 3.1e, f respectively. SnCl$_2$ is easily hydrolyzed in water (SnCl$_2$ (aq) + H$_2$O (l)$\rightarrow$Sn(OH)Cl (s) + HCl (aq)). In the preparation of HS-A, the initially clear urea aqueous solution was changed slowly into an opaque suspension by the addition of SnCl$_2$ due to the hydrolysis of SnCl$_2$ to Sn(OH)Cl. Sn(OH)Cl was unstable and consequently decomposed to tetragonal SnO (JCPDS card no. 85-0423), which was confirmed by XRD measurements (Figure 3.1e). SEM examination showed mostly random NPs in the precipitate (Figure 3.1a). Hydrothermal treatment converted the precipitate to HS-A, a collection of large 5-10 µm plates and small 100-200 nm NPs (Figure 3.1b). The large plates were mostly likely formed by the aggregation of the random NPs under hydrothermal conditions.

The XRD pattern of HS-A is also indexable to tetragonal SnO. When the SnCl$_2$ precursor was added to an alkaline solution of urea in the preparation of HS-B, the solution turned turbid quickly with the formation of a white precipitate. XRD confirmed the white precipitate as Sn$_6$O$_4$(OH)$_4$ (JCPDS card no.84-2157) (Figure 3.1e). The facile formation of Sn$_6$O$_4$(OH)$_4$ from Sn(II) at pH>7 has been shown before. (Uchiyama et al. 2006) Similar to the HS-A precursor the HS-B precursor was also proliferated with random NPs (Figure 3.1c). Hydrothermal treatment converted this precursor to HS-B, a mixture of hierarchical structures of NSs (vide infra) amidst a
few large plates (Figure 3.1d). XRD measurements indicated the presence of both tetragonal SnO and tetragonal SnO₂ (JCPDS card no. 41-1445). SnO was formed by the decomposition of Sn₆O₄(OH)₄ whereas SnO₂ was formed by the oxidation of Sn(II) in the soluble coordination complex Sn₆O₄(OH)₄+x⁻ by dissolved oxygen in the solution product, as shown by the redox reactions below (Allen et al. 2001):

\[
\begin{align*}
O_2 + 2H_2O + 4e^- &\rightarrow 4OH^- & 0.40 \text{ V} \\
Sn^{4+} + 2e^- &\rightarrow Sn^{2+} & 0.15 \text{ V}
\end{align*}
\]

The SnO₂ in HS-C (vide infra) was also formed in the same way.

HS-C was by far the most interesting sample. In the preparation of HS-C, the solution did turn turbid after the addition of SnCl₂ but re-clarified after 20 min of uninterrupted stirring. The dissolution of Sn₆O₄(OH)₄ in excess OH⁻ as the coordination complex Sn₆O₄(OH)₄+x⁻ created a uniform reaction environment for hydrothermal processing to result in a product with higher regularity. The flower-like morphology of HS-C in Figure 3.2a-c was indeed a hierarchical structure 2-3 µm in size assembled from 500 nm long and 40 nm thick NSs. XRD indicated HS-C as anorthic Sn₂O₃ (JCPDS card no. 25-1259). The primary crystallite size of ~43 nm calculated from the Scherrer Equation based on the (011) diffraction agrees well with the thickness of the NSs. The partial oxidation of Sn(II) in the hydrothermal reaction was again caused by dissolved oxygen in the solution. The analysis of these tin oxide products formed under different conditions suggests that the precipitation of Sn(II) as an insoluble salt should be avoided in the preparation in order to facilitate self-assembly into a hierarchical structure under hydrothermal conditions. Figure 3.3 is a postulation of the pH dependent formation mechanism.
Figure 3.1  SEM images of a) HS-A precursor before hydrothermal reaction, b) HS-A, c) HS-B precursor before hydrothermal reaction, d) HS-B, e) XRD patterns of HS-A and HS-B precursors before hydrothermal reaction, and f) XRD patterns of HS-A, HS-B.
Figure 3.2  SEM images of a) HS-C at low magnification, b) HS-C at high magnification, c) TEM images of HS-C and d) XRD patterns of HS-C.

Figure 3.3  Proposed formation mechanisms of HS-A, HS-B and HS-C.
3.3.2 Morphology Control by Reactant Concentrations

The packing density in the flower-like hierarchical structures could be changed by increasing or decreasing the reactant concentrations (urea, NaOH and SnCl₂) while keeping their ratios fixed. When the reactant concentrations were reduced to half of the values used in the preparation of HS-C, the NSs in the flower-like hierarchical structure were loosely packed (HS-D). (Fig. 3.4a-c) Isolated NSs not involved in any packed structure could also be found. The NSs were ~30-40 nm in thickness and ~400-
500 nm in length. XRD identified them as a mixture of tetragonal SnO$_2$ (JCPDS card no. 41-1445) and anorthic Sn$_2$O$_3$ (JCPDS card no. 25-1259) (Figure 3.4g). Since all preparations were carried out using the same volume of reaction mixture and hence the same dissolved oxygen content, the O$_2$/Sn(II) ratio in the preparation of HS-D was higher than that in the preparation of HS-C due to the decreased Sn(II) content. The higher Sn(IV) content in HS-D than in HS-C could be understood as such. Conversely, the product formed by doubling all reactant concentrations (HS-E) was 2-3 µm flower-like hierarchical structures with a much higher packing density than HS-C(Fig. 3.4 d-e). The NSs in this case were ~40-50 nm in thickness and 500-600 nm in length. Plate-like, nest-like and bipyramid-like hierarchical structures consisting of SnO NSs of different sizes have been reported before.(Ning et al. 2009) The proximity of the NSs suggests that the hierarchical structures were formed by layer-by-layer construction. The flower-like structure in this study is different. It consisted of a large number of aggregated sheets nearly perpendicular to one another. It was a more open structure with a greater free volume to accommodate the volume changes. XRD result showed mostly anorthic Sn$_2$O$_3$ (JCPDS card no. 25-1259) with only a trace amount of tetragonal SnO (JCPDS card no. 85-0423). The dearth of Sn(IV) content could be attributed to a (low) O$_2$/Sn(II) ratio inadequate for the complete oxidation of Sn(II) to Sn(IV). Some semispherical flowers indicative of a higher packing density were also present in HS-E (the inset in Figure 3.4d)). Hence, it may be concluded that NSs was formed first in the hydrothermal reaction first and then assembled into flow-like hierarchical structures. Increase in reactant concentrations also increased the packing density due to the increase in the number of primary particles formed; and hence the increase in the building blocks (which were NSs formed from the primary particles) in the fully assembled structure. Figure 3.4h shows the proposed mechanism for the
formation of flower-like hierarchical structures of different packing densities by changing the reactant concentrations.

![Figure 3.5](image)

**Figure 3.5** SEM images of a) HS-H b) HS-G precursor before hydrothermal reaction, c) HS-G, d) XRD patterns of HS-H, HS-G precursor before the hydrothermal reaction and HS-G.

### 3.3.3 The Morphology Evolution Process

The products formed very early into the reaction were also characterized by SEM and XRD to reconstruct the morphology evolution process. Figure 3.5a is the typical image of the product (HS-H) formed within a very short time of the hydrothermal treatment (0.5 h). The assembly of NSs into a flower-like hierarchical structure had already taken place. The size of the flower-like particles was the same as the product after 6 h of reaction. Some of the hierarchical structures were however semi-spherical (incomplete
assembly) but no unassembled NSs were found. This suggests that the assembly of NSs into flower-like hierarchical structures was facile and occurred as soon as the NSs were formed. XRD measured a mixture of tetragonal SnO (JCPDS card no. 85-0423) and tetragonal SnO$_2$ (JCPDS card no. 41-1445). When this is compared with the predominance of Sn$_2$O$_3$ in HS-C, one could postulate the conversion of these two phases into the more stable form of Sn$_2$O$_3$ with increasing reaction time. The stability of Sn$_2$O$_3$ has been confirmed in a previous calculation. (Maki-Jaskari et al. 2004) This could also explain the strong presence of Sn$_2$O$_3$ in products HS-C, D, and E.

The effects of urea were also examined. Under reaction conditions which were similar to those in the preparation of HS-C except the presence of urea (HS-F), no solid product was formed after the hydrothermal treatment. This indicates that urea was necessary for the formation of nucleation sites in the hydrothermal reaction. To prove this urea was replaced by ammonia carbonate (HS-G). Urea only forms NH$_4^+$ and CO$_3^{2-}$ at temperatures above 60 °C whereas ammonia carbonate can immediately form these species upon dissolution in water (Equation 3-3 and 3-4).

\[
\text{NH}_2-(\text{C}=\text{O})-\text{NH}_2+2\text{H}_2\text{O} \rightarrow 2\text{NH}_4^++\text{CO}_3^{2-} \tag{3-3}
\]

\[
(\text{NH}_4)_2\text{CO}_3 \rightarrow 2\text{NH}_4^++\text{CO}_3^{2-} \tag{3-4}
\]

The replacement of urea by ammonia carbonate formed a persistent white precipitate upon SnCl$_2$ addition, which remained insoluble even after 1 h of stirring. SEM showed the presence of NPs which were confirmed by XRD to be Sn$_6$O$_4$(OH)$_4$. This indicates that NH$_4^+$ could promote the precipitation of Sn$_6$O$_4$(OH)$_4$, probably by removing the excess OH$^-$ in Sn$_6$O$_4$(OH)$_4+x^-$ which rendered the complex soluble. Different from the case of HS-A and HS-B where nucleation was fast, the decomposition of urea
controlled the release of NH$_4^+$ and CO$_3^{2-}$ in the solution (Adachi-Pagano et al. 2003; Boschini et al. 2003) and hence the rates of nucleation of HS-C, HS-D and HS-E precursors could be regulated by the rate of urea hydrolysis. The HS-G product formed after hydrothermal reaction consisted of very large (30 µm) microplates of tetragonal SnO (JCPDS card no. 85-0423) with only a trace amount of SnO$_2$ (JCPDS card no. 41-1445). This was yet another demonstration that a fast precipitation of Sn(II) was not favorable for self-assembly.

### 3.3.4 Reversible Lithium Storage Properties

The effects of morphology on electrochemical performance were examined by evaluating products HS-A, HS-C, HS-D and HS-E (i.e., products with uniform morphologies) at 0.5 A/g and 1 A/g in the 0.01-2 V (versus Li/Li$^+$) voltage window. The first 2 cycle discharge/charge curves of these four products are shown in Figure 3.6. The first cycle discharge and charge capacities were 1197 and 768 mAh/g (or ICL of 35.8%) for HS-C at 0.5 A/g; 1091 and 649 mAh/g (or ICL of 40.5%) for HS-C at 1 A/g. The ICL of HS-C is significantly lower than the typical literature value of 45-50% (Park et al. 2007; Deng et al. 2008; Wang et al. 2011). One possible cause was the presence of Sn(II) which reduced the ICL of tin oxide reduction to tin. The other reason was a smaller surface area for SEI formation which will be explained later. The higher ICL at high current density could be due to other factors such as Li ion entrapment in the material. Hence, the lower current density of 0.5 A/g was used for the comparison of ICL values. The ICL of tin-oxide anodes is known to consist of two components: tin oxide reduction to tin and SEI formation (Deng et al. 2008). The ICL associated with tin oxide reduction to tin could be estimated from the capacity in the 1.0-0.7 V voltage plateau of the discharge curve in Figure 4.6b (Han et al. 2005;
Demir-Cakan et al. (2008) The value calculated as such was 250 mAh/g. The ICL from SEI formation could then be calculated as the difference between the measured ICL and the ICL of tin oxide reduction. For HS-C this value amounted to 179 mAh/g. Since products HS-D and HS-E also contained primarily Sn$_2$O$_3$ (the amounts of SnO$_2$ in HS-D and SnO in HS-E were too small to have any consequences), the ICL of tin oxide reduction could likewise be assumed to be 250 mAh/g. On the other hand HS-A contained mostly SnO and its ICL due to tin oxide reduction could be estimated theoretically as $250/3 \times 2 = 167$ mAh/g. The first cycle discharge and charge capacities, the overall ICL, the ICL due to tin oxide reduction and SEI formation respectively calculated on the above basis are summarized in Table 3.2.

**Figure 3.6** Discharge and charge curves of a) HS-A, b) HS-C, c) HS-D and d) HS-E at 0.5 A/g and 1A/g in the 0.01-2 V (versus Li/Li$^+$) voltage window.
Table 3.2  Summary of electrochemical properties of HS-A, HS-B, HS-C and HS-D

<table>
<thead>
<tr>
<th>Sample</th>
<th>a [mAh/g]</th>
<th>b [mAh/g]</th>
<th>c</th>
<th>d [mAh/g]</th>
<th>e [mAh/g]</th>
<th>f [mAh/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5A/g</td>
<td>1A/g</td>
<td>0.5A/g</td>
<td>1A/g</td>
<td>0.5A/g</td>
<td>0.5A/g</td>
</tr>
<tr>
<td>HS-A</td>
<td>1250</td>
<td>999</td>
<td>680</td>
<td>559</td>
<td>54.4%</td>
<td>56.0%</td>
</tr>
<tr>
<td>HS-C</td>
<td>1197</td>
<td>1091</td>
<td>768</td>
<td>649</td>
<td>64.2%</td>
<td>59.5%</td>
</tr>
<tr>
<td>HS-D</td>
<td>1328</td>
<td>1265</td>
<td>726</td>
<td>685</td>
<td>54.7%</td>
<td>54.2%</td>
</tr>
<tr>
<td>HS-E</td>
<td>1296</td>
<td>1254</td>
<td>771</td>
<td>714</td>
<td>59.5%</td>
<td>57.0%</td>
</tr>
</tbody>
</table>

- a. 1st cycle discharge capacity
- b. 1st cycle charge capacity
- c. Columbic efficiency
- d. Overall ICL
- e. ICL due to reduction of tin oxide to tin
- f. ICL due to SEI formation

From Table 3.2 the ICLs of hierarchical structures (HS-C and HS-E) for SEI formation were all smaller than those of unassembled NPs or NSs of tin oxide (HS-A and HS-B). HS-C had the highest first cycle columbic efficiencies at both 0.5 A/g or 1 A/g. Its ICL due to SEI formation was also the lowest, at 179 mAh/g. Since SEI is a surface process, a low ICL due to SEI formation may be taken to indicate the reduction in surface area on which electrolyte decomposition could freely occur. Despite similar columbic efficiencies, the ICL from SEI formation was much higher for HS-A than HS-D. This could be attributed to the larger surface area of HS-A (100-200 nm unassembled NPs) relative to HS-D (unassembled NSs 30-40 nm in thickness and ~400-500 nm in length). The ICL from SEI formation on HS-E was also higher than that in HS-C even though the packing density was higher in the former. This could be related to the presence of incomplete hierarchical structures in HS-E.
Figure 3.7  Cycling stability of a) HS-A, b) HS-C, c) HS-D and d) HS-E at 0.5 A/g and 1A/g in the 0.01-2 V (versus Li/Li⁺) voltage window.

The cycling stability of these differently structured tin oxide products is compared in Figure 3.7. The charge capacities after 30 cycles of discharge and recharge were 201 mAh/g for HS-B, 428 mAh/g for HS-C, 320 mAh/g for HS-D and 372 mAh/g for HS-E respectively. The two products with hierarchical structures were clearly more cyclable than the two unstructured products. This can be attributed to the structural stability of hierarchical constructions. (Yin et al. 2010; Sun et al. 2011; Zhang et al. 2011) The cycling stability of HS-E was not as good as that of HS-C probably because the packing density could be too high to maintain good contact of the flower interior with the electrolyte. Hence, it may be concluded that the organization of active materials into hierarchical structures with a moderate packing density would generally benefit the electrochemical performance. It is worthwhile to mention that the hierarchically structured tin oxide products, despite their large overall size, could cycle...
well at high current densities. The best product, HS-C, could deliver a charge capacity of 327 mAh/g at 1 A/g (most tin oxide NPs could not cycle well at >100 mA/g). Therefore hierarchical structures not only could lower the ICL of SEI formation, but could also improve the rate performance of the active material.

3.4 Conclusion

Through careful control of the preparation conditions, tin oxide particles with hierarchical structures could be fabricated by a two-step process - hydrolysis of a Sn(II) precursor at sufficiently high pH followed by assembly of the tin oxides formed under hydrothermal conditions. The hierarchical structures had a generally flower-like appearance, and were assembled from NSs with packing density that could be increased by increasing reactant concentrations. It is postulated that the assembly of NSs was fast and occurred immediately after the NSs were formed by the aggregation of primary NPs. The driving force for the assembly was the reduction of surface energy. The dissolution of Sn$_6$O$_4$(OH)$_4$ in excess OH$^{-}$ as the coordination complex Sn$_6$O$_4$(OH)$_{4+x^-}$ created a uniform reaction environment in hydrothermal processing to result in products with a higher regularity. Urea was important in the preparation as its hydrolytic decomposition removed the excess OH$^{-}$ in Sn$_6$O$_4$(OH)$_{4+x^-}$, precipitating Sn slowly and uniformly as Sn$_6$O$_4$(OH)$_4$. The nucleation of HS-C, HS-D and HS-E precursors could then be controlled by the hydrolysis rate of urea. Sn$_6$O$_4$(OH)$_4$ then decomposed to tin oxides with hierarchical structures under hydrothermal conditions. Hierarchically structures of tin oxide with a moderate packing density showed very high first cycle columbic efficiencies at 0.5 A/g or 1 A/g (the columbic efficiency of HS-C was 64.2% whereas the typical literature values for tin oxide are ~46%-55%). The ICL due to SEI formation was only 179 mAh/g measured at 0.5 A/g. It also had
the best cycling performance. (428 mAh/g of charge capacity after 30 cycles at 0.5 A/g). Hence, the organization of active materials into hierarchical structures with a moderate packing density could increase the Li storage reversibility of the material in battery applications (decrease in irreversible side reactions (SEI formation), higher capacity, rate performance and cyclability).
CHAPTER 4 CONFORMAL GRAPHENE
ENCAPSULATION OF TIN OXIDE
NANOPARTICLE AGGREGATES FOR
IMPROVED REVERSIBILITY OF
LITHIUM ION STORAGE

4.1 Introduction

Among the anode materials under consideration, tin-based compounds with their high theoretical capacities (782 mAh/g for SnO$_2$; 994 mAh/g for Sn) and low toxicity, continue to be a material of interest to the battery community. Downsizing the tin-based anodes to the nanoscale has improved the performance of Sn for reversible Li ions storage.(Wang et al. 2004; Ning et al. 2009; Wang et al. 2011) As there is a strong tendency for tin NPs to aggregate during use, the preservation of the nanometre length scale advantage of the active material is important for a consistent application performance.

Tin oxide is often compounded with graphite(Fan et al. 2004) or various forms of disordered carbon(Derrien et al. 2007; Deng et al. 2009; Deng et al. 2010; Liu et al. 2010) to compensate for some of its innate deficiencies. Generally a carbon matrix connects up the Sn/SnO$_2$ NPs electrically. Carbon is also an effective medium for stress and strain relief in discharging and charging reactions by the alloying
mechanism. The cycling performance of Sn-based anodes is often improved this way but their rate performance still leaves room for improvement because of the limited conductivity of some of these carbonaceous materials. (Mattia et al. 2006)

Graphene would be an excellent form of carbon to composite with high capacity anode materials. First, it has good electrical conductivity. Second, its relatively low mass will minimize the ‘dead weight effect’ of the compounding medium (i.e., graphene) in the composite. Lastly, its high surface area (2600 m²/g theoretically) ensures good electrical contact with the active anode material with only a small amount of graphene. Hence, there have been quite a number of studies on tin oxide/graphene composites targeted at lithium ion batteries applications. (Paek et al. 2009; Wang et al. 2009; Yao et al. 2009; Du et al. 2010; Kim et al. 2010; Li et al. 2010; Wang et al. 2010; Wang et al. 2010; Zhang et al. 2010; Huang et al. 2011; Liang et al. 2011; Liang et al. 2011; Wang et al. 2011; Zhang et al. 2011; Zhong et al. 2011) The most common composite structure is dispersions of tin oxide NPs on graphene sheets. If this structure is produced by simply mixing tin oxide NPs with graphene sheets, the common incompatibility between inorganic and organic compounds would result in weak interactions between tin oxide and graphene; and consequently poor composite stability. (Paek et al. 2009) If the composite is produced by mixing GO with a tin precursor followed by reduction, (Zhang et al. 2010; Zhang et al. 2011; Zhong et al. 2011) the attachment of tin oxide to the graphene sheets is improved by the presence of oxygen-containing groups on GO. However, such affinity diminishes when the oxygen-containing groups are removed in the reduction step. The aggregation of tin oxide NPs therefore occurs in cycling due to the lack of adequate confinement. Previously, our group has developed an electrostatic self-assembly procedure which
averted many of these problems in the preparation of graphene-encapsulated hollow aggregates of Fe₃O₄ NPs. (Chen et al. 2011) The resulting composite delivered large reversible Li ions storage capacity together with good rate performance. The graphene encapsulation prevented NP coalescence at the aggregate level although not all of the aggregates were graphene-encapsulated. Recently Zhou et al. (Zhou et al. 2011) reported a different method for fabricating metal oxide@graphene core–shell nanostructures. Their results showed that the α-Fe₂O₃@graphene core–shell NPs were also graphene-encapsulated aggregates with multiple cores per shell.

Herein, we provide a method to prepare tin oxide NP aggregates individually wrapped by graphene sheets (SnO₂@TRGO (thermally reduced graphene oxide) composites). The preparation method involves self-assembly driven by both electrostatic interaction and chemical cross-linking. In this method, a mixture of poly(allylamine hydrochloride) (PAH) and tin oxide NP aggregates is vigorously ultrasonicated so that the SnO₂ surface can be completely covered with amine terminating groups to repulse the coalescence of NP aggregates. This allows the graphene sheets to approach individual SnO₂ NP aggregates closely and folds their surface under electrostatic interaction. At the same time, the amine groups on the PAH-modified NPs can cross-link with the epoxy groups of two or more GO layers to form covalent C-N linkages between the NPs and graphene. (Zhou et al. 2011) The resistance of the C-N bonds to thermal reduction imparts stability to the composite structure. This particular construction method maximizes the contact between the tin oxide NP aggregates and graphene sheets. The resulting electrical conductivity is good enough that carbon black conductive additive is no longer needed for electrode formulation. The graphene encapsulation of individual SnO₂/Sn NP aggregates also keeps the NP aggregates
electrically connected even when the active anode material undergoes volume expansion and contraction during discharging and charging, and inhibits the growth of tin particles by coalescence. On the other hand, the uniform distribution of tin oxide NPs in the graphene sheets also prevents the restacking of graphene sheets, which is a common problem in the application of graphene. Consequently, the SnO$_2$@TRGO composites displayed excellent cycling performance: stabilization of the discharge/charge capacities by the 3$^{\text{rd}}$ cycle, practically no capacity fading for 50 cycles; and a reversible charge capacity of 700 mAh at 0.1 Ah/g and 423 mAh/g at a ten fold increase in current density to 1 Ah/g. Through electrochemical characterizations the good performance of the composites can be understood in terms of the importance of across-plane diffusion of Li ions in the graphene sheets on the NPs, a finding that can lead to more effective designs of other active material/graphene composites where diffusion of an ionic species is crucial to the application performance.

4.2 Experimental Section

4.2.1 Synthesis of Tin Oxide NP Aggregates

The synthesis of tin oxide NP aggregates began with dissolving 1 g potassium stannate trihydrate (K$_2$SnO$_3$.3H$_2$O, Aldrich, 99.9%) and 3 g glucose (Aldrich, 99.0%) in 60 mL water. The solution was transferred to a Teflon-lined stainless steel autoclave (100 mL), sealed and hydrothermally processed at 160 $^\circ$C for 4 h in an electric oven, and then cooled to room temperature naturally. The brown precipitate formed was harvested by centrifugation, washed with deionized water and ethanol, and dried at 100 $^\circ$C for 4 h. The dry brown powder was then heated in air at 500 $^\circ$C for 2 h in a combustion boat. A white tin oxide powder was obtained.
4.2.2 Synthesis of SnO$_2$@GO Composites

GO synthesized from natural graphite powder (Merck) by a modified Hummers method (Hummers et al. 1958) was ultrasonically dispersed in water until a transparent solution was formed. 100 mg of the SnO$_2$ powder prepared above was ultrasonically dispersed in 30 mL 1 g/L PAH solution for 10 min followed by another hour of stirring. The solid phase after treatment was recovered by centrifugation and redispersed ultrasonically in 10 mL deionized water for 10 min. 30 mL of the GO solution was then added with stirring. Mixing continued for 2 more hours after the end of addition. The light gray precipitate (SnO$_2$@GO core-shell composites) recovered at the end of these procedures was dried at 100 °C for 8 h.

4.2.3 Synthesis of SnO$_2$@TRGO Composites

SnO$_2$@TRGO composites were prepared by the thermal reduction of the SnO$_2$@GO core-shell composites prepared above. In a typical preparation, 80 mg SnO$_2$@GO composite was placed in a combustion boat and heated at 600 °C in 200 sccm of a 5% H$_2$ – 95% N$_2$ gas mixture for 3 h. The gas supply was then switched to pure nitrogen and the furnace cooled down naturally.

4.2.4 Materials Characterization

The structure and morphology of the product and semi-products were characterized by TEM on a Philips FEG-CM300 operating at 200 kV, FESEM and scanning transmission electron microscopy (STEM) on a JEOL JSM-6700F operating at 5 and 25 kV respectively, and by energy-dispersive X-ray spectroscopy (EDX) on a JEOL JSM-840 operating at 15 kV. Powder XRD patterns were measured by a Bruker D8
Advance spectrometer using a Cu Kα1 radiation source (λ = 0.15406 nm). X-ray photoelectron spectroscopy (XPS) was conducted on a Kratos Axis Ultra DLD spectrometer. All binding energies were referenced to the C1s carbon peak at 284.5 eV. Thermogravimetric analysis (TGA) measurements were performed in air on a Shimadzu DTG-60H from 25 to 800 °C at a heating rate of 10 °C/min.

4.2.5 Electrochemical Measurements

The electrochemical properties of tin oxide NP aggregates, TRGO and SnO₂@TRGO composites as the anode of lithium ion batteries were evaluated using Swagelok-type cells and constant current charging and discharging. TRGO and SnO₂@TRGO composites electrodes were fabricated by coating copper foils with a mixture of 90 wt% active material and 10 wt% PVDF without any conductive additive. For the preparation of the tin oxide NP aggregates electrode; the mixture was 80 wt% active material, 10 wt% PVDF and 10 wt% carbon black (Timcal). The pasted electrodes after pressing were dried in vacuum at 120 °C overnight. Test cells were assembled in a Mbraun Ar-filled glove box using the pasted electrode as the working electrode, metallic Li as the counter cum reference electrode, 1 M LiPF₆/ EC+DEC (1:1 w/w) electrolyte and Celgard 2400 polypropylene separator. The cells were discharged and charged galvanostatically between 0.005 and 2 V (versus Li/Li⁺) on a Maccor Series 2000 battery tester at various current densities. Electrochemical impedance spectroscopy (EIS) was performed on an AutoLab Electrochemical System (±5 mV AC, frequency range 100 kHz–0.1 Hz).
4.3 Results and Discussion

4.3.1 Structure Analysis

The process flow for the synthesis is summarized in Figure 4.1. The aggregation of NPs into a hierarchical structure has the advantage of increasing the density of the active material (and hence volumetric capacity) and decreasing the surface area where SEI may form. Graphene encapsulation is easier with NP aggregates than with individual NPs because of the stiffness in graphene folding. However, encapsulation needs to be individual for each NP aggregate in order to be effective. Graphene encapsulation also addresses the problem of graphene restacking, which is a common cause of the instability of graphene composites.
The tin oxide NP aggregates in this work were prepared by the hydrolysis of potassium stannate, leveraging on the slow hydrolysis rate of stannates for more process controllability. The material incompatibility between graphene sheets and inorganic compounds was first addressed by using GO. Affinity binding between GO and tin oxide was also improved by modifying the surface of the latter with amine terminating groups which can cross-link with the epoxide groups in GO by the following reaction:

\[
\text{CH}_2=\text{CH}_2 + \text{R}-\text{NH}_2 \rightarrow \text{H}_2\text{C} - \text{C} - \text{NH} - \text{R} \rightarrow \text{SnO}_2
\]

Hence, PAH, a water soluble cationic polyelectrolyte, was used as the amination agent. The PAH modification of pristine tin oxide NP aggregates also avoided the coalescence of tin oxide NP aggregates by imparting positive charge to the latter.(Chen et al. 2011) GO is highly negatively charged when dispersed in water due to the ionization of its surface carboxylic acid and phenolic hydroxyl groups.(Li et al. 2008) The electrostatic interaction between positively charged PAH-modified tin oxide NP aggregates and negatively charged GO was sufficient to prevent the aggregation of the nanocomposites.
aggregates and negatively charged GO was complemented by chemical cross-linking between amine and epoxide groups to yield a compact core–shell assembly. (Zhou et al. 2011) The PAH modification had to be carried out under strong ultrasonication so that the surface of the tin oxide NP aggregates could be fully functionalized and subsequent encapsulation by the graphene sheets could be conformal. The extent of graphene encapsulation on the structure and electrochemical performance of graphene encapsulated tin oxide was evaluated by using GO solutions of different concentrations in the synthesis. Based on the weight percents of graphene in the products, SnO$_2$@GO composites with 5 and 10 wt% graphene (SnO$_2$@GO-5 and SnO$_2$@GO-10) were prepared and the corresponding SnO$_2$@TRGO composites were SnO$_2$@TRGO-5 and SnO$_2$@TRGO-10.

![Figure 4.3](image.png)

**Figure 4.3** Linescan image of three representative SnO$_2$@TRGO-5 particles.
The tin oxide NP aggregates were prepared by the Lou method (Lou et al. 2009) with their carbon coating removed by calcination in air. A hollow core was clearly visible within the aggregate interior after calcination. This was caused by the compaction of tin oxide NPs in the surface region into a shell by the forces from the outward diffusion of CO2. (Deng et al. 2008) The calcined tin oxide NP aggregates were fairly uniform in size and shape with diameters around 90 nm, and were composed of several 15 nm primary NPs (Figure 4.2a-c). The TEM, FESEM and STEM images of SnO$_2$@GO-5 confirm the successful coating of GO layers on the NP aggregates (Figure 4.2d-f). The GO coating was very thin. Figure 4.2h-g suggest that thermal reduction also converted some tin oxide into tin and this was confirmed by the linescan image of three representative SnO$_2$@TRGO-5 particles (Figure 4.3). Based on our own experience and the findings of others, (Lou et al. 2009) unhindered melting of tin during calcination could cause the formation of large particles with irregular shapes.
Hence, the same basic size and shape of the particles in SnO$_2@$TRGO-5 as the pristine tin oxide NP aggregates suggests that the aggregation of molten tin was inhibited after graphene encapsulation; and this was possible only if the tin oxide NP aggregates were individually wrapped in graphene sheets. Likewise the presence of a graphene shell is also visible in the SEM images of SnO$_2@$GO-10 (Figure 4.4a-c). The graphene sheets in this case were thicker because of more GO layers. Different from SnO$_2@$TRGO-5, no tin NPs could be identified in SnO$_2@$TRGO-10 (Figure 4.4d-f). This is indication that the shell was too thick to allow the reducing gas access to the particle interior for tin oxide reduction.

![C1s XPS spectra](image)

**Figure 4.5**  C1s XPS spectra of GO, SnO$_2@$GO-5 and SnO$_2@$TRGO-5.
4.3.2 XRD/XPS Analysis

The chemical changes in GO due to cross-linking with PAH-modified tin oxide NP aggregates and thermal reduction were characterized by XPS analysis of GO, SnO$_2$@GO composites and SnO$_2$@TRGO composites. The C1s spectra of GO, SnO$_2$@GO-5 and SnO$_2$@TRGO-5 are shown in Figure 4.5. The C1s spectrum of GO has three distinctive peaks at 284.5, 286.6 and 288.3 eV. The peak positions are in good agreement with those of pristine carbon (C-C), oxygenated carbon (e.g., C–OH and epoxide) and carbon in carbonate ions (\(\sigma^-\)) respectively.(Li et al. 2011) The intensity of the oxygenated carbon peak is high, suggesting that the oxidation degree was very high for GO prepared by the Hummers method. The un-reduced GO coating in SnO$_2$@GO produced an additional C1s peak at $\sim$285.6 eV which could be attributed to the C-N bond.(Kuper et al. 1999) Thermal reduction did not remove this particular carbon species. Hence, the C-N cross-links between GO and PAH-modified SnO$_2$ NP aggregates were resistant to thermal reduction. On the contrary the peak corresponding to oxygenated carbon at $\sim$ 286.6 disappeared after the thermal reduction of SnO$_2$@GO-
and decreased in intensity after the thermal reduction of SnO$_2$@GO-10 (Figure 4.6b). Hence, only oxygenated carbon species were removable by the thermal reduction procedure of this study. A thicker graphene shell, with increased mass transfer resistance, would limit the diffusion of the reducing gas to the particle interior and consequently, the tin oxide in the core area was less likely to be reduced to Sn. The survey scan spectrum shows the presence of C, O, Sn and Si (background) and no evidence of other elements present as impurities (Figure 4.6a).

Figure 4.7 a) XRD patterns of GO, tin oxide, SnO$_2$@GO-5, SnO$_2$@TRGO-5 and SnO$_2$@TRGO-10. b) TGA curves of SnO$_2$@TRGO-5 and SnO$_2$@TRGO-10.

The XRD patterns of GO, tin oxide, SnO$_2$@GO-5, SnO$_2$@TRGO-5 and SnO$_2$@TRGO-10 are shown in Figure 4.7a. The broad peak at $2\theta=10^\circ$ in the GO
sample was caused by the (001) diffraction of GO. (Cai et al. 2007) The absence of this peak in the tin oxide composites with GO or TRGO indicates that the GO encapsulation of PAH-modified tin oxide NP aggregates also effectively prevented the re-stacking of the graphene sheets (and hence no, or limited constructive diffractions from ordered graphene sheets). The four main diffraction peaks of cassiterite (the tetragonal crystalline phase of tin oxide (JCPDS 41-1445)), i.e., the (110), (101), (211), and (301) diffractions, are all present in the powder diffraction patterns of pristine tin oxide, SnO$_2$@GO-5, SnO$_2$@TRGO-5 and SnO$_2$@TRGO-10. The crystallite size of primary tin oxide NPs calculated from the {101} diffraction of pristine tin oxide by the Scherrer Equation was $\sim$16 nm, in good agreement with the TEM measurement. For SnO$_2$@TRGO-5 in particular, peaks at $2\theta = 30.4^\circ$, $31.9^\circ$, $43.8^\circ$, and $44.8^\circ$ indexable to crystalline metallic tin (JCPDS 04-0673) were also found. This confirms the partial conversion of tin oxide to tin in SnO$_2$@GO-5. For TGA measurements of the graphene contents in the composites, samples were heated from 25-800 °C at a rate of 10 °C/min under air atmosphere. (Figure 4.7b) The 2.5% weight loss below 150 °C for SnO$_2$@TRGO-10 could be attributed to moisture content. The carbon contents in SnO$_2$@TRGO-10 and SnO$_2$@TRGO-5 were estimated to be 9% and 5.2% by weight (dry basis) respectively. It should be mentioned that the carbon content of tin-containing SnO$_2$@TRGO-5 could be overestimated due to the weight gain from tin re-oxidation. The carbon content of SnO$_2$@TRGO-5 according to EDX measurements was 5 wt%. The difference between these values was used to deduce a Sn content of 20.8 wt% in SnO$_2$@TRGO-5.
Figure 4.8  Discharge and charge curves of a) tin oxide, b) TRGO at 200 mA/g in the 0.005-2 V (versus Li/Li⁺).

Figure 4.9  a) 1ˢᵗ and 2ⁿᵈ cycle discharge and charge curves of SnO₂@TRGO-5 and SnO₂@TRGO-10 at 200 mA/g in the 0.005-2 V (versus Li/Li⁺) voltage window. b) Cycling performance of tin oxide, TRGO, SnO₂@TRGO-5 and SnO₂@TRGO-10. (Test conditions: 200 mA/g, 0.005-2 V versus Li/Li⁺).
4.3.3 Reversible Lithium Storage Properties

Constant current discharging and charging of the SnO$_2$@TRGO composites was first measured at a current density of 200 mA/g in the 0.005-2 V (versus Li/Li$^+$) voltage window. The performance of pristine tin oxide and TRGO was also evaluated under the same conditions for comparison. From the first 2 cycle discharge/charge curves of tin oxide (Figure 4.8a) and TRGO (Figure 4.8b), the first cycle discharge and charge capacities of tin oxide were 1394.3 and 723.7 mAh/g respectively resulting in a first cycle ICL of 47.8%. This ICL was caused by tin oxide reduction to tin as well as SEI formation.(Deng et al. 2008) The ICL related to the former could be estimated from the capacity in the 1.0-0.8 V voltage window of the discharge curve of pristine tin oxide in Figure 4.8a. The value calculated as such was 300 mAh/g. The ICL due to SEI formation could then be calculated as the difference between the measured ICL and the ICL due to tin oxide reduction. For pristine tin oxide this value was 371 mAh/g. The first cycle discharge and charge capacities of TRGO were 648.2 and 122.7 mAh/g. The large ICL of 81.1% is typical for the graphene anodes in lithium ion batteries applications.(Wang et al. 2009; Choi et al. 2011) An earlier report has attributed this to Li interactions with the residual oxygen-containing functional groups within the graphene sheet, SEI formation and the barrier in Li ions diffusion out of a well-ordered graphene structure.(Persson et al. 2010) The first cycle discharge and charge capacities calculated from the discharge/charge curves in Figure 4.9a were 1326.1 and 749.9 mAh/g (or ICL of 43.4%) for SnO$_2$@TRGO-5; and 1141.2 and 435.0 mAh/g (or ICL of 61.9%) for SnO$_2$@TRGO-10. Assuming the ICL caused by tin oxide reduction remained the same as 300 mAh/g for tin oxide in the SnO$_2$@TRGO composites, the ICL corresponding to the reduction of tin oxide to tin in SnO$_2$@TRGO-5 was calculated to be 300 mAh/g×(1-0.05-0.21)=222 mAh/g, while the corresponding value
for SnO$_2$@TRGO-10 was 300 mAh/g$\times$(1-0.09)=273 mAh/g. The ICL contributed by the graphene shell on the tin oxide surface was calculated to be 354.2 mAh/g for SnO$_2$@TRGO-5 and 433.2 mAh/g for SnO$_2$@TRGO-10 respectively. Since SEI formation should occur to the same extent on these two SnO$_2$@TRGO composites due to the compactness of the graphene shell, their difference (79 mAh/g) in ICL could be attributed to a greater content of residual oxygen-containing functional groups and/or the difficulty of Li ions diffusion in SnO$_2$@TRGO-10. The discharge capacity of SnO$_2$@TRGO-10 in the first cycle was also smaller than SnO$_2$@TRGO-5, suggesting that the ICL difference was mainly caused by the greater difficulty of Li ions diffusion in SnO$_2$@TRGO-10.

Other than the differences in ICL, voltage hysteresis in cycling could also be used to indicate the transport limitations in electron and/or Li ions transfer (Palacin 2009). The following order was found in the voltage hysteresis of the composites: SnO$_2$@TRGO-10 > SnO$_2$@TRGO-5 ~ SnO$_2$. Since there was good electrical contact between SnO$_2$ and TRGO in the composites, the larger voltage hysteresis in SnO$_2$@TRGO-10 was caused primarily by the resistance of a thick graphene sheet in Li ions transport. The effect was particularly noticeable because of the extensiveness of graphene encapsulation used in the study (individual wrapping of active particles). In these composite particles Li ions could only diffusion across the basal plane of the graphene sheets. The anisotropic diffusion of Li ions in graphite is relatively well known, e.g., a previous study has shown high Li ions diffusivity in the direction parallel to the graphene plane ($\sim$10$^{-7}$-10$^{-6}$ cm$^2$/s) as opposed to across the basal plane ($\sim$10$^{-11}$ cm$^2$/s). Hence, the resistance to across-plane Li ions diffusion should increase with thickness. On the other hand, the in-plane vacancies formed
during graphene oxidization could actually benefit Li ions diffusion as they could serve as the additional entry points for Li ions passage. The thermal reduction of GO to TRGO was unlikely to fully remediate these defects. This was likely the case for SnO$_2$@TRGO-5. The likelihood of these defects forming a contiguous ‘leak’ path for Li ions was smaller for a thick TRGO layer. Hence, the greater resistance of SnO$_2$@TRGO-10 to Li ions diffusion could be understood on ground of two reasons: increase in passage resistance with thickness and the smaller number of Li ions leak paths in thick layers.

**Figure 4.10**  a) TEM, b) FESEM and c) STEM images, d) C1s XPS spectrum and e) cycle stability of SnO$_2$@CRGO-5. SnO$_2$@CRGO-5 was prepared by the following procedure: 50 mg SnO$_2$@GO-5 was dispersed in 10 mL hydrazine (N$_2$H$_4$, 53%) for 0.5 h with stirring. The recovered solid was washed by DI water for 3 times.

From the cycle stability comparison in Fig 4.9b, SnO$_2$@TRGO composites were clearly an improvement over pristine SnO$_2$. However, the side effect of graphene
encapsulation is also evident: decrease in specific capacity (the capacity of SnO₂@TRGO-10 was lower than that of SnO₂ for the first 30 cycles, it only surpassed the latter in prolonged cycling – 461 mAh/g in the 50th cycle vs. 379 mAh/g for SnO₂). A comparison between the first and second cycles showed that Li ions transport was more difficult in the first cycle perhaps due to the insertion of Li into a host previously uninhabited by Li ions. SnO₂/graphene composites in previous studies often took more than 20 cycles to stabilize the discharge/charge capacities. (Paek et al. 2009; Zhang et al. 2010; Liang et al. 2011; Zhang et al. 2011) There was also report of significant charge capacity decrease (from ~800 mAh/g in 2nd cycle to ~600 mAh/g in 20th cycle). (Liang et al. 2011) On the contrary the charge capacity of SnO₂@TRGO composites in this study was stable from the 3rd cycle onwards. The difference could be attributed to a more effective SEI formation process in our case. Stabilization of SEI is difficult on Sn surfaces because the large volume excursion in discharging and charging exposes new surfaces where SEI needs to be reformed. SEI formation is however very stable and effective on graphitic surfaces (SEI on graphene is similar to that on graphite). (Ji et al. 2011) In SnO₂@TRGO composites where the surface of tin oxide/tin was fully covered by graphene sheets, a stable SEI layer could be formed relatively quickly. The cycle stability of SnO₂@TRGO-10 led us to conclude that 9 wt% graphene was adequate to completely encapsulate the SnO₂ surface for stable SEI formation. The capacity fading in SnO₂@TRGO-5 (charge capacity of 729 mAh/g in the 2nd cycle and 517 mAh/g in the 50th cycle) could be caused by the disruption of intSnO₂-graphene contact during the partial reduction of tin oxide to tin. This was confirmed experimentally by reducing SnO₂@GO-5 with hydrazine hydrate. The resulting product was designated as SnO₂@CRGO-5. No tin oxide was reduced to tin by this procedure although XPS confirmed the reduction of GO to graphene (Figure
4.10). The cycling performance of SnO$_2$@CRGO-5 was much better although the capacity was substantially lower than that of SnO$_2$@TRGO-5. This could be attributed to the lower Li ions across-plane diffusivity in chemically reduced GO compared with thermally reduced GO - the defects in oxidation could be more easily remediated by chemical reduction than thermal reduction thereby eliminating Li ions diffusion through the defect channels. (Gao et al. 2009)

Figure 4.11 a) Rate performance of SnO$_2$@TRGO-5 and SnO$_2$@TRGO-10 electrodes at current densities from 100 to 1000 mA/g. b) Nyquist plots of SnO$_2$, SnO$_2$@TRGO-5, SnO$_2$@CRGO-5 and SnO$_2$@TRGO-10 electrodes before cycling at a discharged potential of 1.6 V (versus Li/Li$^+$) in the 100 kHz to 0.1 Hz frequency region.
The rate performance of SnO$_2$@TRGO composites was evaluated by varying the current density from 0.1 to 1 A/g in the same 0.005-2 V voltage window (Figure 4.11a). The rate performance of SnO$_2$@TRGO-5 was noticeably higher than that of SnO$_2$@TRGO-10 because of the aforementioned good Li ion conductance of a thinner graphene sheet. SnO$_2$@TRGO-5 was able to maintain stable recharge and delivered 423 mAh/g at a current density of 1 A/g in the 20th cycle, while the corresponding value for SnO$_2$@TRGO-10 was only 144 mAh/g. At the ‘standard’ current density of 0.1 A/g, the charge capacity of SnO$_2$@TRGO-5 was ~700 mAh/g in the 30th cycle. It should be emphasized that this good rate performance was achieved without any carbon additive, and was measured in a narrower voltage window (0.005-2 V) than previously reported SnO$_2$-graphene composites (0-3 V) (Zhang et al. 2010; Zhong et al. 2011).

For additional insights the electrochemical impedance spectra of SnO$_2$, SnO$_2$@TRGO-5, SnO$_2$@CRGO-5 and SnO$_2$@TRGO-10 before cycling were measured in the 100 kHz to 0.1 Hz frequency range (Figure 4.11b). The Nyquist plots of the results show a depressed semicircle in the high to middle frequency region and an inclined straight line in the low frequency region. According to Abe and co-workers, (Yamada et al. 2009) the impedance representing the resistances in Li ions storage could consist of: (i) Li ions transport in the electrolyte ($R_{\text{sol}}$), (ii) Li ions transport through the SEI ($R_{\text{SEI}}$), (iii) Li ions transfer at the host/electrolyte interface ($R_{\text{ct}}$), (iv) Li ions transport in the host material, and (v) electron transport in the host and at host material/current collector interface ($R_{\text{e}}$). They believed that Li ions transport in the electrolyte (i) and electron transport (v) are generally efficient and appear collectively as the $Z’$ intercept on the $Z’$ axis at the high frequency end. In the event that electron transport in the
electrode (consisting of electron transport in the host, between the host particles and at the host/current collector interface) is not effective, the limitations would also contribute to the semicircle in the high to middle frequency region. At the open circuit potential of 1.6 V where SEI was not yet formed, Li ions transport in the SEI (ii) could be omitted in the analysis. Li ions diffusion in SnO₂ (iv) would give rise to a classical Warburg impedance response (an inclined straight line at low frequencies). Hence, the semicircles in Figure 4.11b could be attributed to mostly a combination of factors (iii) and (v) and the difference in the semicircle diameter (described generically as ‘charge transfer resistance’) to the difference in Li ions transport across the basal planes of graphene and electron transport in the electrode. The EIS measurements indicate lower charger-transfer resistance in all of the SnO₂/graphene composites than in graphene-free SnO₂. Hence, the as-prepared SnO₂@TRGO structure was more electrically conductive. Charge transfer resistance was higher in SnO₂@TRGO-10 because of a thicker graphene sheet, which increases the resistance to Li ions transport. Hence, it may be concluded that SnO₂@TRGO-5 had the better balance of electrical and Li ions transport properties. Charge transfer resistance was also measured after 50 discharge-charge cycles (Figure 4.12). There was a significant increase in the charge-transfer resistance of the SnO₂-only electrode while the SnO₂@TRGO-5 electrode showed no significant difference. This is indication of the preservation of the good electrical contact between Sn/SnO₂ NPs and graphene sheets and the absence of NP coalescence, which explains the good cycle stability and good rate performance of SnO₂@TRGO-5. The electrical conductivity of chemically reduced GO was higher than that of thermally reduced GO because of a lower defect content, yet the measured charge-transfer resistance of SnO₂@CRGO-5 was higher than that of SnO₂@TRGO-5. This was probably because of the small Li ions across-plane diffusivity of the former as
discussed before. From the above comparison, it is obvious that thermally reduced GO layers provide the good electronic conductivity to improve the electrical connectivity of the active materials while at the same time decrease the resistance to Li ions transport in graphene to improve the accessibility of the Li storage host (Sn).

Figure 4.12 Nyquist plots of SnO2, SnO2@TRGO-5 after 50 discharge/charge cycles at a discharged potential of 1.6 V (versus Li/Li⁺). Frequency range: 100 kHz to 0.1 Hz.

4.4 Conclusion

Good electrochemical reversibility for Li ions storage was shown by SnO2@TRGO core-shell composites with SnO2 NP aggregates individually wrapped in graphene shells of different thicknesses. The SnO2@TRGO composite with 9 wt% graphene coating (SnO2@TRGO-10) had outstanding cycling stability with little or no capacity fading between the 2nd and the 50th cycle (charge capacity was 488 mAh/g in the 2nd cycle and 463 mAh/g in the 50th cycle). The SnO2@TRGO composite with 5 wt% graphene coating (SnO2@TRGO-5) delivered even higher discharge/charge capacities (charge capacity was 729 mAh/g in the 2nd cycle and 517 mAh/g in the 50th cycle) but
some capacity decay was noticeable probably due to some impairment of the graphene-SnO$_2$ connectivity while SnO$_2$ was partially reduced to tin during the thermal treatment. Nonetheless a higher rate performance (charge capacity of 423 mAh/g at a current density of 1 A/g) was possible with this composite because of a better balance of electrical conductivity and ionic conductivity. We also found that thermally reduced GO was more suitable than chemically reduced GO to compound with high capacity anode materials for lithium ion battery applications.
CHAPTER 5  LITHIUM TITANATE

SURFACE COATING OF TIN-BASED HIGH CAPACITY Li ION ANODE MATERIALS

5.1 Introduction

The current interest in electric vehicles and energy storage for grid-scale applications has driven up the demand for lithium ion batteries with higher energy densities. Materials innovations are the most promising approach to deliver the necessary breakthrough in technology. Lithium-alloying elements such as Sn and Si can easily increase the Li ions storage capacity of the anode by a factor of two to ten over the current carbon-based anodes. However, earlier discussions have pointed out three significant challenges in the development of high-capacity anode materials: high ICL, poor capacity retention in long-term cycling and low rate performance. (Han et al. 2005; Kim et al. 2005; Lou et al. 2006; Sun et al. 2006) The solution to these problems is continually being improved through materials design and synthesis. (Wang et al. 2006; Wang et al. 2006; Derrien et al. 2007; Park et al. 2007; Yu et al. 2007; Chan et al. 2008; Chen et al. 2008; Deng et al. 2008; Kim et al. 2008; Kim et al. 2008; Deng et al. 2009) For example, nanostructuring has been used to decrease the Li ions diffusion length and to increase the tolerance to strains caused by the Li ions insertion/extraction reactions. (Kim et al. 2005; Cui et al. 2007; Lee et al. 2007; Kim et al. 2008) Compositing the active material with a softer material capable of stress absorption and strain relief is another approach. (Noh et al. 2005; Wang et al. 2006; Wang et al. 2006;
For the latter carbon has been the most commonly used compositing medium. Due to the low graphization degree of carbon in the composite, the ICL of the composite is often rather large. (Sun et al. 2006; Lou et al. 2009; Lou et al. 2009; Deng et al. 2010) Other composites such like SnO$_2$/TiO$_2$, (Chen et al. 2010) Si/SnO$_2$ (Lee et al. 2010) have also been investigated as anode materials for LiONs.

SnO$_2$ has a high Li ions storage capacity and is relatively easy to synthesize by environmentally friendly methods from low cost resources. (Courtney et al. 1997) Hence, it has been extensively studied as an anode material for the LiONs. Spinel LTO was also identified as an alternative anode material. It has very good reversibility (it incurs zero strain in Li insertion and extraction reactions) and excellent rate performance, and no SEI formation in the 1.0-2.0 V voltage window. (Jiang et al. 2007) SEI, however, does form at potentials below 1.0 V. (Shu 2008; Shu 2009) Cycling LTO between 0.0-2.0 V was found to cause a first cycle ICL of about 70 mAh/g but capacity in this lower potential region was stable from the 2$^{nd}$ cycle onwards. (Shu 2009) SnO$_2$/Li$_x$Ti$_5$O$_{12}$ (Wang et al. 2008) and Sn/Li$_x$Ti$_5$O$_{12}$ (Cai et al. 2010; Sivashanmugam et al. 2011) composites have been explored as anode materials before but the composites in these early studies were random mixtures and as a result the electrochemical performance was not satisfactory. The specific capacity was generally low (the highest charge capacity in the 1$^{st}$ cycle was 321mAh/g). We hypothesize that LTO could be used more effectively as a protective coating on high capacity anode materials to reduce the ICL and to concurrently improve the electrochemical performance of the latter. LTO has several advantages as a protective coating. Firstly, compared with high quality carbon coatings which can only be prepared at high
temperature or pressure in an inert atmosphere, a LTO coating can be prepared in air at lower temperatures (Jiang et al. 2007); Secondly, LTO with its high Li ions mobility (Wagemaker et al. 2008) may also facilitate the transport of Li ions to the active material, and hence improving the rate performance of the active material.

![Figure 5.1 Schematic illustration showing hollow tin oxide particles with and without the LTO coating. For the uncoated hollow tin oxide particles, an unstable SEI layer is formed in the 1st cycle resulting in a larger irreversible consumption of Li ions. With the LTO coating, a more stable SEI layer is formed in the 1st cycle; reducing the irreversible consumption of Li ions and also improving material cyclability. The high Li ions mobility in LTO could also facilitate Li ions transport to the core to increase rate performance.](image)

The viability of using LTO to decrease the ICL and to improve other aspects of tin oxide particles in LiON applications is investigated in this part of the thesis study. SnO\textsubscript{2} is very amenable to the LTO modification. Specifically, tin oxide particles with a hollow core and a porous shell aggregated from primary tin oxide NPs were used as the active Li ions storage compound. The hollow interior and the porosity in the shell provided the space for volume excursion in Li-Sn reactions during discharging and charging. The LTO coating shielded most of the direct contact between tin oxide and the electrolyte and as such the ICL due to SEI formation was reduced to that of LTO. The SEI formed was also more stable than that on a native Sn-based anode resulting in some cyclability improvement. Furthermore, there was also an increase in the rate
performance. Figure 5.1 is a simplified illustration of the advantages of LTO surface coating.

5.2 Experimental Section

5.2.1 Preparation of Hollow SnO$_2$/Li$_4$Ti$_5$O$_{12}$ Core-shell Composite Particles

Hollow tin oxide NPs were prepared by the Lou method (Lou et al. 2006) with some modifications. Specifically calculated amounts of urea and potassium stannate trihydrate ($\text{K}_2\text{SnO}_3\cdot3\text{H}_2\text{O}$) were dissolved in 35 mL of an ethanol/water mixture (40% ethanol by volume) to final concentrations of 0.1 M and 16 mM, respectively. After stirring for 5 min and aging for 40 min, a white translucent solution was formed. The solution was transferred to a 50 mL Teflon lined stainless steel reactor and hydrothermally treated at 150 $^\circ$C for 24 h. A white precipitate was obtained which could be recovered by centrifugation followed by washing with ethanol and deionized water, and drying in vacuum at 50 $^\circ$C for 12 h.

The hollow tin oxide NPs formed by the above procedures were deposited with titantia by two methods. In the first method, 1 g titanium isopropoxide (TTIP) was dissolved in 30 mL ethanol and stirred for 2 min. 0.5 g of hollow tin oxide was added to the TTIP solution and ultrasonicated for 15 min. After stirring for 0.5 h the mixture was placed on an orbital shaker and incubated for 12 h. The mixture was then centrifuged to remove the excess titania sol. The solid phase separated as such was condensed with ethanol/water (1:1) under magnetic stirring for 2 h at room temperature. The final sediment was collected by centrifugation and washed with deionized water and ethanol. It was then vacuum dried at 50 $^\circ$C for 12 h.
The second coating method was based on the procedure of Tang. (Wang et al. 2006) In this case, 0.2 g hollow tin oxide was ultrasonically dispersed in 40 mL of a ethanol/acetonitrile mixture (3:1 v/v). 0.3 mL ammonia solution (32%) was then added under vigorous stirring at room temperature. Finally, 0.5-0.8 mL of titanium tetrabutoxide (TBOT) in 10 mL ethanol/acetonitrile (3:1 v/v) was slowly added to the above suspension with stirring. After stirring for 2 h, the solid product was recovered by centrifugation followed by washing with deionized water twice. It was then dried in a vacuum oven at 50 °C for 12 h.

The titania coating was then converted to a LTO shell by the following procedure: 6 mmol LiOH was dissolved in 30 mL deionized water with stirring. The titania-coated hollow tin oxide NPs were ultrasonically dispersed in the LiOH aqueous solution. The mixture was transferred to a 50 mL Teflon-lined reactor and sealed. The reactor was heated to 180 °C and kept at this temperature for 20 h to form a LTO coating on the hollow tin oxide particles. The solid phase was recovered by centrifugation followed by washing with ethanol and deionized water; and vacuum drying at 50 °C for 12 h. The final product was obtained after calcination at 800 °C for 2 h.

5.2.2 Characterization

The intermediate and final products prepared above were characterized by FESEM and STEM on a JEOL JSM-6700F operating at 5 and 25 kV respectively. High-resolution TEM (HRTEM) and EDX were performed on a Philips FEG-CM300 operating at 200 kV. Powder XRD was recorded on a Shimadu XRD-6000 using Cu Kα radiation.
5.2.3 Electrochemical Measurements

The candidate anode material was mixed with 10 wt% PVDF binder and 10 wt% Super P (Timcal) in NMP into a homogeneous slurry. The slurry was applied to a copper disc current collector and dried in vacuum at 120 °C overnight. Li test cells were assembled in an argon-filled glove box using a Li metal foil doubled as the counter and reference electrodes; and 1 M LiPF₆/ EC+DEC (1:1 w/w) as the electrolyte. The cells were tested on a Maccor Series 2000 battery tester at ambient conditions at constant charge and discharge current densities in the 5 mV to 2 V voltage window. CV was performed on an AutoLab Electrochemical System in the 0-3 V window at 0.2 mV/s. EIS was also carried out on the same equipment using a FRA2 add-on module. The frequency range for the impedance measurements was 100 kHz to 0.01 Hz. The perturbation amplitude was ± 5 mV AC.

5.3 Results and Discussion

5.3.1 Structure Analysis

Hydrothermal processing was selected in this project to construct the designed core-shell structure. Classical epitaxial deposition or solution deposition method was unable to achieve the same in this case. This is because LTO could only be formed under high temperature or high pressure conditions, making it difficult to apply the usual kinetic control strategy for the heterogeneous nucleation of the shell on the core. The LTO coating was prepared by a two-step process: a titania shell was first created by the hydrolysis-condensation of titanium alkoxide in the presence of preformed tin oxide NPs. It was then converted into LTO by reacting with LiOH under hydrothermal conditions.
Figure 5.2  

The major steps in the preparation process and the evolution of the composite are illustrated in Figure 5.2a. Hollow tin oxide NPs were first prepared by a template-free method (Lou et al. 2006) which involved the hydrothermal treatment of stannate in an ethanol-water mixture and inside-out Ostwald ripening. Titania was then coated on the exterior of the preformed tin oxide NPs by controlling the hydrolysis rate of TTIP or TBOT. A LTO shell was then formed by the reaction between the titania shell and lithium hydroxide in water at 180 °C under hydrothermal conditions for 20 h. In the last process, excess LiOH was used to ensure the complete conversion of titania to
LTO. Finally, the SnO$_2$/LTO composite was calcined in air to increase the crystallinity of the final composite product.

![Figure 5.3](image)

**Figure 5.3** Line scan image of a SO/LTO-30 particle.

Figure 5.2b, c are typical TEM (b) and SEM (c) images of the SnO$_2$ NPs. These spherical hollow NPs were 300–800 nm in size with a shell thickness of 50-150 nm. Upon closer examination the shell was found to be aggregated from small primary NPs about 10 nm in diameter (Figure 5.2c). For the first coating method, the hollow SnO$_2$ NPs were aged in a titantia sol for 12 h and then condensed by an ethanol/water mixture (SO/TO-5). A thin uniform coating could be confirmed by STEM imaging (Figure 5.2d). The thickness of the coating on the SnO$_2$ NPs was estimated to be about 5 nm. Due to the low affinity between tin oxide and TTIP, the coating formed by this method was relatively thin. A thicker uniform coating layer could however be formed by the Tang’s method. (Wang *et al.* 2006) Here stable SnO$_2$@TiO$_2$ core-shell particles were prepared by the hydrolysis of TBOT catalyzed by ammonium ions in the mixed solvent (SO/TO-15 and SO/TO-30). The thickness of the coating could be varied by controlling the amount of TBOT used (0.5 mL for SO/TiO-15 and 0.8 mL for SO/TiO-
30). In the TEM images of SO/TO-15 and SO/TO-30 in Figure 5.2e, f; a shell thickness of 15 nm for SO/TO-15 and 30 nm for SO/TO-30 could be measured. The titania coating also imparted a smoother texture to the hollow tin oxide particle exterior. This could be explained by the adsorption of \( \text{NH}_4^+ \) on the surface of the tin oxide particles, enabling a more uniform distribution of the negatively charged titania precursor in the surrounding and consequently a more homogenous condensation process leading to uniform deposition. The uniform coating was formed under diffusion-controlled kinetics with the mixed solvent controlling the rate of diffusion of the titania precursor.

In the final step of the preparation SO/TO-5, SO/TO-15 and SO/TO-30 were reacted with LiOH and calcined to form \( \text{SnO}_2@\text{Li}_4\text{Ti}_5\text{O}_{12} \) core-shell composites (SO/LTO-5, SO/LTO-15 and SO/LTO-30). The morphology of the thin shelled SO/LTO-5 composite is shown in Figure 2g, j. The LTO coating could not be easily identified because of the thinness of the shell. The LTO coating was more visible in SO/LTO-15 and SO/LTO-30. TEM (Figure 5.2h, i) estimated thickness of \( \sim15 \) nm for SO/LTO-15 and 30 nm for SO/LTO-30. The uniformity of the coating was also confirmed. In the HRTEM mode, lattice fringes could also be detected in the coating on SO/LTO-30. The interplanar spacing of 4.8 Å corresponds well with the \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) (111) planes. SEM examination (Figure 5.2j-l) revealed more particle rupture in SO/LTO-15 and SO/LTO-30 than SO/LTO-5. This was most likely caused by the differential expansion of the core and shell components during hydrothermal processing, which was more severe in composites with a thicker shell.
Figure 5.4 Element mapping of a) SO/LTO-15, b) SO/LTO-30.
5.3.2 EDX/XRD Analysis

The core-shell structure and the composition of the composite were also confirmed by other methods. The element maps from EDX spectroscopy were used to ascertain the core-shell structure. Using SO/LTO-30 as a typical example, three SO/LTO-30 particles were used to sample the distributions of tin, oxygen and titanium. A line scan image shows the concentration of Ti in the shell area outside the hollow SnO\(_2\) core (Figure 5.3). Figure 5.4 further confirmed that the presence of titanium was confined to the shell area. The Ti:Sn ratios in SO/LTO-5, SO/LTO-15 and SO/LTO-30 were determined to be 1:33, 1:5.7, 1:4.2 by EDX, consistent with the increasingly thicker shells. The corresponding weight fractions of LTO in these composites were 1.8\%, 9.7\% and 12.7\% respectively. XRD was used to determine the material phases in SnO\(_2@\)Li\(_4\)Ti\(_5\)O\(_{12}\). All the peaks in the XRD pattern of calcined hollow tin oxide spheres (800 °C for 2 h in air, labeled as SO in Figure 5.5) could be indexed to
crystalline SnO\textsubscript{2} (cassiterite, JCPDS Card No. 41-1445). The broad fwhm (full width at half-maximum) of the diffraction peaks is indication of the smallness of the constituent primary crystalline SnO\textsubscript{2} NPs. For the SnO\textsubscript{2}@Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} composite, four additional peaks appeared at 18.5°, 35.6°, 43.4° and 62.9°, which correspond well with the (111), (311), (400) and (440) diffractions of spinel LTO (JCPDS Card No. 26-1198). The intensity of these LTO peaks increased as the thickness of the coated layer increased.

5.3.3 Reversible Lithium Storage Properties

For the examination of the effects of LTO coating on the electrochemical performance of SnO\textsubscript{2}, hollow tin oxide NPs after calcination (800 °C for 2 h in air) and SnO\textsubscript{2}@Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} composites with different shell thicknesses were used as the anodes in half cell measurements. Testing was carried out under constant current conditions (100 mA/g) in the 5 mV-2 V voltage at room temperature. The first cycle discharge and charge capacities and ICL for each of these materials are summarized in Table 5.1. The ICL due to SEI formation and the discharge capacity in the 30\textsuperscript{th} cycle of SO, SO/LTO-5, SO/LTO-15 and SO/LTO-30 are also shown in Figure 5.6. Figure 5.7a shows the first cycle charge/discharge curves of pristine hollow tin oxide and SO/LTO-15 (the first cycle charge/discharge curves of other SnO\textsubscript{2}@Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} composites are similar in features). The first cycle charge and discharge capacities of SO/LTO-15 were 600.0 and 1030.9 mAh/g respectively, while the corresponding values for the uncoated SnO\textsubscript{2} hollow NPs were 614.3 and 1340.0 mAh/g measured at the same current density. The overall ICL therefore decreased from 725.7 to 430.9 mAh/g. The voltage plateau around 1.0-0.8 V for the hollow tin oxide and around 0.9-0.7 V for the SnO\textsubscript{2}@Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} composite in the discharge curves of Figure 5.7a could be attributed to the reduction of tin oxide to tin(Han et al. 2005; Demir-Cakan et al.)
2008). The corresponding ICL as measured from Figure 4a for the hollow tin oxide NPs was 300 mAh/g. Since the SnO$_2$@Li$_4$Ti$_5$O$_{12}$ composite contained both Sn and Ti, the ICL corresponding to the reduction of tin oxide to tin in SnO$_2$@Li$_4$Ti$_5$O$_{12}$ was calculated from the measured values by the equation below. In the equation R is the atomic ratio of Sn:Ti in the SnO$_2$@Li$_4$Ti$_5$O$_{12}$ composite; and 150.71 g/mol and 459.1 g/mol are the molecular weights of SnO$_2$ and Li$_4$Ti$_5$O$_{12}$ respectively.

\[
C_{\text{reduction of tin oxide to tin}} = \frac{300 \text{ mAh/g} \times R \times \frac{150.71 \text{ g/mol}}{\text{mol}}}{R \times \frac{150.71 \text{ g/mol}}{\text{mol}} + \frac{1}{5} \times \frac{459.1 \text{ g/mol}}{\text{mol}}}
\]  

(5-1)

The ICL due to SEI formation could then be calculated as the difference between the measured ICL and the ICL attributable to tin oxide reduction. The calculated values were 425.7 mAh/g for the hollow tin oxide NPs and 159.5 mAh/g for SO/LTO-15. Hence, a LTO coating could reduce the ICL associated with SEI formation by as much as 62.5%. This is confirmation that a LTO coating could effectively reduce losses associated with SEI formation on Sn surfaces. However, the value of ICL is still higher than the ICL on LTO in the literature (Shu 2009), suggesting that some tin oxide was still exposed to the electrolyte. Due to the low specific capacity of LTO, composite particles with thicker shell thickness would result in lower discharge capacities; which is evident in Table 5.1. The ICL due to SEI formation for SO/LTO-5 and SO/LTO-30 were 171.4 and 142.3 mAh/g respectively. The effect of shell thickness on ICL due to SEI formation was therefore not very significant. This suggests that a dense LTO layer which could satisfactorily insulate the underlying tin surface from the contact with electrolyte. It also implies the LTO coating should be as thin as possible from the aforementioned specific capacity considerations. The thinnest LTO that could be formed and delivered the ICL reduction functionality in this study was ~5 nm in thickness (i.e., SO/LTO-5).
Table 5.1 Summary of electrochemical performance of SO and SO/LTO composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>a [mAh/g]</th>
<th>b [mAh/g]</th>
<th>c</th>
<th>d [mAh/g]</th>
<th>e [mAh/g]</th>
<th>f [mAh/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO</td>
<td>1340.0</td>
<td>614.3</td>
<td>45.8%</td>
<td>725.7</td>
<td>300.0</td>
<td>425.7</td>
</tr>
<tr>
<td>SO/LTO-5</td>
<td>1155.2</td>
<td>689.2</td>
<td>59.7%</td>
<td>466.0</td>
<td>294.6</td>
<td>171.4</td>
</tr>
<tr>
<td>SO/LTO-15</td>
<td>1030.9</td>
<td>600.0</td>
<td>58.2%</td>
<td>430.9</td>
<td>271.4</td>
<td>159.5</td>
</tr>
<tr>
<td>SO/LTO-30</td>
<td>983.8</td>
<td>580.3</td>
<td>59.0%</td>
<td>403.5</td>
<td>261.2</td>
<td>142.3</td>
</tr>
</tbody>
</table>

a. 1st cycle discharge capacity  
b. 1st cycle charge capacity  
c. Columbic efficiency  
d. Overall ICL  
e. ICL due to reduction of tin oxide to tin  
f. ICL due to SEI formation

The cycling performance of the composites was also measured at 100 mA/g and Figure 5.7b shows their comparison. The presence of a LTO coating was also found to improve the cycling performance of hollow tin oxide NPs. For example, the discharge capacity of uncoated hollow tin oxide NPs decreased to 75.6 mAh/g by the 30th cycle whereas the corresponding value for SO/LTO-5 was 284.8 mAh/g. This could probably be attributed to the quality of the SEI formed on LTO. However, the LTO shell in the current implementation was not totally resistant to the volume excursion in the core area; and hence exfoliation of the LTO coating could occur during cycling. This was most noticeable for SO/LTO-5 which had the thinnest LTO coating. For SO/LTO-15 and SO/LTO-30, the discharge capacities were 656.7 and 621.5 mAh/g in the second cycle, and decreased to 457.1 and 431.5 mAh/g in the 30th cycle. The better performance of SO/LTO-15 and SO/LTO-30 relative to SO/LTO-5 was clearly a shell thickness effect. The specific capacity of SO/LTO-15 was higher than that of SO/LTO-30 because of its lower LTO content. Although capacity decay could still be observed, the cycling performance of tin oxide NPs with LTO coating layer showed significant
improvements over the uncoated tin oxide NPs. The capacity decay was mostly caused by the exfoliation of the LTO coating layer after repetitive expansion and contraction of the anode. We believe through further work, the LTO coating can be optimized to provide a more stable cycling performance.

Figure 5.6  ICL due to SEI formation and discharge capacity in the 30\textsuperscript{th} cycle of SO, SO/LTO-5, SO/LTO-15 and SO/LTO-30.

The cyclic voltammograms (CVs) of hollow tin oxide NPs and SO/LTO-15 in Figure 5.8 show the electrochemical changes that occurred in the initial cycling of these materials. In the first cycle, two cathodic peaks corresponding to reduction of tin oxide to tin and the lithiation of tin appeared at 0.5 and 0.01 V for pristine SnO\textsubscript{2}; and at 0.64 and 0.07 V for the SO/LTO-15 composite.(Aurbach \textit{et al.} 2002) The shift could be attributed to the facilitated transport of Li ions through the LTO layer. A feeble cathodic peak at 1.5 V for SO/LTO-15 in the first cycle could be due to Li ions intercalation into LTO. The peak corresponding to the reduction of tin oxide to tin was greatly reduced in the second and third cycles. The broad cathodic feature in the 1.3-0.8 V region may be assigned to SEI formation. It was more subdued in SO/LTO-15, indicating a lower extent of SEI formation on the LTO coated composite. The
prominent anodic peak at ~0.6 V common to both electrodes may be attributed to the delithiation reaction. The other anodic peak at 1.0-1.8 V is likely to be due to the decomposition of Li₂O. (Aurbach et al. 2002; Han et al. 2005; Demir-Cakan et al. 2008)

**Figure 5.7**  
a) Voltage profiles of SO and SO/LTO-15 at 100 mA/g. b) Cycling performance of SO, SO/LTO-5, SO/LTO-15 and SO/LTO-30 at 100 mA/g.
The cycling performance of SO/LTO-15 at the higher current densities of 200 and 1000 mA/g is shown in Figure 5.9. The uncoated tin oxide NPs was unable to release the stored Li ions at these high current densities. Similar discharge/charge capacities were obtained. Despite some increase in the ICL at 1000 mA/g, an average discharge capacity of 439 mA/g was available for at least 30 cycles at this high current density. Such display of good rate performance could be due to the LTO coating acting as a funnel to draw the Li ions towards the active material. (Reitmeier et al. 2009)

The stability of the core-shell structured SnO₂/LTO composite was also evaluated by EIS. Specifically the impedance of SO/LTO-15 at the end of a complete cycle (taken at open circuit conditions (~1.5 V) after the cell was rested for 5 h) in continuous cycling was measured. (Figure 5.10). The resulting Nyquist plot shows the typical response of a semi-circular arc in the mid-to-high frequency range and an inclined straight line at the low frequency end. By usual assignments the semi-circular arc may be attributed to the charge transfer resistance at the electrode (consisting of electrode kinetics and electron transport in the electrode, see Chapter 4); the inclined straight line to the
limitations in transport processes. Impedance measurements recorded a gradual decrease in the charge transfer resistance from the 3rd to the 30th cycle. The decrease in charge transfer resistance with cycling has been reported before (Feng et al. 2009) and was used to suggest electrode stability. At the minimum there was no increase in the charge transfer resistance to suggest particle aggregation. The structural stability of the composite was also examined by comparing the morphology of the SO/LTO-15 electrode before and after 30 cycles (Figure 5.11). The results showed good retention of the overall spherical morphology without indication of shell rupture. This may be attributed to the containment effect of the LTO layer – keeping the tin based material within the hollow core area while the free volume in the latter accommodated the volume changes in cycling.

![Figure 5.9](image)

**Figure 5.9** Cycling performance of SO/LTO-15 at 200 and 1000 mA/g.
Figure 5.10  Nyquist plot of SO/LTO-15 at the end of 3\textsuperscript{rd}, 10\textsuperscript{th} and 30\textsuperscript{th} cycles. Impedance measurements were taken at the open circuit condition after the cell was rested for 5 h after cycling.

Figure 5.11  SEM micrographs of a) the as-prepared SO/LTO-15 electrode, b) a SO/LTO-15 electrode after 30 cycles.

5.4 Conclusion

In conclusion, SnO$_2$@Li$_4$Ti$_5$O$_{12}$ core-shell composite particles with different shell thicknesses were prepared; which improved the electrochemical performance of the
uncoated particles. The coating was effective in reducing the ICL due to SEI formation on the anode surface. Specifically a LTO coating on hollow tin oxide nanoparticle aggregates could lower the ICL for SEI formation from 425.7 mAh/g to 142.3 mAh/g. The cycling performance of hollow SnO$_2$@Li$_4$Ti$_5$O$_{12}$ was also a significant improvement over the pristine uncoated hollow tin oxide NPs. The discharge capacity of hollow tin oxide particles was only 75.6 mAh/g in the 30$^{th}$ cycle whereas the corresponding value for SO/LTO-15 was 457.1 mAh/g. Unlike some other studies, the specific capacities were calculated based on the weights of the composite, and not on the weights of active materials only. A LTO layer ~5 nm in thickness was sufficient to shield the contact between tin oxide and electrolyte. However, thicker LTO layers were more resistant to exfoliation caused by the volume excursion of the core material during cycling. Hence, there exists some optimal shell thickness which balances the two opposing effects. Moreover, the LTO layers were also found to improve the rate performance of the active material. The LTO coating method is generic, and can be a new strategy for improving the electrochemical performance of other high capacity anode materials.
CHAPTER 6  ANODE MATERIALS FOR LITHIUM ION BATTERIES WHICH CAN BE USED WITHOUT CONDUCTIVE ADDITIVES

6.1 Introduction

Lithium ion batteries are undoubtedly the rechargeable battery with the highest energy density in the market today. New applications such as full or hybrid electric vehicles; and the energy storage systems in distributed power generation/smart grids require both high energy density and high power density (i.e., the ability to charge and discharge quickly). Supercapacitors surpass batteries in power density but are limited in energy density. Consequently, batteries and supercapacitors can be integrated at the systems level to provide the solution to high energy density concurrently with high power density. A more appealing solution is to increase the power density of lithium ion batteries at the materials level. In this regard some studies have shown the feasibility of improving the rate performance of cathode materials by various strategies such as modifying the crystal structure (Kang et al. 2006), creating a fast ion-conductive surface phase(Kang et al. 2009), or forming a self-assembled three-dimensional bicontinuous nanoarchitecture(Zhang et al. 2011). However, the improvement of the rate performance of anode materials while keeping their specific capacity intact remains a significant challenge.
The reduction in the active material length scale is an effective method to increase the rate performance of the electrode material. This is because the time constant for diffusion $t$ in a material is proportional to the square of the diffusion length $L \approx \sqrt{t L^2/D}$. Hence, many nanomaterials in a variety of morphologies have been fabricated and applied as the anode of lithium ion batteries. The nanomaterials can be hollow (Lai et al. 2012), porous (Jia et al. 2011; Xue et al. 2011; Chen et al. 2012), or hierarchical structured (Sun et al. 2011; Zhang et al. 2011; Li et al. 2012) and be fabricated by self-assembly or template synthesis. The conventional approach to maintaining electrical connectivity and mechanical integrity of a battery electrode is to use a formulated mixture of at least three functional components: the active material, a conductive additive and a polymer binder. Since most electrode materials do not have good intrinsic conductivity, a substantial amount of conductive additive, such as Super P, is added to provide high inter-particle electrical conductivity. In some research, the amount of the carbon additive in the electrode was as high as 20 wt% (Chen et al. 2010; Chen et al. 2010; Ding et al. 2010; Wu et al. 2011) The high additive content can significantly decrease the volumetric and gravimetric capacities of the lithium ion batteries. Furthermore, the uniform dispersion of conductive additive in the active material can be difficult in view of the strong aggregation tendency of nanomaterials. Hence, the material performance in some studies could have been adversely affected by the limited electrical conductivity of the electrode caused by high inter-particle resistance (Nelson et al. 2012) Consequently, conductive additive may be used in excess of the amount required for complete percolation. Some new electrode configurations have therefore been proposed as alternatives. For example Simon and co-workers (Taberna et al. 2006) grew an electrochemically active $\text{Fe}_3\text{O}_4$ film directly
on a nanoarchitected Cu current collector to ensure good current collector/active material contact. Such methods are however not amenable to the mass production of the electrodes for commercial purposes.

The rate performance of an electrode can be significantly improved if each nanoparticle of the active material is furnished with its own current collector to keep the inter-particle resistance to electron transport at a minimum. Previous reports have shown that the partial reduction of Ti$^{4+}$ could create a conductive phase. (Armstrong et al. 2005; Song et al. 2012) This finding has motivated us to design a SnO$_2$/TiO$_2$ composite which can be used as a lithium ion battery anode without any external conductive additive. Different from other SnO$_2$ composites such as SnO$_2$/carbon where the compositing medium (carbon) serves primarily as an electron collector and hence only makes discontinuous contact with the tin oxide surface, TiO$_2$ is a Li ion and electron conductor and as an oxide, can completely encapsulate the SnO$_2$ surface without hindering electron and Li ion transport. A conductive Li$_y$Ti$_{1-y}$O$_2$ layer was used in this study as the current collector for each single NP aggregate to provide a high electrical conductivity throughout the electrode even with the volume changes in the active material (Figure 6.1). The specific capacity of the electrode could be higher because there was no need for conductive carbon addition in electrode formulation. The design is also easier to implement than the use of controlled off-stoichiometry to create a fast ion-conducting surface phase. (Kang et al. 2009) The composite prepared as such could deliver a charge capacity of 514 mAh/g at 1 A/g even after 30 cycles. Impedence measurements indicated that the charge transfer resistance of the composite without any external conductive additive was even smaller than that of pristine tin oxide mixed with an external conductive additive. The good electrical
conductivity of the composite at the materials level could be the main reason for the superior rate performance of the SnO₂/TiO₂ composite.

Figure 6.1  Explanation for the excellent rate performance of the core-shell SnO₂/TiO₂ composite in this study.

6.2  Experimental Section

6.2.1  Electrode Fabrication

SnO₂ NP aggregates were synthesized by the procedures in Chapter 4. Briefly, SnO₂ nanocolloids coated with a thin layer of glucose-derived, carbon-rich polysaccharide were first prepared by a hydrothermal reaction. The brown precipitate obtained as such was calcined at 800 °C for 1 h in air to form a white tin oxide powder (SO). The coating of tin oxide with titania followed the procedures of Tang which were used in Chapter 5. (Wang et al. 2006) Specifically the composite was prepared from 0.2 g SO and 0.6 mL of TBOT. The solid product formed was transferred to a Teflon-lined stainless steel autoclave (50 mL) and added with 30 mL DI. Hydrothermal treatment was then carried out at 200 °C for 12 h to crystallize the titania coating. After cooling
to room temperature, the product was rinsed with distilled water and dried at 100 °C for 12 h (SO@TO). It was fabricated into an electrode (the SO@TO electrode) by mixing the SO@TO powder and PVDF in a weight ratio of 90:10 and then vacuum dried at 120 °C for 12 h. A reference tin oxide electrode (SO/C) was also prepared by mixing the tin oxide powder, acetylene black (Super P, from Timcal) and PVDF in the weight ratio of 80:10:10. For comparison a tin oxide electrode was also prepared without the conductive carbon (SO).

6.2.2 Material Characterization

The morphology of all samples was examined by HRTEM and EDX (Philips FEG-CM300) operating at 200 kV, by SEM (JEOL JSM-6700F) and STEM on a JEOL JSM-6700F operating at 5 and 25 kV respectively. Powder XRD with Cu Kα radiation (Shimadu XRD-6000) was used to determine the phase composition. Swagelok-type cells were assembled in an argon-filled glove box using the tin oxide based electrode as the positive electrode, Li metal as the negative electrode, Celgard 2400 separator, and 1 M LiPF₆/EC+DEC (1:1 w/w) electrolyte. The cycling stability of the cells was tested on a Maccor Series 2000 battery tester at different current densities in the fixed voltage window of 0.005-2 V. CV at 0.2 mV/s was used to identify the redox reactions in the 0-3 V (versus Li/Li⁺) voltage range on an AutoLab Electrochemical System. EIS was performed on the same equipment in the frequency range 100 kHz–0.1 Hz with ±5 mV AC. For the EIS measurements of cells in different states of Li intercalation, the cells were discharged or charged to a predetermined potential at a given current density, and then rested for 5 h to fully dissipate spurious polarization effects.
6.3 Results and Discussion

6.3.1 Structure Analysis

Figure 6.2  SEM images of a) pristine SnO$_2$, b) electrode fabricated by casting a mixture of SnO$_2$, conductive carbon and PVDF. The inset in figure a) shows the TEM image of pristine SnO$_2$.

Figure 6.3  a) TEM image, b) SEM image of SnO$_2$/amorphous TiO$_2$.

One of the design principles is that the core should contain sufficient free volume to accommodate the volume excursion in discharging and charging reactions so that the shell will not exfoliate. In this study hollow porous tin oxide NP aggregates were used as the core of a core-shell construction, making use of the cavity in the tin oxide aggregates to provide such free volume. The cavity in the tin oxide aggregates could be
varied by the calcination temperature. From the discussion in Chapter 4, the shell was formed by the compression of tin oxide NPs in the surface region by forces generated from the outward diffusion of CO\textsubscript{2} formed by the oxidation of carbon-rich polysaccharides on the NPs. (Deng et al. 2008) Hence, increase in the calcination temperature would increase the rate of CO\textsubscript{2} formation; creating a greater compression effect to result in a larger internal cavity. This is confirmed by Figure 6.2a which shows a larger hollow core than the tin oxide NP aggregates calcined at a more lower temperature of 500 °C in Chapter 4. The diameter of the tin oxide NP aggregates here was around 80 nm. Figure 6.2b shows the FESEM image of the mixture cast from a slurry of the tin oxide NP aggregates, Super P and PVDF after drying at 100 °C for 12 h. This slurry had been continuously stirred for 3 days to increase the degree of homogenization. Yet the FESEM image still shows segregation of tin oxide aggregates and conductive carbon particles. Hence, there are more contacts between the active particles than between the active particles and conductive particles in an actual electrode.

A mixture of solvents (acetonitrile and ethanol) was used to regulate the hydrolysis rate of TBOT for a complete coverage of the SnO\textsubscript{2} surface by titania. Figure 6.3 shows the TEM and SEM images of tin oxide NP aggregates coated with amorphous TiO\textsubscript{2}. The coating was very uniform and some coating layers also spanned over two or more nanoparticle aggregates. The coating process was a typical sol-gel reaction consisting of the hydrolysis of the metal alkoxide, TBOT, (Equation 6-1) and the condensation reaction of the hydrolyzed species (Equation 6-2):

\[
\text{Ti(OC}_4\text{H}_9)_4 + \text{H}_2\text{O} \rightarrow \text{Ti-OH} + \text{C}_4\text{H}_9\text{OH}
\]  
(6-1)
Ti-OH + Ti-OH $\rightarrow$ Ti-O-Ti + H$_2$O  \hspace{1cm} (6-2)

Sol-gel derived precipitates are often amorphous and heat treatment is required to induce crystallization. (Wang et al. 1999) Hydrothermal treatment is an alternative to calcination for promoting crystallization at lower temperatures. High crystallinity is important as previous reports have shown irreversible insertion of Li ions in structural and chemical defect sites of amorphous titania. (Ortiz et al. 2008) In this study DI water and a temperature of 200 °C were used to form crystalline anatase TiO$_2$ by hydrothermal treatment, according to the recommendation of a previous report. (Cheng et al. 1995) A conformal coating layer was formed after the hydrothermal treatment. SEM shows that the core-shell composite prepared as such was quite uniform in size and shape (Figure 6.4a). The coating thickness as determined from the light borders on the dark particle cores in the STEM image was ~11 nm (Figure 6.4b). The HRTEM image of a single SO@TO particle and its fast Fourier transform (FFT) pattern in the region of interest are shown in Figure 6.4c, d. The interplanar spacing of 3.5 Å corresponds well with the anatase TiO$_2$ (101) planes. Element mapping of oxygen, tin, and titanium in SO@TO further confirmed the presence of titanium and the uniformity of the shell (Figure 6.4e).

6.3.2 XRD/XPS Analysis

XRD patterns of pristine tin oxide (SO), tin oxide/titania (SO@TO) and SO@TO after discharging/charging for 10 cycles are shown in Figure 6.5a. All the peaks in the XRD pattern of pristine tin oxide could be indexed to crystalline SnO$_2$ (cassiterite, JCPDS Card No. 41-1445). There were no additional peaks in the XRD pattern of SO@TO probably because the coating layer was too thin to produce a coherent diffraction. The peaks in SO@TO after charging could be indexed to crystalline metallic tin (JCPDS
04-0673). This is consistent with the alloying storage mechanism after tin was formed from tin oxide in the first discharge cycle. The phase composition of SO@TO was also examined by XPS. The survey spectrum showed the presence of Ti, Sn and O (Si and C were from the background and substrate). The atomic ratio of Ti: Sn of 1.74:1 indicates a Ti-enriched surface. The high resolution XPS Ti 2p spectrum showed the characteristic doublet of the Ti$^{4+}$ oxidation state at binding energies of 458.2 eV (2p$_{3/2}$) and 464.4 eV (2p$_{1/2}$). (Garfunkel et al. 1995) All of these measurements are consistent with an anatase titania surface coating layer.
Figure 6.4  a) FESEM image, b) STEM image, c) HRTEM image, d) corresponding FFT pattern of the region of interest and e) elemental maps of SO@TO.
Figure 6.5  a) XRD patterns of SO, SO@TO and SO@TO charged to 2 V after 10 cycles. b) Survey scan spectrum of SO@TO. The inset is the high-resolution Ti 2p XPS spectrum of SO@TO.

6.3.3 Reversible Lithium Storage Properties

Figure 6.6 shows the first three cycle CV of SO/C and SO@TO electrodes in the 0-3 V voltage window (versus Li/Li⁺) at 0.2 mV/s. For the SO@TO electrode, there was no reduction peak at ~1.7 V to indicate the intercalation of Li ions into anatase TiO₂.(Ye et al. 2010) The small amount of TiO₂ in the composite could have caused this process unnoticeable. The reduction peaks in the 1-1.3 V region in 2nd and 3rd cycles could be caused by SEI formation. They did not appear in the 1st cycle because their formation from electrolyte reductive decomposition probably required a Sn surface.(Menkin et al. 2009) The less conspicuous SEI formation on SO@TO suggests that the SEI layer could be thinner on TiO₂ than on Sn. Unlike pristine SnO₂ where the free surface
moving inwards or outwards in response to the volume changes in cycling could cause SEI rupture thereby necessitating restitution, the titania coating on the SO@TO surface, which did not undergo volume changes, protected the integrity of the SEI layer. The distinct reduction peak between 0.5-1.0 V in the cathodic scan in the 1st cycle which disappeared in the 2nd and 3rd cycles could be attributed to the reduction of tin oxide to tin concurrent with Li$_2$O formation. It should be stated that Li ions intercalation in TiO$_2$ below 1 V has not been reported. The reduction peak between 0-0.4 V could be safely attributed to the formation of Li-Sn alloys. According to Feng et al., the more prominent lithiation peak in SO@TO could be an indication of a higher Li ions diffusion rate. (Feng et al. 2009) Li ions diffusivity should be same for SO/C and SO@TO but the diffusion rate could be affected by the effectiveness of electron transport. Hence, it may be deduced that the faster diffusion of Li ions in SO@TO was due to the better electrical conductivity of the latter. The oxidation peak between 0-1.0 V in the anodic scan caused by the delithiation of Li-Sn alloys was also larger for SO@TO and corresponded well with the larger cathodic peak of Li alloying in the cathodic scan below 1 V. The oxidation peak beyond 1 V has been attributed to the reaction of Li$_2$O with Sn to form SnO/SnO$_2$. (Han et al. 2005)

Figure 6.7a is the comparison of the first cycle discharge/charge curves of SO@TO, SO/C. The first cycle discharge and charge capacities were 1623 and 743 mAh/g for SO@TO (ICL: 54.2% or 880 mAh/g), 1329 and 712 mAh/g (ICL: 46.4% or 617 mAh/g) for SO/C, and 1344 and 629 mAh/g (ICL: 53.3% or 715 mAh/g) for SO. All measurements were taken at 200 mA/g. It should be mentioned that all specific capacities were normalized by the composite mass rather than the mass of the active material alone. Furthermore the electrode specific capacity could also be increased by
~10 wt% since carbon was not needed in electrode formulation. The 1st cycle discharge capacities of the electrodes were therefore arranged in the following order: SO@TO > SO ~ SO/C while the order for the 1st cycle charge capacities was SO@TO > SO/C > SO. The high discharge and charge capacities of SO@TO were accompanied by an ICL which was the highest among the three. Since Li ions insert in anatase TiO₂ between 1.0-1.7 V and are extracted mainly at ≥ 2.0 V. (Ortiz et al. 2008; Chen et al. 2010), the large ICL of SO@TO could be caused by the difficulty of Li ion extraction from TiO₂ in a narrower voltage range (0.005-2 V). If the difference in the 1st cycle charge capacity was caused by the difference in the electrical conductivity of the electrodes, it may then be inferred that the SO@TO electrode has the best conductivity and the SO electrode had the lowest. The variations in specific gravimetric capacity of the three electrodes with cycle number are shown in Figure 6.7b. The cycling stability of SO@TO and SO/C were about the same from the second cycle onwards. The charge capacities of SO@TO were 722 mAh/g in the 2nd cycle and 518 mAh/g in the 30th cycle, while the corresponding values of SO/C were 711 mAh/g in the 2nd cycle and 520 mAh/g in the 30th cycle. On the contrary the pristine tin oxide electrode without any carbon (SO) sustained severe capacity fading. Its charge capacity of 617 mAh/g in the 2nd cycle was decreased to 141 mAh/g in the 30th cycle. This comparison clearly shows that tin oxide NP aggregates without conductive carbon additive could not reversibly store Li ions due to the low electrical conductivity caused by high inter-particle resistances. Since the SO@TO electrode demonstrated reversibly storage of Li ions without conductive carbon, the coating layer had to be able to reduce the inter-particle resistance to improve the electrical conductivity of the electrode.
Figure 6.6  CVs of SO/C and SO@TO at a scan rate of 0.2 mV/s in the 0-3 V range (versus Li/Li$^+$). The solid lines are for SO/C and the dash lines are for SO@TO.

Figure 6.7  a) 1$^{\text{st}}$ cycle discharge and charge curves of SO@TO, SO and SO/C. b) Cycling performance of SO@TO, SO and SO/C. Test conditions: current density=200 mA/g, voltage range=0.005-2 V versus Li/Li$^+$. The electrochemical performance of SO@TO, SO/C and SO was also evaluated at higher current densities (1 A/g and 3 A/g). SO and SO/C could not successfully extract Li ions at these high current densities. The rate performance of SO@TO is shown in Figure 6.8. The discharge and charge curves for the first two cycles at 1 A/g and 3 A/g are shown in Figure 6.8a. A discharge capacity of 1582 mAh/g and a charge capacity of 735 mAh/g could still be delivered by SO@TO in the first cycle at 1 A/g; showing
no significant decreases from the capacities measured at 200 mA/g. The charge capacity decreased to 514 mAh/g after 30 cycles (Figure 6.8b). Capacity fading was more severe at 3 A/g, yet a charge capacity of 378 mAh/g, which is higher than the theoretical capacity of graphite, was still possible.

![Figure 6.8](image)

**Figure 6.8** a) Discharge and charge curves of SO@TO in the first two cycles. b) Cyclability of SO@TO at 1 A/g and 3 A/g. Test conditions: voltage range=0.005-2 V versus Li/Li⁺.

The effect of titania coating on the electrochemical performance of SO@TO composite was also investigated by EIS (Figure 6.9). The impedance of a SO/C electrode was also measured for comparison. In the EIS study, the SO@TO and SO/C electrodes were working electrodes paired with a Li foil counter electrode and a reference electrode. The cells were discharged and charged to specific potentials in the 1st cycle at 0.2 A/g and then rested at these potentials for 5 h before the collection of impedance data. The results when presented as Nyquist plots all showed a semicircle in the middle frequency region and a slanted straight line in the low frequency region (Figure 6.9). It is generally accepted that the intercept on the $Z'$ axis at the high frequency end measures the resistance of the electrolyte. (Yamada et al. 2009) The values measured as such were 4 Ω·mg for the SO@TO electrode and 8 Ω·mg for the SO/C electrode. The difference was caused by the need to use an extra separator layer in the SO/C cell.
(for the prevention of self-discharge which was not evident in the SO@TO cell). In general the Nyquist plot could display two semicircular arcs – a high frequency arc due to Li ions migration through the SEI layer and a middle frequency arc due to the charge transfer resistance of the active electrode. Invariably the low frequency response is dominated by a slanted line indicating some form of transport limitations (Li ion diffusion in bulk materials). (Aurbach et al. 2002; Subramanian et al. 2006) The EIS spectra of SO@TO and SO/C in the 1st cycle at different states of discharge and charge contained only one mid-frequency semicircle. This is consistent with the ‘delayed’ formation of the SEI layer in the discussion of the voltammetry results. The charge transfer resistance of the SO@TO electrode in open-circuit conditions was higher than that of SO/C. This was because of the limited electrical conductivity of SO@TO at high potentials whereas the conductive carbon in SO/C could impart some conductivity to the electrode. The two electrodes were then discharged and charged to different potentials at 200 mA/g. The resistance of SO/C was nearly unchanged after discharging to 2 V whereas the decrease in the resistance of SO@TO was more substantial. This is believed to be due to the partial reduction of Ti$^{4+}$ to the conductive Li$_y$Ti$_{1-y}$O$_2$ phase. (Song et al. 2012) The trend of decreasing resistance continued with discharging to 1 V when more conductive Li$_y$Ti$_{1-y}$O$_2$ phase was formed. Discharging to 0.005 V found the equalization of the two charge transfer resistances. This could be understood as the reduction of tin oxide to tin in the 0.7-1.0 V window and the completion of the formation of conductive Li$_x$Sn alloys at low potentials. In the reverse process of charging, the resistance of SO/C increased when it was charged to 1 V. This could be due to the partial loss of electrical contact between tin oxide NPs and the conductive carbon during to the volume changes in the former. (Liu et al. 2011) The resistance of SO@TO also increased when it was charged to 1 V but for a different
reason – the decreasing conductivity of the conductive Li$_y$Ti$_{1-y}$O$_2$ phase when it was progressively delithiated. Nonetheless the resistance of SO@TO at 1 V was still lower than that of SO/C, confirming the contribution of the titania coating to the reduction of inter-particle resistance resulting in the improvement of the electrical conductivity of the electrode.

**Figure 6.9** Nyquist plots of SO/C and SO@TO electrodes in different stages of discharge and charge. a) SO/C, b) SO@TO at open-circuit condition, 1$^{st}$ cycle discharge to 2 V, 1 V, 0.005 V and 1$^{st}$ cycle charge to 1 V at 200 mA/g. c) SO/C, d) SO@TO in the 10$^{th}$ cycle discharged to 2 V, 1 V, 0.005 V and then charged to 1 V at 1 A/g.
The EIS spectra of the two electrodes in different states of discharge and charge after 10 cycles at 1 A/g were also recorded to analyze the impact of high current density. Two semicircles appeared in SO/C with the new semicircle (at the high frequency) attributable to the resistance of the SEI layer. The semicircle due to SEI was not conspicuous in SO@TO. This is another demonstration of the stability (and hence thinness) of the SEI layer on titania resulting in lower resistance for Li ions passage, as was delineated previously. The charge transfer resistance of SO@TO in all stages of discharge/charge was smaller than the corresponding values of SO/C. Hence, the presence of conductive carbon in SO/C to increase the conductivity of the electrode was not as effective as having each active particle (tin oxide NP aggregates) covered with a conductive phase to decrease the inter-particle contact resistance. As a result the charge transfer resistance of the electrode, which is the composite of kinetic and transport effects, can be significantly reduced. The titania coating of tin oxide was also more effective than carbon coating because of the natural affinity between two oxide materials (carbon is hydrophobic and does not naturally affine to the oxide surface unless the surfaces are modified). The tight titania coating also formed a more compact SEI layer to reduce the resistance of Li ions migration through it; as has been shown by the good rate performance of the SO@TO electrode. Titania coating also resulted in a more stable electrode. Figure 6.10 shows the TEM image of SO@TO discharged to 0.005 V after 10 cycles of discharge and charge. The active material still exhibited a core-shell structure confirming the integrity of the titania coating layer and its protection against the pulverization of the tin-based core materials.
6.4 Conclusion

In conclusion, a tin oxide based anode with good power density has been developed which could be used without any conductive carbon additive. The anode material was designed as a tin oxide/titania core-shell composite and could deliver a charge capacity of 735 mAh/g at 1A/g in the first cycle. The charge capacity was as high as 514 mAh/g after 30 cycles. EIS measurements showed that the SO@TO electrode had lower charge transfer resistance than an electrode of tin oxide NP aggregates and conductive carbon. It is believed that the titania layer was converted into a more conductive form (Li_yTi_{1-y}O_2) during cycling which served as the ‘current collector’ for each tin oxide NP aggregate. The inter-particle resistance to both electron and Li ions transport was reduced resulting in an overall smaller charge transfer resistance for the electrode. The removal of carbon conductive additive in the electrode effectively increased the energy and power densities by 10 wt%. The natural affinity between oxides led to a thinner coating (especially in relation to a SnO_2/carbon composite). The
thin titania layer was fairly robust because of its small volume change during cycling. Consequently, the core-shell composite could withstand cycling without structural collapse. The titania coating method could be a new approach for the preparation of high power density anode materials.
CHAPTER 7 CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

Materials innovations are important to the improvement of the performance of lithium ion batteries for energy and power intensive applications such as electric vehicles and smart grid energy storage systems. Previous research has shown that the use of tin nanomaterials or tin nanocomposites to substitute for the existing carbon-based anodes can increase the anode specific capacity by many folds. Good capacity retention is also possible if the nanostructure is designed to provide adequate free volume to accommodate the expansion and contraction of the storage material during cycling. However, tin-based anode nanomaterials are still beset with problems of large ICL and poor rate performance. This thesis study is focused on improving the electrochemical reversibility of tin-based anode materials to deliver a balance performance in practice. The following tin nanomaterials/nanocomposites were demonstrated at the conclusion of this study: hierarchical tin oxide with different packing densities (Chapter 3), tin oxide NP aggregates individually wrapped in graphene sheets (Chapter 4), tin oxide@LTO core-shell composites (Chapter 5), and tin oxide@titania core-shell particles (Chapters 6). The major findings of this thesis study include the following:

1. Through careful control of the preparation conditions, tin oxide particles with hierarchical structures were produced by a two-step process - hydrolysis of a
Sn(II) precursor at sufficiently high pH followed by the assembly of the tin oxides formed under hydrothermal conditions. The hierarchical structures had a generally flower-like appearance and were assembled from NSs. The packing density of the assembly could be increased by increasing the reactant concentrations. It is postulated that the assembly of NSs was fast and occurred immediately after NSs were formed by the aggregation of primary NPs. The driving force for the assembly was the reduction of surface energy. The dissolution of Sn$_6$O$_4$(OH)$_4$ in excess OH$^-$ as the coordination complex Sn$_6$O$_4$(OH)$_{4+x}^{x-}$ created a uniform reaction environment in hydrothermal processing to result in products with higher regularity. Urea was important in the preparation as its decomposition extracted the excess OH$^-$ in Sn$_6$O$_4$(OH)$_{4+x}^{x-}$, thereby precipitating Sn as Sn$_6$O$_4$(OH)$_4$. The nucleation rates of HS-C, HS-D and HS-E precursors could therefore be regulated by controlling the hydrolysis rate of urea. Sn$_6$O$_4$(OH)$_4$ which then decomposed to tin oxides under hydrothermal conditions. Hierarchically structured tin oxide with a moderate packing density showed very high first cycle columbic efficiencies at 0.5 A/g or 1A/g. The columbic efficiency could be as high as 64.2% measured at 0.5 A/g, which compares favorably with the typical value of 46%-55% for tin oxide nanoparticles. The ICL due to SEI formation was only 179 mAh/g, smaller than those of unassembled NPs or NSs of tin oxide. It also had good cycle stability (428 mAh/g of charge capacity after 30 cycles at 0.5 A/g). Hence, organizing an active material into hierarchical structures with a moderate packing density is an effective strategy to increase the reversibility of the material in electrochemical reactions (decrease in irreversible side reactions (SEI formation), and increase in capacity, rate performance and cyclability).
2. Good electrochemical reversibility for Li ion storage was also demonstrated by wrapping aggregates of SnO$_2$ NPs individually in graphene sheets of different thicknesses (SnO$_2$@TRGO core-shell composites). The SnO$_2$@TRGO composite with 9 wt% of graphene had outstanding cycling stability with little or no capacity fading from the 2$^{nd}$ to the 50$^{th}$ cycle (charge capacity was 488 mAh/g in the 2$^{nd}$ cycle and 463 mAh/g in the 50$^{th}$ cycle). The SnO$_2$@TRGO composite with 5 wt% graphene delivered even higher discharge/charge capacities (charge capacity was 729 mAh/g in the 2$^{nd}$ cycle and 517 mAh/g in the 50$^{th}$ cycle) but some capacity decay was noticeable probably due to some impairment of the graphene-SnO$_2$ connectivity while SnO$_2$ was partially reduced to tin during the thermal treatment. Nonetheless a higher rate performance (charge capacity of 423 mAh/g at a current density of 1 A/g) was possible with this composite because of a better balance of electrical conductivity and ionic conductivity. We also found that thermally reduced GO was more suitable than chemically reduced GO to compound with high capacity anode materials for lithium ion battery applications.

3. SnO$_2$@Li$_4$Ti$_5$O$_{12}$ core-shell composite particles with different shell thicknesses were also prepared; which showed improvements over the electrochemical performance of uncoated particles. The coating was effective in reducing the ICL due to SEI formation on the anode surface. Specifically a LTO coating on hollow tin oxide nanoparticle aggregates could lower the ICL for SEI formation from 425.7 mAh/g to 142.3 mAh/g. The cycling performance of hollow SnO$_2$@ Li$_4$Ti$_5$O$_{12}$ was also superior to that of uncoated hollow tin
oxide NPs. The discharge capacity of hollow tin oxide particles was reduced to 75.6 mAh/g in the 30\textsuperscript{th} cycle whereas the corresponding value for the SnO\textsubscript{2}@Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} core-shell composite with 15 nm shell was 457.1 mAh/g. Unlike other studies, the specific capacities here were normalized by the weights of the composites, and not the weights of active materials only. A LTO layer ~5 nm in thickness was sufficient to shield the contact between tin oxide and electrolyte. However, thicker LTO layers were more resistant to exfoliation caused by the volume excursion of the core material during cycling. Hence, there exists some optimal shell thickness which balances the two opposing effects. Moreover, the LTO layers were also found to improve the rate performance of the active material. The LTO coating method is generic; and can be a new strategy for improving the electrochemical performance of other high capacity anode materials.

4. A tin oxide based anode with good power density has been developed which could be used without any conductive carbon additive. The anode material was designed as a tin oxide/titania core-shell composite and could deliver a charge capacity of 735 mAh/g at 1 A/g in the first cycle. The charge capacity was as high as 514 mAh/g after 30 cycles. EIS measurements showed that the SnO\textsubscript{2}@TiO\textsubscript{2} core-shell composite electrode had lower charge transfer resistance than an electrode of tin oxide NP aggregates and conductive carbon. It is believed that the titania layer was converted into a more conductive form (Li\textsubscript{y}Ti\textsubscript{1-y}O\textsubscript{2}) during cycling which served as the ‘current collector’ for each tin oxide NP aggregate. The inter-particle resistance to both electron and Li ions transport was reduced resulting in an overall smaller charge transfer resistance.
for the electrode. The removal of carbon conductive additive in the electrode effectively increased the energy and power densities by 10 wt%. The natural affinity between oxides led to a thinner coating (especially in relation to a SnO₂/carbon composite). The thin titania layer was fairly robust because of its small volume change during cycling. Consequently, the core-shell composite could withstand cycling without structural collapse. The titania coating method could be a new approach for the preparation of high power density anode materials.

7.2 Future Work

This thesis study demonstrated that hierarchical tin based materials could be prepared by hydrothermal synthesis with tunable morphologies by changing the reaction conditions. More importantly the electrochemical performance of tin oxide in reversible Li ion storage could be improved through compositing and morphology control. During the course of this thesis study I grew to believe that Li ions could be stored in tin oxide besides the classical alloy mechanism. While most tin nanomaterials have been designed with some free volume to accommodate the volume change in the host material during cycling, the optimal amount of free volume which balances cyclability with high volumetric capacity has not been systematically determined. These, together with some other ideas for future work, are briefly outlined below.
1. Re-examining Li storage in tin oxides

Alloy formation is the classical mechanism for Li storage in tin and the use of tin oxide would necessarily involve the irreversible reduction of tin oxide to tin. However some of our experimental results suggest that the reduction of tin oxide to tin could be partially reversible. There has been some evidence to this effect in the literature. For example, Han \textit{et al.} measured reversible specific capacity of 120 mAh/g when tin oxide was cycled in the 0.8-2 V window.(Han \textit{et al.} 2005) Tin could not be formed in this voltage range and hence the capacity could only arise from the direct storage of Li ions in tin oxide. In another research,(Li \textit{et al.} 2012) very high specific capacity more so than what is possible with the alloy storage mechanism was reported. Although not mentioned by the authors, the reversibility of tin oxide reduction to tin could explain the high specific capacity. Assuming that the reduction of tin oxide to tin is completely reversible, the theoretical specific capacity of tin oxide could then be increased from 781 to 1491 mAh/g based on the following reactions:

\[ \text{SnO}_2+4\text{Li}^++4e^- \rightarrow \text{Sn}+2\text{Li}_2\text{O} \]  \hspace{1cm} (7-1)

\[ \text{Sn}+x\text{Li}^++xe^- \rightarrow \text{Li}_x\text{Sn} \ (0 \leq x \leq 4.4) \]  \hspace{1cm} (7-2)

Hence, more research on the reversibility of tin oxide reduction is needed. Understanding the conditions under which the first reaction is completely reversible can be very rewarding. It is likely that the size, morphology and structure of the tin oxide and conductivity of the electrode during cycling are important factors to consider.

2. Constructing tin/graphene composites with variable graphene structure
Chapter 4 shows that the arrangement of graphene sheets in the composite; and properties such as thickness and the type and concentration of defects in graphene can significantly impact the electrochemical performance of the composite. For example individual wrapping of NP aggregates with graphene sheets is more effective than multi-core wrapping. In addition a small Li ion across-plane diffusivity in graphene can translate into a large Li ion transfer resistance in the composite. As shown by the example of thermally reduced graphene oxide (TRGO), in-plane vacancies formed during graphene oxidization could actually benefit Li ion diffusion as they provide more entry points for the passage of Li ions so that the overall transport process is not inhibited by small Li ion conductivity. Some proposed future works may include methods which can judiciously vary the graphene in-plane vacancies to achieve the best balance between electrical and Li ion conductivities. This can in principle be done by controlling the degree of oxidization in GO or by post-synthesis irradiation damage.

3. Control of the composite free volume

It is generally believed that a Li storage host that undergoes large volume changes in cycling needs to be provided with free volume to accommodate the volume changes. Apparently too low a free volume would not serve the purpose but too much of free volume could reduce the volumetric capacity imprudently. The optimization of free volume has yet to be attempted and hence trial and error approach dominated in many of the ‘composite designs’. The problem is due to the lack of knowledge of the minimum free volume needed to sustain cycle stability. The volume change in cycling is about 359\% for bulk tin.(Courtney et al. 1997) Many of the current nanostructured materials do not have that quantum of free volume and yet they cycle quite satisfactorily. Hence, the volume change in nanoscale materials may either be smaller,
or nanoscale materials are stronger in stress and strain tolerance. The minimum free volume needs to be established before a rational design and/or optimization of free volume in the composite becomes possible. This could be an iterative process since the free volume is likely to be geometry dependent in view of possible anisotropic mechanical properties of the nanomaterials. For nanocomposites with the core shell architecture (e.g., tin oxide@lithium titanate core-shell composites in Chapter 5, and tin oxide@titania core-shell composites in Chapter 6), the knowledge of free volume would allow a design that supports the expansion of the core without rupturing the outer shell layer, therefore stabilizing the SEI on the shell surface and at the same time without wastage of space in the composite (i.e., the volumetric capacity can be as high as possible).
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