Investigation on Advanced Metal Oxides as Electrode Materials for Electrochemical Energy Storage

Qiannan Liu
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Investigation on Advanced Metal Oxides as Electrode Materials for Electrochemical Energy Storage

This thesis is presented as part of the requirement for the Award of the Degree of Philosophy

From the University of Wollongong

by

Qiannan Liu, M. Sc.

Institute for Superconducting and Electronic Materials (ISEM)

Faculty of Engineering

September 2017
Declaration

I, Qiannan Liu, declare that this thesis, submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting & Electronic Materials (ISEM), Faculty of Engineering, University of Wollongong, New South Wales (NSW), Australia, is wholly an original work unless otherwise referenced or acknowledged. In addition, this thesis has not been submitted to any other academic institutions for qualifications.

Qiannan Liu

September 20, 2017

Wollongong, Australia
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Abstract

Due to the continuously increasing worldwide depletion of fossil fuels and the demand for large-scale storage devices, electrical energy-storage systems have become a hot research topic for energy conversion from renewable resources, such as wind and solar power, to the energy grid to store the intermittent renewable energy. Rechargeable metal ion batteries have been paid great attention since the emergence of the lithium-ion battery, which has now conquered the portable electronic market and is forecast to continue to be the main choice for energy storage systems for the next generation. In addition, the sodium ion battery is attracting more and more attention due to its similar chemistry to the lithium ion battery, since Na and Li are in the same group of the periodic table of elements. In this doctoral thesis, different metal oxides, including hierarchical SnO$_2$ hollow spheres with or without carbon coating, ZnCo$_2$O$_4$ microspheres and Zn$_{0.85}$Co$_{0.15}$O/C nanoparticles, multi-angular Na$_{0.44}$MnO$_2$ rods, and layered P2-type Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ are studied as electrode materials, either as anode or cathode, for the lithium ion battery (LIB) or the sodium ion battery (SIB). The microstructure, composition, electrochemical performance, and reaction mechanism of each material have been systematically investigated with the result that metal oxides show their promising potential as electrode materials for next-generation rechargeable metal ion batteries.

Three-dimensional hierarchical SnO$_2$ hollow spheres composed of nanosheets were synthesized by a hydrothermal method, and their electrochemical performance were tested as an anode material for LIBs. The electrochemical performance of bare SnO$_2$ electrodes was further improved by coating a thin layer of carbon on the nanosheets. In addition, carboxymethyl cellulose (CMC) binder, which is water soluble and inexpensive, was used instead of the conventional polyvinylidene difluoride (PVDF) binder, making the whole fabrication process for the electrode environmentally friendly and low in cost. As a result, the
as-prepared SnO$_2$/C composite exhibited synergistic properties arising from its nanostructures and conductive carbon, and it thus demonstrated superior electrochemical performance with good cycling performance and large reversible capacity when used as anode for rechargeable lithium ion batteries.

Hierarchical ZnCo$_2$O$_4$ microspheres and Zn$_{0.85}$Co$_{0.15}$O/C nanoparticles were successfully obtained from a facile microemulsion-based method. The homogeneously dispersed ZnCo$_2$O$_4$ microspheres are further composed of uniform sized and closely interconnected ZnCo$_2$O$_4$ nanoparticles. When trying to study the effect of carbon modification, Zn$_{0.85}$Co$_{0.15}$O and carbon composite (Zn$_{0.85}$Co$_{0.15}$O/C) nanoparticles were finally obtained. High reversible capacities of 616.7 and 741.9 mA h g$^{-1}$ was maintained after repetitive 100 cycles for ZnCo$_2$O$_4$ microspheres and Zn$_{0.85}$Co$_{0.15}$O/C nanoparticles, respectively, demonstrating their capabilities as anode candidates for lithium ion batteries.

Monophasic tunnel-type Na$_{0.44}$MnO$_2$ with multi-angular shaped rods were synthesized by a modified reverse microemulsion method and studied as cathode material for SIBs. This structure offers a suitable size that increases the contact area between the material and the electrolyte, guarantees fast sodium ion diffusion, and helps release strains resulting from de-insertion/insertion of Na$^+$ ions in multiple directions. When used as cathode material in SIBs, the as-prepared multi-angular Na$_{0.44}$MnO$_2$ rods featured stable cycling performance, excellent high-rate capability, and long cycle life at 8.3 C. With the benefits of multi-angular morphology, suitable size, and fast sodium ion diffusion, the Na$_{0.44}$MnO$_2$ rods prepared at 850°C as a cathode material for SIBs demonstrated stable cycling performance with capacity of 72.8 mAh g$^{-1}$ and capacity retention of 99.6% after 2000 cycles at 8.3 C. The as-designed multi-angular Na$_{0.44}$MnO$_2$ provides new insight into the development of tunnel-type electrode materials and their application in rechargeable sodium-ion batteries.
Moreover, layered P2-type Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ was successfully synthesized and characterized as a cathode material for SIBs. *In-situ* X-ray diffraction and the galvanostatic intermittent titration technique were also used to better understand the mechanism and sodium ion diffusion during the sodium intercalation and de-intercalation processes, which provide new experimental evidence of the structural evolution during cycling tests under different cut-off voltages. Due to its different phase transformations and sodium ion diffusion rates, it was clear that the electrochemical performance of this material is strongly related to the particular cut-off voltage and electrolyte that are used. The as-prepared P2-Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ exhibited an initial discharge capacity as high as 179.7 mAh g$^{-1}$ when cycled between 4.5-2.0 V. Great capacity fading was observed in this voltage, however. In the voltage range of 4.0-1.5 V, the electrode exhibited an initial capacity of 151.0 mAh g$^{-1}$ with slight capacity fading due to the structural distortion caused by the Jahn-Teller Mn$^{3+}$ ions. When cycled in the range of 4.0-2.0 V, the electrode maintained a capacity of 93 mAh g$^{-1}$ with good cycling stability and excellent structural preservation even after 1000 cycles at 1 C. The capacity retention was 71.2% even after 1200 cycles at 10 C.

In summary, all the hierarchical SnO$_2$ hollow spheres with or without carbon coating, ZnCo$_2$O$_4$ microspheres and Zn$_{0.85}$Co$_{0.15}$O/C nanoparticles, multi-angular Na$_{0.44}$MnO$_2$ rods, and layered P2-type Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ exhibit good electrochemical performances as electrode materials for LIBs or SIBs, demonstrating the great potential of different metal oxides for electrochemical energy storage.
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### List of Abbreviations

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<thead>
<tr>
<th>Abbreviation</th>
<th>Full name</th>
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<tbody>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
</tr>
<tr>
<td>3D</td>
<td>Three dimensional</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>LIBs</td>
<td>Lithium ion batteries</td>
</tr>
<tr>
<td>SIBs</td>
<td>Sodium ion batteries</td>
</tr>
<tr>
<td>CMC</td>
<td>Sodium carboxymethyl cellulose</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>FEC</td>
<td>Fluoroethylene carbonate</td>
</tr>
<tr>
<td>VC</td>
<td>Vinylene carbonate</td>
</tr>
<tr>
<td>VEC</td>
<td>Vinyl ethylene carbonate</td>
</tr>
<tr>
<td>TMOBX</td>
<td>Trimethoxyboroxine</td>
</tr>
<tr>
<td>TMB</td>
<td>Trimethyl borate</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>GITT</td>
<td>Galvanostatic intermittent titration technique</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>BSE</td>
<td>Back-scattered electrons</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electrons</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected-area electron diffraction</td>
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### List of Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
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<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>SXRD</td>
<td>Synchrotron X-ray diffraction</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectra</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray adsorption near the edge structure</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>NMO</td>
<td>( \text{Na}_{0.44}\text{MnO}_2 )</td>
</tr>
<tr>
<td>NNMO</td>
<td>( \text{Na}<em>{2/3}\text{Ni}</em>{1/3}\text{Mn}_{2/3}\text{O}_2 )</td>
</tr>
<tr>
<td>cm</td>
<td>Centimetre</td>
</tr>
<tr>
<td>mm</td>
<td>Millimetre</td>
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<tr>
<td>nm</td>
<td>Nanometre</td>
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### List of Symbols

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<th>Name</th>
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<tr>
<td>(\theta)</td>
<td>Detection angle in XRD</td>
<td>(^\circ)/degree</td>
</tr>
<tr>
<td>(R)</td>
<td>Gas constant = 8.314</td>
<td>( \text{J K}^{-1} \text{mol}^{-1} )</td>
</tr>
<tr>
<td>(\lambda)</td>
<td>Wavelength</td>
<td>( \text{nm} )</td>
</tr>
<tr>
<td>(N_A)</td>
<td>Avogadro constant = (6.022 \times 10^{23})</td>
<td>( \text{mol}^{-1} )</td>
</tr>
<tr>
<td>(F)</td>
<td>Faraday’s constant = 96485</td>
<td>( \text{C mol}^{-1} )</td>
</tr>
<tr>
<td>(S_{\text{BET}})</td>
<td>Specific BET surface area</td>
<td>( \text{m}^2 \text{ g}^{-1} )</td>
</tr>
<tr>
<td>(R_{\text{ct}})</td>
<td>Charge transfer resistance</td>
<td>( \Omega )</td>
</tr>
<tr>
<td>(R_f)</td>
<td>Film resistance</td>
<td>( \Omega )</td>
</tr>
<tr>
<td>(R_s)</td>
<td>Electrolyte resistance</td>
<td>( \Omega )</td>
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<tr>
<td>C-rate</td>
<td>Charge/discharge rate</td>
<td>( \text{mA g}^{-1} )</td>
</tr>
<tr>
<td>(W)</td>
<td>Warburg impedance</td>
<td>( \Omega )</td>
</tr>
<tr>
<td>(Z_{\text{re}})</td>
<td>Real part of the impedance</td>
<td>( \Omega )</td>
</tr>
<tr>
<td>(Z_{\text{im}})</td>
<td>Imaginary part of the impedance</td>
<td>( \Omega )</td>
</tr>
<tr>
<td>(D_{\text{Na}^+})</td>
<td>Sodium-ion diffusion coefficient</td>
<td>( \text{cm}^2 \text{ s}^{-1} )</td>
</tr>
<tr>
<td>(f)</td>
<td>Frequency</td>
<td>( \text{Hz} )</td>
</tr>
<tr>
<td>(Q)</td>
<td>Specific capacity</td>
<td>( \text{mAh g}^{-1} )</td>
</tr>
<tr>
<td>(Q_c)</td>
<td>Specific charge capacity</td>
<td>( \text{mAh g}^{-1} )</td>
</tr>
<tr>
<td>(Q_d)</td>
<td>Specific discharge capacity</td>
<td>( \text{mAh g}^{-1} )</td>
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List of Nomenclature

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<th>Description</th>
<th>Unit</th>
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<tr>
<td>$Q_T$</td>
<td>Theoretical capacity</td>
<td>mAh g$^{-1}$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Ionic conductivity</td>
<td>S cm$^{-1}$</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K or °C</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>h or s</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Coulombic efficiency</td>
<td>%</td>
</tr>
<tr>
<td>$I$</td>
<td>Current density</td>
<td>A cm$^{-2}$</td>
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List of Organizations

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<tr>
<td>ISEM</td>
<td>Institute for Superconducting and Electronic Materials</td>
</tr>
<tr>
<td>EMC</td>
<td>Electron Microscopy Centre</td>
</tr>
<tr>
<td>AIIM</td>
<td>Australian Institute of Innovative Materials</td>
</tr>
<tr>
<td>UOW</td>
<td>University of Wollongong</td>
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Chapter 1. Introduction

1.1 Background

Energy storage has been a growing global concern over the past several decades, resulting from increased energy demand, the increased price of refined fossil fuels, and the environmental issues arising from fossil fuel usage. These have led to a strong demand for environmentally friendly alternative sources for both energy generation and storage. Among the several technologies that are suitable for large-scale energy storage, electrochemical energy storage (EES) technologies based on batteries are presenting considerable promise resulting from many breakthroughs in the last few years. Batteries, in particular, represent a viable energy storage technology for the integration of renewable resources that provide intermittent energy into the grid. The extension of battery technology to large-scale storage will become necessary as intermittent renewable energy generating technologies such as wind, wave, and solar power become more prevalent and are integrated into the electrical grid.¹⁻³

Among the various effective energy storage technologies, the Li-ion battery (LIB), which has conquered the portable electronic market, is the leading candidate for electric and plug-in electric vehicles and is forecast to continue to be the technology of choice for energy storage systems for the next generations. LIBs have many advantage: (1) the largest energy density and output voltage of all the rechargeable battery technologies in use; (2) high load capabilities; (3) long cycle life and extended shelf-life; (4) high capacity, low internal resistance, and good coulombic efficiency; (5) simple charge algorithms and reasonably short charge times; and (6) low self-discharge. Moreover, Li-ion technology relies on a versatile chemistry leading to a wide range of attractive electrode materials for both cathode (LiCoO₂, LiMn₂O₄, LiFePO₄, etc.) and anode materials (C, Sn, Si, etc.).⁴
Chapter 1. Introduction

While Li-ion battery technology is quite mature, there still remain questions regarding its safety, lifetimes, limited abundance (0.0007 percent of the Earth’s crust), cost, and poor low-temperature performance. Furthermore, the increasing demand for Li mineral resources, which are also geographically constrained, is greatly driving up prices. Limitations on the availability of the transition metals for cathode materials are also of concern, driving development towards more sustainable elements, so that Na-based compounds have become an alternative choice. The use of Na instead of Li in rocking chair batteries could mitigate shortages of Li in an economical way, due to the relatively unlimited nature of Na sources, the ease of recovering it, and its lower price, as compared with Li, as is shown in Table 1.1. Moreover, Na is in the same group as Li in the periodic table of elements. For positive electrode materials, sodium intercalation chemistry is very similar to that of Li counterpart, thus making it possible to use very similar compounds for both kinds of systems. Sodium ion batteries (SIBs) are gaining more and more attention for the next generation of rechargeable energy storage.

Table 1.1 Comparison of characteristics of Li and Na.\textsuperscript{5}

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>lithium</th>
<th>sodium</th>
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<tr>
<td>Price (for carbonates)</td>
<td>$5000/ton</td>
<td>$150/ton</td>
</tr>
<tr>
<td>Voltage vs. SHE</td>
<td>-3.0 V</td>
<td>-2.7 V</td>
</tr>
<tr>
<td>Ionic radius</td>
<td>0.76 Å</td>
<td>1.02 Å</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>6.9 g mol\textsuperscript{-1}</td>
<td>23 g mol\textsuperscript{-1}</td>
</tr>
<tr>
<td>Capacity</td>
<td>3829 mAh g\textsuperscript{-1}</td>
<td>1165 mAh g\textsuperscript{-1}</td>
</tr>
<tr>
<td>Melting point</td>
<td>180.5 °C</td>
<td>97.7 °C</td>
</tr>
<tr>
<td>Coordination preference</td>
<td>Octahedral and tetrahedral</td>
<td>Octahedral and prismatic</td>
</tr>
</tbody>
</table>

* SHE is standard hydrogen electrode.

Up to this point, scientists, inventors, and battery companies have been continually seeking ways to explore how to make use of available resources to store electricity. The process of finding such ways and studying how to generate energy will probably be never-ending.
1.2 Current issues and challenges

Current research on batteries is focused on obtaining a significant increase in power and energy density, as well as an increased lifetime. Although LIBs have shown outstanding commercial success in portable devices, there are still significant improvements needed to meet the requirements of large-scale applications. SIBs are facing the same technical barriers, including a safety problems as LIBs, since they are operated based on similar chemistry.

For anode materials, irreversible capacity loss normally occurs during the initial charge process. This irreversible capacity loss comes from electrolyte decomposition, which results in the formation of solid electrolyte interphase (SEI) on the surface of the electrode during the first cycle, and further electrolyte decomposition is prevented by the SEI. Meanwhile, there are volume changes accompanying the delithiation/lithiation or desodiation/sodiation reactions, which severely reduce the capacity retention and cycle life of the electrode. Surface modification and particular structural designs are viable options to solve the problem of capacity loss and low cycling stability. In addition, there are two main difficulties for SIBs as opposed to LIBs, arising from the bigger ionic radius of Na than Li. One is that some conversion reactions occur at relatively high potentials, eventually resulting in decreases in the overall cell voltage, especially in the cases of oxides, fluorides, chlorides, etc. The other is that the volume expansion is even larger for SIBs than that for their Li-based equivalents, causing mechanical degradation and thus poor cycle life.

For cathode materials, their specific capacity, rate capability, low initial coulombic efficiency, and safety issues need to be considered for the next generation of metal ion batteries. Layered LiCoO$_2$ is widely used in commercial LIBs, but it shows a limited specific capacity (140 mAh g$^{-1}$), is partially toxic, and also is expensive. In the case of spinel LiMn$_2$O$_4$, it is a serious challenge to control the capacity decay associated with Mn dissolution and the Jahn-
Teller distortion of Mn$^{3+}$ ions.\textsuperscript{7} When choosing cathode materials for SIBs, the main challenge is that the intercalation of Na$^+$ is so difficult compared with Li$^+$ that the specific energy and power density of SIBs are smaller compared with LIBs. Considerable study of suitable positive electrode materials with high capacity and high operating voltages is required to further increase the energy density of SIBs.

It is crucial to find advanced new electrode materials with superior energy density and to enhance their electrochemical properties through various strategies, including controlling the morphology, structure, and size of the particles, and forming compounds and composites.

1.3 Objectives of this work

In this doctoral work, the main goal has been to study and search for promising metal oxides as electrode materials with high capacity, long cycle life, and environmental-friendliness. Hierarchical SnO$_2$ was prepared with and without carbon coating and characterized as an anode material for LIBs. Moreover, zinc cobalt oxide microspheres or nanoparticles were also studied and investigated as anode for LIBs. Improved electrochemical performance was obtained after carbon modification, which effectively accommodated the volume changes during the cycling process and enhanced the electronic conductivity of the active materials. Two kinds of sodium-manganese metal oxides (Na$_{0.44}$MnO$_2$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$) were investigated as cathode materials. The effects of the morphology, cut-off voltage, and electrolyte on the electrochemical performance were considered, and the electrochemical mechanism is discussed in detail, based on in-suit synchrotron tests.

1.4 Outlines of thesis

The outline of this doctoral work is briefly summarized as follows:
Chapter 1. Introduction

Chapter 1 briefly introduces the general background of LIBs and SIBs, the goals of this doctoral research, and an outline of this doctoral study.

Chapter 2 presents a literature review on LIBs and SIBs, including their development history, fundamental concepts, and progress of date in battery research.

Chapter 3 presents the chemicals and methods applied for the synthesis of different electrode materials in this doctoral work. The characterization methods used are also introduced, including X-ray diffraction (XRD), synchrotron X-ray diffraction (SXRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), energy dispersive X-ray spectroscopy (EDS), Brunauer-Emmet-Teller (BET) surface area measurements, and various electrochemical measurements, including cyclic voltammetry (CV), galvanostatic charge-discharge cycling, and electrochemical impedance spectroscopy (EIS).

Chapter 4 investigates hierarchical SnO$_2$ hollow spheres self-assembled from nanosheets and prepared with and without carbon coating as anodes for lithium-ion batteries. The combination of their nanosized architecture, hollow structure, and a conductive carbon layer endows the SnO$_2$-based anode with improved specific capacity and cycling stability, making them particularly promising for use in lithium ion batteries.

Chapter 5 presents the ZnCo$_2$O$_4$ microspheres and of Zn$_{0.85}$Co$_{0.15}$O/C nanoparticles as anode materials for lithium-ion batteries. The complex structures of ZnCo$_2$O$_4$ with nanostructured constituent units and carbon modification of Zn$_{0.85}$Co$_{0.15}$O/C is favourable for the diffusion of lithium ions possess. When applied as anode materials for lithium ion batteries, the hierarchical ZnCo$_2$O$_4$ microspheres and Zn$_{0.85}$Co$_{0.15}$O/C nanoparticles exhibited good cycling
performance with slowly increasing capacity over cycling. The capability of metal oxides for lithium storage is further demonstrated.

Chapter 6 reports multi-angular rod-shaped Na$_{0.44}$MnO$_2$ prepared via a reverse microemulsion method as cathode materials for sodium-ion batteries. With the benefits of multi-angular morphology, suitable size, and fast sodium ion diffusion, the as-prepared Na$_{0.44}$MnO$_2$ rods prepared at 850°C possess stable cycling performance with capacity of 72.8 mAh g$^{-1}$ and capacity retention of 99.6% after 2000 cycles at 8.3 C. The as-designed multi-angular Na$_{0.44}$MnO$_2$ provides new insight into the development of tunnel-type electrode materials and their application in rechargeable sodium-ion batteries.

Chapter 7 presents layered P2-type Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ synthesized as a cathode material for the sodium ion battery. The effects of cut-off voltages, current density, and fluroethylene carbonate (FEC) additive on the cycling stability and coulombic efficiency are discussed in detail. In situ XRD and the galvanostatic intermittent titration technique were also used to better understand the mechanism and sodium ion diffusion during the sodium intercalation and de-intercalation process. Due to the different phase transformations and sodium ion diffusion rates, the electrochemical performance is demonstrated to be strongly related to the particular cut-off voltage and electrolyte that are used.

Chapter 8 provides an overall summary of the doctoral work and the outlook for further research work related to next-generation LIBs and SIBs.
Chapter 2. Literature Review

2.1 Development history of the battery

The word “battery” comes from the old French word ‘baterie’, meaning “action of beating,” and relates to a group of cannons in battle. In the endeavour to find an energy storage device, scientists in the 1700s adopted the term “battery” to represent multiple electrochemical cells connected together.\(^8\)

In 1800, Alessandro Volta invented the voltaic pile, the first "wet cell battery" that produced a reliable, steady electrical current. It was constructed of alternating discs of zinc and copper with pieces of cardboard soaked in brine between the metals. The voltaic pile could not deliver an electrical current over a long period of time. In 1836, John F. Daniell invented the Daniell cell, which used two electrolytes: copper sulfate and zinc sulfate. This battery lasted longer than the Volta cell or pile, and it was used to power objects such as telegraphs, telephones, and doorbells, remaining popular in homes for over 100 years. In 1839, William Robert Grove developed the first fuel cell that could produce electricity by combining hydrogen and oxygen. Then batteries using liquid electrodes to produce electricity were invented. In 1859, Gaston Plante developed the first practical lead-acid battery that could be recharged (secondary battery). In 1866, the carbon-zinc wet cell battery was invented by a French engineer, Georges Leclanche. The cathode consisted of crushed manganese dioxide with a little carbon mixed in. The negative electrode was a zinc rod. The cathode was packed into a pot, and a carbon rod was inserted to act as a current collector. The anode and the pot were then immersed in an ammonium chloride solution. The liquid electrolyte readily seeped through the porous cup and made contact with the cathode material. Georges Leclanche then further improved this design by substituting ammonium chloride paste for the liquid electrolyte and invented a method of sealing the battery, inventing the first dry cell, which
was now transportable. In 1899, Waldmar Jungner invented the first nickel-cadmium rechargeable battery. Then in 1901, Thomas Alva Edison invented the alkaline storage battery, which had iron as the anode material and nickelic oxide as the cathode material. The alkaline-manganese battery was developed by Lew Urry in 1949. In 1954, the first solar cell, which converts the sun's energy into electricity, was invented. The inventors created an array of several strips of silicon, placed them in sunlight, captured the free electrons and turned them into electrical current. The development history of the battery is summarized in Figure 2.1.

![Figure 2.1 Schematic illustration of the development history of the battery.](image)

In the case of the commercially accepted Li ion battery, the first studies took place in 1912 under G.N. Lewis, but it was not until the early 1970s that the first non-rechargeable lithium batteries became commercially available. Attempts to develop rechargeable lithium batteries followed in the 1980s, but they failed because of instability in the metallic lithium used as the anode material. Three important developments were vital to the creation of these batteries: the discovery of the LiCoO$_2$ cathode by John Goodenough (1980), the discovery of the graphite anode by Rachid Yazami (1982) and the rechargeable lithium battery prototype produced by Asahi Chemical, Japan. Sony commercialized the lithium ion battery in the early 1990s.
Nowadays, rechargeable batteries play an irreplaceable role in various aspects of our daily life, as shown in Figure 2.2. With the passage of time, various new types of rechargeable ion batteries, including sodium ion batteries, potassium ion batteries, magnesium ion batteries, and so on, have attracted the attention of researchers around the world. Nevertheless, there is a long way to go for them to be commercial.

![Figure 2.2](image)

**Figure 2.2** Representative applications for rechargeable batteries.\(^\text{10}\)

### 2.2 Fundamental concepts of batteries

A battery is a charge-separation device consisting of one or more electrochemical cells, with external connections to power electrical devices such as flashlights, smartphones, and electric cars. It stores electrical energy by separating cations (positively-charged ions) and anions (negatively-charged ions). The fundamental concepts to provide an introduction to the battery are discussed below.

#### 2.2.1 Active material

The active materials represent the materials that take part in chemical reactions and generate electrical current in a battery.

#### 2.2.2 Anode
The anode is the negatively charged electrode in an electrochemical/galvanic cell that experiences oxidation. When connected to an external circuit, the anode will give up electrons, which flow and deliver energy to the connected external device.

\subsection*{2.2.3 Cathode}

The cathode is the positively charged electrode in an electrochemical/galvanic cell. The cathode contains an excess of cations and is the electrode at which a reduction reaction occurs, or the electrode that receives electrons from an external circuit.

\subsection*{2.2.4 Binder}

A binder is any material or substance that holds or draws other materials together to form a cohesive whole, mechanically or chemically, by adhesion or cohesion. In battery production, the binder conglutinates the active materials and the conductive agent together on the metal current collector for an electrode.

Normally, the binders commonly used can be divided into two types: organic and water based binders, based on the solvent (organic solvent or water) used.

\subsection*{2.2.5 Electrolyte}

The electrolyte is a solution through which an electric current may be carried through the motion of ions. It is a transport medium between the cathode and anode, which ensures that alkali ions are effectively transported, allowing the chemical reactions to be completed at the separate terminals and thus delivering energy to the external circuit. The electrolyte ensures good electrical conductivity and minimizes voltage drop, so that the recorded potential corresponds to the actual potential. Many aqueous solutions for electrolytes are available, but typical ones contain alkali metal salts in the form of perchlorates and nitrates. In the case of non-aqueous solvents, the range of electrolytes is more limited.
2.2.6 Separator

The separator is an ion permeable, electronically non-conductive material, which prevents electronic contact between the electrodes of two opposite polarities within the same cell.

2.2.7 Parameters to evaluate battery performance

2.2.7.1 State of charge (SOC)

The state of charge (SOC) (%) of a battery expresses the present capacity as a percentage of maximum capacity, and is generally calculated using current integration to determine the change in battery capacity over time.

2.2.7.2 Depth of discharge (DOD)

The depth of discharge (DOD) (%) of a battery is the percentage of battery capacity that has been discharged, expressed as a percentage of maximum capacity. A discharge to at least 80% DOD is thought of as a deep discharge.

2.2.7.3 Self-discharging

Batteries typically lose certain amounts of their original power even when no load is applied. This self-discharging results from the non-current-producing "side" chemical reactions that occur within the cell. Typically, a battery loses 8 – 20% of its original charge per year when stored at room temperature (20 - 30 °C).

2.2.7.4 Voltage

(1) Open circuit voltage (OCV)
The open circuit voltage of a battery means the voltage between the battery terminals with no load applied, that is, the battery neither charging nor discharging. The OCV depends on and increases with the SOC of battery.

(2) Working voltage

The working voltage is the typical range of voltages of a battery during the discharge process.

(3) Terminal voltage

The terminal voltage is the voltage between the battery terminals with load applied. It varies with the SOC and charge/discharge current.

(4) Cut-off voltage

The cut-off voltage is the minimum allowable voltage of a battery. It generally defines the “empty” state of the battery.

2.2.7.5 Internal resistance

The internal resistance is the resistance within the battery. It is generally different for charging and discharging processes, and also dependent on the SOC of the battery. With increasing internal resistance, the battery efficiency decreases, and the thermal stability is reduced due to more conversion of charging energy into heat.

Because of internal resistance, the terminal voltage of a cell that is discharging is smaller than the OCV, and the terminal voltage of a cell that is charging exceeds the OCV. An ideal cell has negligible internal resistance, would maintain a constant terminal voltage until exhausted, and then drop to zero. In actual cells, the internal resistance increases under discharge, and the OCV also decreases upon discharge.

2.2.7.6 Capacity (Q)
A battery’s capacity is the amount of electric charge it can deliver, in other words the amount of energy that can be extracted from the battery under certain specified conditions. Its unit is amp-hours (Ah).

The capacity of a battery can be calculated using the following equation:

\[ Q = \int_{t_1}^{t_2} I(t) \, dt = nzF \]  

(2.1)

where \( I(t) \) is the current (A), \( t \) is the time (h), \( n \) is the number of the ions (mol), \( z \) is the valence of the ions, and \( F \) is the Faraday constant (96485 C mol\(^{-1}\)).

(1) Specific capacity

For a given active material, the more electrode material is contained in the cell, the greater its capacity will be. A small cell has less capacity than a larger cell. The specific capacity is used to evaluate and compare the energy delivered per unit weight, per unit volume or per unit area of the active material. Correspondingly, it can be described in terms of gravimetric specific capacity (ampere hour per gram: Ah g\(^{-1}\)), volumetric specific capacity (ampere hour per liter: Ah L\(^{-1}\)), and superficial specific capacity (ampere hour per square meter: Ah m\(^{-2}\)).

Normally, the charge specific capacity (\( Q_c \), mAh g\(^{-1}\)) and discharge specific capacity (\( Q_d \), mAh g\(^{-1}\)) are used to evaluate the electrochemical performance of a battery and are calculated per unit weight of the active material during charging or discharging processes. The equation is listed as follows:

\[ Q_c (or \ Q_d) = \frac{\int_{t_1}^{t_2} I(t) \, dt}{m} \times 1000 \]  

(2.2)

where \( I(t) \) is the current (A), \( t \) is the time (h), and \( m \) is the mass of active material (g).

(2) Theoretical specific capacity
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The theoretical capacity \((Q_T, \text{mAh g}^{-1})\) of a cell is the maximum amount of energy that can be extracted from the battery and can be calculated by Faraday’s law:

\[
Q_T = \frac{(nF)}{(3600*{M_w})}*1000
\]

where \(n\) is the number of charge carriers, \(F\) is the Faraday constant \((96485 \text{ C mol}^{-1})\) and \(M_w\) is the molecular weight of the active material \((\text{g mol}^{-1})\).

3) Irreversible capacity

The irreversible capacity is the difference between the charge specific capacity \((Q_c)\) and the discharge specific capacity \((Q_d)\) after each cycle, and is used to evaluate how much capacity is lost during each cycle.

For anode materials, the batteries start from the discharging process. The irreversible capacity of each cycle equals the difference between \(Q_d\) and \(Q_c\) \((Q_d - Q_c)\).

For cathode materials, the batteries start from the charging process. The irreversible capacity of each cycle equals the difference between \(Q_c\) and \(Q_d\) \((Q_c - Q_d)\).

4) Capacity retention

The capacity retention is the ratio of charge or discharge capacity of a later cycle to that in a previous one, which can be obtained by the following equation:

\[
\text{Capacity retention} = \frac{(n^\text{th} \, Q_c)}{(m^\text{th} \, Q_c)} \times 100\% \text{ or } \frac{(n^\text{th} \, Q_d)}{(m^\text{th} \, Q_d)} \times 100\% \ (n > m)
\]

The higher the capacity retention is, the better the energy storage capability of the battery will be.

2.2.7.7 Coulombic efficiency (CE, \(\eta\))

The coulombic efficiency represents the ratio of the output of charge by a battery to the input of charge and is determined by the internal resistance of a cell.
2.2.7.8 Cycle life

The cycle life is the number of discharge-charge cycles a battery experiences before it fails to meet a specific performance criterion. It is estimated for specific discharge and charge conditions. The actual operating life of a battery is affected by the depth and rate of cycling, and by other conditions such as humidity and temperature. The higher the DOD, the shorter the cycle life will be.

2.2.7.9 Rate capability or C-rate

The rate capability, also called the C-rate, is generally used to evaluate the transfer speed of alkali ions during the charging or discharging process at a specific current density. The C-rate is a measure of the rate at which a battery is discharged relative to its maximum capacity. At 1 C, the time for the battery to be completely charged or discharged is 1 h. At 0.5 C, the current is cut in half, and the time is doubled, and at 0.1 C the current is cut to one-tenth and the time is increased 10-fold.

2.2.7.10 Specific energy and energy density

The Specific energy, or gravimetric energy density, defines the nominal battery energy in terms of mass (Wh/kg). The specific energy of an electric vehicle battery, as a characteristic of the battery chemistry and packaging, along with the energy consumption of the vehicle, determines the battery weight required to achieve a given electric range.

Correspondingly, the energy density, or volumetric energy density, defines the nominal battery energy per unit volume (Wh/L). Along with the energy consumption of the vehicle, the energy density determines the battery size required to achieve a given electric range.

2.2.7.11 Specific power and power density
The specific power, or the gravimetric power density, referring to the maximum available power per unit mass, is the ratio of the power available from a cell to its cell mass (W/kg). It determines the battery weight required to achieve a given performance target.

Correspondingly, the power density is the maximum available power per unit volume (W/L). It determines the battery size required to achieve a given performance target.

**2.3 Theory and mechanism of the battery**

Batteries convert chemical energy directly to electrical energy. Each cell of a battery consists of two half-cells connected by a conductive electrolyte. One half-cell includes the electrolyte and the anode to which the anions migrate; the other one includes the electrolyte and the cathode to which the cations migrate.

A schematic illustration of a Li or Na half-cell is presented in Figure 2.3. In a half-cell, the Li or Na metal is used as both the counter and reference electrode for LIBs or SIBs, respectively. The working electrode is prepared by mixing the active materials, conductive agent and
binder together, and the slurry-like mixture is then coated on copper or aluminium foil. The electrodes do not touch each other, but are electrically connected by the electrolyte. In a full battery, the separator allows ions to flow between half-cells. The battery is powered by the redox reactions in the cells.

An illustration of a LIB is shown in Figure 2.4 as an example to illustrate the inner reaction mechanism of the battery. The negative electrode is graphitic carbon, which holds Li ions in its layers, whereas the positive electrode is a Li-intercalation oxide compound, which is often characterized by a layered structure. Li ions can be reversibly inserted and removed at both electrodes. On charging, Li ions are removed or de-intercalated from the layered oxide cathode and intercalated into the layers of graphite. The process is reversed on discharging. The electrodes are separated by a non-aqueous electrolyte, allowing the transport of Li ions between the two electrodes.

As mentioned above, SIBs have attracted increasing attention as a low-cost alternative to LIBs because of the abundance, low cost, and suitable redox potential of sodium. SIBs
experience similar reactions to LIBs during charge-discharge processes since Na and Li are in the same group of the periodic table of elements. In addition, Na ions, as relatively larger ions than Li ions, offer more flexibility in materials design. The larger ionic radius of sodium compared to lithium offers weak solvation energy in polar solvents, and the high ionic conductivity of Na-based electrolyte is also beneficial to obtain better battery performance compared to Li-based electrolyte.\(^{13}\)

When choosing electrode materials for LIBs and SIBs, several criteria, including societal, economic, and technical considerations, are proposed. These include their natural abundance; lack of competition with other industrial applications; and eco-friendliness for processing, usage, and recycling.\(^{14}\) Technologically, the electrode materials must offer a large reversible storage capacity at the desired electrochemical potential. Figure 2.6 shows the potential elements available for use as new electrode materials.

![Figure 2.5 Elements available for the design of new electrode materials. The colored squares are excluded due to their high cost, toxicity, or radioactivity. Despite their toxicity, some transition metals, such as V and Co, are still actively investigated.\(^3\) The table can be revised, as some materials have displayed acceptable electrochemical performance in recent reports,](image_url)
including Sn, Nb, Mo, and W. Different metal oxides have been studied and applied as anodes or cathodes for LIBs or SIBs, details of which together with other electrodes materials will be discussed in the following parts.

### 2.4 Electrode materials for LIBs

Figure 2.6 shows the voltage vs. capacity for different electrode materials that could be used for the next generation of rechargeable Li-based batteries. The choice of electrode materials depends on the particular type of aimed system, whether the aim is a rechargeable Li-metal battery or a Li-ion battery. For the rechargeable Li-metal battery, owing to the use of metallic Li as anode, the cathode electrode does not need to be lithiated before cell assembly. In contrast, for LIBs, because the carbon or other alternative negative electrodes have no lithium, the positive electrode must act as the Li source, so air-stable Li-based intercalation compounds are normally chosen to facilitate the cell operation.

#### 2.4.1 Anode materials for LIBs
In 1982, Yazami and Touzain reported the first successful experiment demonstrating the electrochemical intercalation and release of lithium into/out of graphite.\textsuperscript{16} Since then, graphitic carbon anodes have been and still are being used as the main anode materials in commercial LIBs due to their extremely low cost, excellent cycling stability and reliability, and environmental friendliness. With the increasing demand for larger capacity and higher lithium diffusion rates in LIBs, researchers have focused on finding alternative anode materials in recent years. The aim of developing new anode materials for LIBs is to obtain higher specific capacity than the current 372 mAh g\textsuperscript{-1} of commercially used graphite, while keeping the excellent properties of carbonaceous materials, including low cost, good cycling stability, and good safety features. The alternative anode materials for LIBs can be classified into four major groups: carbonaceous materials, lithium-metal alloy materials, metal oxides, and other materials.

2.4.1.1 Carbonaceous materials

Carbonaceous materials, which have been widely studied, are the most promising candidate anode materials for LIBs. Carbon is the most widespread element in nature and has various forms. The discovery of graphene has propelled the research on carbon into a new era, with special reference to its use in LIBs.\textsuperscript{17-19} Different widely studied types of carbon are illustrated in Figure 2.7. A great number of carbonaceous materials with high theoretical capacities, as well as excellent properties (e.g., high surface area, high conductivity, excellent chemical stability), have been explored as anode materials for LIBs, including one-dimensional (1D) carbon nanotubes, carbon nanowires, and carbon nanofibers, two-dimensional (2D) graphene, and other structures (e.g., amorphous, porous carbon).
Figure 2.7 Different forms of carbon: graphene (top left); graphite (top right); carbon nanotube (bottom left) and buckminsterfullerene ($C_{60}$, bottom right).  

Graphite is regarded as the first successful example of an LIB anode among the carbonaceous anode materials, as mentioned above. In the half-cell reaction coupled with lithium foil, the discharge step involves lithium ion intercalation into graphitic layers without major structural changes, while the de-intercalation process corresponds to the charge process:

$$C_n + xLi^+ + xe^- \leftrightarrow Li_xC_n \ (0 \leq n \leq 6) \quad (2.5)$$

The low theoretical capacity of 372 mAh g$^{-1}$ of graphite, however, is insufficient to provide the high energy required from the LIB system for some applications. In addition, the diffusion coefficient of Li ions in graphite is less than $10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which leads to a low power density.  

The carbon nanotubes (CNTs), with high length-to-diameter ratios (diameter less than 100 nm), are typical representative carbonaceous-based electrode materials due to their high capacities. The capacity for the storage of lithium in CNTs results from the effective diffusion of lithium ions into the sidewalls of the CNT. During the discharge process, lithium ions can be stored in stable sites located on the nanotube surface and/or inside individual
nanotubes, which they access through the end cap or sidewall openings. Conductive, free-standing, binder-free flexible CNT films were prepared by adding the CNTs to a starting dispersion of carbon black and Triton X-100, followed by a vacuum filtration technique. The flexible multi-walled CNT (MWCNT) electrodes show stable cycling behaviour and allow up to a 10 C-rate (Figure 2.8a).

Figure 2.8 (a) Schematic illustration of synthesis and electrochemical performance of free-standing MWCNT film, and (b) schematic illustration and electrochemical performance of core-shell Si/carbon nanowire.

2.4.1.2 Lithium-metal alloy materials

Like carbon materials, elements from groups IV and V in the periodic table can be alloyed with Li metal. The capacities can be extremely high, and they are achieved from (de)alloying reactions as follows:

$$Li_xM \leftrightarrow M + xLi^+ + xe^-$$  \hspace{1cm} (2.6)

where M represents the elements from the carbon and nitrogen families, such as Si, Sn, Ge, Pb, P, As, Sb, and Bi, as well as other metal elements, such as Al, Au, In, Ga, Zn, Cd, Ag, and Mg. Among them, as one of the most promising materials, Si can alloy with lithium
with a saturation composition of Li$_{4.4}$Si ($x = 4.4$ in equation (2.6)), corresponding to a capacity of 4212 mAh g$^{-1}$, which is more than 10 times the capacity of graphite.

The practical utilization of lithium-metal alloy materials for LIBs, however, is severely limited by the huge volume changes during the lithiation/delithiation processes. The significant volume changes will introduce large strains into the electrode, which will cause cracks and crumbling in the electrode and loss of electrical contact between individual particles, degrading the cycling stability of the LIB.$^{25, 28, 30-32}$ Also, new solid-electrolyte interphase (SEI) layers formed on the fresh surfaces arising from the cracks and pulverization would result in low coulombic efficiency. In order to address these issues, various approaches, including the design of nanostructures and carbon composites, have been applied to Si anode to overcome the huge volume changes and maintain the structural integrity. For example, Cui’s group reported silicon nanowire battery electrodes that can accommodate large strain without pulverization, provide good electronic contact and conduction, and display short lithium insertion distances.$^{28}$ The theoretical charge capacity was obtained for this silicon anode and a discharge capacity close to 75% of this maximum with little fading during cycling was maintained. Core-shell carbon nanofibers coated with amorphous silicon were also successfully prepared (Figure 2.8b).$^{25}$ The carbon core experiences less structural damage during lithium cycling and can function as a mechanical support and an efficient electron conducting pathway. The resultant nanowires achieved the high capacity of $\sim$2000 mAh g$^{-1}$ with good cycling life, exhibiting a high coulombic efficiency of 90% for the first cycle and 98-99.6% for the following cycles.

2.4.1.3 Metal oxides

Various metal oxides have been intensively studied as potential anodes for LIBs owing to their high reversible capacities (500 - 1000 mAh g$^{-1}$). According to their reaction mechanisms,
metal oxide anodes can be divided into three categories: 1) intercalation-deintercalation reaction, 2) alloying-dealloying reaction, and 3) conversion (redox) reaction. Figure 2.9 shows some metal oxides with different reaction mechanisms as anodes for LIBs.

![Figure 2.9 Metal oxides with different reaction mechanism as anodes for LIBs.](image)

Metal oxide anodes with the insertion reaction mechanism are used for LIBs due to their low cost and non-toxicity. The drawback of these anodes is that the number of lithium ions involved in the insertion reaction is normally less than one per formula unit. This is because lithium can only occupy the vacant sites of these crystal frameworks, resulting in low specific capacity. Ti-based oxide compounds (such as TiO$_2$ and Li$_4$Ti$_2$O$_12$) are typical metal oxides which store lithium through the insertion reaction mechanism. For example, the reaction between TiO$_2$ and lithium ions can be described as follows:
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\[ TiO_2 + xLi^+ + xe^- \leftrightarrow Li_xTiO_2 (x \leq 1) \]  (2.7)

TiO\(_2\) has a theoretical capacity of 335 mAh g\(^{-1}\) and a high lithium intercalation potential (1.75 V vs. Li\(^+\)/Li), offering enhanced safety due to the elimination of the lithium plating that appears below ~1 V vs. Li\(^+\)/Li. Anatase TiO\(_2\) nanotube anode is generally considered the most attractive anode material.\(^{34}\) Myung et al. prepared anatase TiO\(_2\) nanorods by hydrothermal reaction of amorphous TiO\(_2\) in NaOH solution, followed by ion exchange in HCl solution and dehydration at 400°C.\(^{35}\) When cycled between 1 and 3 V at 50 mA g\(^{-1}\), the initial discharge and charge capacities were 320 and 265 mAh g\(^{-1}\), respectively. A reversible capacity of 225 mAh g\(^{-1}\) was also maintained after 50 cycles.

For the Li-alloying reaction compounds, Sn-based oxides (such as SnO and SnO\(_2\)) are typical representatives. The basic reactions of SnO\(_2\) could be written as follows:

\[ SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O \]  (2.8)
\[ Sn + 4.4Li_2O \leftrightarrow Li_{4.4}Sn \]  (2.9)

The first step is irreversible or partly reversible. In this two-step reaction, SnO\(_2\) provides a theoretical capacity of 783 mAh g\(^{-1}\), which is less than for the elemental Sn (992 mAh g\(^{-1}\)). SnO\(_2\), however, is easier to handle and store due to its higher melting point and stability. Moreover, the electrochemically induced Li\(_2\)O could buffer the initial Sn aggregation and hold reduced Sn particles during the Li insertion process. At present, porous SnO\(_2\) nanostructures,\(^{36}\) SnO\(_2\) nanoboxes,\(^{37}\) SnO\(_2\) nanowires,\(^{38}\) and SnO\(_2\)-based nanocomposites\(^{39-41}\) have been prepared to alleviate the Sn aggregation issue. For example, mesoporous graphene-based TiO\(_2\)/SnO\(_2\) hybrid nanosheets (TiO\(_2\)@SnO\(_2\)@GN) were successfully prepared by Tang et al.\(^{40}\) The volume expansion and agglomeration of SnO\(_2\) during the Li-alloying/dealloying processes are effectively suppressed by the structure of both the SnO\(_2\) and the TiO\(_2\) nanoparticles that are loaded on a conductive graphene substrate in a 2D mesoporous manner. The TiO\(_2\)@SnO\(_2\)@GN retained a reversible capacity of 600 mAh g\(^{-1}\), which is stable and
even shows an increase after 300 cycles. Liu et al. fabricated a binder-free graphene film decorated with spindle-like Fe$_2$O$_3$@SnO$_2$ nanoparticles using vacuum filtration of a Fe$_2$O$_3$@SnO$_2$ and graphite oxide (GO) mixed solution with a subsequent thermal reduction treatment. The core-shell structured Fe$_2$O$_3$@SnO$_2$ nanoparticles exhibited initial discharge and charge capacities of 2063 and 1255 mAh g$^{-1}$, respectively, retaining a reversible capacity of 1015 mAh g$^{-1}$ after 200 cycles.

**Figure 2.10** Theoretical (black bars), first discharge (dark grey), and charge (light grey) specific capacities of different metal oxides that react with lithium through a conversion reaction.

Considering the redox reaction mechanism, there are a large number of transition metal oxides (M$_x$O$_y$, where M = Cr, Mo, Mn, Fe, Ru, Co, Ni, Cu, etc.) that experience the redox reaction through the conversion reaction mechanism with lithium. Figure 2.10 presents different specific capacities of metal oxides reacting with lithium through a conversion reaction mechanism, which can be expressed as follows:

$$M_xO_y + 2yLi^+ + 2ye^- \leftrightarrow xM + yLi_2O$$

(2.10)
Their electrochemical performance is summarized in Figure 2.8. For instance, since the high theoretical capacity of 890 mAh g$^{-1}$ for Co$_3$O$_4$ was first reported in 2000, a great number of Co$_3$O$_4$ materials with different morphologies, including nanowires, nanocages, needle-like nanotubes and nanosheets, have been prepared and proved to achieve stable and reversible capacities of 800-900 mAh g$^{-1}$.

2.4.1.4. Other materials

Layered metal sulphides, MS$_2$ (M = Mo, W, Ti, Sn, Nb, and Fe) have a similar structure to graphitic carbon and have thus been considered as anode materials for LIBs. For example, MoS$_2$ was synthesized with expanded layers and studied as LIB anode in an ether-based electrolyte. By limiting the cut-off voltage to 1.0 V, the as-prepared MoS$_2$ achieved 96% capacity retention even after 1400 cycles and showed good electrochemical performance with LiCoO$_2$ as the counter electrode in a full cell. In addition, transition metal nitrides, transition metal phosphides, transition metal fluorides and some polyanionic systems have shown their potential for application as anode in LIBs. In addition, due to their low-voltage redox activity, organic compounds have attracted attention and been investigated as electrodes for LIBs. Michel et al. prepared two organic salts, Li$_2$C$_8$H$_4$O$_4$ (Li terephthalate) and Li$_2$C$_6$H$_4$O$_4$ (Li trans-trans-muconate), with carboxylate groups conjugated within the molecular core. These two organic compounds were respectively able to react with two and one extra Li per formula unit at potentials of 0.8 and 1.4 V, delivering reversible capacities of 300 and 150 mA h g$^{-1}$.

2.4.2 Cathode materials for LIBs

Cathode materials for LIBs have been considered one of the biggest obstacles to the goal of obtaining perfect electrochemical performance. A wide range of materials can be chosen as cathodes for LIBs, although the ideal cathode material is the one that exhibits no structural
change during cycling. Several reviews focused on the cathode materials for LIBs have been published, such as reviews by Nazar’s group \textsuperscript{61}, Doron Aurbach’s group \textsuperscript{62}, and Goodenough’s group \textsuperscript{63}. The key requirements when a material is chosen as a cathode material for LIBs must be considered carefully as follows:\textsuperscript{19}

1) The discharge reaction should have a large negative Gibbs free energy (high discharge voltage);

2) The host must have low molecular weight and the ability to intercalate a large amount of lithium (high energy capacity);

3) The host must have a high lithium diffusion coefficient (high power density);

4) The structural modifications during charge and discharge processes should be as small as possible (long cycle life);

5) The material should be chemically stable, non-toxic and inexpensive;

6) The handling of material should be easy.

The anode materials for LIBs are divided into several groups here and discussed, namely, metal oxides, vanadium oxides, polyanionic compounds, and other materials.

2.4.2.1 Metal oxides

Based on their structure, three types of metal oxides, namely, layered, spinel and olivine lithium metal oxide, constitute the metal oxide family of cathode materials for LIBs.\textsuperscript{60} Illustration of the structures of different metal oxides are presented in Figure 2.11,\textsuperscript{64} and the representative compounds are LiCoO\textsubscript{2} with the layered structure, LiMn\textsubscript{2}O\textsubscript{4} with the spinel structure and LiFePO\textsubscript{4} with the olivine structure, respectively. Figure 2.12 shows the formulae, structures, and potential profiles during the discharging process of several typical metal oxides as cathodes for LIBs.
Figure 2.11 Schematic illustrations of various crystallographic structures of (a) LiMO$_2$ (layered structure observed along the (111) plane, blue: MO$_6$ octahedron, M: transition metal), (b) LiFePO$_4$ (olivine structure observed along the [010] direction, light purple: PO$_4$ tetrahedron, brown: FeO$_6$ octahedron), and (c) LiMn$_2$O$_4$ (spinel structure observed along the <110> direction, purple: MnO$_6$ octahedron). The small green balls represent Li$^+$.\textsuperscript{64}

Figure 2.12 Formulae, structures, and potential profiles during the discharging process of several typical metal oxides as cathodes for LIBs.\textsuperscript{14}

Owing to its simple and scalable production, high theoretical capacity (274 mAh g$^{-1}$), reasonable rate performance, and good cycle life, layered structured LiCoO$_2$ is commercially used as the cathode material of choice for LIBs.\textsuperscript{65} Nowadays, the combination of LiCoO$_2$ as
cathode and graphite as anode gives the commercial lithium-ion battery. The practical reversible capacity of LiCoO$_2$ is \(\sim140 \text{ mAh g}^{-1}\) when the cut-off voltage is 4.2 V (Li$_x$CoO$_2$, \(0.5 < x < 1\)). To increase the specific reversible capacity, the cells have to be charged above 4.2 V (\(x < 0.5\)), but the capacity retention will deteriorate with increasing cut-off voltage. LiNiO$_2$, LiMnO$_2$, and their solid solutions are also widely studied cathode materials for LIBs with layered structure.\(^{66-70}\)

LiMn$_2$O$_4$, originally proposed by Thackeray et al.\(^71\) has a spinel-framework structure (Figure 2.11c) and has been developed as a possible alternative to commercial LiCoO$_2$ because it shows a flat operating voltage of 3.95–4.1 V with theoretical capacity of 148 mAh g$^{-1}$. High-quality single-crystalline cubic spinel LiMn$_2$O$_4$ nanowires were successfully synthesized using Na$_{0.44}$MnO$_2$ nanowires as a self-template.\(^72\) These single crystalline LiMn$_2$O$_4$ nanowires showed high thermal stability and excellent performance at high rates, even 20 A g$^{-1}$, with both a relatively flat charge-discharge plateau and excellent cycling stability. Another spinel structured compound, Li$_4$Ti$_5$O$_{12}$, is also under consideration as anode for LIBs due to its \(\sim1.55\) V charging potential, as there is no danger of the lithium metal deposition that might occur on graphitic carbon at high rates. Carbon-coated spinel Li$_4$Ti$_5$O$_{12}$ anode material was prepared by heat-treating a mixture of TiO$_2$ (anatase), Li$_2$CO$_3$ and sugar.\(^73\) Compared to its bare counterpart, the carbon-coated Li$_4$Ti$_5$O$_{12}$ displays a larger diffusion coefficient for lithium ions, high rate capability, and excellent reversibility with capacity of approximately 160 mAh g$^{-1}$ at 0.1 C.

As one of the most popular of the olivine family, since its proposal by Goodenough’s group, olivine structured LiFePO$_4$ has attracted particular interests due to the low cost and the environmental compatibility of its basic constituents.\(^{74-79}\) A nanocomposite of LiFePO$_4$ nanoparticles embedded in a nanoporous carbon matrix (LFP-NP@NPCM) was synthesised by Wu et al. (Figure 2.13).\(^80\) The as-prepared LFP-NP@NPCM cathode showed that it could
be fully charged or discharged within a period of less than 30 s, similar to a supercapacitor, but with more energy density. The specific capacity retained was ~100 mAh g$^{-1}$ after 700 cycles with coulombic efficiency of almost 100%. Olivine structured LiMnPO$_4$ nanoplates have been synthesized via a novel, single-step, solid-state reaction in molten hydrocarbon.\textsuperscript{81} Porous LiMnPO$_4$ nanoplates with a thickness of ~50 nm were assembled and grew into nanorods along the [010] direction in the (100) plane. After carbon coating, the thus-prepared LiMnPO$_4$ cathode demonstrated a flat potential at 4.1 V (vs. Li$^+/Li$) with a stable specific capacity as high as 168 mAh g$^{-1}$.

\textbf{Figure 2.13} Electrochemical characterization of the LFP-NP@NPCM nanocomposite: a) charge/discharge profiles cycled at the rate of C/9; b) charge/discharge curves with different charge/discharge times and discharge energy densities; c) rate performance at different power densities, with the inset showing the Ragone plots for the nanocomposite and commercially available supercapacitor electrodes; and d) cycling performance of the LFP-NP@NPCM
nanocomposite cycled at a rate of 1.5 C between 2.2 and 4.2 V (vs. Li\(^+\)/Li), with the inset showing the corresponding coulombic efficiency profile. 

2.4.2.2 Vanadium oxides

![Structure of vanadium oxides](image)

**Figure 2.14** Structures and relations between different vanadium oxides. 

There are many vanadium oxides: VO\(_2\), V\(_2\)O\(_3\), V\(_2\)O\(_5\), and V\(_n\)O\(_{2n-1}\), etc., among which, VO\(_2\)(B) (isostructural to TiO\(_2\)(B)) and V\(_2\)O\(_5\) have been investigated for use as anode materials for LIBs via an intercalation mechanism. Figure 2.14 presents the structures of and relations between different vanadium oxides. The layered structures of vanadium oxides predominantly consist of MO\(_6\) octahedra, which normally share corners and/or edges (and in a few cases faces), to form 2D sheet structures. These sheets may be one octahedron thick, as in V\(_2\)O\(_3\) itself, or two octahedra thick, as in the \(\delta\)-phases, M\(_x\)V\(_4\)O\(_{10}\). V\(_2\)O\(_4\) is formed in the absence of any vacancies. V\(_2\)O\(_5\) has attracted the most interest among the vanadium oxide species, owing to its low cost and high theoretical capacity (437 mAh g\(^{-1}\)). It suffers from
capacity fading, however, resulting from the decomposition of electrolyte or the dissolution of $\text{V}_2\text{O}_5$, which generates irreversible phases [$\varepsilon$-$\text{Li}_x\text{V}_2\text{O}_5$ $(0.35 < x < 0.7)$ and $\delta$-$\text{LiV}_2\text{O}_5$] during cycling.\textsuperscript{87} While doping could improve the cycling stability of the vanadium oxides, the doped materials suffer from lower capacity.\textsuperscript{88}

Another type that has been of much interest is $\text{Li}_{1+x}\text{V}_3\text{O}_8$, which is composed of quadruple chains of $\text{VO}_6$ octahedra connected by double chains of $\text{VO}_5$ square pyramids through terminal corners. In 1983, Panero et al. found that, at current densities ranging from 0.5 to 2 mA cm$^{-2}$, $\text{Li}_{1+x}\text{V}_3\text{O}_8$ with low $x$ values could reversibly insert three $\text{Li}^+$ ions per formula unit and deliver a steady capacity of more than 100 mAh g$^{-1}$ over many cycles.\textsuperscript{89} The lithium insertion behaviour of $\text{Li}_{1.2}\text{V}_3\text{O}_8$ was investigated under ambient conditions and at the high temperature of 100°C using both chemical and electrochemical methods. According to the open-circuit voltage dependence on the Li content in $\text{Li}_{1+x}\text{V}_3\text{O}_8$, the lithiation proceeds as a single-phase reaction for $1+x \leq 3$. A constant value was observed in the region of $2.0 < x < 3.0$, and a two-phase plateau appears up to the $\text{Li}_4\text{V}_3\text{O}_8$ composition, which has a disordered rock-salt structure.\textsuperscript{90}

2.4.2.3 Polyanionic compounds
The safety, cost, and environmental issues for LiCoO$_2$/C cells have raised the demand for new positive electrode materials with minimal cobalt content, such as polyanionic compounds composed of iron and manganese, which offer substantial safety and environmental benefits. The polyanionic compounds mentioned here do not include the olivines LiFePO$_4$ and LiMnPO$_4$, which have already been discussed. Other polyanionic compounds (fluorophosphates, fluorosulfates and silicates), including LiFePO$_4$F, LiVPO$_4$F, and LiFeSO$_4$F, Li$_2$FeSiO$_4$, and Li$_2$MnSiO$_4$ have been investigated. Their crystal structures are shown in Figure 2.15. LiVPO$_4$F holds promise as a two-electron redox material, with its lithium extraction/insertion based on the reversibility of the V$^{3+}$/V$^{4+}$ and V$^{2+}$/V$^{3+}$ redox couples at 4.2 and 1.75 V, respectively. Compared to the corresponding transition metal olivines, the silicates have lower potentials. For example, the electrochemistry of Li$_2$FeSiO$_4$ prepared at 750$^\circ$C showed a plateau at 3.10 V vs. Li/Li$^+$ on the initial charge, but this plateau shifted to 2.80 V on subsequent cycles.

2.1.2.4 NASICON type

The Sodium Super Ionic Conductor (NASICON) family of compounds is particularly attractive because of its inherently high ionic conductivity. They are of the general formula $A_xMM'(XO_4)_3$ ($A$ = alkali ion; $M$, $M'$= transition metal; $X$ = S, P, Mo, and W) and comprise a three dimensional framework of $MO_6$ and $M'O_6$ octahedra sharing corners with $XO_4$ tetrahedra. This structure allows for extensive substitution on the octahedral ($M$ and $M'$) and tetrahedral ($X$) sites, and the thus-formed large interstitial channels can effectively accommodate alkali cations, among which, Li$_3$V$_2$(PO$_4$)$_3$ is a typical representative, and its
crystal structure is shown in Figure 2.16. Its three-dimensional network consists of slightly distorted metal octahedra and phosphorus tetrahedra linked together via common apical oxygens to form a (M-O-P-O)_n bonding arrangement. When cycled in the 3.0-4.8 V voltage window, Li_3V_2(PO_4)_3/C composite showed itself to be a high energy material (average potential of 3.85 V vs. Li) with a specific energy density of 2330 mWh cm^{-3}, which is comparable to other materials such as LiCoO_2 (2750 mWh cm^{-3}) and LiFePO_4 (2065 mWh cm^{-3}).

Figure 2.16 (a) Crystal structure (along the [010] direction) and (b) voltage-composition plot for Li_3V_2(PO_4)_3 at the rate of 1C in the voltage window 3.0-4.8 V.

2.4.3 Electrolytes for LIBs

The electrolyte plays an indispensable role in batteries, providing electrical conductivity and acting as a transport medium between the cathode and anode. Electrolytes are mainly composed of salts and solvents. There are different kinds of electrolytes used in the LIB system, including inorganic liquid electrolyte, organic liquid electrolyte, ionic liquid electrolyte, organic solid electrolyte, and inorganic solid electrolyte. Table 2.1 shows the important properties of typical electrolytes used in LIBs. In general, for an ideal electrolyte, the following conditions should be fulfilled:
(1) High chemical and thermal stability of the electrolyte/electrode interface during cycling;

(2) No reactivity towards the cell;

(3) Large anodic-cathodic stability window;

(4) High ionic conductivity ($\sigma_{Li} > 10^{-4}$ S cm$^{-1}$) and low electronic conductivity ($\sigma_{e} < 10^{-10}$ S cm$^{-1}$);

(5) Transference number $\sigma_{Li^+}/\sigma_{total} \approx 1$ (with $\sigma_{total}$ including the conductivities of all the other ions in the electrolyte, as well as $\sigma_{Li^+}$);

(6) Suitability for broad ambient temperature ranges;

(7) Non-toxic, non-flammable, and environmentally friendly;

(8) Low cost.

Table 2.1 Properties of typical electrolytes in LIB system.

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Example of classical electrolytes</th>
<th>Ionic conductivity ($\times 10^{-7}$ S/cm) at room temp</th>
<th>Electrochemical window (V) vs Li$^+/Li^0$</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid organic</td>
<td>1M LiPF$_6$ in EC:DEC (1:1)</td>
<td>7$^3$</td>
<td>1.3$^7$</td>
<td>4.5$^9$ Flammable</td>
</tr>
<tr>
<td>Ionic liquids</td>
<td>1M LiPF$_6$ in EC:DMC (1:1)</td>
<td>10$^{13}$</td>
<td>1.3$^{15}$</td>
<td>$&gt;5.0^{3}$</td>
</tr>
<tr>
<td>Polymer</td>
<td>LiTFSI-P(EO)MEEGE, LiClO$_4$−PEO$_8$ + 10 wt % TiO$_2$</td>
<td>0.1$^{24}$</td>
<td>&lt;0.0$^{24}$</td>
<td>4.5$^{54}$ Flammable</td>
</tr>
<tr>
<td>Inorganic solid</td>
<td>Li$<em>{1-x}$C$<em>6$C$</em>{6-x}$, $x = 0.75$, 0.05Li$</em>{2}$SO$_4$, 0.57Li$_2$S + 0.38Si$_2$</td>
<td>2.2$^{28}$</td>
<td>&lt;0.0$^{28}$</td>
<td>$&gt;5.0^{28}$ Non-flammable</td>
</tr>
<tr>
<td>Inorganic liquid</td>
<td>LiAlCl$_4$ + SO$_2$</td>
<td>70$^{20}$</td>
<td>-</td>
<td>4.4$^{90}$ Non-flammable</td>
</tr>
<tr>
<td>Liquid organic + Polymer</td>
<td>0.04LiPF$_6$ + 0.2EC + 0.62DMC + 0.14PAN, LiClO$_4$ + EC + PC + PVdF</td>
<td>4.2$^{38}$</td>
<td>-</td>
<td>4.4$^{38}$ Flammable</td>
</tr>
<tr>
<td>Ionic liquid + Polymer</td>
<td>1M LiTFSI + P$_3$TFSI + PVdF-HFP</td>
<td>0.18$^{63}$</td>
<td>&lt;0.0$^{63}$</td>
<td>5.8$^{63}$ Less flammable</td>
</tr>
<tr>
<td>Ionic liquid + Polymer + Liquid organic</td>
<td>56 wt % LiTFSI−P$_3$TFSI + 30 wt % PVdF−HFP + 14 wt % EC/PC</td>
<td>0.81$^{64}$</td>
<td>1.5$^{64}$</td>
<td>4.2$^{44}$ Less flammable</td>
</tr>
<tr>
<td>Polymer + Inorganic solid</td>
<td>2 vol % LiClO$_4$−TEC−19 + 98 vol % 95 (0.6Li$_2$S + 0.4Li$_2$S) + 5Li$_2$SO$_4$</td>
<td>0.0$^{66}$</td>
<td>&lt;0.0$^{66}$</td>
<td>$&gt;4.5^{46}$ Non-flammable</td>
</tr>
<tr>
<td>Ionic liquid + Liquid organic</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

In addition, additives, such as vinylene carbonate (VC), fluoroethylene carbonate (FEC), vinyl ethylene carbonate (VEC), trimethoxyboroxine (TMOBX), trimethyl borate (TMB), etc., are often used in the electrolyte to tune the composition of the SEI, enhance its stability,
and create a functional electrolyte, e.g. reduce flammability, prevent overcharging, and assist the wetting of electrodes. The additives can be targeted towards safety oriented properties, originating in the electrolyte, but not reaching sufficient chemical and electrochemical stability, or be more performance oriented, such as to expand the operating window in terms of voltage or increase the C-rate by reducing the viscosity.

2.5 Electrode materials for SIBs

![Figure 2.17 Schematic illustration of a Na-ion battery system.](image)

In order to construct high-performance SIBs, it is essential to find potential electrodes providing sufficiently big interstitial spaces for insertion and extraction of Na⁺ ions. Figure 2.17 is a schematic illustration of the components of a Na-ion battery system. Different types of materials are under investigation and have been studied as electrode materials for SIBs. Commonly, Na compounds and their Li analogues form similar crystal structures with small differences in lattice parameters, distortion, and local environment, but in some cases, they form completely different structures. Figure 2.18 shows the voltage-capacity plots of some typical anodes and cathodes used for SIBs. The differences in structure between Li and Na compounds provide opportunities for new Na-intercalation materials. For example, in the
case of layered AMO$_2$ ($M = V, Cr, Fe, Mn; A = \text{alkali metal}$), NaMO$_2$ shows good electrochemical performance, whereas its Li equivalents LiMO$_2$ shows almost no discharge capacity after the first charge.

![Figure 2.18](image)

**Figure 2.18** Relationship between voltage and capacity of electrode materials for NIBs.  

2.5.1 Anode materials for SIBs

Sodium metal anodes are commonly used on the laboratory scale to evaluate the performance of cathode materials. Similar to Li metal, Na metal as an anode for SIBs is very reactive to organic electrolyte solvents and would produce dendrites during Na metal deposition. Moreover, the use of Na metal electrode at ambient temperatures presents a significant safety hazard in devices due to the low melting point of Na (98 °C). Thus, it is essential to find anode alternatives to sodium metal for SIBs.$^{115}$ A very recent review has given a comprehensive account for present and future for SIBs.$^{113}$ The alternative anodes for SIBs
can be divided into carbonaceous materials, sodium-metal alloy materials, metal oxides and sulphides, and organic compounds.

2.5.1.1 Carbonaceous materials

![Figure 2.19](image.png)

**Figure 2.19** Discharge capacity of hollow carbon nanowire (HCNW) electrode at different charge–discharge current densities.\(^{117}\)

Unlike the successful application of graphite in LIBs, electrochemical sodium insertion into graphite has been proven to be unfavourable.\(^{118-120}\) Nevertheless, a variety of carbon-based materials, including hard carbon,\(^{118, 121-123}\) carbon black,\(^{124}\) petroleum coke,\(^{125-127}\) macroporous carbon,\(^{128}\) carbon microspheres,\(^{129}\) carbon nanowires,\(^{117}\) carbon nanospheres,\(^{130}\) and graphene,\(^{131}\) have been demonstrated to facilitate the insertion/extraction of Na ions into/from the host frameworks of SIBs. For instance, Dahn’s group reported that “house of cards” carbon could deliver an initial capacity as high as ~ 300 mAh g\(^{-1}\) because of the efficient sodium intercalation into the nanopores of carbon during the discharge process.\(^{132}\) Figure 2.19 presents hollow carbon nanowires (HCNWs) prepared through pyrolyzation of a hollow polyaniline nanowire precursor.\(^{117}\) The HCNWs delivered a high reversible capacity of 251 mAh g\(^{-1}\) and 82.2% capacity retention over 400 cycles between 1.2 and 0.01 V (vs.
Na⁺/Na) at a constant current of 50 mA g⁻¹. Furthermore, heteroatom doping (N, B, and P) of carbon nanomaterials have been demonstrated to significantly enhance the electrical conductivity and surface hydrophilicity of carbon-based electrodes to facilitate the charge transfer and electrolyte–electrode interactions. For example, Wang et al. prepared functionalized N-doped carbon nanofibers (FN-CNFs) using polypyrrole as precursor.¹³³ The FN-CNFs anode delivered a capacity of 134.2 mAh g⁻¹ at a high current density of 200 mA g⁻¹ after 200 cycles and retained a capacity of 73 mAh g⁻¹, even at an extremely high current density of 20 A g⁻¹.

2.5.1.2 Sodium-metal alloy materials

![Figure 2.20](image)

**Figure 2.20** Theoretical equilibrium redox potentials of (a) Na–Si, (b) Na–Ge, (c) Na–Sn, and (d) Na–Pb. ¹³⁴

Most Group IV and V elements have the ability to form binary alloy compounds with Na, including Sn, Sb, Ge, P, and Pb.¹³⁵ Figure 2.20 presents the theoretical equilibrium redox potentials of Na with Si, Ge, Sn, and Pb. The most significant feature of these alloy elements is that their theoretical capacities are very high due to their ability to combine a single atom
with multiple Na atoms. Si and Ge can alloy with one Na ion to form NaX-type compounds. Sn and Pb have the ability to form Na$_{15}$X$_4$-type compounds, while P, Sb, and Bi can form Na$_3$X-type compounds. Anodes based on these elements, such as SnSb, Sn$_{4+x}$P$_3$, and SnGeSb have also been investigated as anode materials for sodium ion batteries. Among them, there is no report, however, on the formation of NaSi in a Na cell at the moment. Pb and Bi achieve initial sodiation close to the theoretical values but present very poor cyclability because of their huge volume expansion of 250% and 365%, respectively. With a theoretical capacity of 790 mAh g$^{-1}$ and an average voltage of 0.3 V vs. Na$^+/Na$, Sn is a more promising candidate. Despite a volume expansion of 420%, composite electrodes consisting of Sn powder with a polyacrylate binder exhibited a reversible capacity of 500 mAh g$^{-1}$ over 20 cycles at a slow cycling rate. Phosphorus electrochemically reacts with Na to form Na$_3$P at an attractive potential and can achieve a higher theoretical capacity of 2596 mAh g$^{-1}$ than any other anodes presently available for SIBs. Amorphous red-P and orthorhombic black-P are being widely studied as anodes for SIBs. Kim et al. reported an amorphous red-P/C composite, which exhibited an appropriate redox potential of ~0.4 V (vs. Na/Na$^+$) with a reversible capacity of 1890 mAh g$^{-1}$ and good rate capability delivering 1540 mAh g$^{-1}$ at a high current density of 2.86 A g$^{-1}$. Similar to LIBs, many metal oxide materials have been tested as anodes for SIBs in recent years. FeO, CoO, and NiO, however, show almost no electrochemical activity in SIBs. According to the sodium storage mechanism, metal oxide anodes for SIBs can be classified into two groups: intercalation type and conversion type. Intercalation type metal oxides include TiO$_2$, Na$_2$Ti$_3$O$_7$, Na$_2$Ti$_6$O$_{13}$, Na$_4$Ti$_5$O$_{12}$, and P2- Na$_{0.66}$[Li$_{0.22}$Ti$_{0.78}$]O$_2$ etc. The sodium insertion potentials for most of them, however, are too high to be of practical use. The lowest intercalation potential reported to date is for the sodium titanate Na$_2$Ti$_3$O$_7$, which
provides a capacity of 178 mAh g$^{-1}$ at 0.3 V (vs. Na$^+/Na$). Furthermore, owing to the limited number of storage sites in their frameworks, the intercalation type metal oxides deliver low reversible capacity of less than 300 mAh g$^{-1}$. In contrast, the conversion type metal oxides could deliver high theoretical specific capacities of more than 600 mAh g$^{-1}$. The conversion mechanism concept for SIB anodes was first demonstrated for the spinel NiCo$_2$O$_4$, which was found to provide reversible capacity of $\sim$200 mAh g$^{-1}$ after an initial discharge of 600 mAh g$^{-1}$. The conversion type metal oxides can be divided into two groups based on whether the metal in the oxides is active. In the first group, the metal in the oxides, such as Fe$_3$O$_4$, Fe$_2$O$_3$, CuO, NiCo$_2$O$_4$, and CoO, is electrochemically inactive.$^{150-153}$ The sodiation/desodiation reaction can be described by the following equation:

$$MO_x + 2xNa^+ + 2xe^- \leftrightarrow xNa_2O + M$$  \hspace{1cm} (2.11)$$

For NiCo$_2$O$_4$, the equation is:

$$NiCo_2O_4 + 8Na^+ + 8e^- \rightarrow Ni + 2Co + 4Na_2O$$  \hspace{1cm} (2.12)$$

Due to the inactivity of M, most of these metal oxides deliver low capacities of less than 400 mAh g$^{-1}$, despite their high theoretical capacities. In the second group, including SnO$_2$$^{154}$ and Sb$_2$O$_4$$^{155}$, the metal M in the oxides is electrochemically active and can further react with Na ions. Their conversion reactions with sodium ions can be described by the following two-step reactions:

$$MO_x + 2xNa^+ + 2xe^- \leftrightarrow xNa_2O + M$$  \hspace{1cm} (2.13)$$

$$xNa_2O + M + yNa^+ + ye^- \leftrightarrow xNa_2O + Na_yM$$  \hspace{1cm} (2.14)$$

For SnO$_2$, the whole equations is:$^{154}$

$$(4+x)Na^+ + 4SnO_2 + (4+x)e^- \leftrightarrow Na_0Sn + 2Na_2O$$  \hspace{1cm} (2.15)$$

SnO$_2$ nanocrystals (NCs) were bound with nitrogen-doped reduced graphene oxide (N-RGO) sheets by means of an in-situ hydrazine monohydrate vapour reduction method (Figure 2.21).$^{156}$ Bonds formed between graphene and SnO$_2$ nanocrystals limit the aggregation of formed
the Sn nanoparticles formed in situ, leading to a stable hybrid anode material showing a reversible charge capacity as high as 1346 mAh g$^{-1}$ after 500 cycles.

![Figure 2.21 Morphology and cycling performance of SnO$_2$NC@N-RGO.](image)

Metal sulphides, including MoS$_2$, TiS$_2$, FeS$_2$, Ni$_3$S$_2$, SnS$_2$, NbS$_2$, and Sb$_2$S$_3$, have become an intensively studied family for SIB anodes in recent years.$^{157-164}$ MoS$_2$ is, as one of the most popular members of the transition metal chalcogenide family. According to the different layer-stacking sequences, MoS$_2$ can be divided into the two-layer-stacked hexagonal polymorph 2H-MoS$_2$, the one-layer-stacked trigonal 1T-MoS$_2$, and the three-layer-stacked rhombohedral 3R-MoS$_2$. As shown in Figure 2.22, the mechanism for bulk MoS$_2$ samples as anode for SIBs was investigated by in-situ X-ray diffraction (XRD), ex situ XRD, and scanning transmission electron microscopy (STEM) characterization, and the electrochemical reaction was summarized as follows.$^{165}$

\[
2H-MoS_2 + 0.5Na \rightarrow 2H-Na_{0.5}MoS_2 (0.85 \text{ V})
\]  
(2.16)

\[
2H-Na_{0.5}MoS_2 + (x-0.5)Na \rightarrow 1T-Na_xMoS_2 (x < 1.5, 0.75 \text{ V})
\]  
(2.17)

\[
1T-Na_xMoS_2 (4-x)Na \rightarrow Mo + Na_2S (\text{below 0.2 V})
\]  
(2.18)
Figure 2.22 (a) High-angle annular dark-field (HAADF) image of commercial MoS$_2$ along the [001] zone axis. The purple, yellow, and blue circles are overlaid in the image for Mo, S, and Na atoms, respectively; (b) initial discharge potential profile of Na intercalation; and (c) in-situ XRD patterns of commercial MoS$_2$.\textsuperscript{165}

2.5.1.4 Organic compounds

Electroactive organics or polymers that have reversible redox reactions are promising candidates as electrode materials because of their tremendous variety of chemical compounds, high theoretical capacity, safety, sustainability, environmental friendliness, and potential low cost.\textsuperscript{55, 166-168} Recently, the organic tetrasodium salt of 2,5-dihydroxyterephthalic acid (Na$_4$C$_8$H$_2$O$_6$) was prepared through a green one-pot method.\textsuperscript{169} When investigated in the potential window of 0.1–1.8 V (vs. Na$^+$/Na), as the negative electrode, it delivered a compatible and stable capacity of $\sim$ 180 mAh g$^{-1}$ with excellent cycling performance. In the potential window of 1.6–2.8 V, a Na$_4$C$_8$H$_2$O$_6$/Na half-cell demonstrated similar excellent
performance. A combination of electrochemical, spectroscopic, and computational studies revealed that reversible uptake/removal of two Na\textsuperscript{+} ions is associated with the enolate groups at 1.6–2.8 V (Na\textsubscript{2}C\textsubscript{8}H\textsubscript{2}O\textsubscript{6}/Na\textsubscript{4}C\textsubscript{8}H\textsubscript{2}O\textsubscript{6}) and the carboxylate groups at 0.1–1.8 V (Na\textsubscript{4}C\textsubscript{8}H\textsubscript{2}O\textsubscript{6}/Na\textsubscript{6}C\textsubscript{8}H\textsubscript{2}O\textsubscript{6}), as shown in Figure 2.23. There still remain three major challenges limiting the development of organic electrodes when compared with high performance carbonaceous and/or inorganic compounds: (1) sluggish kinetics from the extremely low electronic conductivity, (2) particle pulverization induced by large volume changes during the Na\textsuperscript{+} ion insertion/de-insertion process, and (3) chemical instability in the organic solvent upon cycling.

Figure 2.23 (a) Electrochemical redox reaction mechanism of Na\textsuperscript{+} ions with Na\textsubscript{4}C\textsubscript{8}H\textsubscript{2}O\textsubscript{6}; (b) voltage-capacity profile and (c) cycling performance of Na\textsubscript{4}C\textsubscript{8}H\textsubscript{2}O\textsubscript{6}/Na half-cell in the voltage range of 0.1–1.8 V vs. Na\textsuperscript{+}/Na.

2.5.2 Cathode materials for SIBs

The cathode materials for SIBs that have been mainly investigated belong to two major groups: oxide compounds Na\textsubscript{x}MO\textsubscript{y} (M = transition metal) and polyanionic compounds...
Na$_x$M$_y$X$_z$ (M = transition metal, X = PO$_4$, SO$_4$, P$_2$O$_7$, PO$_4$F, SO$_4$F). Meanwhile, another two groups, metal hexacyanometalates and organic compounds, have been paid increasing attention recently.

2.5.2.1 Metal oxides

![Figure 2.24: Structural patterns of various transition metal oxides:](image)

Transition metal oxides for use as cathodes for SIBs can be divided into two types of structures, namely, layered structures and tunnelled structures, as illustrated in Figure 2.24. The layered structured compounds Na$_x$MO$_{2+y}$ (M = transition metal and combinations thereof) were extensively investigated during the 1970s and 1980s. The layered structure is built up from sheets of edge-sharing MO$_6$ octahedra, which provide two-dimensional channels for alkali ion extraction and insertion between them. Delmas and co-workers first classified Na$_x$MO$_2$ compounds based on the stacking arrangements of alkali ions between the layers,
namely, the O2 type and P3 type, where the symbols O or P denote the octahedral or prismatic environment for Na sites, and the number 2 or 3 indicates the minimum number of transition metal layers in the repeating cell units. Figure 2.25 shows charge–discharge profiles of several typical layered sodium metal oxides. A reversible phase transition of $O_3 \rightarrow O'3 \rightarrow P'3$ was proposed within a Na content range of $0.5 \leq x \leq 1$ for the $O_3$-NaCoO$_2$ (Figure 2.25a). An in-situ XRD experiment showed that the structure evolution of $P_2$-Na$_{2/3}$CoO$_2$ included various single- or two-phase domains with different Na$^+/V_{Na^+}$ patterns based on Na concentration (Figure 2.25b). Monoclinic $\alpha$-NaMnO$_2$ (C2/m) exhibited an initial capacity of 185 mAh g$^{-1}$ (0.8 Na) in the voltage range of 2.0–3.8 V. Its capacity decayed rapidly, however, in subsequent cycles (Figure 2.25c). $P_2$-Na$_{0.6}$MnO$_2$ was reported with a capacity of 140 mAh g$^{-1}$ over the initial few cycles, but also with rapid capacity decay (Figure 2.25d). Reversible Na storage in NaFeO$_2$ was achieved at 3.3 V by limiting the cut-off voltage (Figure 2.25e). P2-Na$_{0.67}$Fe$_{0.5}$Mn$_{0.5}$O$_2$ (Figure 2.25f) was also proposed to be able to provide reversible Fe$^{4+}$/Fe$^{3+}$ conversion with a reversible capacity of 190 mAh g$^{-1}$. $O_3$-NaNi$_{0.5}$Mn$_{0.5}$O$_2$ was reported to exhibit a capacity of 105-125 mAh g$^{-1}$ between 2.2 V and 3.8 V (Figure 2.25g). $P_2$-Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ was demonstrated to be able to deliver a capacity as high as 160 mAh g$^{-1}$, with nearly all Na removed from the slab (Figure 2.25h). A large capacity of 185 mAh g$^{-1}$ was even obtained when it was charged to 4.5 V. Rapid capacity fading also occurred, however. O3-NaNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ was also demonstrated to exhibit reversible intercalation of 0.5 Na (120 mA h g$^{-1}$) in the voltage range of 2.0–3.75 V with good cycling performance (Figure 2.25i), although its instability in air limits its applications. P2-Na$_{0.45}$Ni$_{0.22}$Co$_{0.11}$Mn$_{0.66}$O$_2$ (Figure 2.25j) exhibited a capacity of ~140 mAh g$^{-1}$ with moderate rate and good cycling performance. The partial capacity delivered at ~ 2.3 V was compensated by the Na anode during the first discharge process.
Figure 2.25 Charge–discharge profiles of different layered sodium metal oxides: (a) O3-NaxCoO2; (b) P2-NaxCoO2; (c) O3-NaMnO2; (d) P2-Na0.6MnO2; (e) O3-NaFeO2; (f) P2-NaxFe0.5Mn0.5O2; (g) O3-NaNi0.5Mn0.5O2; (h) P2-Na2/3Ni1/3Mn2/3O2; (i) O3-NaNi1/3Mn1/3Co1/3O2; and (j) P2-Na0.45Ni0.22Co0.11Mn0.66O2.\textsuperscript{115,172-181}
As shown in Figure 2.24e, tunnel-structured NaₓMO₂ is an orthorhombic structure, in which the edge-sharing MO₅ sites are connected by one triple and two double MO₆ octahedral chains at the vertices, forming an S-shaped tunnel. In contrast to most layered transition metal oxides, the tunnel-type transition metal oxides are extremely stable in air and have been widely studied. Na₀.₄₄MnO₂ is a representative tunnel-type metal oxide. Ti-substituted Na₀.₄₄MnO₂ was systematically investigated on the atomic scale by high-resolution XRD, electron energy loss spectroscopy (EELS) and STEM energy dispersive spectroscopy (EDS). As shown in Figure 2.26, the tunnel-type Na₀.₄₄Mn₁₋ₓTiₓO₂ shows different charge/discharge curves with increasing Ti content. The Na₀.₄₄[Mn₀.₄₄Ti₀.₅₆]O₂ can deliver a high reversible capacity of ~150 mAh g⁻¹. It was proven that Ti substitution could break the charge ordering, lower the storage voltage, and significantly smooth the discharge/charge curves of Na₀.₄₄MnO₂.

![Figure 2.26](image)

**Figure 2.26** The 1ˢᵗ, 5₀ᵗʰ, and 1₀₀ᵗʰ discharge/charge curves of (a) Na₀.₄₄MnO₂, (b) Na₀.₄₄[Mn₀.₇₈Ti₀.₂₂]O₂, and (c) Na₀.₄₄[Mn₀.₄₄Ti₀.₅₆]O₂ at a current rate of C/10 between 1.5 and
3.8 V (vs. Na⁺/Na); (d) In situ XRD patterns collected during the first discharge/charge of the Na/Na₀.₄₄[Mn₀.₄₄Ti₀.₅₆]O₂ cell under a current rate of C/10 within the voltage range of 1.5-3.9 V; and (e) responding evolution of the lattice parameters during charge/discharge process. \(^{182}\)

Another tunnel-type family, Na₉Fe₉Ti₂₉O₄ (x = 1, 0.875) with the Pnma space group was reported. \(^{183}\) Only ~ 0.24 Na could be electrochemically extracted from NaFeTiO₄ when it was charged up to 4.5 V, which might relate to the Fe⁴⁺/Fe³⁺ redox couple, while ~ 0.37 Na could be extracted from Na₀.₈₇₅Fe₀.₈₇₅Ti₁.₁₂₅O₄, showing better kinetics, which may be associated with higher conductivity resulting from the increased number of Na vacancies and/or suitable transport channels.

2.5.2.2 Polyanionic Compounds

**Figure 2.27** Crystal structures of various polyanionic compounds: (a) Na₃V₂(PO₄)₃, (b) NaFePO₄, (c) Na₂FePO₄F, and (d) NaFeSO₄F (Na: yellow, V/Fe: blue, O: red, F: grey). \(^{114}\)
Figure 2.28 (a) Cyclic voltammograms for the first 3 cycles and (b) charge-discharge profiles for selected cycles (inset: rate performance) of Na$_3$V$_2$(PO$_4$)$_3$/C composite.\cite{184}

As shown in Figure 2.27, owing to their crystal structures with open channels, polyanion compounds, including phosphates, fluorophosphates, pyrophosphates and sulfates, as cathode materials for SIBs have already started to receive more attention.\cite{114, 185} A carbon-coated Na$_3$V$_2$(PO$_4$)$_3$ sample was successfully synthesized by a one-step solid state reaction (Figure 2.28). This Na$_3$V$_2$(PO$_4$)$_3$/C composite shows two flat voltage plateaus at 3.4 V and 1.63 V, respectively. When tested in the voltage range of 2.7–3.8 V as a cathode, the Na$_3$V$_2$(PO$_4$)$_3$/C composite delivered initial charge/discharge capacities of 98.6/93 mAh g$^{-1}$, respectively.\cite{184}

With a theoretical capacity close to 100 mAh·g$^{-1}$, the Na$_2$FeP$_2$O$_7$ cathode could operate at an average voltage of 3 V (vs. Na/ Na$^+$), and delivered a reversible capacity of 82 mAh·g$^{-1}$ with good rate capability (Figure 2.29a and d).\cite{186} The layered structure of NaFe(SO$_4$)$_2$ consists of octahedral Na$^+$ and Fe$^{3+}$ ions bridged by SO$_4^{2-}$ polyanions in the ab-plane. It demonstrated a reversible single phase reaction at a voltage of 3.2 V with a capacity of 80 mAh g$^{-1}$ at the 0.1 C rate (Figure 2.29b and e).\cite{187} Electrochemically active, high cell voltage, substitutional solid solutions of the form Na$_2$(Mg$_w$Fe$_x$Co$_y$Ni$_z$)PO$_4$F ($w + x + y + z = 1$) were reported by Nazar’s group.\cite{188} The compositionally identical, but structurally distinct Na$_2$MnPO$_4$F, however, exhibits very poor electrochemical behaviour despite an open
pathway for alkali migration. In sharp contrast to the olivine LiFePO$_4$, distinct two-phase behaviour of Na$_2$FePO$_4$F is not observed (Figure 2.29 c and f), which may be driven by electron localization of Fe$^{2+}$/Fe$^{3+}$ in the Na$_{1.5}$FePO$_4$F intermediate phase.$^{188}$

Figure 2.29 Schematic illustration of crystal structures and charge-discharge profiles of (a and d) Na$_2$FeP$_2$O$_7$ (viewed normal to the $bc$-plane, with tunnels favoring Na$^+$ ion migration as highlighted by black dotted rectangles, and the FeO$_6$ octahedra, PO$_4$ tetrahedra, and Na atoms shown in green, light purple, and yellow, respectively)$^{186}$, and the corresponding differential capacity plot shown in the inset to (d); (b and e) NaFe(SO$_4$)$_2$, $^{187}$ and (c and f) Na$_2$FePO$_4$F (viewed along the [010] direction, with the FeO$_6$ octahedra, PO$_4$ tetrahedra, and Na atoms shown in blue, yellow, and green, respectively). $^{188}$

2.5.2.3 Metal Hexacyanometalates
Hexacyanometallates \((A_xM_1[M_2(CN)_6]_{y-z}H_2O; A = \text{alkaline metal}; M_1 \text{ and } M_2 = \text{transition metal ions}; \square = [M_2(CN)_6] \text{ with vacancies occupied by coordinating water}; 0 \leq x \leq 2, y \leq 1)\) have attracted great interest. Prussian blue (PB) and its analogues (PBAs) have been widely investigated as cathode materials for SIBs.\(^{189-194}\) Figure 2.30 presents the crystal structure of PBAs. Most of the PBAs exhibit an open and zeolite-like structure composed of a cubic framework of transition metal cations bound by hexacyanometallate groups, and allow alkali cations \((\text{Li}^+, \text{Na}^+, \text{and } \text{K}^+)\) to be inserted/extracted rapidly through their wide channels. The ideal electrochemical reaction can achieve maximum ion storage \((xA^+)\) and is expressed as follows:

\[
A_xM_1^{II}[M_2^{II}(CN)_6] \leftrightarrow xA^+ + xe^- + M_1^{III}[M_2^{III}(CN)_6]
\] (2.19)

When applied as cathodes for SIBs, PBAs have the following advantages: (1) the rigid open framework with large interstitial sites can ensure effective \(\text{Na}^+\) mobility and accommodate volume variation during the \(\text{Na}^+\) extraction/insertion processes; (2) the theoretical specific capacity of PB is as high as 170 mA h g\(^{-1}\) [based on \(\text{Na}_2\text{FeFe(CN)}_6\)], resulting from a theoretical two-electron redox reaction; and (3) the facile synthetic procedure, nontoxicity, and low cost of PB make it suitable for large-scale production. Figure 2.31 shows the charge-discharge profiles of several kinds of PBAs, including \(\text{Na}_{0.61}\text{Fe}[\text{Fe(CN)}_6]_{0.94},\)\(^{195}\) \(\text{Na}_2\text{Mn}^{II}[\text{Mn}^{II}(CN)_6],\)\(^{196}\) and \(\text{Na}_2\text{Zn}_3[\text{Fe(CN)}_6]_{-x}H_2O.\)\(^{197}\)
The presence of vacancies and coordinating water in PBAs could break down the bridging of the M₁-CN-M₂ framework, resulting in distorted lattices, which would cause low efficiency and structural instability of the PB compounds during the charge-discharge process. It is important to prepare PBAs with few vacancies or coordinating water. The interstitial H₂O was removed from Na₂MnFe(CN)₆·zH₂O by Goodenough’s group.¹⁹⁸ The dehydrated phase delivered a reversible capacity of 150 mAh g⁻¹ in a Na half-cell and 140 mAh g⁻¹ in a full cell with a hard-carbon anode. At a rate of 20 C, the half-cell capacity was 120 mAh g⁻¹, and the cell exhibited 75% capacity retention after 500 cycles at 0.7 C.

Figure 2.31 Charge–discharge profiles of (a) Na₀.₆₁Fe[Fe(CN)₆]₀.₉₄,¹⁹⁵ (b) Na₂Mn²⁺[Mn²⁺(CN)₆]¹⁹⁶ and (c) Na₂Zn₃[Fe(CN)₆]·xH₂O, with the corresponding differential capacity plot in the inset.¹⁹⁷

2.5.2.4 Organic Compounds

Currently available organic cathode materials for SIBs mainly consist of aromatic carbonyl derivatives, organosulfur compounds, pteridine derivatives, and functional polymers. Figure 2.32 shows some representative organic cathode materials.¹⁴³ As mentioned above, a Na₄C₈H₂O₆/Na cell as SIB cathode delivered a stable capacity of ~ 180 mAh g⁻¹ with excellent cycling performance in the voltage window of 1.6-2.8 V.¹⁶⁹ Full cells using organic electrode as anode or cathode were studied and a summary is shown in Figure 2.33.¹⁶⁸ Nonetheless, their easy dissolution in organic liquid electrolytes, low thermal stability, poor
electronic conductivity, and sluggish kinetics are still obstructing their application as cathode for SIBs.

Figure 2.32 Representative organic cathode materials with high specific capacities or high operating potentials.\textsuperscript{143}

Figure 2.33 A summary of full SIB cells with organic electrode materials as anode or cathode.\textsuperscript{168}
2.5.3 Electrolyte for SIBs

Figure 2.34 Electrochemical potential window of stability (black bars and upper y axis) and thermal range (green bars and lower y axis) values of (a) propylene carbonate (PC) based electrolytes with 1 M of various Na salts and (b) electrolytes based on 1 M NaClO$_4$ dissolved in various solvents and solvent mixtures.\textsuperscript{199}

Since many chemical and physical properties of SIBs are analogous to those of LIBs, there are several electrolytes used in LIBs that could also be tried in the SIBs.\textsuperscript{112,199,200} While the combinations of salts and solvents may differ between LIBs and SIBs, there is as yet no specific solvent developed specifically for SIBs, and thus, most of the information below is generic to both. For SIB electrolytes, the same prospective anions, such as ClO$_4^-$, PF$_6^-$, BF$_4^-$,
CF$_3$SO$_3^-$, (Tf)$^-$ and [N(CF$_3$SO$_2$)$_2$)$_2^-$ (TFSI), are found as are applied in the field of LIB electrolytes. As many of the resulting properties are more often dependent on the anions than on the cations, the advantages and drawbacks are more or less the same. The most commonly used electrolyte for SIBs is NaClO$_4$ or NaPF$_6$ salts in carbonate ester solvents, particularly propylene carbonate (PC). For example, Ponrouch et al. investigated hard carbon as anode for SIBs using several solvents (tetrahydrofuran (THF), dimethyl carbonate (DMC), PC, diethyl carbonate (DEC), dimethoxyethane (DME), and triethylene glycol dimethyl ether (triglyme)) and solvent mixtures (EC:DEC, EC:DMC, EC:DME, EC:PC, and EC:triglyme) in combination with different Na salts, namely NaClO$_4$, NaPF$_6$, and NaTFSI. They found that hard carbon electrodes delivered reversible capacities of 200 mAh g$^{-1}$ in 1 M NaPF$_6$ or NaClO$_4$ in EC:PC electrolyte.$^{199}$ Figure 2.34 shows the electrochemical potential windows of stability and thermal range values of PC based electrolytes with 1 M of various Na salts and electrolytes based on 1 M NaClO$_4$ dissolved in various solvents and solvent mixtures. The use of organic liquid electrolytes leads to practicality and safety issues, however. Corrosion of metallic sodium anodes corrosion takes place continuously in the presence of these organic electrolytes, rather than forming a stable SEI.

Developing aqueous electrolytes instead of organic electrolytes could offer an alternative solution. Nevertheless, an aqueous electrolyte system is more complicated than an organic system because of problems related to (1) the elimination of residual O$_2$ from the electrolyte; (2) the maintenance of electrode stability in the aqueous electrolyte; (3) inhibition of H$_3$O$^+$ co-intercalation into the electrode; and (4) the efficiency of the internal consumption of H$_2$ and O$_2$ produced from the anode and cathode sides when the cell is overdischarged, overcharged or improperly operated in a closed aqueous battery system.$^{200}$ More investigations are needed to help address these issues.
Chapter 3. Experimental

The flow chart of the whole experiment of this work is summarized in Figure 3.1. Details of each process will be discussed in the following sections.

![Flow chart of the experiment](image)

Figure 3.1 Process diagram of the experiments.

### 3.1 Materials and chemicals

Materials and chemicals used in this doctoral thesis are listed in Table 3.1.

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3.2 Materials preparation
The preparation methods used in this doctoral work include the hydrothermal, reverse microemulsion and sol-gel methods. All the methods are briefly described below.

3.2.1 Hydrothermal method

Hydrothermal method involves the various techniques to crystallize substances from high-temperature aqueous solutions at rather high pressures. The synthesis of single crystals depends on the solubility of reactants in water under high temperature and high pressure, and the crystal growth is performed in a steel pressure vessel called autoclave.

The hydrothermal method has many advantages over other types of crystal growth technique: (1) conducive to create crystalline phases which are unstable at their melting points; (2) favourable for the growth of materials with a high vapour pressure near the melting points; and (3) suitable for the preparation of good-quality crystals while keeping control of their composition. Meanwhile, the disadvantages of the hydrothermal method include the high cost of autoclaves, and the impossibility of observing the growth process of prepared crystal.

3.2.2 Reverse microemulsion method

The reverse microemulsion process includes fully dispersing a water phase into an oil phase to constitute thermodynamically stable microemulsion droplets, among which each droplet may act as an independent micro-reactor to grow into the desired compound. Normally, the oil phase consists of a surfactant and a co-surfactant. After the equilibrium state is reached, nano-sized microemulsion droplets (reverse micelles) are formed. Each tiny droplet acts as an independent microreactor for the production of desired compounds and provides a confinement effect preventing particle-to-particle contact, constraining particle nucleation, growth, and coagulation. This method can synthesize small particles with narrow size distribution.
3.2.3 Sol-gel method

The sol-gel process is a wet-chemical technique used to fabricate both glassy and ceramic materials. In this process, the sol (or solution) evolves gradually and form a gel-like network containing both a solid phase and a liquid phase. Precursors undergo hydrolysis and polycondensation reactions to form a colloid. Removal of the remaining solvent from the gel requires a further drying process, which is typically accompanied by a large amount of shrinkage and densification. Afterwards, a thermal treatment is often performed to realize further polycondensation and enhance structural stability through final sintering, densification and grain growth.

3.3 Battery assemble

3.3.1 Electrode preparation

The prepared active materials were mixed with conductive agent (super P) and binder (CMC or PVDF) in distilled water or NMP solvent respectively with a weight ratio of 80: 10: 10 to form a slurry, which then was coated on copper foil for anode materials or aluminium foil for cathode materials. Then the thus-prepared foil was dried in a vacuum oven overnight, cut and pressed to form working electrode.

3.3.2 Cell assemble

The coin cells CR2032 were assembled in an argon-filled glove box with water and oxygen concentration of less than 0.1 ppm. Lithium foil or sodium foil was used as both the counter electrode and reference electrode.

For lithium ion batteries, the electrolyte used was 1M LiPF₆ in an ethylene carbonate (EC) – diethyl carbonate (DEC) (1:1 v/v) solution.
For sodium ion batteries, the electrolyte used was 1M NaClO$_4$ with in an EC – DEC (1:1 v/v) solution with or without 5 vol. % of fluoroethylene carbonate (FEC).

### 3.4 Morphology and structural characterization

#### 3.4.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an efficient thermal analytic way to investigate the effects of temperature on the chemical and physical properties of samples. It is mainly employed to study the contents of composition of composites by measuring the weight change. TGA can collect information on various physical phenomena, such as second-order phase transitions, including vaporization, sublimation, absorption, adsorption, and desorption. Also, TGA can provide information on chemical phenomena, including desolvation (especially dehydration), chemisorption, decomposition, and solid-gas reactions.

#### 3.4.2 X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) is a fast analytical technique which primarily used for phase identification of a crystalline material, and can provide information about average composition and structure of the analysed material with a high degree of resolution.

X-rays can be considered as waves of electromagnetic radiation with a wavelength from 0.01 to 10 nanometers while crystals are considered as regular arrays of atoms scattering X-ray waves through the atoms’ electrons. An X-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as elastic scattering, and the electron is regarded as the scatterer. A regular array of scatterers produces a regular array of spherical waves. The scattering from all the different sets of planes results in a pattern unique to the crystal structure of a given compound. A plane with spacing $d$ is determined by Bragg’s law:
Here $d$ is the spacing between diffracting planes, $\theta$ is the incident angle, $n$ is any integer, and $\lambda$ is the wavelength of the beam. These specific directions appear as spots on the diffraction pattern called reflections.

### 3.4.3 Synchrotron powder XRD (SPXRD)

In synchrotron X-ray powder diffraction (SPXRD), X-rays generated from a synchrotron facility is at least 5 orders of magnitude of the best X-ray laboratory source. In comparison with laboratory XRD, SXRD has some significant advantages: 1) high photon wavelength resolution; 2) tuneable photon energy, ideal for acquiring fluorescence-free XRD data and better diffraction peaks separation; 3) angular (FWHM) resolution better than 0.01°; 4) d-spacing resolution better than 0.35 Å; 5) ultra-fast data collection (millisecond scale); and 6) very high counting statistics (millions of counts) in a few seconds. *In situ* synchrotron XRD can effectively trace the phase transformation of electrode materials happening during the cycling processes.

### 3.4.4 Scanning electron microscope (SEM)

A scanning electron microscope (SEM) is a type of electron microscope used to produce images by scanning samples with focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that help identify information about the sample's surface topography, composition and other surface properties. The types of signals produced by SEM include those from secondary electrons (SE, most common), back-scattered electrons (BSE), characteristic X-rays, specimen currents, and transmitted electrons. By scanning the sample and collecting the SE emitted using a special detector, an image displaying the topography of the surface is created.
3.4.5 Transmission electron microscope (TEM) and selected area electron diffraction (SAED)

Transmission electron microscopy (TEM) is a microscopy technique where a beam of electrons is transmitted through an ultra-thin specimen to interact with the atoms of specimen while passing through. TEM can be used to observe the morphology, crystal structure, and electronic structure of a specimen, and is capable of imaging at a significantly higher resolution than light microscopes.

Selected area electron diffraction (SAED) is a crystallographic experimental technique performed inside a TEM, and was used as a complementary technique to XRD for identification of crystalline samples. It can be employed to examine crystal defects and crystal structures of the specimen. When the high energy electrons are transmitted through the ultra-thin sample, part of the electrons will be scattered at different angles depending on the crystal structure, generating a characteristic pattern of diffraction spots.

3.4.6 Brunauer Emmett Teller (BET) adsorption

Brunauer-Emmett-Teller (BET) is an important analysis technique to measure the specific surface area and/or pore size distribution of a material. The BET surface area analysis is based on the theory of physical adsorption of gas molecules on a solid surface, which was first proposed by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller. It is conducted at liquid nitrogen temperature (77 K) under various pressures atmospheres. The mass of the original powder is normally in the range of 50-1000 mg. The BET theory is an extension of the Langmuir theory for monolayer molecular adsorption. When exploring multilayer adsorption, the BET theory proposed the following hypotheses: 1) gas molecules are physically adsorbed on the surface of a solid in potentially infinite layers; 2) there is no
interaction between different adsorption layers; and 3) the Langmuir theory can be applied to each layer.

3.4.7 X-ray absorption near the edge structure (XANES)

X-ray absorption spectroscopy (XAS) is a widely used quantitative analytical technique to collect information about energy emissions and electron excitations initiated by the absorption of X-ray energy. The experiment is usually performed at synchrotron radiation sources, which provide atomic-scale information about a wide range of liquid or solid systems by using a crystalline monochromator to tune the photon energy to a range where core electrons can be excited (0.1-100 keV photon energy). Because of probing short and medium-range order and being able to measure disordered samples, it is a complementary method to XRD.

X-ray absorption near edge structure (XANES), also known as near edge X-ray Absorption Fine Structure (NEXAFS), is loosely defined as the analysis of the spectra obtained in X-ray absorption spectroscopy experiments, indicating the XAS features of condensed matter due to the photo absorption cross section for electronic transitions from an atomic core level to final states in the energy region of 50–100 eV above the selected atomic core level ionization energy. It is an element-specific and local bonding-sensitive spectroscopic analysis that determines the partial density of the empty states of a molecule, providing information about the oxidation state and coordination chemistry of a particular element.

3.5 Electrochemical measurements

3.5.1 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) is an electrochemical technique which is widely used to investigate the thermodynamics and kinetics of electron transfer at the electrolyte-electrode interface. It
is performed by cycling the potential of a working electrode linearly versus time, and records
the resulting current in an electrochemical cell. It is often used to study the redox processes,
to determine the stability of reaction products, the presence of intermediates in redox
reactions, electron transfer kinetics, and the reversibility of a reaction. CV can also be used to
determine the electron stoichiometry of a system, the formal reduction potential and diffusion
coefficient of an analyte.

3.5.2 Galvanostatic charge-discharge (GCD)

The galvanostatic charge-discharge test is the most fundamental test for battery materials,
normally including the cycling performance at a stable current density and rate performance
at different current densities, to evaluate the electrochemical performance of active materials
when used as working electrodes for batteries. The discharge/charge specific capacity ($Q$)
equal to the total electron charge in the corresponding process and can be calculated from the
applied current ($I$) and the total time ($t$) according to the formula $Q = I \times t$.

3.5.3 Electrochemical impedance spectroscopy (EIS)

EIS is an important experimental measurement technique which can be employed to test the
inner resistance and characterize the energy storage and dissipation properties of
electrochemical systems. The information obtained from EIS can include information about
the charge transfer resistance, ohmic resistance and double layer capacitance. Normally, the
impedance spectrum is composed of a semicircle at low frequency related to the kinetic
process and a tail at high frequency resulting from the diffusion of ions from the electrolyte
into the electrode materials. Moreover, EIS can help to measure the ion diffusion and
apparent energy activation of the electrode.

3.5.4 Galvanostatic intermittent titration technique (GITT)
In a typical GITT test, some thermodynamic information of the active material in the working electrode can be obtained, together with its diffusion coefficient. The GITT test consists of a series of current pulses, each followed by a relaxation time, during which no current passes through the cell. The current is positive during charge processes and negative during discharge processes. If sufficient small currents are applied for short time intervals, the chemical diffusion coefficient can be calculated based on the following formula:

\[
D = \frac{4}{\pi\tau} \left( \frac{n_m V_m}{S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_t} \right)^2
\]  

(3.2)

Here, \(\tau\) is the duration of the current pulse (s), \(n_m\) is the number of moles (mol), \(V_m\) is the molar volume of the electrode (cm\(^3\) mol\(^{-1}\)), \(S\) is the electrode/electrolyte contact area (cm\(^2\)), \(\Delta E_s\) is the steady-state voltage change during the current pulse and \(\Delta E_t\) is the voltage change during the constant current pulse, eliminating the iR drop.
Chapter 4. Carbon-coated Hierarchical SnO$_2$ Hollow Spheres as an Anode for Lithium Ion Batteries

4.1 Introduction

Recently, a new generation of electrode materials with higher energy density and better rate capability has been achieving more and more attention for rechargeable lithium ion batteries (LIBs). SnO$_2$ has been regarded as a promising anode material for the next-generation LIBs due to its environmentally friendly fabrication and high theoretical capacity (782 mAh g$^{-1}$), which is more than twice that of commercial graphite anode (370 mAh g$^{-1}$). The practical application of SnO$_2$, however, is inhibited by its large initial capacity loss and severe capacity fading, arising from the huge volume changes and agglomeration of tin nanoparticles during alloying and de-alloying processes with lithium ions, which causes pulverization and loss of electrical contact in the electrodes.

It has been suggested that fabricating unique nanostructured SnO$_2$, especially with hollow structures, could alleviate these drawbacks, because the introduced void space can buffer the volume variation, improving the storage properties of SnO$_2$ materials. Moreover, these nanostructures with large exposed surfaces can shorten the diffusion length and interact more efficiently with Li$^+$ ions. Among them, three-dimensional (3D) hierarchical structures with low dimensional nanoscale building blocks are being paid special attention. Ordered 3D hierarchical structures possess the advantages of the pristine building blocks, and more importantly, also could exhibit new physicochemical properties arising from their secondary constituent. For example, a hierarchical SnO$_2$ architecture with hollow structures assembled from nanosheets, which was prepared by Yin et al., delivered a reversible capacity of 545 mAh g$^{-1}$ after 50 cycles at the current density of 100 mA g$^{-1}$. In addition, the introduction of a stable layer, such as by coating an amorphous carbon layer on
the SnO$_2$, could also provide an elastic matrix which can help to effectively counteract the pulverization and increase the conductivity of electrode materials.$^{36,214-218}$ Both of these two design strategies have been used to improve the cyclability of SnO$_2$-based anode materials. In most cases, however, each approach on its own leads to only limited improvement. It is still a significant challenge to achieve reasonable design and facile synthesis of SnO$_2$-based battery materials for highly reversible lithium storage.

In accordance with our previous work on self-assembled transition metal oxides$^{210,219}$, herein, we report 3D hierarchical SnO$_2$ hollow spheres composed of nanosheets synthesized by a modified reaction, and test their electrochemical performance as an anode material for the lithium ion battery. The electrochemical performance of bare SnO$_2$ electrodes is further improved by coating a thin layer of carbon on the nanosheets. In addition, carboxymethyl cellulose (CMC) binder, which is water soluble and inexpensive, is used instead of the conventional polyvinylidene difluoride (PVDF) binder, making the whole fabrication process for the electrode environmentally friendly and low in cost.$^{220,221}$ As a result, the prepared SnO$_2$/C composite exhibits synergistic properties arising from the nanostructures and conductive carbon, and it possesses superior electrochemical performance with good cycling performance and large reversible capacity when used as anode for rechargeable lithium ion batteries.

4.2 Experimental details

4.2.1 Materials preparation

Synthesis of hierarchical SnO$_2$ hollow spheres. 0.2 g polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO20-PPO70-PEO20, Pluronic P123) was first dissolved in 3 g absolute ethanol, and then 2 g H$_2$O and 20 mL of ethylene glycol (EG) were added successively to form a homogeneous solution. After that, 0.225 g SnCl$_2$·2H$_2$O and 0.14 g
hexamethylenetetramine (HMTA) were added into the solution under vigorous stirring for 30 min. The final solution was transferred into a 45 mL autoclave, which was then heated at 150°C for 5 h. After cooling down naturally, the obtained particles were washed with distilled water and ethanol several times and then dried at 80°C overnight. The product was calcined at 400 °C in air for 2 h to obtain hollow microspheres with high crystallinity.

Synthesis of hierarchical SnO$_2$/C hollow spheres. 100 mg SnO$_2$ hollow microspheres and 500 mg glucose were dissolved in 5 mL and 15 mL of distilled water, respectively. Then the SnO$_2$ suspension and 10 mL ethanol were added to the glucose solution and mixed under magnetic stirring. The resulting solution was transferred into a 45 mL Teflon autoclave and then heated at 180°C for 12 h. The dark grey products were centrifuged, washed with distilled water and ethanol several times, and then dried at 80°C overnight. The as-prepared powders were calcined in a tube furnace at 600°C for 3 h under flowing N$_2$.

4.2.2 Materials characterization

The morphologies and structures of the synthesized powders were investigated by field-emission scanning electron microscopy (FESEM; JEOL JSM-7500FA) and transmission electron microscopy (TEM; JEOL ARM200F). The crystalline structures of the synthesized powders were characterized by powder X-ray diffraction (XRD; GBC MMA diffractometer) with Cu $K_{\alpha}$ radiation. The carbon content of the carbon-coated sample was determined by a Mettler–Toledo thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) STARre System from 25°C to 800°C in air with a ramp rate of 5°C min$^{-1}$. The Brunauer–Emmett–Teller (BET) test was performed using a Micromeritics Tristar II 3020 Surface Area Analyzer.

4.2.3 Electrochemical measurements
Chapter 4. Carbon-coated Hierarchical SnO$_2$ Hollow Spheres for Lithium Ion Batteries

The electrodes were prepared by mixing the active material (SnO$_2$ or SnO$_2$/C hollow spheres), Super P, and CMC binder in a weight ratio of 80:10:10 to form a slurry, which then was coated on copper foil. The thus-prepared working electrode was then dried in a vacuum oven at 80°C overnight, and then pressed at 20 MPa. The electrolyte used was 1.0 mol L$^{-1}$ LiPF$_6$ in an ethylene carbonate – diethyl carbonate (1:1 v/v) solution. The coin cells were assembled in an argon-filled glove box. The cycling performance and rate stability of the cells were tested with a Land Test System between 0.01 V and 3.0 V (vs. Li$^+$/Li) at different constant current densities. The specific capacity of SnO$_2$ or SnO$_2$/C is calculated based on the total mass of the hierarchical SnO$_2$ or SnO$_2$/C hollow spheres, including the amorphous carbon support that typically shows negligible capacity. Cyclic voltammetry at a scan rate of 0.1 mV s$^{-1}$ in the potential range of 0.01–2.5 V (vs. Li$^+$/Li) and electrochemical impedance spectroscopy from 100 kHz to 100 mHz were performed using a CHI 660b electrochemistry workstation.

4.3 Results and discussions
Chapter 4. Carbon-coated Hierarchical SnO\textsubscript{2} Hollow Spheres for Lithium Ion Batteries

Figure 4.1 SEM images (a, b, c, d) and HRTEM images (e, f) of SnO\textsubscript{2} and SnO\textsubscript{2}/C hollow spheres: (a, c, e) SnO\textsubscript{2} hollow spheres; (b, d, f) SnO\textsubscript{2}/C hollow spheres. (The dashed line in (f) indicates the edge of a single particle.)

The morphologies and structures of the hierarchical SnO\textsubscript{2} and SnO\textsubscript{2}/C hollow spheres were investigated by scanning and transmission electron microscopy (SEM and TEM), as shown in Figure 4.1. SnO\textsubscript{2} hollow spheres with a diameter of about 220 nm, self-assembled from nanosheets about 5 nm in thickness, were obtained, as shown in Figure 4.1(a, c, e). A typical high resolution TEM (HRTEM) image of SnO\textsubscript{2} (Figure 4.1(e)) was taken from the edge of one single sphere. It can be seen that the nanosheets are further composed of smaller nanoparticles. The lattice fringes of these particles are distinct, with \(d\)-spacing of 3.35 Å and 2.64 Å, corresponding to the (110) planes and (101) planes of SnO\textsubscript{2}, respectively. The synthesis mechanism of the hierarchical hollow spheres is discussed in Figure 4.2. Such a hierarchical structure could be beneficial for rechargeable batteries. Firstly, the 2D
Chapter 4. Carbon-coated Hierarchical SnO$_2$ Hollow Spheres for Lithium Ion Batteries

Nanosheets can shorten the lithium ion diffusion length and facilitate contact between the active material and the electrolyte, serving as extra spaces and increasing the number of active sites for lithium-ion storage. Moreover, the void space in the secondary hollow spheres can accommodate the large volume changes and improve the accessibility of the electrolyte. After carbon coating, the morphology of the SnO$_2$/C nanocomposite does not change much, and a uniform layer of carbon is coated on the surfaces of the SnO$_2$ hollow spheres, as can be seen from Figure 4.1(b, d, f). Figure 4.1(d) and (f) were collected after grinding the powders. It can be seen that the carbon layer has a thickness of 3 nm and is closely attached onto the surfaces of the sheet-like subunits. The coated thin carbon layer could provide increased electrical conductivity of SnO$_2$ matrix, alleviate the big volume change and would help to counteract the pulverization during discharge-charge processes.$^{222, 223}$

Figure 4.2 Schematic phase diagram of surfactant–water–oil system showing the two-step self-assembly design by first forming the desired units in composition “A” and then assembling them into the final spherical morphology by adjusting the composition to “B”. $^{224}$
The synthesis of hierarchically-ordered nanostructures via a particular one-pot two-step self-assembly is proposed and summarized.\textsuperscript{219, 224, 225} Based on the surfactant-water-oil system in Figure 4.2, specially shaped constituent oligomers or nanostructured subunits, such as lamellar subunits and so on, are firstly formed from structure-defined surfactant, and then the obtained architectural units are further assembled into the final morphologies in the presence of a second co-surfactant. Different well-defined scalable two-dimensional transition metal oxide nanosheets have been successfully prepared using this universal method.\textsuperscript{226} In this work, the nanosized SnO\textsubscript{2} particles are firstly assembled into the lamellar structure due to the template effect of P123 surfactant, and then the formed nanosheets are self-organized into the final hierarchical SnO\textsubscript{2} hollow spheres with the addition of co-surfactant ethylene glycol.

\textbf{Figure 4.3} XRD spectra of hierarchical SnO\textsubscript{2} and SnO\textsubscript{2}/C hollow spheres: (a) SnO\textsubscript{2} hollow spheres; (b) SnO\textsubscript{2}/C hollow spheres.

Figure 4.3 presents the X-ray diffraction (XRD) patterns of the hierarchical SnO\textsubscript{2} and SnO\textsubscript{2}/C hollow spheres, which can both be assigned to the tetragonal phase with the space group P42/mnm (PDF No. 41–1445, \(a = 4.738\) Å, \(b = 4.728\) Å, and \(c = 3.187\) Å). All peaks of the
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Hierarchical hollow SnO$_2$ and SnO$_2$/C samples are broad, demonstrating their nanocrystalline nature, consistent with the results of TEM.

![TGA curve of SnO$_2$/C hollow spheres.](image)

**Figure 4.4** TGA curve of SnO$_2$/C hollow spheres.

![N$_2$ adsorption/desorption isotherms (insets: corresponding pore size distribution) of (a) SnO$_2$ and (b) SnO$_2$/C.](image)

**Figure 4.5** N$_2$ adsorption/desorption isotherms (insets: corresponding pore size distribution) of (a) SnO$_2$ and (b) SnO$_2$/C.

TGA was conducted to determine the carbon content in the SnO$_2$/C nanocomposite, as shown in Figure 4.4. The weight loss between 225°C and 535°C is attributed to combustion of the outer carbon layer resulting from carbonization of glucose. The weight percentage of carbon in the SnO$_2$/C sample can be estimated to be 4.9%, which is much lower than in other
This is also in good agreement with the thin carbon layer observed in the HRTEM image in Figure 4.1(f). The Brunauer-Emmett-Teller (BET) measurements were performed and the results are shown in Figure 4.5. The BET surface area of SnO$_2$ and SnO$_2$/C are close to each other and calculated to be 51.3 and 55.9 m$^2$/g, respectively. Pore size distribution shows that SnO$_2$/C has more mesopores compared to SnO$_2$, which may provide more active sites for Li$^+$ storage.

![Cyclic voltammograms (CVs) for selected cycles of SnO$_2$ and SnO$_2$/C](image)

**Figure 4.6** Cyclic voltammograms (CVs) for selected cycles of (a) SnO$_2$ and (b) SnO$_2$/C at a scan rate of 0.01 mVs$^{-1}$ between 0.01 V and 2.5 V (vs. Li$^+$/Li).

The electrochemical properties of the SnO$_2$ and SnO$_2$/C hollow spheres were investigated as anodes for LIBs. Cyclic voltammograms (CVs) were collected and are shown in Figure 4.6. The CV behaviour of bare SnO$_2$ anode is generally consistent with what has been reported in the literature$^{220}$, in reports which also used CMC as binder, indicating the same electrochemical reaction pathways. Specifically, three reduction peaks at 0.72 V, 0.45 V, and 0.12 V are formed during the first cathodic scan of the SnO$_2$ electrode as shown in Figure 4.6(a). The peak at 0.72 V is attributed to the formation of the solid electrolyte interphase (SEI) layer and the initial reduction of SnO$_2$ to Sn. The reaction is expressed as follows:

\[
SnO_2 + 4Li^+ + 4e^- \leftrightarrow Sn + 2Li_2O \quad (4.1)
\]
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and the peak shifts into a broad peak from 1.03 to 1.27 V in the following cycles. The small peak at 0.45 V corresponds to the formation of $\beta$ phase Sn during the reaction process and shifts to 0.56 V in the following cycles.\textsuperscript{220} While the one at 0.12 V comes from the alloying of Sn with Li$^+$ ions as represented in Equation (4.2):

$$Sn + xLi^+ + xe^- \leftrightarrow Li_xSn \quad (0 \leq x \leq 4.4)$$ (4.2)

which is repetitive. Correspondingly, three oxidation peaks at 0.54 V, 1.25 V, and 1.84 V are formed during the anodic scan process. The peak at 0.54 V can be assigned to the de-alloying process from Li$_x$Sn as described in Equation (4.3):

$$Li_xSn \leftrightarrow Sn + xLi^+ + xe^- \quad (0 \leq x \leq 4.4)$$ (4.3)

and the broad peak at 1.25 V results from partial reversible formation of SnO$_2$.\textsuperscript{12} The peak around 1.84 V is due to the lithium ion diffusion out of/into the interspaces between the nanoparticles. The anodic and cathodic peaks almost overlap in the following cycles, indicating the good reversibility of the electrochemical reactions.

For the SnO$_2$/C electrode, the CV curves of which show similar profiles to those of the pure SnO$_2$ electrode as depicted in Figure 4.6(b). The reduction peaks of first cycle move to higher voltage of 0.79 V, 0.53 V, and 0.17 V, respectively, demonstrating the decreased voltage polarization resulting from the improved electrical conductivity provided by the carbon coating. The anodic processes of SnO$_2$/C show negligible change compared with those of SnO$_2$. Also, the intensity and peak positions of SnO$_2$/C show better repeatability compared to those of SnO$_2$ during the different cycling processes, indicating its better cycling stability.
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Figure 4.7 Electrochemical performance of SnO$_2$ and SnO$_2$/C: (a) discharge-charge profiles for the 1$^{\text{st}}$, 2$^{\text{nd}}$, and 5$^{\text{th}}$ cycles of SnO$_2$; (b) discharge-charge profiles for the 1$^{\text{st}}$, 2$^{\text{nd}}$, and 5$^{\text{th}}$ cycles of SnO$_2$/C; (c) cycling performances of SnO$_2$, SnO$_2$/C, and commercial SnO$_2$, and coulombic efficiency of SnO$_2$/C at a current density of 100 mA g$^{-1}$; and (d) rate performances of SnO$_2$ and SnO$_2$/C.

The discharge-charge profiles of SnO$_2$ and SnO$_2$/C at a current density of 100 mA g$^{-1}$ are presented in Figure 4.7(a) and (b), respectively. In accordance with the CV results shown in Figure 4.6, three defined plateaus can be recognized in the first discharge process, and the peaks at 0.72 V and 0.79 V of SnO$_2$ and SnO$_2$/C, respectively, disappear in the following cycle. Also, the profile of SnO$_2$/C shows much better repeatability than that of bare hierarchical SnO$_2$.

The cycling performances of bare SnO$_2$ and SnO$_2$/C were also evaluated at 100 mA g$^{-1}$, as shown in Figure 4.7(c). As expected, the SnO$_2$/C electrode exhibits superior cyclability.
compared to the SnO₂ electrode. The irreversible capacity at the first cycle of SnO₂/C is slightly lower than that of SnO₂ due to the presence of low-capacity carbon and more side reactions. Specifically, the initial discharge and charge capacities of SnO₂ anode are 1506.5 mAh g⁻¹ and 953.2 mAh g⁻¹, respectively, while SnO₂/C gives 1486.7 and 1239.3 mAh g⁻¹ in the first discharge and charge processes, respectively. The larger capacity in the first cycle than the theoretical one results from the partly reversible Eq.(1), and the formation of the SEI layer, which are common for most anode materials.²¹¹,²²⁸,²²⁹ The SnO₂/C delivers discharge capacity of 900 mAh g⁻¹ in the 50th cycle, corresponding to 71.4% of the discharge capacity in the second cycle, and retains a coulombic efficiency of 98.2%. Under the same test conditions, the SnO₂ exhibit faster capacity fade, and only around 607.2 mAh g⁻¹ of discharge capacity is left after 50 cycles. Moreover, we investigated the electrochemical performance of commercial SnO₂ powders under the same conditions. The cycling data is also shown in the Figure 4.7(c). As expected, this electrode suffers from severe capacity fade, and the retained discharge capacity in the 50th cycle is only 382.0 mAh g⁻¹, which is worse than for the SnO₂/C sample and even worse than for the SnO₂ sample. This result exactly demonstrates the advantages of the synergetic effects of the hierarchical hollow sphere structure and the homogeneous carbon coating.

![Graph](image)

**Figure 4.8** Discharge-charge profiles of (a) SnO₂ and (b) SnO₂/C at different current densities.
The rate capacities of SnO$_2$ and SnO$_2$/C at different current densities are shown in Figure 4.7(d), in which each current density is maintained for 10 cycles. The corresponding discharge-charge profiles are shown in Figure 4.8. The capacities of the SnO$_2$ hollow sphere anode are 1098.6, 825.5, 688.1, 589.7, and 459.8 mAh g$^{-1}$ at 100, 200, 500, 1000, and 2000 mA g$^{-1}$, respectively. The SnO$_2$/C electrode delivers high capacities of 1307.4, 1156.9, 903.6, 794.9, and 669.9 mAh g$^{-1}$ at 100, 200, 500, 1000, and 2000 mA g$^{-1}$, respectively. It can be also seen that the hierarchical SnO$_2$ electrode delivers good high rate performance, which is further improved by the carbon coating in SnO$_2$/C. For example, a stable discharge capacity of 670 mAh g$^{-1}$ is maintained at a high current density of 2000 mA g$^{-1}$ for SnO$_2$/C, 200 mAh g$^{-1}$ more than that for pure SnO$_2$ anode. This capacity increase arising from the carbon coating is similar to other examples,$^{41,218,223,230,231}$ undoubtedly demonstrating the benefit of the nanosized carbon coating.

Figure 4.9 Electrochemical impedance spectra of SnO$_2$ and SnO$_2$/C from 100 kHz to 100 mHz (inset: equivalent circuit).

Electrochemical impedance spectra of the hierarchical SnO$_2$ and SnO$_2$/C were collected and are shown in Figure 4.9. The equivalent circuit is shown in the inset, in which $R_s$ represents
the solution resistance of the electrolyte, and the constant phase element (CPE) is used to replace an ideal capacitance. The depressed semicircle in the high frequency region is attributed to the charge transfer resistance \( R_{ct} \). In the low frequency region, the sloping line is associated with the Warburg impedance \( Z_w \). The \( R_s \) of SnO\(_2\) and SnO\(_2\)/C is fitted to be 2.826 \( \Omega \) and 2.565 \( \Omega \), respectively. The \( R_{ct} \) of SnO\(_2\)/C (226 \( \Omega \)) is much smaller than that of SnO\(_2\) (473 \( \Omega \)), resulting from the rational nano-design and conductive carbon layer, which facilitate the electrochemical reaction kinetics.

4.4 Conclusion

In summary, hierarchical SnO\(_2\) and SnO\(_2\)/C hollow spheres assembled from nanosheets were synthesized through hydrothermal synthesis and subsequent calcination. The uniform coating of nanosized carbon on the SnO\(_2\) matrix of SnO\(_2\)/C can improve the reversible capacity, rate stability, and cycle life. Combining the advantages of the low-dimensional nanosized building blocks, hollow structure, and elastic carbon buffering layer, the design of SnO\(_2\)/C offers a promising route to improve the electrochemical performance of SnO\(_2\)-based anode materials.
Chapter 5. Hierarchical Zinc Cobalt Oxides Microspheres and Nanoparticles as Anode Materials for Lithium Storage

5.1 Introduction

Since the discovery of 3d transition-metal oxides with good performance as anode for Li-ion battery, an enormous and worldwide effort has been made to improve their capacity, cycling performance, and initial cumbic efficiency. Moreover, due to the higher electrical conductivity and relatively low activation energy of electron transfer than single one, the mixed metal oxides have been widely studied as electrode materials for high performance lithium ion batteries.\(^{232}\)

Co-based anodes for LIBs included partially replacing Co with more ecofriendly and cheaper alternative metals to form MCo_2O_4 (M = Zn, Cu, Ni, Mg, and Fe) without sacrificing its electrochemical performance.\(^{232}\) ZnCo_2O_4 (ZCO), whose structure is same with Co_3O_4, has been considered and widely studied as an attractive candidate to substitute the conventional graphite anode in LIB due to its superiorities such as improved reversible capacities, enhanced cycling stability, and good environmental benignity.\(^{233-236}\) It is a normal spinel with the Zn\(^{2+}\) ions occupying the tetrahedral sites in the cubic spinel structure and Co\(^{3+}\) ions occupying the octahedral sites, as shown in Figure 5.1(a).\(^{237}\) ZCO can store Li\(^+\) through not only the conversion reaction, but also the alloying/dealloying reaction between Zn and Li, which results in a high theoretical capacity of \(\sim 900 \text{ mAh g}^{-1}\).\(^{235}\) However, the intrinsic poor electric conductivity and low cycling stability due to drastic volume change during lithium insertion/extraction process still limit its practical application. Until now, many types of ZCO, including nanowires,\(^{238}\) nanosheets,\(^{239}\) and 3D hierarchically porous structures\(^{240}\), have been synthesized to be used as anode for Li ion battery with good reversible capacity. However,
Chapter 5. Hierarchical Zinc Cobalt Oxides Microspheres and Nanoparticles as Anode Materials for Lithium Storage

the poor electric conductivity and large volume change of the ZCO nanostructures during the electrochemical reaction processes led to fast capacity decrease. Carbon modification is also performed to improve the cycling performance of ZCO. Meanwhile, another kind of zinc cobalt oxide, Zn$_{1-x}$Co$_x$O (x=0.05, 0.10 and 0.15) has been widely studied as magnetic materials, but rarely as electrode materials. The crystal structure of Zn$_{1-x}$Co$_x$O is shown in Figure 5.1b, in which Co ions enter into the inner lattice of ZnO and the oxidation state of Co ions is +2 valence, which are tetrahedrally coordinated. It is reported that the doping of Co does not change the wurtzite structure of ZnO with doping concentrations below 25%. Thus the XRD pattern of Zn$_{1-x}$Co$_x$O is similar to that of ZnO.

![Figure 5.1](image)

**Figure 5.1** The crystal structure of (a) spinel ZnCo$_2$O$_4$ in the (220) plane, showing the arrangements of zinc tetrahedrons and cobalt octahedrons and (b) Zn$_{1-x}$Co$_x$O.

In this work, hierarchical ZCO microspheres have been successfully synthesized by a facile microemulsion-based method. The homogeneously dispersed ZCO microspheres are further composed of uniform sized and closely interconnected ZCO nanoparticles. The relatively
large micrometer size is good to improve the volumetric energy density. When trying to study the effect of carbon modification, nanoparticles of $\text{Zn}_{0.85}\text{Co}_{0.15}\text{O}$ and carbon composite ($\text{Zn}_{0.85}\text{Co}_{0.15}\text{O}/\text{C}$) was finally obtained. Microstructure, composition and electrochemical performance of ZCO and $\text{Zn}_{0.85}\text{Co}_{0.15}\text{O}/\text{C}$ were studied and discussed in details.

5.2 Experimental details

5.2.1 Materials preparation

Synthesis of hierarchical ZCO microspheres. 0.2 g polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO20-PPO70-PEO20, Pluronic P123) was first dissolved in 3 g absolute ethanol and 20 mL of EG were added later to form the oil phase. After that, zinc nitrate hexahydrate and cobalt nitrate hexahydrate with a ratio of 0.5 were dissolved successively in deionized water to form the water phase. After stirring for 30 minutes, the water phase was gradually dropped into the oil phase under continuous stirring. The obtained precursor was heated at 80°C to vaporize the water and then heated in a muffle furnace at 500°C for 3 h to obtain the final products.

Synthesis of $\text{Zn}_{0.85}\text{Co}_{0.15}\text{O}/\text{C}$ nanoparticles. A certain amount of glucose were dissolved into the above mentioned microemulsion precursor under continuous stirring to perform carbon modification. After pre-drying at 80°C, the as-prepared powders were calcined in a tube furnace at 500°C for 3 h under flowing N$_2$ to obtain the final products.

5.2.2 Materials characterization

The morphologies and structures of the synthesized samples were investigated by field-emission scanning electron microscopy (FESEM; JEOL JSM-7500FA). The crystalline structures and compositon of the synthesized powders were characterized by powder X-ray
diffraction (XRD; GBC MMA diffractometer) with Cu $K_\alpha$ radiation together with the EDX analysis. The carbon content of the composite was further determined by using an elemental analyzer (German, Vario EL CUBE) and a Mettler-Toledo thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) STARe System from 40°C to 1000°C in air with a ramp rate of 5°C min$^{-1}$.

5.2.3 Electrochemical measurements

The electrodes were prepared by mixing the active material (ZCO or $\text{Zn}_{0.85}\text{Co}_{0.15}\text{O}/\text{C}$), Super P, and PVDF binder in a weight ratio of 80:10:10 to form a slurry, which then was coated on copper foil. The thus-prepared working electrode was then dried in a vacuum oven at 120°C overnight, and then pressed at 20 MPa. The electrolyte used was 1.0 mol L$^{-1}$ LiPF$_6$ in an ethylene carbonate–diethyl carbonate (1:1 v/v) solution. The coin cells were assembled in an argon-filled glove box with the content of O$_2$ and H$_2$O are both less than 0.1 ppm. The cycling performance and rate stability of the cells were tested with a Land Test System between 0.01 -3.0 V (vs. Li$^+/\text{Li}$) at different constant current densities. Cyclic voltammetry at a scan rate of 0.1 mV s$^{-1}$ in the potential range of 0.01–3.0 V (vs. Li$^+/\text{Li}$) was performed using a CHI 660b electrochemistry workstation.

5.3 Results and discussions
Figure 5.2 SEM morphologies of (a-c) hierarchical ZCO microspheres and (d, e) Zn$_{0.85}$Co$_{0.15}$O/C nanoparticles.

Figure 5.2 shows SEM morphologies of the prepared hierarchical ZCO microspheres and Zn$_{0.85}$Co$_{0.15}$O/C nanoparticles. The prepared ZCO microspheres with ~1 μm in diameter showed homogeneous distribution and were further composed of uniform sized and closely interconnected nanoparticles. Its homogeneity was also demonstrated by the EDX element analysis as shown in Figure 5.3. While the Zn$_{0.85}$Co$_{0.15}$O/C had an absolute different morphology with ZCO, it was consisted of nanoparticles with several hundreds of nanometres in diameter. The existence of Zn, Co, O and C elements were also proved by EDX analysis as shown in Figure 5.4. This carbon modification for Zn$_{0.85}$Co$_{0.15}$O/C does not exhibit same morphology and composition with ZCO as that in chapter 4 for SnO$_2$ and SnO$_2$/C, possibly due to the different carbon modification method. The addition of glucose in the initial step, to some extent, destroyed the formation of micelle subunits.
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Figure 5.3 EDX images of ZCO microspheres showing homogeneous distribution of Zn, Co and O elements.

Figure 5.4 EDX images of Zn_{0.85}Co_{0.15}O/C nanoparticles showing homogeneous distribution of Zn, Co, C and O elements.
Figure 5.5 (a) XRD spectra and (b, c) EDX patterns with element ratio inset of ZCO and Zn$_{0.85}$Co$_{0.15}$O/C.

Figure 5.6 TGA curve of Zn$_{0.85}$Co$_{0.15}$O/C nanoparticles.
Figure 5.5 shows the composition of ZCO and Zn0.85Co0.15O/C tested from XRD and EDX analysis. The XRD pattern of ZCO can be assigned to ZnCo$_2$O$_4$ (PDF# 23-1390). The Zn0.85Co0.15O/C is a composite of CoO and Zn$_{1-x}$Co$_x$O (PDF# 89-0510 of ZnO). EDX results demonstrated that the molar ratio of Zn/Co for ZCO is 0.46, corresponding with the 0.5 of Zn/Co ration for ZnCo$_2$O$_4$. While the Zn/Co ration of Zn$_{0.85}$Co$_{0.15}$O/C is 1.78 resulting from the coexistence of CoO and Zn$_{1-x}$Co$_x$O. The C peak in EDX spectra and elemental distribution came from the carbon in Zn$_{0.85}$Co$_{0.15}$O/C and conductive tape used in the test. TGA test was performed to explore the carbon content in Zn$_{0.85}$Co$_{0.15}$O/C sample and is shown in Figure 5.6. The weight increase during the whole process comes from the oxidation of CoO to Co$_3$O$_4$. And weight loss in stage II results from combustion of the carbon, which is larger than the increase caused by CoO. Based on the TGA result, EDX distribution together with the additional elemental analysis of Zn$_{0.85}$Co$_{0.15}$O/C, the carbon content in Zn$_{0.85}$Co$_{0.15}$O/C was determined to be 3.51 wt%. The content of CoO was calculated to be 31.9 wt%. Thus the x in Zn$_{1-x}$Co$_x$O can be determined to be 0.15, which means the Zn$_{0.85}$Co$_{0.15}$O/C was finally prepared.

Figure 5.7 (a) Cyclic voltammograms (CV) at a scan rate of 0.1 mV/s between 0.01-3.0 V and (b) discharge-charge profiles of the 1st, 2nd, and 100th cycles for ZCO between 0.01-3.0 V.
Figure 5.7a illustrates the cyclic voltammograms of first 5 cycles for the ZCO electrode at a scan rate of 0.1 mV s$^{-1}$. In the first cathodic scan, the obvious peak centred at 0.52 V can be clearly observed, which results from the decomposition of ZCO to metallic Co and Zn (equation (5.1)), and the alloying of Zn and Li (equation (5.2)) together with the formation of SEI layers. The significant intensity decrease of this peak in the following cycles indicates the irreversible electrochemical reaction in the initial cycle. Meanwhile, two broad peaks in the first anodic scan located at ~1.7 and 2.0 V corresponded to the oxidation of Zn to ZnO and Co to CoO. Apparently, the differences in the second cycle indicate a different and electrochemical mechanism from the first anodic process. The lithium insertion/extraction reactions for electrode might be described as follows:

\[
\begin{align*}
\text{ZnCo}_2\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- & \rightarrow \text{Zn} + 2\text{Co} + 4\text{Li}_2\text{O} \\
\text{Zn} + x\text{Li}^+ + xe^- & \leftrightarrow \text{Li}_x\text{Zn}(x \leq 1) \\
\text{Zn} + \text{Li}_2\text{O} & \leftrightarrow \text{ZnO} + 2\text{Li}^+ + 2\text{e}^- \\
\text{Co} + \text{Li}_2\text{O} & \leftrightarrow \text{CoO} + 2\text{Li}^+ + 2\text{e}^- \\
\text{CoO} + 1/3 \text{Li}_2\text{O} & \leftrightarrow 1/3 \text{Co}_3\text{O}_4 + 2/3\text{Li}^+ + 2/3\text{e}^- 
\end{align*}
\]

Figure 5.7b presents the charge-discharge profiles of discharge-charge profiles of the 1$^{st}$, 2$^{nd}$, and 100$^{th}$ cycles for ZCO between 0.01-3.0 V. In the first discharge curve, a long plateau starting from 1.0 V can be observed, which is consistent with the CV result and can be ascribed to the transformation of ZCO into Zn, Co and Li$_2$O, as well as the formation of SEI film. The initial discharge and charge capacities are 1145 and 808.2 mAh g$^{-1}$, respectively, corresponding to a coulombic efficiency of 70.6%. The irreversible capacity loss in the following cycles can be mainly attributed to the formation of the SEI film. The long discharge plateau became showing a steeper one starting from 1.25 V in the 2$^{nd}$ cycle, which is consistent with the shift of cathodic peak from the 1$^{st}$ to 2$^{nd}$ scan.
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Figure 5.8 (a) Cycling performance and coulombic efficiency at a current density of 100 mA g\(^{-1}\) and (b) rate performance at different current densities of ZCO.

Figure 5.8 shows the cycling performance and rate performance of ZCO. The initial coulombic efficiency is 70.6% resulting from the charge-discharge capacities of 1145/808.2 mAh g\(^{-1}\). From the second cycle afterwards, the coulombic efficiency improves remarkably, reaching 86.7% in the 2nd cycle (discharge capacity of 702.3 mAh g\(^{-1}\) and charge capacity of 810 mAh g\(^{-1}\)) and achieving 97.8% in the 5\(^{th}\) cycle. The gradually increasing reversible capacities can be clearly observed during cycling, which is also seen for some other transitional metal oxide anode materials and may be ascribed to a gradual activation process of electrodes as well as reversible reactions between metal particles and electrolytes.\(^{245}\) The ZCO delivered discharge capacity of 616.7 mAh g\(^{-1}\) in the 100\(^{th}\) cycle, corresponding to 87.8% of the discharge capacity in the second cycle, and retains a coulombic efficiency of 99.2%. The irreversible loss during the first charge is commonly attributed to irreversible side reactions on the surface of electrodes, such as formation of SEI layer, electrolyte decomposition and possible incomplete restoration of metallic Zn and Co into the original oxides. From Figure 5.8b, it can be seen that the reversible discharge capacities of ZCO are 495, 407.2, 348.7 and 289.9 mAh g\(^{-1}\) at 200, 500, 1000, and 2000 mA g\(^{-1}\), respectively. And
the capacity recovered to 535.9 mAh g\(^{-1}\) when the current density went back to 100 mA g\(^{-1}\), exhibiting good rate performance.

**Figure 5.9** (a) Cyclic voltammograms (CV) at a scan rate of 0.1 mV/s between 0.01-3.0 V and (b) discharge-charge profiles for the 1\(^{\text{st}}\), 2\(^{\text{nd}}\), and 100\(^{\text{th}}\) cycles of Zn\(_{0.85}\)Co\(_{0.15}\)O/C between 0.01-3.0 V.

For the Zn\(_{0.85}\)Co\(_{0.15}\)O/C nanoparticles, the CV curves (Figure 5.9a) show similar profiles with those of ZCO, including the main cathodic peak at 0.5 V in the first cycle which shifted to higher potential in the subsequent cycles, and two broad anodic peaks at ~1.6 and 2.0 V, which indicates similar electrochemical reactions among these two materials. In detail, the cathodic peak at 0.5 V in the initial cycle can be attributed to the decomposition of Zn\(_{0.85}\)Co\(_{0.15}\)O/C, formation of Zn and Co and formation of SEI film as that for ZCO. The other seen small peaks may come from the different composition of ZnCo\(_2\)O\(_4\) and Zn\(_{0.85}\)Co\(_{0.15}\)O, of which the distinct peak centred at 0.34 V could be assigned to the reduction of Co\(^{2+}\) to metallic Co (CoO + 2Li\(^+\) + 2e\(^-\) ↔ Co + Li\(_2\)O) resulting from the existence of CoO.\(^{245}\) In the anodic scan, similar to that of ZCO, the broad peak at 1.05–1.65 V is ascribed to the oxidation of Zn to Zn\(^{2+}\), and the peak at ~ 2.1 V corresponds to the oxidation of Co to Co\(^{2+}\).\(^{246}\) From the 2\(^{\text{nd}}\) to the 5\(^{\text{th}}\) cycle, these peaks overlapped well with each other, suggesting the good reversibility of the Li\(^+\) storage process.
Figure 5.7b presents the charge-discharge profiles of discharge-charge profiles of the 1st, 2nd, and 100th cycles for Zn\(_{0.85}\)Co\(_{0.15}\)O/C in the voltage window of 0.01-3.0 V. The plateau of the profiles in the first cycle is consistent with the CV result and can be ascribed to the transformation of ZCO into Zn, Co and Li\(_2\)O, as well as the formation of SEI film. The irreversible capacity loss in the following cycles is also mainly ascribed to the formation of the SEI film.

Figure 5.10 (a) Cycling performance and coulombic efficiency of Zn\(_{0.85}\)Co\(_{0.15}\)O/C at a current density of 100 mA g\(^{-1}\) and (b) rate performance at different current densities of Zn\(_{0.85}\)Co\(_{0.15}\)O/C.

Cycling performance at a current density of 100 mA g\(^{-1}\) and rate performance at different densities for Zn\(_{0.85}\)Co\(_{0.15}\)O/C are shown in Figure 5.10. The Zn\(_{0.85}\)Co\(_{0.15}\)O/C delivered high first-cycle discharge and charge capacities of 911.3 and 610.9 mAh g\(^{-1}\), respectively, corresponding to a coulombic efficiency of 67%. The specific capacities keep increasing slowly after 15 cycles and the discharge capacity reached 741.9 mAh g\(^{-1}\) in the 100th cycle, corresponding to a capacity retention of 81.4%. The charge capacity of the 120th cycle (783.4 mAh g\(^{-1}\)) is higher than that of the 2nd cycle. The reversible discharge capacities are 591.4, 493.9, 429.7, 409.4 mAh g\(^{-1}\) at 200, 500, 1000, and 2000 mA g\(^{-1}\), respectively. And the
capacity recovered to 653.8 mAh g\(^{-1}\) when the current density went back to 100 mA g\(^{-1}\), showing good rate performance as anode for LIB.

5.4 Conclusion

Hierarchical ZnCo\(_2\)O\(_4\) microspheres and Zn\(_{0.85}\)Co\(_{0.15}\)O/C nanoparticles were successfully prepared via a microemulsion method. The complex structures of ZnCo\(_2\)O\(_4\) with nanostructured constituent units and carbon modification of Zn\(_{0.85}\)Co\(_{0.15}\)O/C is favourable for the diffusion of lithium ions possess. When applied as anode materials for lithium ion batteries, the hierarchical ZnCo\(_2\)O\(_4\) microspheres and Zn\(_{0.85}\)Co\(_{0.15}\)O/C nanoparticles exhibited good cycling performance with slowly increasing capacity over cycling. High reversible capacities of 616.7 and 741.9 mA h g\(^{-1}\) was maintained after repetitive 100 cycles for ZCO and Zn\(_{0.85}\)Co\(_{0.15}\)O/C, respectively, demonstrating their lithium storage capacity as anode materials for lithium ion batteries.
Chapter 6. Multi-angular Rod-Shape Na\textsubscript{0.44}MnO\textsubscript{2} as Cathode Materials with High-Rate and Long-Life for Sodium-Ion Batteries

The demand for large-scale energy storage devices has been growing significantly due to the continuous depletion of energy resources.\textsuperscript{11} Sodium ion batteries (SIBs), a new generation of large-scale rechargeable energy storage devices, are attracting more and more attention because of the low cost and abundant availability of sodium resources. Nevertheless, the sluggish electrochemical reaction kinetics resulting from the large diameter of the Na\textsuperscript{+} ion makes it very difficult to find suitable host materials for rapid and reversible Na\textsuperscript{+} insertion and extraction.\textsuperscript{247} Therefore, it is highly desirable to develop effective Na-host materials for high performance SIBs with high specific capacity, high rate capability, and long-term cycling stability.\textsuperscript{5, 143, 158, 245, 248, 249}

6.1 Introduction

Considering the cost factor, the sodium manganese oxides (Na\textsubscript{x}MnO\textsubscript{2}), such as NaMnO\textsubscript{2}, Na\textsubscript{0.60}MnO\textsubscript{2} and Na\textsubscript{0.44}MnO\textsubscript{2}, have been studied as promising cathode materials for SIBs since they were reported by Parant \textit{et al.} in 1971.\textsuperscript{250} For Na\textsubscript{x}MnO\textsubscript{2}, a tunnel-type structure is formed at 0.22 ≤ x ≤ 0.44, a mixture of tunnel and layered structures is formed at 0.44 < x ≤ 0.66, and a fully layered structure is formed at 0.66 < x ≤ 1.\textsuperscript{251} Among these structures, the tunnel-structured Na\textsubscript{0.44}MnO\textsubscript{2} is particularly attractive due to its unique three-dimensional (3D) crystal structure, which is made up of MnO\textsubscript{5} pyramids and MnO\textsubscript{6} octahedra, and is able to tolerate some stress during structural change.\textsuperscript{252-256} Na\textsubscript{0.44}MnO\textsubscript{2}, with a theoretical discharge capacity of 121 mAh g\textsuperscript{-1} (1 C = 121 mA g\textsuperscript{-1}), has a framework containing large S tunnels and small tunnels, and among them, the S tunnels can provide an abundance of vacancies, where 0.22 Na\textsuperscript{+} can be reversibly extracted along the c-axis.\textsuperscript{257-259} The crystal
structure of Na$_{0.44}$MnO$_2$ is shown in Figure 6.1. It is difficult, however, for the Na$_{0.44}$MnO$_2$ lattice to well accommodate the structural changes during the insertion/extraction of Na$^+$, leading to poor rate capability, which severely restricts its practical applications. Sauvage et al. prepared Na$_{0.44}$MnO$_2$ with an initial capacity of 80 mAh g$^{-1}$ at 0.1 C.$^{260}$ The capacity faded rapidly, however, with only half of the initial capacity retained after 50 cycles. Many strategies, such as nanosizing and metal substitution, have been tried to alleviate this disadvantage. Cao et al. reported Na$_{0.44}$MnO$_2$ nanowires with a discharge capacity of 84.2 mAh g$^{-1}$ over 1000 cycles at 0.5 C.$^{261}$ Wang et al. prepared Ti-substituted Na$_{0.44}$MnO$_2$ with capacity retention higher than 96% after 1100 cycles at 0.1 C.$^{182}$ There is no report, to the best of our knowledge, on Na$_{0.44}$MnO$_2$ with both excellent high-rate (more than 5 C) capacity and long cycling life for sodium storage.

Figure 6.1 Schematic crystal structure of orthorhombic Na$_{0.44}$MnO$_2$. The manganese octahedra are plotted in purple, oxygen atoms are shown in red and sodium in yellow.

Na$_{0.44}$MnO$_2$ can be prepared via facile synthetic methods such as hydrothermal,$^{262}$ solid-state,$^{260}$ sol-gel,$^{263}$ polymer-pyrolysis,$^{143}$ and reverse microemulsion method$^{259}$ etc. The preparation methods and electrochemical performance of the Na$_{0.44}$MnO$_2$ as cathode for SIBs are summarized in Table 6.1. The products obtained by different methods display different electrochemical performance. Among those methods, the reverse microemulsion process involves thoroughly dispersing a water phase into an oil phase consisting of a surfactant and a co-surfactant, to form thermodynamically stable microemulsion droplets (reverse micelles),
in which each droplet acts as an independent microreactor to help produce the desired compound.\textsuperscript{264} It can help to synthesize small particles with a narrow size distribution.\textsuperscript{265}

**Table 6.1** Summary of Na\textsubscript{0.44}MnO\textsubscript{2} prepared by different methods as sodium-ion battery cathodes.

<table>
<thead>
<tr>
<th>Method</th>
<th>Calcination temperature time</th>
<th>Morphology</th>
<th>Voltage (V vs. Na\textsuperscript{+}/Na)</th>
<th>Current density (rate)</th>
<th>Specific capacity/cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pechini method</td>
<td>800°C for 9 h</td>
<td>rod</td>
<td>2.0 – 3.8 V</td>
<td>0.1 C</td>
<td>65 mAh g\textsuperscript{-1}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 C</td>
<td>32 mAh g\textsuperscript{-1}</td>
</tr>
<tr>
<td>Sol-gel method</td>
<td>450°C for 6 h; 900°C for 15 h</td>
<td>slab</td>
<td>2.0 – 4.0 V</td>
<td>0.1 C</td>
<td>~ 110 mAh g\textsuperscript{-1}/100</td>
</tr>
<tr>
<td>Hydrothermal method</td>
<td>205°C for 96 h</td>
<td>nanowire</td>
<td>2.0 – 4.0 V</td>
<td>8.3 C</td>
<td>~ 90 mAh g\textsuperscript{-1}/20</td>
</tr>
<tr>
<td>Solid state method</td>
<td>300°C for 8 h; 800°C for 9 h</td>
<td>rod</td>
<td>2.0 – 3.8 V</td>
<td>0.1 C</td>
<td>~ 40 mAh g\textsuperscript{-1}/45 for Na\textsubscript{0.44}MnO\textsubscript{2}/C electrode</td>
</tr>
<tr>
<td>Polymer-pyrolysis method</td>
<td>750°C for 24 h</td>
<td>nanowire</td>
<td>2.0 – 4.0 V</td>
<td>0.5 C</td>
<td>84.2 mAh g\textsuperscript{-1}/1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 C</td>
<td>82 mAh g\textsuperscript{-1}/1000</td>
</tr>
<tr>
<td>Reverse microemulsion method</td>
<td>750°C for 24 h</td>
<td>rod</td>
<td>2.0 – 3.8 V</td>
<td>0.83 C</td>
<td>80.2 mAh g\textsuperscript{-1}/50</td>
</tr>
<tr>
<td>Our work</td>
<td>850°C for 20 h</td>
<td>multi-angular rod</td>
<td>2.0 – 3.8 V</td>
<td>0.1 C</td>
<td>99.1 mAh g\textsuperscript{-1}/1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.3 C</td>
<td>82.1 mAh g\textsuperscript{-1}/1000</td>
</tr>
</tbody>
</table>

In this work, we have prepared monophasic Na\textsubscript{0.44}MnO\textsubscript{2} with multi-angular shaped rods by a modified reverse microemulsion method.\textsuperscript{259} To the best of our knowledge, this is the first time that Na\textsubscript{0.44}MnO\textsubscript{2} with multi-angular images has been reported. This structure with suitable size increases the contact area between the material and the electrolyte, guarantees fast sodium ion diffusion and helps release strains resulting from de-insertion/insertion of Na\textsuperscript{+} ions in multiple directions. When used as cathode material in SIBs, the as-prepared multi-angular Na\textsubscript{0.44}MnO\textsubscript{2} rods feature stable cycling performance, excellent high-rate capability, and long cycle life at 8.3 C.

### 6.2 Experimental section
6.2.1 Materials preparation

Multi-angular rod-shaped Na$_{0.44}$MnO$_2$ was synthesized through a reverse microemulsion method. All the chemicals were used as purchased. Sodium nitrate and manganese nitrate tetrahydrate with a Na/Mn ratio of 0.44 were dissolved successively in 9 mL deionized water to form the water phase. 0.2 g polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO20-PPO70-PEO20, Pluronic P123, surfactant) was dissolved in 3 g absolute ethanol with 20 mL ethylene glycol (EG, cosurfactant) added later to form the oil phase. After stirring for 30 minutes, the water phase was gradually dropped into the oil phase under continuous stirring. Then, the obtained microemulsion was heated at 80°C to vaporize the water. The obtained gel precursor was then heated in a muffle furnace at 700°C (NMO700), 750°C (NMO750), 800°C (NMO800), 850°C (NMO850), or 900°C (NMO900) for 20 h in air to obtain the final products.

6.2.2 Structural Characterization

The morphologies of the as-prepared samples were investigated by field-emission scanning electron microscopy (FESEM, JEOL JSM-7500) and transmission electron microscopy (TEM, JEOL ARM 200F). TEM samples were prepared after sonication treatment. The microstructures of the as-prepared powders were characterized on a synchrotron X-ray diffraction beamline with a wavelength ($\lambda$) of 0.6885 Å calibrated with the National Institute of Standards and Technology (NIST) LaB$_6$ 660b standard reference material and laboratory X-ray diffraction (XRD, GBC MMA diffractometer) with Cu K$_{\alpha}$ radiation. The thermal property of the precursor before calcination was characterized by a Mettler–Toledo thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) STARRe System under air over a temperature range of 40–1000 °C with a ramp rate of 5°C min$^{-1}$. 
6.2.3 Electrochemical measurements

The electrodes were prepared by mixing 80 wt% active materials, 10 wt% Super P, and 10 wt% polyvinylidene fluoride (PVDF) binder to form a slurry, which was then coated on an aluminium foil. Next, the aluminium foil was dried in a vacuum oven overnight at 120°C. After that, the working electrodes were cut out and pressed under a pressure of 20 MPa. The electrolyte used was 1.0 mol L\(^{-1}\) NaClO\(_4\) in an ethylene carbonate (EC) – diethyl carbonate (DEC) solution (1:1 v/v) with 5 vol.% of fluoroethylene carbonate (FEC). Sodium foil was cut from a sodium bulk stored in mineral oil and used as both the counter and reference electrode. The cells were assembled in an argon-filled glove box. The electrochemical performances were tested on a Land Test System in the voltage range of 3.8-2.0 V (vs. Na\(^+\)/Na) at different current densities. Cyclic voltammetry (CV) at a scan rate of 0.1 mV s\(^{-1}\) and electrochemical impedance spectroscopy (EIS) from 100 kHz to 100 mHz were performed using a CHI 660b electrochemistry workstation between 4.0-2.0 V. In situ synchrotron XRD data were collected at the Australian Synchrotron with a wavelength (\(\lambda\)) of 0.6885 Å, calibrated with the NIST LaB\(_6\) 660b standard reference material. The cell used was charged at a current density of 12.1 mA g\(^{-1}\) (0.1 C), and the cutoff voltage was 3.8-2.0 V. The diffusion coefficient of Na\(^+\) ions was studied using the galvanostatic intermittent titration technique (GITT) and EIS. For the GITT measurement, the cells were charged and discharged at 0.1 C for 360 s followed by an open circuit relaxation for 1 h. The procedure was maintained until the voltage reached 3.8 V or 2.0 V. All the electrochemical testings were conducted at room temperature.

6.3 Results and discussions
Figure 6.2 (a) TGA curve of the gel precursor between 40 – 1000°C with a ramp rate of 5°C min⁻¹ (inset is an enlargement of Zone 3); (b) synchrotron powder XRD spectra of NMO samples calcined at different temperatures. The 2θ angle has been converted to values corresponding to the more common laboratory Cu Kα radiation.

Figure 6.3 X-ray diffraction patterns collected with Cu Kα radiation of NMO powders calcined at different temperatures.
The shape-defined cathode material, Na$_{0.44}$MnO$_2$, was synthesized via a reverse microemulsion method from the mixed solution of P123, EG, ethanol and water. A gel precursor was formed after removing the water from the precursor solution by heating at 80°C, and then the targeted material could be obtained by further heating the precursor at a higher temperature in air. The TGA/DSC test was employed to study the chemical reactions and crystallization behaviours of the gel precursor during calcination. Figure 6.2a is the TGA curve of the gel precursor between 40 and 1000°C. Two distinct weight losses were observed during heated to 370°C (Zone 1 and Zone 2), which can be attributed to the removal of remnant water and ethylene glycol, respectively. Further heating to 1000°C, as shown in the magnified image of Zone 3 (~1% weight loss), slight weight variations occurred at around 750°C and 850°C were monitored.

Figure 6.2b presents synchrotron XRD spectra of the powders calcined at different temperatures, which indicates the change on the compositions and crystal structures of the products after heating. At 700°C, Na$_{0.44}$MnO$_2$ (Na$_4$Mn$_9$O$_{18}$) together with Na$_{0.4}$MnO$_2$ (Na$_2$Mn$_5$O$_{10}$) was obtained due to a slight loss of Na during the preparation process. It was reported that the psilomelane Na$_{0.4}$MnO$_2$ decomposes at temperatures above 750°C based on the equation below:\[^{250}\]

$$0.44\ Na_{0.4}MnO_2 \rightarrow 0.40\ Na_{0.44}MnO_2 + 0.02\ Mn_2O_3 + 0.01O_2 \uparrow$$ \hspace{1cm} (6.1)

which caused a small change in the weight loss at 750°C in the TGA curve. There were still Na$_{0.4}$MnO$_2$ residues detected for NMO800. Another phase transformation took place from 800 to 850°C, and the Na$_{0.4}$MnO$_2$ phase almost disappeared in NMO850. Meanwhile, traces of unknown phases were detected in NMO850 and became less in NMO900. Those transformations are in accordance with the change in the weight loss at and after 850°C in the TGA curve. No other phases apart from Na$_4$Mn$_9$O$_{18}$ and Na$_2$Mn$_5$O$_{10}$ could be detected in the
XRD patterns shown in Figure 6.3, indicating that the content of impurities was less than 5 mol%. All the Na$_{0.44}$MnO$_2$ peaks can be indexed to the orthorhombic phase with space group Pbam (JCPDS No. 27-750, $a = 9.100$ Å, $b = 26.340$ Å, and $c = 2.821$ Å). The intensities of the Na$_{0.44}$MnO$_2$ peaks become stronger with increasing temperature, indicating the better crystallinity and larger crystallite size of the sample. The (3 5 0) reflection of all the Na$_{0.44}$MnO$_2$ samples split into two Bragg peaks for (0 10 0) and (3 5 0) with changing relative intensity for samples calcined at different temperatures in both patterns. Rietveld refinement was performed on the synchrotron XRD pattern collected from NMO850 as a single phase,$^{266}$ and is shown in Figure 6.4. The structural formula is fitted to Na$_{4.34}$Mn$_9$O$_{18}$, indicating more sodium existing in the composite than Na$_4$Mn$_9$O$_{18}$. Since the impurity phase is very little, we can not get the exact phase through the Rietveld refinement.

![Rietveld refinement XRD pattern of NMO powders calcined at 850°C. The peaks marked with V are unknown impurities.](image)

**Figure 6.4** Rietveld refinement XRD pattern of NMO powders calcined at 850°C. The peaks marked with V are unknown impurities.
Chapter 6. Multi-angular Rod-Shape $\text{Na}_{0.44}\text{MnO}_2$ as Cathode Materials with High-Rate and Long-Life for Sodium-Ion Batteries

**Figure 6.5** SEM morphologies of NMO samples calcined at (a) 750°C; (b) 800°C; (c) 850°C; and (d) 900°C.

The morphologies of samples calcined at different temperatures are shown in **Figure 6.5**. All the samples presented well-distributed multi-angular rod-shape morphology with grooves on the surfaces. It can be seen that the rods of NMO750 were well-isolated with diameters in the range of 0.1-0.5 μm and lengths of 0.5-2.5 μm. With increasing sintering temperature, the rods become bigger and longer and the grooves become more obvious. This growth is consistent with the increasing intensity of the XRD results. The multi-angular rods tend to fuse together to decrease the surface energy at 850 and 900°C. The edges of the grooves tend to be deeper and sharper for NMO850 but smoothened when calcined at 900°C.
Figure 6.6 Laboratory X-ray diffraction patterns collected with Cu Kα radiation of NMO powders calcined at 850°C without the addition of P123 or ethylene glycol (EG).

Figure 6.7 SEM morphologies of NMO samples prepared at 850°C without the addition of P123: (a) low magnification, (b) high magnification; and without the addition of ethylene glycol: (c) low magnification, (d) high magnification.
To understand the effects of P123 and EG, we prepared samples without the addition of P123 or EG, while the other conditions were maintained as the same with NMO850. The XRD patterns and SEM morphologies of the samples obtained without the addition of P123 or EG are shown in Figure 6.6 and Figure 6.7, respectively. It can be clearly seen that the rods obtained from the solution without P123 formed with manganese oxide impurities, and are shorter and thicker comparing with those prepared with the addition of P123 as shown in Figure 6.5c. The grooves on the surfaces are far less obvious than those in Figure 6.5c, which may result from the lack of morphology controlling effect of surfactant P123 to form shape-defined grooves. Moreover, without the addition of EG, the multi-angular rods are Na_{0.44}MnO_2 with Mn_2O_3 impurities, the content of which is much larger than 5 mol%, as shown in Figure 6.6. The rods are longer and thinner than those shown in Figure 6.5c and Figure 6.7a and 6.7b. EG helps to inhibit the formation of superabundant Mn_2O_3. Therefore, the addition of P123 and EG is essential for synthesizing pure-phase multi-angular Na_{0.44}MnO_2 product.
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Figure 6.8 TEM images of NMO samples calcined at (a) 800°C (inset: lower magnification); (b) 850°C; and (c) 900°C; HRTEM images of samples calcined at (d) 800°C; (e) 850°C (inset: corresponding SAED pattern); and (f) 900°C.

TEM investigations were also carried out to study the microstructures of samples calcined at different temperatures, as shown in Figure 6.8. It can be seen that the diameter is \(~0.5\ \mu\text{m}\) of one single rod for all samples. The image contrast observed on the rods in the TEM images and the corresponding high-resolution TEM images (HRTEM) is ascribed to the variations in the thickness of the samples resulting from the grooves on the surface. The rods of NMO850 and NMO900 tightly fused together and remained adhesive after sonication, as shown in Figure 6.8b and 6.8c, which are consistent with the SEM results. All the rods calcined at different temperatures show clear lattices in the HRTEM images (Figure 6.8d-f). All of the lattice fringes have a spacing of 0.455 nm, corresponding to the (200) planes of Na$_{0.44}$MnO$_2$. The selected area electron diffraction (SAED) pattern (inset of Figure 6.8e) of NMO850
reveals that the rods are single-crystalline Na$_{0.44}$MnO$_2$ with orientation along the [001] direction, which is consistent with other reports.$^{267, 268}$ The impurity content is too low to be detected. Similar SAED patterns also exist for NMO800 and NMO900 (not shown).

The $\vec{c}$ ([001]) direction, along which a Na$_{0.44}$MnO$_2$ crystal grows much faster than in other directions, is the main path for sodium diffusion of Na$_{0.44}$MnO$_2$.\textsuperscript{269, 270} Therefore, Na$_{0.44}$MnO$_2$ tends to grow into rod- or wire-like shapes, as summarized in Table 6.1. To the best of our knowledge, this is the first time that multi-angular Na$_{0.44}$MnO$_2$ rods are reported. The multi-angular structure is theoretically favourable for materials intended as electrodes for batteries. In this case, it can not only increase the contact area between the Na$_{0.44}$MnO$_2$ rods and the electrolyte, but also accelerate the diffusion of sodium ions in the bulk of the material. The aligned grooves on the surface of the 1D rods can endorse the material enhanced wettability and directional diffusion of the electrolyte along the grooves.\textsuperscript{271} Also, the multi-angular structure can help release strains resulting from de-insertion/insertion of Na$^+$ ions in multiple directions. The relatively large particle size is also good to improve the volumetric energy density.
Figure 6.9 Electrochemical performances of NMO850 and NMO900: (a) cyclic voltammograms (CV) between 4.0-2.0 V; (b) charge-discharge profiles at 0.1 C; (c) cycling performance and coulombic efficiency of NMO850 and cycling performance of NMO900 at 8.3 C (inset: amplification image up to 200 cycles); and (d) rate capacity between 3.8-2.0 V.

Figure 6.10 Cyclic voltammograms (CV) of the NMO sample calcined at 850°C for the first five cycles at a scan rate of 0.1 mV s⁻¹ in the potential window of 4.0-2.0 V.
NMO850 and NMO900 were chosen for further electrochemical testing since they are mainly composed of Na$_{0.44}$MnO$_2$ without Na$_{0.4}$MnO$_2$. Figure 6.9a shows CV curves of NMO850 and NMO900. For NMO850, the voltage peaks in the oxidation process for the initial cycle were centred at 3.09, 3.31, and 3.51 V, respectively. The cathodic scan shows six peaks at 3.37, 3.13, 2.93, 2.61, 2.36, and 2.15 V, which is consistent with the reported six biphasic transitions, implying a complex multiphase transition mechanism during Na-ion insertion and extraction processes.$^{261}$ Six highly reproducible redox processes can be clearly seen in the following cycles, as shown in Figure 6.10. There is little difference between the first cycle and the subsequent cycles, demonstrating the stable charge and discharge processes. This result is different from some other reports, in which the initial anodic scans are stronger than those in the subsequent cycles.$^{253, 256}$ This can be attributed to the strain tolerance of the multi-angular structure for Na$^+$ de-insertion/insertion. It can be seen that the CV curves of NMO900 shows similar transitions and same position of reduction peaks compared with NMO850. The voltage peaks in the oxidation process, however, exhibit values higher than those of NMO850 and were observed at 3.13, 3.34, and 3.54 V respectively, indicating its more serious polarization. This may be responsible for the difference in the discharge capacity between them.

The charge-discharge curves (Figure 6.9b) of NMO850 and NMO900 at 0.1 C also display six plateaus, which are consistent with the CV results and could be attributed to the extraction of Na$^+$ from different sites.$^{173, 255}$ It was reported that the Na ions located in the S-shape tunnels can produce a theoretical capacity of 50 mAh g$^{-1}$.$^{272}$ In our work, the initial charge capacity of NMO850 at 0.1 C is 49.4 mAh g$^{-1}$, corresponding to the extraction of 0.18 Na$^+$ from the Na$_{0.44}$MnO$_2$ framework.
Figure 6.11  Cycling performances of NMO samples sintered at 850 and 900°C between 3.8-2.0 V at a current density of 12.1 mA g\(^{-1}\) (0.1 C).

The cycling performances of NMO850 and NMO900 were investigated at the high current density of 8.3 C, as shown in Figure 6.9c. It can be seen that both the samples exhibit a stable cycling performance with negligible decay within 1000 cycles. In detail, NMO850 and NMO900 deliver initial discharge capacities of 73.1 and 27.9 mAh g\(^{-1}\), respectively. From the inset amplification image, it can be found that both the discharge capacity kept increasing during the first 200 cycles, arising from an activation process. The discharge capacities were 82.1 and 39.8 mAh g\(^{-1}\) after about 1000 cycles for NMO850 and NMO900, respectively. In particular, NMO850 retained a discharge capacity of 72.8 mAh g\(^{-1}\) after 2000 cycles, corresponding to a high capacity retention of 99.6% of the initial capacity. Moreover, the coulombic efficiency was 212% in the first cycle and remained stable at nearly 100% up to 2000 cycles. The cycling performances of NMO850 and NMO900 at 0.1 C are shown in Figure 6.11. Both the samples exhibit good cycling performance at 0.1 C, especially the one obtained at 850°C, the discharge capacity of which increases gradually over 100 cycles. In detail, NMO850 and NMO900 delivered initial discharge capacities of 97.6, and 77.2 mAh g\(^{-1}\) in the first cycle, respectively. After an activation process, NMO850 retained a discharge
capacity of 99.1 mAh g\(^{-1}\) over 100 cycles, corresponding to capacity retention of 101.5\% of the initial discharge capacity. At both 8.3 C and 0.1 C, NMO850 exhibits high capacity and good cycling stability owing to its composition, unique morphology, and suitable particle size. NMO900, however, shows lower reversible specific capacity due to the greater strains resulting from its bigger particle size and smoother surface. The capacity and stability related to the size of Na\(_{0.44}\)MnO\(_2\) was also testified by Zhan et al.\textsuperscript{259} and Cao et al.\textsuperscript{261}

The rate capacities of NMO850 and NMO900 are shown in Figure 6.9d. It was observed that NMO850 retained specific capacities of 101.3, 95.1, 90.2, 84.8, 78.6, 68.8, and 54.7 mAh g\(^{-1}\) at 0.1, 0.2, 0.5, 1, 2, 5, and 10 C, respectively, and it can return back to 97.1 mAh g\(^{-1}\) at 0.1 C after cycling at 10 C. By contrast, NMO900 delivered much lower capacities. The good cycling and rate performance of NMO850 can also be ascribed to the well-defined 3D channel structure of the Na\(_{0.44}\)MnO\(_2\), which effectively facilitates the extraction/insertion of Na\(^+\) ions. To the best of our knowledge, this is the best cycling performance, with long cycle life and high cycling stability at a high current density of 8.3 C, compared with other reported results for Na\(_{0.44}\)MnO\(_2\), as summarized in Table 6.1.
Figure 6.12 (a) GITT curves for the charge and discharge states of the 1st cycle and (b) corresponding sodium ion diffusion coefficient ($D_{Na^+}$) for Na/NMO850 cell cycling at 0.1 C between 3.8-2.0 V; (c) GITT curves for the charge and discharge states of the 1st cycle and (d) corresponding $D_{Na^+}$ of Na/NMO900 cell cycling at 0.1 C between 3.8-2.0 V.

Figure 6.12 show the GITT curves for the first cycle at 0.1 C of Na/NMO850 and Na/NMO900 cell and the corresponding sodium ion diffusion coefficient ($D_{Na^+}$). The peaks or bottoms of $D_{Na^+}$ vs. volatge curves correspond to the plateaus of voltage vs. time curves, indicating the occurrence of phase transformation. It can be calculated that the $D_{Na^+}$ values of electrodes are between $4.9 \times 10^{-16}$ and $2.15 \times 10^{-14}$ cm$^2$ s$^{-1}$ for NMO850, and between $1.0 \times 10^{-16}$ and $1.76 \times 10^{-14}$ cm$^2$ s$^{-1}$ for NMO900 in the range of 2.2 to 3.5 V, respectively. Meanwhile, the sodium ion diffusion coefficients of different electrodes were also
investigated by electrochemical impedance spectroscopy at open circuit potential (OCP). The Nyquist curves and the corresponding $Z_{re}$ vs. $\omega^{-1/2}$ plots in the low-frequency region are shown in Figure 6.13. The calculated $D_{Na^+}$ values are \(2.40 \times 10^{-14}\) and \(1.90 \times 10^{-14}\) cm$^2$ s$^{-1}$ at the OCP for NMO850 and NMO900, respectively. The high $D_{Na^+}$ values well explain the excellent cycling performance of the Na$_{0.44}$MnO$_2$ multi-angular rods. The $D_{Na^+}$ of NMO850 is larger than that of NMO900, indicating its faster sodium ion diffusion, which results from its more suitable size and more distinct multi-angular structure than those of NMO900.

Figure 6.13 (a) Nyquist plots of the NMO samples calcined at 850 and 900°C from 100 kHz to 100 mHz at open circuit potential; (b) $Z_{re}$ vs. $\omega^{-1/2}$ plots for the low-frequency region of NMO samples sintered at 850 and 900°C.

Both the samples show a semicircle in the high frequency area and a sloping line in the low frequency region. The depressed semicircle in the high frequency region is attributed to the charge transfer resistance, which is smaller for the sample calcined at 850°C, indicating its faster speed of electron transfer compared to the sample calcined at 900°C. Through linear fitting of the $Z_{re}$ vs. $\omega^{-1/2}$ plot in the low-frequency region in Figure 6.13(b), the apparent diffusion coefficient of the Na$^+$ ions at open circuit potential can be calculated to be \(2.40 \times\)
$10^{13}$ and $2.08 \times 10^{13}$ cm$^2$ s$^{-1}$ for the samples calcined at 850 and 900°C, respectively, which is consistent with the GITT results in Figure 6.12.

![Image of Figure 6.14](image)

**Figure 6.14** (a) *In situ* X-ray synchrotron diffraction patterns collected at 0.5 C between 3.8-2.0 V during the first charge/discharge process for NMO850; (b) corresponding changes of cell parameters $a$, $b$, and $c$, and the unit cell volume. The $2\theta$ angle has been converted to values corresponding to the more common laboratory Cu K$_\alpha$ radiation.
In-situ X-ray synchrotron diffraction was also conducted to investigate the Na\textsuperscript{+} de-insertion/insertion behaviour during the first charge-discharge process at 0.5 C for NMO850, as shown in Figure 6.14a. Potential drops are related to single-phase domains in a narrow sodium content range and the sloping curves are the signature of solid-solution behaviour. There is no evident formation of new phases or superstructures but solid-solution reaction during the Na extraction/insertion from/into the Na\textsubscript{0.44}MnO\textsubscript{2} framework.\textsuperscript{273} It is clearly seen that all the peaks shift towards larger 2θ values during the charge process, indicating the extraction of Na\textsuperscript{+} from and contraction of the unit cell in the Na\textsubscript{0.44}MnO\textsubscript{2} framework. During the discharge process, those shifted peaks move back to lower degree and the phase can go back to the original one (the same as the XRD of initial Na\textsubscript{0.44}MnO\textsubscript{2}) at ~2.8 V. The intensity of (200) decreased, especially after the phase recovered to the primary one (~2.8 V). Upon further discharging, the NMO framework kept expanding, which would cause the decrease of structure ordering, resulting in the decrease of peak intensity. At the end of discharge process, all the peaks shifted to lower degrees relative to the original ones, resulting from the insertion of more Na\textsuperscript{+} into the Na\textsubscript{0.44}MnO\textsubscript{2} framework during the discharge process than the extracted ones during the charge process. The two split peaks ((3 5 0) and (0 10 0)) around 34° merge into one peak when charged to 3.8 V, and the peak starts splitting again at the beginning of discharge. This could be caused by the changing amount of Na\textsuperscript{+} ions in the structure due to the de-insertion/insertion of Na\textsuperscript{+} ions.\textsuperscript{274} The corresponding change of cell parameters \textit{a}, \textit{b}, \textit{c} and volume are shown in Figure 6.14b. The parameters \textit{a}, \textit{b} and \textit{c} all become smaller during the charge process due to extraction of Na\textsuperscript{+} and turn to be larger during the discharge process. It can be seen that the charge process affects mainly the \textit{b} parameter, while strong variation of \textit{a} and \textit{c} occur during the discharge process, in accordance with the changes in the (2 0 0) and (0 10 0) peaks in Figure 6.14a. Similar trends on the crystal structure parameters change have also been observed by Sauvage \textit{et al.}\textsuperscript{260} The volume change is calculated to be less than
2.53%, demonstrating the excellent structure stability and thus high cycling stability of this material during the charge and discharge processes.

**Figure 6.15** (a) TEM image, (b) HRTEM image, and (c) SAED pattern of NMO850 after cycling for 100 cycles at 0.1 C.

To clarify the stability of the electrode, TEM characterization was performed on NMO850 electrode, which was discharged to 2.8 V after cycling for 100 times at 0.1 C. The same morphology of the bright field TEM image (**Figure 6.15a**) as for Figure 6.5c and Figure 6.8b demonstrates the stable structure of NMO850. The lattice spacing in the HRTEM image (**Figure 6.15b**) can be clearly seen with distances of 0.282 and 0.455 nm, corresponding to the (001) planes and (200) planes of Na$_{0.44}$MnO$_2$, respectively. The same structure of electrode discharged to 2.8 V with the original one is in accordance with the *in-suit* synchrotron XRD result, and further demonstrates the robust structure of NMO850. The corresponding SAED pattern (**Figure 6.15c**) indicates that the sample retains its single-crystalline nature in the [0-10] direction. The high stability of this robust multi-angular structure is crucial for the superior cycling performance of Na$_{0.44}$MnO$_2$.

**6.4 Conclusion**
In summary, we synthesized multi-angular rod-shaped Na$_{0.44}$MnO$_2$ via a reverse microemulsion method and studied the electrochemical performance as cathode materials for sodium-ion batteries. With the benefits of multi-angular morphology, suitable size, and fast sodium ion diffusion, the as-prepared Na$_{0.44}$MnO$_2$ rods prepared at 850°C as a cathode material for SIBs possess stable cycling performance with capacity of 72.8 mAh g$^{-1}$ and capacity retention of 99.6% after 2000 cycles at 8.3 C. The as-designed multi-angular Na$_{0.44}$MnO$_2$ provides new insight into the development of tunnel-type electrode materials and their application in rechargeable sodium-ion batteries.
Chapter 7. P2-type Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ as Cathode Materials with Good Performance for Sodium Ion Storage

7.1 Introduction

The demand for large-scale energy storage systems has been growing significantly due to the requirement for the applications such as smart grid. Among the diverse energy storage technologies, the secondary battery is one of the most promising means to store electricity on a large-scale.\textsuperscript{11, 247, 275} Due to the low cost and abundant sources of sodium, the sodium ion batteries (SIBs) may have the potential to meet the increasing demand for electric devices, and has attracted more and more attention.\textsuperscript{13, 115, 116, 143, 276} Nevertheless, the large diameter of the Na$^+$ ion makes it difficult to find suitable host materials for rapid Na$^+$ extraction and insertion due to the sluggish reaction kinetics. It is highly essential to develop effective cathodes for high performance SIBs with large Na storage, high rate capability, and long-term cycling stability.

Researches on cathode materials for SIBs have been focused on compounds ranging from polyanions to layered transition metal oxides.\textsuperscript{5, 277} and it is suggested that layered sodium transition metal oxides show outstanding electrode properties. Moreover, the barrier for Na$^+$ migration can potentially be lower than that for Li$^+$ migration in the layered structures and the higher vacancy concentrations of sodium layered oxides can offer larger capacity.\textsuperscript{104, 278} Layered sodium transition metal oxides are classified into several groups such as O3- and P2-types based on the location of the Na-ions (O: octahedral and P: prismatic).\textsuperscript{13, 171} It is reported that P2-structured sodium intercalated materials show better Na storage and cyclability than O3-featured ones owing to the larger residing sites for sodium ions, less favorability in phase transition and faster ion diffusion in trigonal prismatic environment vs. octahedral one.\textsuperscript{177, 279}
Layered sodium manganese bronzes, Na$_x$Mn$_{1-y}$M$_y$O$_2$ (A = Co, Ni, Fe, etc.) with the P2-structure, normally with high Na storage capacity, have been studied by many researchers. Among those, Na$_x$Mn$_{1-y}$Ni$_y$O$_2$ and some metal substituted or doping materials, have been widely studied since last century due to the high operating voltage based on a Ni$^{2+}$/Ni$^{4+}$ redox reaction, including the Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$, NaNi$_{0.5}$Mn$_{0.3}$Ti$_{0.2}$O$_2$, Na$_{0.5}$Ni$_{0.25}$Mn$_{0.75}$O$_2$, Na$_{0.67}$Mn$_{0.66}$Ni$_{0.30}$Co$_{0.10}$O$_2$, Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$, and Na$_{0.67}$Ni$_{0.23}$Mg$_{0.1}$Mn$_{0.67}$O$_2$ et al. For the primary Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ (NNMO), all 2/3 of Na ions can be reversibly extracted and intercalated to the host structure providing specific capacity of 173 mAh g$^{-1}$ (1 C = 173 mAh g$^{-1}$). Moreover, water cannot be intercalated into within P2-Na$_{2/3}$[Ni$_{1/3}$Mn$_{2/3}$]O$_2$ framework due to the existence of superlattice ordering Ni atoms within the transition metal layer (TMO$_2$) which apparently induces a very strong interlayer interaction and inhibits the uptake of water. When applied for solid-state SIBs, the NNMO showed a superior stability and high reversibility with a capacity retention of 90% after 10 000 cycles at 6 C. However, good cycling stability can be obtained only with cut-off voltage below 4.0 V due to the phase transformation from P2-O2 above 4.1 V.

In this paper, layered P2-type Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ was successfully synthesized and characterized as a cathode material for sodium ion battery. The effect of cut-off voltages, current density and FEC additive on the cycling stability and coulombic efficiency were discussed in details. In situ XRD and galvanostatic intermittent titration technique were also used to better understand the mechanism and sodium ion diffusion during the sodium intercalation and deintercalation process, which provide new experimental evidence of the structural evolution upon cycling tests under different cut-off voltages. Resulting from different phase transformation and sodium ion diffusion rate, the electrochemical performance is highly related to the cut-off voltage and electrolyte used. The prepared P2-
Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ exhibited an initial discharge capacity as high as 179.7 mAh g$^{-1}$ when cycling between 4.5-2.0 V. However, great capacity fading was observed in this voltage area. In the voltage range of 4.0-1.5 V, the electrode exhibited an initial capacity of 151.0 mAh g$^{-1}$ with slight capacity fading due to the structure distortion caused by the Jahn-Teller Mn$^{3+}$ ions. When cycling in the range of 4.0-2.0 V, the electrode maintained 93 mAh g$^{-1}$ with good cycling stability and excellent structural preservation even after 1000 cycles at 1 C. The capacity retention is 71.2% even after 1200 cycles at 10 C.

7.2 Experimental section

7.2.1 Material preparation

Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ (NNMO) powders were synthesized through a facile sol-gel method. All the chemicals were used as purchased. Sodium nitrate, nickel nitrate hexahydrate and manganese nitrate tetrahydrate with mole ratio of 2.08/1/2 were dissolved successively in deionized water to form a uniform solution. After stirring for 30 minutes, the mixed solution was added dropwise into 20ml of ethylene glycol under continuous stirring. Then, the obtained mixture was heated at 80°C to form a gel precursor, which was then heated in a muffle furnace at 800, 850, or 900°C for 20 h in air to obtain the final products with naturally cooling to room temperature.

7.2.2 Structural characterization

The morphologies of the as-prepared samples were investigated by field-emission scanning electron microscopy (FESEM, JEOL JSM-7500) and transmission electron microscopy (TEM, JEOL ARM 200F). TEM samples were prepared after sonication treatment. The microstructures of the as-prepared powders were characterized on a synchrotron X-ray diffraction beamline with a wavelength (λ) of 0.6885 Å calibrated with the National Institute
of Standards and Technology (NIST) LaB$_6$ 660b standard reference material and laboratory X-ray diffraction (XRD, GBC MMA diffractometer) with Cu K$_\alpha$ radiation. Mn and Ni K-edge X-ray adsorption near the edge structure (XANES) was performed at Pohang Accelerating Laboratory in Republic of Korea using a double Si (111) monochromator. All spectra were normalized to the main edge jump.

7.2.3 Electrochemical measurements

The electrodes were prepared by mixing 80 wt% active materials, 10 wt% Super P, and 10 wt% polyvinylidene fluoride (PVDF) binder to form a slurry, which was then coated on an aluminium foil. Next, the aluminium foil was dried in a vacuum oven overnight at 120°C. After that, the working electrodes were cut out and pressed under a pressure of 20 MPa. The electrolyte used was 1.0 mol L$^{-1}$ NaClO$_4$ in an ethylene carbonate (EC) – diethyl carbonate (DEC) solution (1:1 v/v) with or without fluoroethylene carbonate (FEC) additive. Sodium foil was cut from a sodium bulk stored in mineral oil and used as both the counter and reference electrode. The cells were assembled in an argon-filled glove box. The electrochemical performances were tested on a Land Test System at different current densities. Cyclic voltammetry (CV) at a scan rate of 0.1 mV s$^{-1}$ and electrochemical impedance spectroscopy (EIS) from 100 kHz to 100 mHz were performed using a CHI 660b electrochemistry workstation. The diffusion coefficient of Na$^+$ ions was studied using the galvanostatic intermittent titration technique (GITT). For the GITT measurement, the cells were charged and discharged at 0.1 C for 360 s followed by an open circuit relaxation for 1 h. All the electrochemical testings were conducted at room temperature.

7.3 Results and discussions
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Figure 7.1 XRD pattern and SEM image (inset) of the as-prepared NNMO (wavelength=0.05899 nm).

The XRD Rietveld refinement of the P2-Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ prepared at 850°C was performed, and the refinement results and SEM image are presented in Figure 7.1. The powders obtained are pure NNMO, whose peaks can be indexed to the hexagonal phase system with space group P63/mmc. The $a$ and $c$ parameters are refined to be 2.885 and 11.155 Å, respectively. All the peaks are sharp and well defined, indicating high crystallinity of the prepared sample. From the SEM image shown inset, it can be seen that uniform plate-shaped NNMO, in thickness of ~500 nm and diameter of ~1 μm, were formed. From the EDX images and elements distribution of NNMO prepared at 850°C (Figure 7.2), it can be seen that the elements Na, Ni, Mn and O were uniformly distributed in the sample prepared at 850°C.
Figure 7.2 EDX images and distribution of Na, Ni, Mn and O elements of NNMO prepared at 850°C.
Figure 7.3 SEM morphologies of NNMO powders calcined at different temperatures: (a, b) 800; (c, d) 850; and (e, f) 900°C.

Figure 7.4 XRD patterns of NNMO prepared at different temperatures.

The calcination temperature plays an important role in the synthesis of pure and image-defined NNMO. XRD patterns and morphologies of NNMO powders prepared at different temperature are shown in Figure 7.3 and Figure 7.4, respectively. All the samples show good crystallinity. When calcined at lower temperature of 800°C, the obtained powders are NNMO with plenty of Na_{0.91}NiO_{2} impurities. Further increasing the calcination temperature
to 900°C, Na$_{0.7}$MnO$_2$ impurities are formed instead. Powders obtained at 800°C were irregular and did not have a defined image. Although the surface looked to be smooth, the plates consisted of different layers, which can be seen in the high magnification images. The powders grow to be bigger and thicker after calcination at 900°C. The TEM image and SAED pattern of NNMO prepared at 850°C in Figure 7.5 further demonstrates its layered structure and good crystallinity.

Figure 7.5 TEM images of NNMO prepared at 850°C (inset: SADE pattern).

Figure 7.6 X-ray adsorption near the edge structure (XANES) of as-prepared NMMO powders: (a) Mn K-edges and (b) Ni K-edges.

To determine the valence state of Mn and Ni in NNMO, XANES was conducted and is shown in Figure 7.6. The XANES of MnO$_2$ and NiO are also shown as reference. It can be
seen that the spectrum of Mn in NNMO corresponds well with that of MnO$_2$. Slow cooling leads to the oxygen uptake during the cooling process and presence of manganese vacancies thus a higher concentration of Mn$^{4+}$ which suppresses the cooperative Jahn–Teller distortion.\cite{293,294} The pre-edge peaks in the spectra are indicative of structural distortion in the MnO$_6$ octahedra.\cite{295} Moreover, Ni in NNMO can be determined to stay at +2 valence based on the spectrum of NiO. Thus the Ni and Mn are at +2 and +4 state respectively in NNMO, which is in agreement with previous reports.\cite{296,297} And it can be predicted that in the bifunctional transition-metal layer, Ni$^{2+}$ acts as a double redox-active centre and Mn$^{4+}$ provides stability to the host structure.\cite{298}

![Figure 7.7 Cyclic voltammetry curves of Na/NNMO cells at different cut-off voltages: (a) 4.0-2.0 V and (b) 4.5-1.5 V.](image)

The cyclic voltammetry curves of Na/NNMO cells (corresponding to sodium deintercalation/intercalation from/into Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$, respectively) of Na/NNMO cells with different charge–discharge cut-off voltages are shown and compared in Figure 7.7. The charge–discharge cut-off voltages are set to 4.0/2.0 and 4.5/1.5 V, respectively, to study the phase change happening until high voltage of 4.5 V or low voltage of 1.5 V. A series of
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complicated CV peaks have been observed, indicating a multitude of possible phase transitions accompanying with the deinsertion or insertion of Na$^+$ ions.

When cycling between 4.0 and 2.0 V, six highly reproducible pairs of peaks, having positions centred at 2.04/2.00, 2.34/2.28, 3.21/3.11, 3.38/3.24, 3.70/3.53, 3.74/3.61 V ~vs. Na$^+$/Na respectively of Na/NNMO cell were observed in the CV curves (Figure 7.6a). The four redox peaks between 3.0-4.0 V are associated with the transition of Ni$^{2+}$-Ni$^{3+}$-Ni$^{3.5+}$ along with Na$^+$ extraction/insertion processes. The various minor plateaus between 2.0-3.0 V during the processes come from Na$^+$/vacancy ordering sequence or transitions involving the gliding of oxygen planes. Mn ions stay at +4 state and are electrochemically inert above 2.0 V, which can help effectively maintain the structural stability in the absence of Jahn-Teller active Mn$^{3+}$, therefore leading to the stabilisation of the undistorted P2 hexagonal crystal structure. The overlapped anodic and cathodic peaks demonstrated the electrochemical stability of NNMO between 4.0-2.0 V.

Further sweeping to 4.5 V, a new pair redox peak of 4.3/4.0 V was observed (Figure 7.7b), which shows the worst reproducibility comparing with other peaks. It was reported that there is a transformation from P2 phase to O2 phase starting at 4.18 V since O2-type stacking faults were introduced into the P2 structure. The transformation is obviously partly reversible and may cause severe structural distortion, which may cause great capacity fade. If the low cut-off voltage was set to 1.5 V, according to the reported studies and the obvious oxidation/reduction peaks appearing below 2.0 V (Figure 7.7b), it can be concluded that Mn$^{4+}$ can was activated and reduced to Mn$^{3+}$ after the initial Na$^+$ ions insertion. Mn$^{4+}$/Mn$^{3+}$ redox pair is responsible for the redox peaks below about 2.0 V. The formation of Jahn-Teller active Mn$^{3+}$ results in large structural distortions of MnO$_6$ octahedra which can induce constraints and defects in the active material leading to increased capacity fading.
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undergoes the disproportion reaction forming Mn$^{4+}$ and Mn$^{2+}$ (2Mn$^{3+}_{\text{solid}} \rightarrow$ Mn$^{4+}_{\text{solid}}$ + Mn$^{2+}$) and continuous decomposition of the electrolyte at high voltages. Furthermore, the Mn$^{2+}$ is easily dissolved in the electrolyte which would cause a constant degradation of the active material.\textsuperscript{301} Furthermore, more obvious peaks around 2.0 V than that in Figure 3a suggests a possibility of occurrence of new phase transformation. It can be expected that the electrodes may experience big capacity fade if continually cycled to 4.5 V or 1.5 V.

![Figure 7.8](image_url)

**Figure 7.8** (a-c) Charge-discharge profiles, (d) cycling performance and (e) corresponding coulombic efficiency of Na/NNMO cell at different cut-off voltages at 0.1 C.

Figure 7.8 shows the charge-discharge profiles and electrochemical performance of NNMO cycling at 0.1 C. The charge-discharge cut-off voltages are set to 4.0/2.0, 4.0/1.5 and 4.5/2.0 V to study the effect of high or low voltage on the electrochemical performance of Na/NNMO cell. It can be seen that the charge-discharge cut-off voltage is crucial for the capacity retention and coulombic efficiency of the electrode. The plateau in the charge-
discharge profiles are consistent with the characteristic peaks in the CV curves, and show different degrees of reproducibility during cycling process under different cut-off voltage ranges.

When performing between 4.0 and 2.0 V (Figure 7.8a and d), several voltage plateaus corresponding to the CV peaks are observed, caused by the different staging of the sodium layers. The initial charge and discharge capacity were 93.3 and 93.0 mAh g⁻¹, corresponding to the extraction of 0.361 mol and the insertion of 0.360 mol of Na ions per formula unit, respectively. Thus, the x value in NaₓNi₁/₃Mn₂/₃O₂ was maintained at approximately 0.67, and Na⁺ could be extracted and inserted reversibly after several charge-discharge cycles, which well explains the excellent cyclicity of Na/NNMO cell in Figure 4d. The coulombic efficiency (CE) in the first and following cycles almost equal to 100% during the whole cycling process. There is no visible decay and the capacity retention is 95.7% after 100 cycles.

**Figure 7.9** (a) Cycling performance and (b) corresponding CE of prepared NNMO with different cut-off voltages at 1 C.

In the voltage range of 4.0 and 1.5 V (Figure 7.8b and d), the electrode cycled reversibly with slight capacity decay, but the voltage steps were still reproducible throughout the whole test.
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Comparing with cells cycling between 4.0 and 2.0 V, another long flat voltage slope at ~1.76 V which associated with the redox reaction of the Mn$^{4+}$/Mn$^{3+}$ pairs, was characterized. The initial discharge capacity was increased to 151.0 mAh g$^{-1}$, of which ~38.4% (58 mAh g$^{-1}$) was contributed by the insertion of Na$^+$ below 2 V. The x value in Na$_x$Ni$_{1/3}$Mn$_{2/3}$O$_2$ cycling in the range of 4.0-1.5 V was increased to 0.95 at the end of discharge process after 0.58 mol of Na ions extracted during the charge process per formula unit. This over-insertion of Na$^+$ ions reaches the theoretical Na intercalation limit where the oxidation state of Mn is totally Mn$^{3+}$. The CE was 160% in the first cycle and kept stable at ~99% from the second cycle. Faster capacity fading was observed than that between 4.0-2.0 V due to the increasing distortion of MnO$_6$ octahedra caused by increasing Mn$^{3+}$ ions, which can induce constraints, defects and thus structural deterioration of the material. Phase transformation also happened proven by the in-situ synchrotron test, which will be discussed later.

In Figure 7.8c and d, the initial charge capacity of NNMO was increased to 191.5 mAh g$^{-1}$ when charging to 4.5 V, 18.5 mAh g$^{-1}$ higher than the theoretical capacity due to possible electrolyte decomposition above 4.4 V. A long plateau at 4.18 V indicated the occurrence of a two phase reaction, corresponding to the P2-O2 phase transformation. There was a strong capacity fade during cycling: while 0.70 Na$^+$ ions per formula unit were reintercalated in the first discharge process, only 0.52 Na$^+$ ions were reversibly cycled in the 10$^{th}$ cycle. After 10 cycles, the long plateau at almost disappeared and the capacity retention was only 71.8%. Furthermore, the CE during the whole cycling was much lower and only reached ~90%. The severe capacity fade and low CE could originate from the increasing catalytic decomposition of the electrolyte with increasing the charging voltage and the increasing irreversibility of the electrode material associated to structural changes. The P2-O2 phase transition involves
large volume shrinkage (~23%) coming from an oxygen framework shift, which would cause fast capacity decay during the cycles in Na$_{x}$Ni$_{1/3}$Mn$_{2/3}$O$_2$.\textsuperscript{287}

It can be found that a low 1.5 V or high 4.5 V cut-off voltage does not lead to capacity improvement for long-term cycling, since after about 10 or 60 cycles the capacity value of the cells with $E_{\text{cutoff}} = 4.0/2.0$ V is reached due to the redox reaction of the Mn$^{4+}$/Mn$^{3+}$ ionic pair below 2 V or P2-O2 transformation and electrolyte decomposition above 4.2 V. Meanwhile, the cycling performance of NNMO at 1 C was also characterized at different cut-off voltages and is shown in Figure 7.9. Similar capacity changing trends were found. Interestingly, the CE in the voltage of 4.5-2.0 V was higher than that at 0.1 C. The lower CE at 0.1 C is probably due to the continuous formation of SEI layer for longer time and slower sodium ions diffusion at lower current rate. High current density, to some extent, inhibits the occurrence of side reaction due to the fast sodium ion de-insertion/insertion processes.
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Figure 7.10 Electrochemical properties of Na/NNMO cell between 4.0 and 2.0 V: (a) cycling performance and corresponding coulombic efficiency at 0.1 C and 1 C; (b) rate capacity; (c) cycling performance 5 C and 10 C and (d) cycling performance and corresponding coulombic efficiency using electrolyte without FEC additive.

We then focus on the electrochemical properties of NNMO at 4.0/2.0 V, during which there is no phase transformation from P2 to O2 or formation of Mn$^{3+}$, and the electrode exhibits excellent cycling stability and high coulombic efficiency. Figure 7.10a shows the cycling performance of NNMO at 0.1 C and 1 C. After 100 cycles, the discharge capacity retains 89.0 mAh g$^{-1}$ at 0.1 C, corresponding to a capacity retention of 95.7% of the first cycle. Moreover, the capacity retention at 1 C after 300 cycles can reach 92.6%. Again, the coulombic efficiencies at both current densities are stable and remain almost 100%. The increasing current densities will not deteriorate the CE of NNMO. This phenomenon indicates high
current density can only cause polarization but will not intensify the side reactions.\textsuperscript{303} In the rate capacity shown in Figure 7.10b, the specific capacity reduced gradually with increasing rate, which could be ascribed to an increase in overpotential resulting from less reaction time for the free cation intercalation into the crystal lattice. In details, the discharge capacities are 84.9, 73.5, 67.8, 65.1, 62.2, 60.7, and 58.2 mAh g\textsuperscript{−1} at 0.2, 0.5, 1, 2, 5, 10, and 20 C respectively. The voltage plateaus could be clearly seen at high current densities. Meanwhile, the NNMO electrodes exhibit excellent cycling stability at high current densities of 5 and 10 C, as shown in Figure 7.10c. The capacity retention is 71.2\% even after 1200 cycles at 10 C.

We also study the effect of FEC additive in the electrolyte on the electrochemical performance of NNMO electrode. As shown in Figure 7.10d, without the addition of FEC, the reversible discharge capacity did not change much comparing with that with FEC additive. The charge capacity, however, are 110 and 79 mA g\textsuperscript{−1} at 0.1 C and 1 C respectively, which are higher than those using FEC additive, resulting in lower coulombic efficiencies. It was reported that FEC additive can suppress the electrolyte decomposition, enhance the reversibility of Na and improve the SEI passivation capability,\textsuperscript{304} thus decreasing the occurrence of irreversible capacity. Again, the CE at 1 C is higher than that at 0.1 C due to the faster sodium ions diffusion.
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Figure 7.11 *In-suit* synchrotron XRD patterns of NNMO cycling in the voltage range of (a) 4.5-2.0 V and (b) 4.0-1.5 V at 0.5 C, the 2θ has been converted based on the Cu wavelength for convenience.

*In-suit* synchrotron XRD were performed in the voltage range of 2.0-4.5 V to study the evolution of NNMO during cycling and are shown in Figure 7.11a. The pristine Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ has an ordered hexagonal structure. During the charging process, the (00l) peaks shift to a lower angle with decreasing intensity, indicating the expansion of sodium
content sensitive $c$ parameter and thus the interplanar distance. The decrease of $a$ parameter, the M-M is indicated by the shift to lower angle of (100) peak. The successive extraction of Na$^+$, which is located between the transition metal layers, leads to a large repulsion of the oxygen anions and, therefore, results in the increase of the $c$-axis parameter as well as the decrease of $a$ parameter,\cite{181} in agreement with the investigation by Lu et al.\cite{179} While the (100), (102), (103), (110) and (112) peaks moved to higher angles, the (104) and (106) peaks in our study moved to lower angles. This evolution is different with the former report,\cite{179} in which all (10$l$) peaks shift to a lower angle, indicating the different evolution degrees of lattice parameters. All the peaks became broader with decreasing intensity along with the extraction of sodium ions. There is no new phase formed and only solid-solution behaviour occurs below 3.8 V. A multiple of new Bragg peaks observed at 21 and 70° were formed above 4.2 V, indicating the formation of O2 phase, which is in agreement with the previous report.\cite{179} It was reported that the TMO$_2$ slabs glide to form octahedral sites after extraction of the Na ions, leading to the formation of a new O2-type phase with stacking faults and a unique oxygen packing.\cite{300} The (100) split and (10$l$) peaks become broader as more O2 stacking faults are introduced in the slabs.\cite{305} But another phase appearing at 4.0 V indicated by the peaks at ~12 and 25° might be attributed to the intercalation of water, solvent molecules and/or salt ions in the interstitial space between the TMO$_2$ slabs.\cite{306,307} And the intercalation is reversible in the 2nd cycle. It was reported that there was Z phase formed during the charge to 4.3 V of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$.\cite{295} However, there is no Z phase observed in our study. The progressive disappearance of the high-voltage plateau above 4.25 V upon cycling (Figure 7.8c) suggests that the transition to O2 phase might be responsible for the capacity fading. Similar phenomena were also observed in some other P2 type cathode materials and O3 type layered compounds.\cite{177,179,278,305,308-310}
Upon discharging, the O2 phase gradually disappeared and a reversible evolution took place. The Bragg diffraction peaks shifted to the opposite direction to that of the charge process, indicating a reversible structural evolution during the charge/discharge process. However, the intensity of peaks decreased and could not return to its primary phase, indicating big irreversibility which would result in great capacity fading during the de-insertion/insertion of Na ions. As Na\(^+\) inserts between the MnO\(_6\) layers, the negative charges of the oxygen between different layers are screened, which moves the layers closer together, leading to the decrease of c parameter. The (100) shift to lower angle reflects the expansion of a and b parameters, resulting from a decrease of the oxidation state of manganese and thus an expansion of the MnO\(_6\)-octahedra during discharge.\(^{280}\)

*In-suit* synchrotron XRD of NNMO cycling between 4.0-1.5 V was also characterized to study the evolution in low voltage area (Figure 7.11b). In the initial charge to 4 V, the evolution is same with Figure 7.11a. Only solid solution mechanism occurred during this voltage range. Limit the voltage to 4 V excludes the formation of O2 phase and electrolyte decomposition, resulting in slower capacity fading compared with that of being charged to 4.5 V. During the following discharge, a solid solution mechanism was observed at the beginning. However, when discharged to or below 2 V, the (002), (100), (102) and (112) peaks split into two peaks along with the peak intensity decrease, which is indicative of a biphasic mechanism. The appearance of two diffraction peaks at about 15.9 and 32.0° correspond to the (002)\(_{P2}\) and (004)\(_{P2}\) reflections in the hexagonal pattern.\(^{308}\) The appearance of a small new phase (orthorhombic P2’ phase) below 2 V is attributed to increasing distortion caused by the increasing concentration of Mn\(^{3+}\) formed from reduction of Mn\(^{4+}\). The biphasic domain between the P2 and P2’ phase is observed for a Na content of 0.85 < x
< 0.95 in Na$_x$Ni$_{1/3}$Mn$_{2/3}$O$_2$. The bi-phasic mechanism here is reversible and the phase return to its initial situation during the discharge process.

**Figure 7.12** (a) GITT curves for the charge and discharge states of the first cycle and (b) corresponding sodium-ion diffusion coefficient ($D_{Na^+}$) for Na/NNMO cell cycling between 4.5 and 2.0 V; (c) GITT curves for the charge and discharge states of the first cycle and (d) corresponding $D_{Na^+}$ of Na/NNMO cell cycling between 4.0 and 1.5 V.

**Figure 7.12** shows the GITT curves for the first cycle at 0.1 C of Na/NNMO cell and the corresponding sodium-ion diffusion coefficient ($D_{Na^+}$) with different cut-off voltages. It is found that the $D_{Na^+}$ values are highly related to the phase transformation and structural evolution during the charge-discharge process. The $D_{Na^+}$ were stable with a high value of $\sim10^{-10}$ cm$^2$ s$^{-1}$ at the beginning of Na extraction during charge process (Figure 7.12b and d)
and began to drop obviously at the phase transformation (P2-O2) area. The value was only $6.39 \times 10^{-14}$ cm$^2$ s$^{-1}$ when charged to 4.5 V. Upon discharging, both $D_{Na^+}$ show a minimum ($\sim 10^{-12}$ cm$^2$ s$^{-1}$) as the arrows indicate due to the Na$^+/vacancy$ ordering at around 2.3 V, corresponding to the CV peaks and voltage plateaus between 3.0-2.0 V. Similarly, $D_{Na^+}$ began to drops when the P2-P2' transformation happened below 2.0 V in Figure 7.12d.

Figure 7.13 (a) Nyquist plots of prepared NNMO at 850$^\circ$C before and after 700 cycles at 1 C (inset: equivalent circuit); and (b) corresponding $Z_{re}$ vs. $\omega^{-1/2}$ plots in the low frequency region.

Table 7.1 Values of different parameters obtained from EIS.

<table>
<thead>
<tr>
<th></th>
<th>$R_s$ (Ω)</th>
<th>$R_f$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$D_{Na^+}$ (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before cycle</td>
<td>53.32</td>
<td>882.9</td>
<td>1161</td>
<td>$9.02\times10^{-12}$</td>
</tr>
<tr>
<td>After 700 cycles at 1 C</td>
<td>52.99</td>
<td>41.44</td>
<td>178.5</td>
<td>$7.15\times10^{-12}$</td>
</tr>
</tbody>
</table>

Meanwhile, the $D_{Na^+}$ of NNMO was also investigated by electrochemical impedance spectroscopy for electrodes before and after cycled at 1 C for 700 cycles between 4.0-2.0 V. The Nyquist curves and the corresponding $Z_{re}$ vs $\omega^{-1/2}$ plots in the low-frequency region of prepared NNMO before and after 700 cycles at 1 C between 4.0-2.0 V are shown in Figure
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7.13. The equivalent circuit inset at the open circuit potential (OCP) are presented inset and values of parameters fitted are shown in Table 7.1. The Nyquist plot consists of two semicircles at high frequency area corresponding to the film resistance ($R_f$) and charge transfer resistance ($R_{ct}$), respectively. The inclined line at low frequency region is related to the Warburg impedance ($Z_w$) associated with Na$^+$ diffusion. The value of $R_f$ and $R_{ct}$ both decreased after 700 cycles at 1 C, resulting from the enhanced contact between the electrolyte and cathode material and the stabilized layers of cathode material. The low $R_{ct}$ at the electrode/electrolyte interface is favourable for the transfer of Na$^+$ ions and electrons at the surface and the diffusion of liquid electrolyte. The apparent Na$^+$ diffusion coefficient ($D_{Na^+}$) can be calculated by the $Z_{re}$ vs. $\omega^{-1/2}$ plots in the low frequency region (Fig. 7.13b). The $D_{Na^+}$ calculated for electrode before and after 700 cycles at 1 C at OCP are 9.02×10$^{-12}$ and 7.15×10$^{-12}$ cm$^2$ s$^{-1}$, respectively. The high $D_{Na^+}$ values well explain the excellent cycling performance of the prepared NNMO. Even after cycling for 1000 cycles at 1 C, the layer structure of NNMO can still be observed in the electrode (Figure 7.14), indicating its superior structure stability.
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Figure 7.14 Electrodes before (a, b) and after (c, d) 1000 cycles at 1 C with super P and PVDF binder around.

Figure 7.15 (a) Charge-discharge profiles and (b) cycling performance of Na/NNMO cell between 0.2-3.0 V at 17 mA g$^{-1}$.

Based on the CV peaks appeared below 2.0 V, in addition to work as a cathode through the high-voltage redox couple Ni$^{4+}$/Ni$^{2+}$ with capacity of 173 mA h g$^{-1}$ (x from 2/3 to 0), by selectively activating the redox couple Mn$^{3+}$/Mn$^{2+}$ at $\sim$1.76 V, as the Figure 7.15 shows,
NNMO is supposed to function as an anode with capacity of 86.5 mAh/g (x from 2/3 to 1). Further study is needed for NNMO for application as anode materials for SIBs.

7.4 Conclusion

In summary, layered P2-type Na_{2/3}Ni_{1/3}Mn_{2/3}O_2 was successfully synthesized through a facile sol-gel method and subsequent heat treatment. Resulting from different phase transformation and sodium ion diffusion rate, the electrochemical performance is highly related to the cut-off voltage and electrolyte used. When the cut-off voltage is set up to 4.5 V or low to 1.5 V, capacity fade happens due to the occurrence of P2-O2 transformation and electrolyte decomposition or the redox reaction of the Mn^{4+}/Mn^{3+} ionic pair and P2-P2’ transformation. The electrode maintained 93 mAh g^{-1} with good cycling stability and excellent structural preservation even after 1000 cycles at 1 C between 4.0-2.0 V. The capacity retention is 71.2% even after 1200 cycles at 10 C. It can be expected that P2-type Na_{2/3}Ni_{1/3}Mn_{2/3}O_2 is very promising as a cathode material for sodium ion battery.
Chapter 8. Conclusions and Outlook

8.1 Conclusions

Metal oxides have shown their promising potential for use either as anode or cathode materials, as introduced in the literature review. The available global lithium reserves are limited and often located in remote or politically sensitive areas. There is a great opportunity for SIBs development because of its similar chemical properties to the LIBs and abundant sodium resources. Similar and comparative studies exist between rechargeable LIBs and SIBs system. This doctoral work aims to investigate some advanced metal oxides used as anode or cathode materials for LIBs or SIBs.

Hierarchical SnO$_2$ hollow spheres combined with conductive carbon showed good cycling performance and excellent rate capability when studied as anode for LIBs. The excellent lithium storage capability come from its highly enhanced electron or lithium transport within the electrode and buffering of the volume expansion by the carbon coating layer to extend the cycling life. Carbon modification is proven to be an effective and generally used method to enhance electronic conductivity and improve electrochemical performance of electrode materials.

Another anode material for LIBs, zinc cobalt oxides, hierarchical ZnCo$_2$O$_4$ microspheres and Zn$_{0.85}$Co$_{0.15}$O/C nanoparticles also exhibited good cycling performance. The complex structures of ZnCo$_2$O$_4$ with nanostructured constituent units and carbon modification of Zn$_{0.85}$Co$_{0.15}$O/C is favourable for the diffusion of lithium ions possess. High reversible capacities of 616.7 and 741.9 mA h g$^{-1}$ and good rate performances were maintained after repetitive 100 cycles for ZCO and Zn$_{0.85}$Co$_{0.15}$O/C, respectively. The potential of metal oxides as electrode materials was further demonstrated and will be continuously studied.
When studied as cathode materials for SIBs, multi-angular rod-shaped Na$_{0.44}$MnO$_2$ synthesized via a reverse microemulsion method show excellent electrochemical performance. With the benefits of multi-angular morphology, suitable size, and fast sodium ion diffusion, the as-prepared Na$_{0.44}$MnO$_2$ rods prepared at 850°C as a cathode material for SIBs possess stable cycling performance with capacity of 72.8 mAh g$^{-1}$ and capacity retention of 99.6% after 2000 cycles at 8.3 C. The as-designed multi-angular Na$_{0.44}$MnO$_2$ provides new insight into the development of tunnel-type electrode materials and their application in rechargeable sodium-ion batteries.

Layered P2-type Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ synthesized through a facile sol-gel method and subsequent heat treatment were also investigated as cathode for SIBs. Resulting from different phase transformation and sodium ion diffusion rate, the electrochemical performance is found to be highly related to the cut-off voltage and electrolyte used. When the cut-off voltage is set up to 4.5 V or low to 1.5 V, capacity fade happens due to the occurrence of P2-O2 transformation and electrolyte decomposition or the redox reaction of the Mn$^{4+}$/Mn$^{3+}$ ionic pair and P2-P2' transformation. The electrode maintained 93 mAh g$^{-1}$ with good cycling stability and excellent structural preservation even after 1000 cycles at 1 C between 4.0-2.0 V. The capacity retention is 71.2% even after 1200 cycles at 10 C. It can be expected that P2-type Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ is very promising as a cathode material for sodium ion battery.

8.2 Outlook

The principal issues challenging the development of batteries for electric vehicles are cost, safety, energy density, charge/discharge rate, and service life. Researches on LIBs are always and will keep going on its way besides its commercialization. The limited dynamics and theoretical capacity of the current electrode materials (especially cathode materials), are the
main challenges that need to be addressed. Considerable study of suitable positive electrode materials with high capacity and high operating voltages is highly required to further increase the energy density and realize further breakthroughs for rechargeable metal ion batteries.

Developments in LIBs technology and its understanding are strongly influencing and accelerating the development of SIBs. Further understanding and experimental and theoretical studies are needed not only for the electrode materials but also for electrolytes, additives and electrode/electrolyte interphase before commercializing practical SIBs: (1) Development of appropriate electrolytes with a wide electrochemical window, high anodic stability, low volatility, low flammability, and good environmental friendliness, especially for high voltage cathode materials; (2) development of ideal binders (e.g., CMC and alginate) for intimate adherence between the current collector and electrode materials for improved electrochemical performance and enhanced stability during electrochemical cycling; and (3) establishment of a combined computational and experimental approach to identify and predict electrode materials with high capacity, high energy density, and low cost. Future development of low-cost LIBs or SIBs should combine with and focus on investigation of electrode material with excellent cycling stability, high rate capability, large gravimetric and volumetric energy densities, and improved safety characteristics.
References

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References


References


References

References


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References


Appendix

Appendix A: List of publications


**Appendix B: Awards**

[1] International Postgraduate Tuition Award (IPTA), 2014-2017, University of Wollongong;
[3] Excellent Poster Award, the International Symposium on Next-Generation Batteries 2016;